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INFRARED SPECTROSCOPIC OBSERVATIONS ON THE FATE OF ORGANOPHOSPHORUS COMPOUNDS EXPOSED TO ATMOSPHERIC MOISTURE

PART III. PHOSPHINES, PHOSPHITES, PHOSPHONITES, PHOSPHINITES, PHOSPHORIC ACIDS, PHOSPHONIC ACIDS, PHOSPHINIC ACIDS, PHOSPHINE OXIDES, PHOSPHONIC HALIDES, PHOSPHONATES, PHOSPHINIC HALIDES, PHOSPHINATES, PHOSPHATES, P-N COMPOUNDS, P=S (THIONO) COMPOUNDS, P-S (THIOLO) COMPOUNDS, P=Se COMPOUNDS, P-O-P (PYRO) COMPOUNDS, OTHER P-COMPOUNDS, AND INORGANIC COMPOUNDS

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RESEARCH AND TECHNOLOGY DIRECTORATE

May 2007

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14. ABSTRACT
This report is part three in a three part series dedicated to observing the degradation of organophorus compound-exposure to atmospheric moisture as a function of time. The investigation continues with Phosphines, Phosphites, Phosphonites, Phosphinites, Phosphoric Acids, Phosphonic Acids, Phosphinic Acids, Phosphine Oxides, Phosphonic Halides, Phosphonates, Phosphinic Halides, Phosphinates, Phosphates, P-N Compounds, P=S (Thiono) Compounds, P-S (Thiolo) Compounds, P=Se Compounds, P-O-P (Pyro) Compounds, other P-Compounds, and Inorganic Compounds. Experimental observation of chemical degradation is interpreted from the measured infrared over the 4000 to 400 wavenumber region. Infrared band assignments are reported and newly formed compounds are identified. The final fate of the compound from starting material is reported. Infrared stack plots are provided illustrating the chemical changes as a function of time.

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Infrared, Inorganic, Fate, Halides, Organophosphorus

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PREFACE

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TABLE

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INFRARED SPECTROSCOPIC OBSERVATIONS ON THE FATE OF ORGANOPHOSPHORUS COMPOUNDS EXPOSED TO ATMOSPHERIC MOISTURE. PART III

1. INTRODUCTION

Many infrared spectra have been collected over the years pertaining to organophosphorus chemical agents and related compounds (precursors, impurities and decomposition products)[a] as well as organophosphorus compounds of general interest. After initial spectra were obtained for many of these compounds the original pure material was allowed to remain between salt windows and repeated scans made with time as the material sat (in a fume hood) exposed to ambient atmospheric conditions. This report will present and discuss the spectra obtained for many organophosphorus compounds as they sat exposed to atmospheric conditions. These spectra should be of interest to the Chemical Weapons (CW) treaty verification program. This data should be of value as part of the verification regime that includes on-site inspection of declared chemical warfare related facilities. Infrared analysis of bulk (neat) hazardous material is rapid and efficient and offers minimal sample preparation.

2. EXPERIMENTATION

2.1 Instrumentation

All the spectra included in this report were determined on either a Nicolet Model 10 DX (Nicolet Analytical Instruments, Madison, WI) or on a Perkin-Elmer Model 1750 (Perkin-Elmer Corporation, Norwalk, CT) Fourier Transform spectrometer. The spectra were saved on individual magnetic floppy disks that were resident to the particular instrument used. The spectra were also transferred to a Zenith PC via a Sprouse Scientific Micro-Trace program (Sprouse Scientific Systems, Incorporated, Paoli, PA) for inclusion into a central search system. Hard copies of the spectra were plotted on a Hewlett-Packard Model 7475A plotter (Hewlett-Packard, Palo Alto, CA). Some spectra were also plotted using Nicolet Omnic® FT-IR software and and Epson *Stylus*® color printer (Epson America, Inc.). The instruments were

[a] Piffath, R.J., Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part I. G-Agents and Related Compounds. Part II. V-Agents and Related Compounds. 1999.

purged with the boil off from a liquid nitrogen cryogenic container. The sample compartments of the instruments were placed inside fume hoods as a safety precaution.

2.2 **Sample Handling**

Liquid samples were determined as capillary films (neat) between 25 mm diameter X 4 mm thick KBr of CsI discs at a resolution of 2 cm^{-1}. After an initial spectrum was obtained, the sample film/salt window sandwich was allowed to sit in the hood air for a period of time, then returned to the sample compartment of the instrument and a spectrum determined. The sample film was returned to the hood air and allowed to sit for another period of time and then another spectrum was determined. This procedure was repeated until the sample was completely hydrolyzed as evidenced by no further changes occurring in the infrared spectrum.

Solid samples were run as either KBr pellets or directly as solids between KBr or CsI windows (discs). Potassium bromide pellets were prepared using infrared grade KBr (Harshaw Chemical Company, Cleveland, OH). The sample KBr matrix was ground in a stainless steel vial with a Wig-L-Bug amalgamator (Crescent Dental Manufacturing Company, Chicago, IL). Some of the solid samples were determined directly (no KBr matrix) by placing a small amount of solid (1 mg or less) between two polished salt discs. The solid was ground by moving the salt discs across one another with a back and forth motion, alternating with a figure-eight motion. This grinding lasted about 20 seconds. An IR spectrum was then determined to see if the grinding was sufficient to produce an acceptable spectrum, one essentially free of distorted band shapes. The spectra thus produced by this second method were smoothed, flattened and ordinate expanded as needed.

2.3 **List of Compounds** (The CAS numbers, where known, are given in the brackets [ ].)

All the following compounds were used as received, with no further purification.

2.3.1 **Phosphines** $P(R)_3$

1. **MD**, methoxydichlorophosphine, CH_3Cl_2OP [676-83-5] **Figs. 1, 2**

2. Dimethylhydroxymethylphosphine, C_3H_9OP [33796-25-7] **Fig. 31**

3. Bis(Hydroxymethyl)methylphosphine, $C_3H_9O_2P$ [20278-51-7] **Fig. 32**

4. Chlorodiethylphosphine (diethylphosphinous chloride), $C_4H_{10}ClP$ [686-69-1] **Figs. 25, 25A-E**

5. Bis(Dimethylamino)methylphosphine(N,N'-tetramethylmethylphosphonous diamide), $C_5H_{15}N_2P$ [14937-39-4] **Figs. 41, 42A-D**

6. Dichlorophenylphosphine (phenylphosphonous dichloride), $C_6H_5Cl_2P$ [644-97-3] **Figs. 7A-B, 8A-B**

7. Dimethoxyphenylphosphine (dimethyl phenylphosphonite), $C_8H_{11}O_2P$ [2946-61-4] **Figs. 14, 15A-B**

8. Dimethylphenylphosphine, $C_8H_{11}P$ [672-66-2] **Figs. 12, 13**

9. Ethylmethylphenylphosphine, $C_9H_{13}P$ [15849-84-0] **Figs. 26, 26A-C**

10. Di-*n*-butylmethylphosphine, $C_9H_{21}P$ [3374-48-0] **Fig. 27**

11. Chlorodiphenylphosphine, $C_{12}H_{10}ClP$ [1079-66-9] **Figs. 3, 4A-C, 5, 6**

12. Diphenylphosphine, $C_{12}H_{11}P$ [829-85-6] **Figs. 5, 10, 11A-B**

13. Tri-*n*-butylphosphine, $C_{12}H_{27}P$ [998-40-3] **Fig. 34**

14. Tris(N,N-diethylamino)phosphine (hexaethylphosphorous triamide), $C_{12}H_{30}N_3P$ [2283-11-6] **Figs. 43, 44A-C**

15. Methyldiphenylphosphine, $C_{13}H_{13}P$ [1486-28-8] **Figs. 19, 20A-C**

16. Diphenylmethoxyphosphine (methyl diphenylphosphinite), $C_{13}H_{13}OP$ [4020-99-9] **Figs. 17, 18A-B**

17. Diphenylvinylphosphine, $C_{14}H_{13}P$ [2155-96-6] **Figs. 24, 24A-D**

18. Ethyldiphenylphosphine, $C_{14}H_{15}P$ [607-01-2] **Fig. 30**

19. Di-*n*-butylphenylphosphine, $C_{14}H_{23}P$ [6372-44-7] **Fig. 28**

20. Diphenyl-2-cyanoethylphosphine, $C_{15}H_{14}NP$ [5032-65-5] **Fig. 21**

21. Isopropyldiphenylphosphine, $C_{15}H_{17}P$ [6372-40-3] **Fig. 23**

22. Butyldiphenylphosphine, $C_{16}H_{19}P$ [6372-41-4] **Fig. 29**

23. Triphenylphosphine, $C_{18}H_{15}P$ [603-35-0] **Fig. 22**

24. Tri-*n*-octylphosphine, $C_{24}H_{51}P$ [4731-53-7] **Fig. 35**

25. **DPM**, Bis(diphenylphosphino)methane, $C_{25}H_{22}P_2$ [2071-20-7] **Fig. 36**

26. 4-(Diisopropylaminomethyl)triphenylphosphine, $C_{25}H_{30}NP$ [98816-60-5] **Fig. 33**

27. **DIPHOS**, Ethylene bis(diphenylphosphine) or 1,2-Bis(diphenylphosphino)ethane, $C_{26}H_{24}P_2$ [1663-45-2] **Fig. 37**

28. 1,3-Bis(Diphenylphosphino)propane, $C_{27}H_{26}P_2$ [6737-42-4] **Fig. 38**

29. 1,4-Bis(Diphenylphosphino)butane, $C_{28}H_{28}P_2$ [7688-25-7] **Fig. 39**

30. **TRIPHOS**, Bis(2-Diphenylphosphinoethyl)phenylphosphine, $C_{34}H_{33}P_3$ [23582-02-7] **Fig. 40**

2.3.2 **Phosphites** $P(OR)_3$

1. Ethyl dichlorophosphite (ethyl phosphorodichloridite), $C_2H_5Cl_2OP$ [1498-42-6] **Figs. 45, 46**

2. Dimethyl phosphite (*see* dimethyl hydrogenphosphonate, dimethyl phosphonate), $C_2H_7O_3P$ [868-85-9] **Figs. 181, 182A-B**

3. Isopropyl dichlorophosphite (isopropyl phosphorodichoridite), $C_3H_7Cl_2OP$ [3140-66-7] **Figs. 47, 48A-B**

4. **TMP**, Trimethyl phosphite, $C_3H_9O_3P$ [121-45-9] **Figs. 61, 62**

5. 2,2,2-Trichloro-1,1-dimethylethyl dichlorophosphite (2,2,2-trichloro-1, 1-dimethylethyl phosphorodichloridite), $C_4H_6Cl_5OP$ [39177-74-7] **Figs. 55, 56A-C**

6. *n*-Butyl dichlorophosphite (*n*-butyl phosphorodichoridite), $C_4H_9Cl_2OP$ [10496-13-6] **Figs. 49, 50**

7. Diethyl chlorophosphite (diethyl chlorophosphonite, diethyl phosphorochloridite) $C_4H_{10}ClO_2P$ [589-57-1] **Figs. 51, 52**

8. Diethyl phosphite (*see* diethyl hydrogenphosphonate, diethyl phosphonate), $C_4H_{11}O_3P$ [762-04-9] **Figs. 183, 184A-B**

9. **MP**, Diethyl methyl phosphite, $C_5H_{13}O_3P$ **Figs. 53, 54A-B**

10. Dimethyl trimethylsilyl phosphite, $C_5H_{15}O_3PSi$ [36198-87-5] **Figs. 76, 77A-C**

11. 2-Chlorophenyl dochlorophosphite (2-chlorophenyl phosphorodichloridite). $C_6H_4Cl_3OP$ [56225-92-4] **Figs. 57, 58A-B**

12. Tris(2,2,2-Trifluoroethyl) phosphite, $C_6H_6F_9O_3P$ [370-69-4] **Figs. 67, 68**

13. Tris(2-Chloroethyl) phosphite, $C_6H_{12}Cl_3O_3P$ [140-08-9] **Figs. 65, 66**

14. **TEP**, Triethyl phosphite, $C_6H_{15}O_3P$ [122-52-1] **Figs. 63, 64**

15. Diisopropyl phosphite (*see* diisopropyl hydrogenphosphonate), $C_6H_{15}O_3P$ [1809-20-7] **Figs. 185, 186A-B**

16. Diethyl trimethylsilyl phosphite, $C_7H_{19}O_3PSi$ [13716-45-5] **Figs. 78, 79A-F**

17. Dibutyl phosphite (*see* dibutyl hydrogenphosphonate), $C_8H_{19}O_3P$ [1809-19-4] **Figs. 187, 188**

18. Di-tert-Butyl phosphite (*see* di-*t*-butyl hydrogenphosphonate), $C_8H_{19}O_3P$ **Figs. 189, 190A-B**

19. Triallyl phosphite, $C_9H_{15}O_3P$ **Figs. 73, 74, 75**

21. Benzyl diethyl phosphite, $C_{11}H_{17}O_3P$ [2768-31-2] **Figs. 59, 60**

22. Diphenyl phosphite (*see* diphenyl hydrogenphosphonate), $C_{12}H_{11}O_3P$ [4712-55-4] **Figs. 196, 197**

23. Tributyl phosphite, $C_{12}H_{27}O_3P$ [102-85-2] **Figs. 71, 72**

24. Dibenzyl phosphite (*see* dibenzyl hydrogenphosphonate), $C_{14}H_{15}O_3P$ [17176-77-1] **Fig. 198**

25. **BIS**, Bis(2-Ethylhexyl hydrogen phosphite), *see* bis(2-ethylhexyl) hydrogenphosphonate, $C_{16}H_{35}O_3P$ [3658-48-8] **Figs. 191, 192A-C**

26. Dilauryl phosphite (*see* dilauryl hydrogenphosphonate), $C_{24}H_{51}O_3P$ [21302-90-9] **Figs. 193, 194**

2.3.3 **Phosphonites** **R-P(OR)$_2$**

1. Diethyl chlorophosphite (diethyl phosphorochloridite, diethyl chlorophosphite), (See Section 3.2.4), $C_4H_{10}ClO_2P$ [589-57-1] **Figs. 51, 52**

2. Dimethyl ethylphosphonite, $C_4H_{11}O_2P$ [2511-19-5] **Figs. 82, 83A-E**

3. **MR**, Ethyl methyl methylphosphonite, $C_4H_{11}O_2P$ **Figs. 80, 81A-C**

4. **TR**, Diethyl methylphosphonite, $C_5H_{13}O_2P$ **Figs. 84, 85A-E**

5. Diethyl ethylphosphonite, $C_6H_{15}O_2P$ [2651-85-6] **Figs. 86, 87A-B**

6. Dimethyl phenylphosphonite (*see* dimethoxyphenylphosphine, Section 3.1.6) $C_8H_{11}O_2P$ [2946-61-4] **Figs. 14, 15A-B**

7. **QL**, Ethyl 2-diisopropylaminoethyl methylphosphonite, $C_{11}H_{26}NO_2P$ [57856-11-8] **Figs. 91A-B, 92A-B**

8. Dibutyl butylphosphonite, $C_{12}H_{27}O_2P$ [2950-47-2] **Figs. 88, 89A-B**

9. Di-*n*-butyl phenylphosphonite, $C_{14}H_{23}O_2P$ **Fig. 90**

10. **LT**, Bis(2-diisopropylaminoethyl) methylphosphonite, $C_{17}H_{39}N_2O_2P$ [57856-12-9] **Figs. 94, 95A-B**

11. Methyl pinacolyl methylphosphonite, $C_8H_{19}O_2P$ **Figs. 96, 97**

2.3.4 **Phosphinites** **$(R)_2P$-OR**

1. Methyl di-*n*-butylphosphinite, $C_9H_{21}OP$ [17383-45-8] **Figs. 98, 99A-B**

2. Methyl di-*tert*-butylphosphinite, $C_9H_{21}OP$ **Figs. 100, 101A-B**

3. Methyl diphenylphosphinite (*see* diphenylmethoxyphosphine, Section 3.1.7), $C_{13}H_{13}OP$ **Figs. 17, 18A-B**

4. Butyl diphenylphosphinite, $C_{16}H_{19}OP$ **Fig. 102**

2.3.5 **Phosphoric Acids** **$(HO)_3P=O$**

1. Phosphoric acid, H_3PO_4 [7664-38-2] **Fig. 103**

2. Di-(2-Ethylhexyl) phosphoric acid, $C_{16}H_{35}O_4P$ [298-07-7] **Fig. 104**

2.3.6 **Phosphonic Acids** **$R-P=O(OH)_2$**

1. Phosphorous acid, H_3O_3P [13598-36-2] **Fig. 105**

2. Trichloromethylphosphonic acid, $CH_2Cl_3O_3P$ [5994-41-2] **Fig. 110**

3. Dichloromethylphosphonic acid, $CH_3Cl_2O_3P$ [13113-88-7] **Fig. 109**

4. Disodium salt of methylphosphonic acid, $CH_3Na_2O_3P$ **Fig. 112**

5. Chloromethylphosphonic acid, CH_4ClO_3P [2565-58-4] **Fig. 108**

6. **Fluoro Acid**, methylphosphonofluoridic acid, CH_4FO_2P [1511-67-7] **Fig. 142**

7. Mono sodium salt of methylphosphonic acid, CH_4NaO_3P **Fig. 111**

8. **MPA**, Methylphosphonic acid, CH_5O_3P [13590-71-1] [993-13-5] **Fig. 106**

9. Hydroxymethylphosphonic acid, CH_5O_4P [2617-47-2] **Fig. 107**

10. Methylenediphosphonic acid, $CH_6O_6P_2$ [1984-15-2] **Fig. 138**

11. Phosphonoacetic acid (carboxymethyphosphonic acid), $C_2H_5O_5P$ [4408-78-0] **Fig. 119**

12. 2-Chloroethylphosphonic acid, $C_2H_6ClO_3P$ [16672-87-0] **Fig. 114**

13. Ethylphosphonic acid, $C_2H_2O_3P$ [6779-09-5] **Fig. 113**

14. Aminoethylphosphonic acid, $C_2H_8NO_3P$ [6323-97-3] **Fig. 115**

15. 2-Aminoethylphosphonic acid, $C_2H_8NO_3P$ [2041-14-7] **Fig. 116**

16. 1,1-Ethylenediphosphonic acid, $C_2H_8O_6P_2$ **Fig. 139**

17. 1,2-Ethylenediphosphonic acid, $C_2H_8O_6P_2$ [6145-31-9] **Fig. 139**

18. 2-Carboxyethylphosphonic acid (3-phosphonopropionic acid), $C_3H_7O_5P$ [5962-42-5] **Fig. 118**

19. **EMPA, VX Acid**, Ethyl methylphosphonic acid, $C_3H_9O_3P$ [1832-53-7] **Fig. 143**

20. Propylphosphonic acid, from the hydrolysis of propylphosphonic dichloride, $C_3H_9O_3P$ **Fig. 120**

21. Isopropylphosphonic acid, $C_3H_9O_3P$ [4721-37-3] **Fig. 121**

22. 3-Aminopropylphosphonic acid, $C_3H_{10}NO_3P$ [13138-33-5] **Fig. 117**

23. Dimethylmethylenediphosphonic acid, $C_3H_{10}O_6P_2$ **Fig. 140**

24. Propylenediphosphonic acid, $C_3H_{10}O_6P_2$ [4671-82-3] **Fig. 141**

25. *n*-Butylphosphonic acid, $C_4H_{11}O_3P$ [3321-64-0] **Fig. 122**

26. *t*ert-Butylphosphonic acid, $C_4H_{11}O_3P$ [4923-84-6] **Fig. 123**

27. **IMPA, GB Acid**, Isopropyl methylphosphonic acid, $C_4H_{11}O_3P$ [5514-35-2] **Fig. 144**

28. **EIPA**, Ethyl isopropylphosphonic acid, $C_5H_{13}O_3P$ **Fig. 145**

29. *n*-Pentylphosphonic acid, $C_5H_{13}O_3P$ [4672-26-8] **Fig. 124**

30. Phenylphosphonic acid, $C_6H_7O_3P$ [1571-33-1] **Fig. 135**

31. Cyclohexylphosphonic acid, $C_6H_{13}O_3P$ [1005-23-8] **Fig. 134**

32. *n*-Hexylphosphonic acid, $C_6H_{15}O_3P$ [4721-24-8] **Fig. 125**

33. 4-Methoxyphenylphosphonic acid, $C_7H_9O_4P$ [21778-19-8] **Fig. 136**

34. **GF Acid**, Cyclohexyl methylphosphonic acid, $C_7H_{15}O_3P$ [1932-60-1] **Fig. 147**

35. *n*-Heptylphosphonic acid, $C_7H_{17}O_3P$ [4721-16-8] **Fig. 126**

36. **GD Acid**, Pinacolyl methylphosphonic acid, $C_7H_{17}O_3P$ [616-52-4] **Fig. 146**

37. 2-Methylcyclohexyl methylphosphonic acid, $C_8H_{17}O_3$ **Fig. 148**

38. *n*-Octylphosphonic acid, $C_8H_{19}O_3P$ [4724-48-5] **Fig. 127**

39. *n*-Nonylphosphonic acid, $C_9H_{21}O_3P$ [4730-79-4] **Fig. 128**

40. *n*-Declyphosphonic acid, $C_{10}H_{23}O_3P$ [6874-60-8] **Fig. 129**

41. 1-Naphthylmethylphosphonic acid, $C_{11}H_{11}O_3P$ **Fig. 137**

42. *n*-Undecylphosphonic acid, $C_{11}H_{25}O_3P$ **Fig. 130**

43. *n*-Tetradecylphosphonic acid, $C_{14}H_{31}O_3P$ [4671-75-4] **Fig. 131**

44. *n*-Heptadecylphosphonic acid, $C_{17}H_{37}O_3P$ **Fig. 132**

45. *n*-Octadecylphosphonic acid, $C_{18}H_{39}O_3P$ [4724-47-4] **Fig. 133**

2.3.7 **Phosphinic Acids** **$HO\text{-}P{=}O(R)_2$**

1. Hypophosphorous acid, H_3O_2P [6303-21-5] **Fig. 149**
2. Dimethylphosphinic acid, $C_2H_7O_2P$ [16391-06-3] **Fig. 150**
3. Bis(Hydroxymethyl)phosphinic acid, $C_2H_7O_4P$ [2074-67-1] **Fig. 151**
4. Diethylphosphinic acid, $C_4H_{11}O_2P$, from the hydrolysis of diethylphosphinic chloride (*see* Section 3.5.9.3) **Fig. 275**
5. Phenylphosphinic acid, $C_6H_7O_2P$ [1779-48-2] **Fig. 153**
6. Di-*n*-butylphosphinic acid, $C_8H_{19}O_2P$ [866-32-0] **Fig. 152**
7. Diphenylphosphinic acid, $C_{12}H_{11}O_2P$ [17077-03-5] **Fig. 154**
8. Bis(4-Methoxyphenyl)phosphinic acid, $C_{14}H_{15}O_4P$ [20434-05-3] **Fig. 155**

2.3.8 **Phosphine Oxides** **$(R)_3P{=}O$**

1. Trimethylphosphine Oxide, C_3H_9OP [676-96-0] **Fig. 156**
2. Tris(Hydroxymethyl)phosphine oxide (phosphinylidynetrimethanol), $C_3H_9O_4P$ [1067-12-5] **Fig. 157**
3. Di-*n*-butylphosphine oxide, $C_8H_{19}OP$ [15754-54-8] **Fig. 158**
4. Diphenylphosphine oxide, $C_{12}H_{11}OP$ [4559-70-0] **Fig. 163**
5. Methyl(*n*-butyl)benzylphosphine oxide, $C_{12}H_{19}OP$ **Fig. 166**
6. Tributylphosphine oxide, $C_{12}H_{27}OP$ [814-29-9] **Fig. 159**
7. Diphenyl(Methoxymethyl)phosphine oxide, $C_{14}H_{15}O_2P$ [4455-77-0] **Fig. 165**
8. Isopropyldiphenylphosphine oxide, $C_{15}H_{17}OP$ **Fig. 162**

9. Triphenylphosphine oxide, $C_{18}H_{15}OP$ [791-28-6] **Fig. 164**

10. Tricyclohexylphosphine oxide, $C_{18}H_{33}OP$ [13689-19-5] **Fig. 161**

11. Tri-*n*-Octylphosphine oxide, $C_{24}H_{51}OP$ [78-50-2] **Fig. 160**

2.3.9 **Phosphonic Halides** **R-P=O(X)$_2$**

1. Methylphosphonic chlorofluoride, CH_3ClFOP **Fig. 167**

2. Dichloromethylphosphonic dichloride, $CHCl_4OP$ **Fig. 170**

3. Chloromethylphosphonic dichloride, CH_2Cl_3OP [1983-26-2] **Figs. 168, 169**

4. **DC**, **Dichlor**, Methylphosphonic dichloride, CH_3Cl_2OP [676-97-1] **Fig. 171**

5. **DF**, **Difluor**, Methylphosphonic difluoride, CH_3F_2OP [676-99-3] **Fig. 172**

6. Methylphosphonocyanidic fluoride, C_2H_3FNOP **Fig. 173**

7. Ethylphosphonic dichloride, $C_2H_5Cl_2OP$ [1066-50-8] **Figs. 174, 175A-B**

8. Propylphosphonic dichloride, $C_3H_7Cl_2OP$ [4708-04-7] **Figs. 176, 177**

9. *tert*-Butylphosphonic difluoride, $C_4H_9F_2OP$ **Fig. 178**

10. Phenylphosphonic dichloride, $C_6H_5Cl_2OP$ [824-72-6] **Figs. 179, 180A-B**

2.3.10 **Phosphonates** **R-P=O(OR)$_2$**

1. Dimethyl hydrogenphosphonate (dimethyl phosphite), $C_2H_7O_3P$ [868-85-9] **Figs. 181, 182A-B**

2. **DMMP**, Dimethyl methylphosphonate, $C_3H_9O_3P$ [756-79-6] **Figs. 199, 200**

3. Ethyl methylphosphonocyanidate, $C_4H_8NO_2P$ **Figs. 202, 203A-B**

4. Dimethyl vinylphosphonate, $C_4H_9O_3P$ [4645-32-3] **Fig. 246**

5. Trimethyl phosphonoformate, $C_4H_9O_5P$ [31142-23-1] **Fig. 259**

6. Diethyl hydrogenphosphonate (diethyl phosphite), $C_4H_{11}O_3P$ [762-04-9] **Figs. 183, 184A-B**

7. **EMMP**, Ethyl methyl methylphosphonate, $C_4H_{11}O_3P$ **Fig. 201**

8. Dimethyl methylthiomethylphosphonate, $C_4H_{11}O_3PS$ **Fig. 224**

9. Dimethyl 2-hydroxyethylphosphonate, $C_4H_{11}O_4P$ [54731-72-5] **Fig. 234**

10. Ethyl 2,2-Dichlorovinyl methylphosphonate, $C_5H_9Cl_2O_3P$ **Fig. 206**

11. Diethyl trichloromethylphosphonate, $C_5H_{10}Cl_3O_3P$ [866-23-9] **Fig. 235**

12. Diethyl cyanophosphonate, $C_5H_{10}NO_3P$ [2942-58-7] **Figs. 236, 237A-C**

13. Dimethyl (2-Oxopropyl)phosphonate, $C_5H_{11}O_4P$ [4202-14-6] **Fig. 257**

14. Trimethyl phosphonoacetate (dimethyl methoxycarbonylmethylphosphonate), $C_5H_{11}O_5P$ [5927-18-4] **Fig. 261**

15. Diethyl chloromethylphosphonate, $C_5H_{12}ClO_3P$ [3167-63-3] **Figs. 217, 218A-B**

16. **TRO, DEMP,* WJ**, Diethyl methylphosphonate, $C_5H_{13}O_3P$ [683-08-9] **Figs. 204, 205**

17. Dimethyl *n*-propylphosphonate, $C_5H_{13}O_3P$ **Fig. 240**

18. Diethyl hydroxymethylphosphonate, $C_5H_{13}O_4P$ [3084-40-0] **Fig. 219**

19. Tetramethyl methylenediphosphonate, $C_5H_{14}O_6P_2$ [16001-93-7] **Fig. 267**

20. Diallyl hydrogenphosphonate (diallyl phosphite), $C_6H_{11}O_3P$ **Fig. 195**

21. Trimethyl 2-phosphonoacrylate, $C_6H_{11}O_5P$ [55168-74-6] **Fig. 265**

***DEMP** has also been used to refer to diethyl methyl phosphite (**MP**), $CH_3OP(OCH_2CH_3)_2$.

22. Dimethyl cyanomethylphosphonate, $C_6H_{12}NO_3P$ [2537-48-6] **Figs. 220, 221A-B**

23. Diethyl isocyanomethylphosphonate, $C_6H_{12}NO_3P$ [41003-94-5] **Figs. 222, 223A-F**

24. Diethyl vinylphosphonate $C_6H_{13}O_3P$ [682-30-4] **Fig. 247**

25. **DEEP**, Diethyl ethylphosphonate, $C_6H_{15}O_3P$ [78-38-6] **Figs. 238, 239A-B**

26. Diisopropyl hydrogenphosphonate (diisopropyl phosphite), $C_6H_{15}O_3P$ [1809-20-7] **Fig. 185, 186A-B**

27. Diethyl (methylthiomethyl)phosphonate, $C_6H_{15}O_3PS$ [28460-01-7] **Fig. 225**

28. Bis(2,2,2-Trifluoroethyl) (methoxycarbonylmethyl)phosphonate $C_7H_9F_6O_5P$ [88738-78-7] **Fig. 229**

29. Diethyl allylphosphonate, $C_7H_{15}O_3P$ [1067-87-4] **Fig. 248**

30. Methyl diethylphosphonoacetate, $C_7H_{15}O_5P$ [1067-74-9] **Fig. 262**

31. Triethyl phosphonoformate (ethyl diethoxyphosphinylformate), $C_7H_{15}O_5P$ [1474-78-8] **Fig. 260**

32. **DIMP**, Diisopropyl methylphosphonate, $C_7H_{17}O_3P$ [1445-75-6] **Figs. 207, 208**

33. Diethyl *n*-propylphosphonate, $C_7H_{17}O_3P$ **Fig. 241**

34. **DEIP**, diethyl isopropylphosphonate, $C_7H_{17}O_3P$ **Fig. 242**

35. Diethyl (ethylthiomethyl)phosphonate $C_7H_{17}O_3PS$ [54091-78-0] **Fig. 226**

36. Disopropyl cyanomethylphosphonate, $C_8H_{16}NO_3P$ [58264-04-3] **Figs. 232, 233**

37. Dimethyl cyclohexylphosphonate, $C_8H_{17}O_3P$ **Fig. 250**

38. Triethyl phosphonoacetate (diethyl ethoxycarbonylmethylphosphonate), $C_8H_{17}O_3P$ [867-13-0] **Fig. 263**

39. Dibutyl hydrogenphosphonate (dibutyl phosphite), $C_8H_{19}O_3P$ [1809-19-4] **Figs. 187, 188**

40. Di-*tert*-butyl hydrogenphosphonate (di-*tert*-butyl phosphite), $C_8H_{19}O_3P$ [13086-84-5] **Figs. 189, 190A-B**

41. Pinacolyl 2,2-Dichlorovinyl methylphosphonate, $C_9H_{17}Cl_2O_3P$ **Figs. 212, 213**

42. Dimethyl (2-oxoheptyl)phosphonate, $C_9H_{19}O_4P$ [36969-89-8] **Fig. 258**

43. Triethyl 2-Phosphonopropionate, $C_9H_{19}O_5P$ [3699-66-9] **Fig. 264**

44. Diethyl pyrrolidinomethylphosphonate, $C_9H_{20}NO_3P$ [51868-96-3] **Fig. 228**

45. Diethyl (trimethylsilyloxycarbonylmethyl)phosphonate (trimethylsilyl P,P-diethylphosphonoacetate, $C_9H_{21}O_5PSi$ [66130-90-3] **Figs. 230, 231A-C**

46. Tetraethyl methylenediphosphonate, $C_9H_{22}O_6P_2$ [1660-94-2] **Fig. 268**

47. Diethyl phenylphosphonate, $C_{10}H_{15}O_3P$ **Fig. 251**

48. Triethyl 4-phosphonocrotonate, $C_{10}H_{19}O_5P$ [20345-62-4] **Fig. 266**

49. Diethyl hexyphosphonate, $C_{10}H_{23}O_3P$ **Fig. 244**

50. Benzyl isopropyl methylphosphonate, $C_{11}H_{17}O_3P$ **Fig. 210**

51. Diethyl benzylphosphonate, $C_{11}H_{17}O_3P$ [1080-32-6] **Figs. 253, 254**

52. Diethyl (phenylthiomethyl)phosphonate, $C_{11}H_{17}O_3PS$ [38006-16-9] **Fig. 227**

53. Diethyl 4-Aminobenzylphosphonate, $C_{11}H_{18}NO_3P$ [20074-79-7] **Fig. 255**

54. D-*n*-butyl allylphosphonate, $C_{11}H_{23}O_3P$ **Fig. 249**

55. Diethyl *n*-heptylphosponate, $C_{11}H_{25}O_3P$ **Fig. 245**

56. **QLO, QB**, Ethyl 2-diisopropylaminoethyl methylphosphonate $C_{11}H_{26}NO_3P$ [71840-26-11] **Fig. 214**

57. Diphenyl hydrogenphosphonate (diphenyl phosphite), $C_{12}H_{11}O_3P$ [4712-55-4] **Figs. 196, 197**

58. **DBBP**, Dibutyl butylphosphonate, $C_{12}H_{27}O_3P$ [78-46-6] **Fig. 243**

59. **DPMP**, Dipinacolyl methylphosphonate [bis(1,2,2-trimethylpropyl) methylphosphonate], $C_{13}H_{29}O_3P$ [7040-58-6] **Fig. 209**

60. Tetraisopropyl methylenediphosphonate, $C_{13}H_{30}O_6P_2$ [1660-95-3] **Fig. 270**

61. Dibenzyl hydrogenphosphonate (dibenzyl phosphite), $C_{14}H_{15}O_3P$ [17176-77-1] **Fig. 198**

62. Dibenzyl methylphosphonate, $C_{15}H_{17}O_3P$ **Fig. 211**

63. **BIS**, Bis(2-Ethylhexyl) hydrogenphosphonate [bis(2-ethylhexyl) hydrogen phosphite], $C_{16}H_{35}O_3P$ [3658-48-8] **Figs. 191, 192A-B**

64. **LTO, LTA,** Bis(2-diisopropylaminoethyl) methylphosphonate, $C_{17}H_{39}N_2O_3P$ **Figs. 215, 216**

65. Bis(4-Nitrophenyl) phenylphosphonate, $C_{18}H_{13}N_2O_7P$ [38872-91-5] **Fig. 256**

66. Tetraethyl decamethylenediphosphonate, $C_{18}H_{40}O_6P_2$ [5943-62-4] **Fig. 269**

67. Dioctyl phenylphosphonate, $C_{22}H_{39}O_3P$ [1754-47-8] **Fig. 252**

68. Dilauryl hydrogenphosphonate (dilauryl phosphite), $C_{24}H_{51}O_3P$ [21302-90-9] **Figs. 193, 194**

2.3.11 <u>Phosphinic Halides</u> $(R)_2P{=}O(X)$

1. Methylphosphinic fluoride, CH_4FOP **Figs. 271, 272**

2. Chloromethylmethylphosphinic fluoride, C_2H_5ClFOP **Fig. 273**

3. Diethylphosphinic chloride (chlorodiethylphosphine oxide), $C_4H_{10}ClOP$ **Figs. 274, 275**

4. Diphenylphosphinic chloride (chlorodiphenylphosphine oxide) $C_{12}H_{10}ClOP$ [1499-21-4] **Figs. 276, 277**

2.3.12 **Phosphinates** **$(R)_2P{=}O(OR)$**

1. **YL**, Ethyl hydrogenmethylphosphinate, $C_3H_9O_2P$ [16391-07-4] **Fig. 278**
2. Ethyl trichloromethylmethylphosphinate, $C_4H_8Cl_3O_2P$ **Fig. 280**
3. Ethyl trifluoromethylmethylphosphinate, $C_4H_8F_3O_2P$ **Fig. 283**
4. Ethyl chloromethylmethylphonphinate, $C_4H_{10}ClO_2P$ **Fig. 281**
5. Isopropyl hydrogenmethylphosphinate, $C_4H_{11}O_2P$ **Fig. 439**
6. Trimethylsilyl methylphosphinate, $C_4H_{13}O_2PSi$ **Figs. 289, 290**
7. **TRX**, Ethyl ethylmethylphosphinate, $C_5H_{13}O_2P$ **Fig. 279**
8. Isobutyl hydrogenmethylphosphinate, $C_5H_{13}O_2P$ **Figs. 287, 288A-C**
9. Cyclopentyl hydrogenmethylphosphinate, $C_6H_{13}O_2P$ **Fig. 440**
10. Ethyl chloromethylphenylphosphinate, $C_9H_{12}ClO_2P$ **Fig. 282**
11. **QA**, 2-Diisopropylaminoethyl methylphosphinate, $C_9H_{22}NO_2P$ [86894-09-9] **Figs. 284, 285A-B**
12. **QC**, 2-Diisopropylaminoethyl ethylmethylphosphinate, $C_{11}H_{26}NO_2P$ **Fig. 286**

2.3.13 **Phosphates** **$(RO)_3P{=}O$**

1. **MDO**, Methyl dichlorophosphate (methyl phosphorodichloridate), $CH_3Cl_2O_2P$ [677-24-7] **Figs. 306, 307**
2. 2,2,2-Tribromoethyl dichlorophosphate, $C_2H_2Br_3Cl_2O_2P$ [53676-22-5] **Figs. 315, 316**
3. 2,2,2-Trichloroethyl dichlorophosphate, $C_2H_2Cl_5O_2P$ [18868-46-7] **Figs. 313, 314A-B**
4. Ethyl dichlorophosphate (ethyl phosphorodichloridate), $C_2H_5Cl_2O_2P$ [1498-51-7] **Figs. 311, 312**

5. **TMP**, Trimethyl phosphate, $C_3H_9O_4P$ [512-56-1] **Figs. 291, 292A-B**

6. **Dichlorvos**, 2,2-Dichlorovinyl dimethyl phosphate, $C_4H_7Cl_2O_4P$ [62-73-7] **Fig. 308**

7. Diethyl chlorophosphate (diethyl phosphorochloridate), $C_4H_{10}ClO_3P$ [814-49-3] **Figs. 309, 310A-B**

8. Diethyl amidophosphate (diethyl phosphoramidate), $C_4H_{12}NO_3P$ (*see* Section 2.3.14 P-N Compounds) **Figs. 364, 365**

9. 2-Chlorophenyl dichlorophosphate (2-chlorophenyl phosphorodichloridate), $C_6H_4Cl_3O_2P$ [15074-54-1] **Figs. 319, 320**

10. 4-Chlorophenyl dichlorophosphate (4-chlorophenyl phosphorodichloridate), $C_6H_4Cl_3O_2P$ [772-79-2] **Figs. 321, 322**

11. Phenyl dichlorophosphate (phenyl phosphorodichloridate), $C_6H_5Cl_2O_2P$ [770-12-7] **Figs. 323, 324**

12. Tris(2-Chloroethyl) phosphate, $C_6H_{12}Cl_3O_4P$ [115-96-8] **Fig. 301**

13. **TEPO**, Triethyl phosphate, $C_6H_{15}O_4P$ [78-40-0] **Figs. 293, 294**

14. 6-Amino-1-hexyl phosphate, $C_6H_{16}NO_4P$ [7564-68-3] **Fig. 317**

15. Triallyl phosphate, $C_9H_{15}O_4P$ **Fig. 304**

16. Tripropyl phosphate, $C_9H_{21}O_4P$ [513-08-6] **Figs. 295, 296**

17. Tris(Trimethylsilyl) phosphate, $C_9H_{27}O_4PSi_3$ [10497-05-9] **Figs. 302, 303**

18. **Paraoxon**, Diethyl *p*-nitrophenyl phosphate, $C_{10}H_{14}NO_6P$ [311-45-5] **Fig. 318**

19. Diphenyl chlorophosphate (diphenyl phosphorochloridate), $C_{12}H_{10}ClO_3P$ [2524-64-3] **Figs. 325, 326**

20. Diphenyl phosphate, $C_{12}H_{11}O_4P$ [838-85-7] **Fig. 327**

21. Diphenyl amidophosphate (diphenyl phosphoroamidate), $C_{12}H_{12}NO_3P$ (*see* Section 2.3.14 P-N Compounds) **Figs. 368, 369A-B**

22. Tri-*n*-butyl phosphate, $C_{12}H_{27}O_4P$ [126-73-8] **Fig. 297**

23. Dibenzl phosphate, $C_{14}H_{15}O_4P$ [1623-08-1] **Fig. 328**

24. Triphenyl phosphate, $C_{18}H_{15}O_4P$ [115-86-6] **Fig. 305**

25. Tris(2-Butoxyethyl) phosphate, $C_{18}H_{39}O_7P$ [78-51-3] **Fig. 300**

26. **TOF**, Tris(2-Ethylhexyl) phosphate, $C_{24}H_{51}O_4P$ [78-42-2] **Figs. 298, 299**

2.3.14 **P-N Compounds**

1. N,N-Dimethylphosphoramidic dichloride, $C_2H_6Cl^2NOP$ [1899-02-1] **Figs. 350, 351**

2. N,N-Dimethylphosphoramidic difluoride, $C_2H_6F_2NOP$ **Figs. 352, 353A-B**

3. 2,2-Dichlorovinyl N,N-Dimethylphosphoramidofluoridate, $C_4H_7Cl_2FNO_2P$ **Fig. 360**

4. N,N-Dimethylmethylphosphonamidic cyanide, $C_4H_9N_2OP$ **Fig. 354**

5. N,N-Diethylphosphoramidous dichloride, $C_4H_{10}Cl_2NP$ [1069-08-5] **Figs. 339, 340**

6. N,N-Diethylphosphoramidous difluoride, $C_4H_{10}F_2NP$ **Fig. 341**

7. Tetramethylphosphorodiamidic chloride, $C_4H_{12}ClN_2OP$ [1605-65-8] **Figs. 355, 356A-C**

8. Diethyl phosphoramidate (diethyl amidophosphate), $C_4H_{12}NO_3P$ [1068-21-9] **Figs. 364, 365**

9. Isopropyl methylphosphonohydrazine [Isopropoxymethylphosphinyl) hydrazine], $C_4H_{13}N_2O_2P$ **Fig. 363**

10. Trimethylsilyl N,N-Dimethylphosphoramidofluoridate, $C_5H_{15}FNO_2PSi$ **Figs. 358, 359A-B**

11. Methylphosphonic bis(Dimethylamide), [N,N,N',N'-tetramethylmethyl-phosphonic diamide], $C_5H_{15}N_2OP$ [2511-17-3] **Figs. 348, 348A-F**

12. N,N'-Tetramethylmethylphosphonous diamide, [Bis(Dimethylamino) methylphosphine], $C_5H_{15}N_2P$ [14937-39-4] **Figs. 329 (41, 42A-D)**

13. Phenyl phosphorodiamidate, $C_6H_9N_2O_2P$ [7450-69-3] **Figs. 366, 367A-C**

14. Methyl N,N-Dethylmethylphosphonamidate, $C_6H_{16}NOP$ **Figs. 332, 333A-B**

15. N,N-Diethyldimethylphosphinamidate, $C_6H_{16}NOP$ **Figs. 344, 345A-B**

16. N,N-Diethylethylphosphinamidate, $C_6H_{16}NOP$ **Figs. 346, 347**

17. **HMPA**, Hexamethylphosphoramide, $C_6H_{18}N_3OP$ [680-31-9] **Fig. 357**

18. **HMPT**, Hexamethylphosphorous triamide, $C_6H_{18}N_3P$ [1608-26-0] **Figs. 330, 331A-B**

19. N,N-Diethylethylmethylphosphinamidate, $C_7H_{18}NOP$ **Figs. 342, 343**

20. Methyl N,N-Diethylethylphosphonamidite, $C_7H_{18}NOP$ **Figs. 334, 335**

21. N,N,N',N'-Tetraethylethylphosponodiamidite, $C_{10}H_{25}N_2P$ **Figs. 336, 337**

22. Diphenylphosphoryl azide, $C_{12}H_{10}N_3O_3P$ [26386-88-9] **Fig. 361**

23. Diphenylphosphinamide, $C_{12}H_{12}NOP$ [5994-87-6] **Fig. 370**

24. Diphenyl phosphoramidate, (diphenyl amidophosphate), $C_{12}H_{12}NO_3P$ [2015-56-7] **Figs. 368, 369A-B**

25. Diethyl phenethylphosphoramidate, $C_{12}H_{20}NO_3P$ [57573-91-3] **Fig. 371**

26. Hexaethylphosphorous triamide, [Tris(N,N-Diethylamino) phosphine], $C_{12}H_{30}N_3P$ **Figs. 338 (43, 44A-C)**

27. Cyanoethyl N,N,N',N'-Tetraisopropylphosphorodiamidite, $C_{15}H_{32}N_3OP$ [102691-36-1] **Fig. 362**

2.3.15 P=S (Thiono) and P-S (Thiolo) Compounds

1. Thiophosphoryl chloride, (phosphorus sulfochloride), Cl_3PS [3982-91-0] **Fig. 372**

2. **TDC,** Methylphosphonothioic dichloride, CH_3Cl_2PS [676-98-2] **Figs. 373, 374A-C**

3. **TDF, Thiono Difluor,** Methylphosphonothioic difluoride, CH_3F_2PS **Figs. 377, 378A-B**

4. Ethyl phosphorodichloridothionate, (ethyl dichlorothiophosphate), $C_2H_5Cl_2OPS$ [1498-64-2] **Figs. 380, 381**

5. **EPTD,** Ethylphosphonothioic dichloride, $C_2H_5Cl_2PS$ **Fig. 379**

6. Dimethylphosphinothioic chloride, C_2H_6ClPS [993-12-4] **Figs. 375, 376A-B**

7. Ethyl hydrogenmethylphosphinothionate, C_3H_9OPS **Fig. 379**

8. Trimethyl thiophosphate (trimethyl phosphorothionate), $C_3H_9O_3PS$ [152-18-1] **Fig. 393**

9. Trimethylphosphine sulfide, C_3H_9PS [2404-55-9] **Fig. 384**

10. Ethyl N,N-Dimethylphosphoramidothionic fluoride, $C_4H_{11}FNOPS$ **Fig. 407**

11. Isopropyl methylphosphonothionic acid, (isopropyl hydrogen methylphosphonothionate), $C_4H_{11}O_2PS$ **Fig. 406**

12. Diethyl dithiophosphate (O,O'-Diethyl S-hydrogen phosphorothiolothionate), $C_4H_{11}O_2PS_2$ [298-06-6] **Figs. 398, 399A-B**

13. Diethyl phosphorothionicacid (diethyl hydrogen phosphorothionate), $C_4H_{11}O_3PS$ **Fig. 405**

14. S,S-Dimethyl N,N-Dimethylphosphoramidodithiolate), $C_4H_{12}NOPS_2$ **Fig. 408**

15. Tetramethyldiphosphine disulfide, $C_4H_{12}P_2S_2$ **Fig. 389**

16. Diethyl dithiophosphate, ammonium salt (diethyl phosphorothiolothionic acid, ammonium salt), $C_4H_{14}NO_2PS_2$ [1068-22-0] **Fig. 400**

17. Ethyl S-(2,2-Dichlorovinyl) methylphosphonothiolate, $C_5H_9Cl_2O_2PS$ **Fig. 414**

18. **TRS,** Diethyl methylphosphonothionate, $C_5H_{13}O_2PS$ [6996-81-2] **Figs. 410, 411A-B**

19. **OSDMP,** O,S-Diethyl methylphosphonothiolate (diethyl methylphosphonothiolate), $C_5H_{13}O_2PS$ [2511-10-6] **Figs. 412, 413A-B**

20. Phenylphosphonothioic dichloride, $C_6H_5Cl_2PS$ [3497-00-5] **Figs. 382, 383**

21. Triethylphosphine sulfide, $C_6H_{15}PS$ [597-51-3] **Fig. 385**

22. Tris(N,N-Dimethylamino)phosphine sulfide (hexamethylphosphorothioic triamide), $C_6H_{18}N_3PS$ **Fig. 409**

23. Ethyl S-(2-Ethoxycarbonyl)vinyl methylphosphonothiolate, $C_8H_{15}O_4PS$ **Figs. 415, 416A-C, 417**

24. Di-*n*-Butylphosphinothionic acid, $C_8H_{19}OPS$ **Fig. 403**

25. Tetraethyldiphosphine disulfide, $C_8H_{20}P_2S_2$ **Fig. 390**

26. **Parathion,** Diethyl *p*-nitrophenyl phosphorothionate, $C_{10}H_{14}NO_5PS$ [56-38-2] **Fig. 395**

27. Diphenylphosphinothionic acid, $C_{12}H_{11}OPS$ **Fig. 404**

28. Diphenylphosphine sulfide, $C_{12}H_{11}PS$ [6591-07-7] **Fig. 397**

29. Diphenylphosphinodithioic acid (diphenylphosphinothiolothionic acid), $C_{12}H_{11}PS_2$ [1015-38-9] **Fig. 401**

30. Dicyclohexylphosphinodithioic acid, (dicyclohexylphosphinothiolothionic acid), $C_{12}H_{23}PS_2$ [2512-58-5] **Fig. 402**

31. Tri-*n*-Butylphosphine sulfide, $C_{12}H_{27}PS$ **Fig. 386**

32. Tetrabutyldiphosphine disulfide, $C_{16}H_{36}P_2S_2$ **Fig. 391**

33. Triphenylphosphine sulfide, $C_{18}H_{15}PS$ [3878-45-3] **Fig. 388**

34. Tricyclohexylphosphine sulfide, $C_{18}H_{33}PS$ **Fig. 387**

35. Tri-*p*-Tolyl thiophosphate (tri-*p*-tolyl phosphorothionate), $C_{21}H_{21}O_3PS$ **Fig. 394**

36. Tetraphenyldiphosphine disulfide, $C_{24}H_{20}P_2S_2$ **Fig. 392**

2.3.16 P=Se Compounds

1. Triethyl selenophosphate, $C_6H_{15}O_3PSe$ **Fig. 418**

2. Triphenylphosphine selenide, $C_{18}H_{15}PSe$ [3878-44-2] **Fig. 419**

2.3.17 Pyro Compounds

1. **Na_2PYRO,** Disodium dimethylpyrophosphonate, $C_2H_6Na_2O_5P_2$ **Fig. 424**

2. Methylphosphinic anhydride, (dihydrogen dimethylpyrophosphonate), $C_2H_8O_5P_2$ **Figs. 422, 423**

3. Diethyl dimethylpyrophosphonate (**VX Pyroester**), $C_6H_{16}O_5P_2$ [32288-17-8] **Fig. 425**

4. Tetraethyl pyrophosphite, $C_8H_{20}O_5P_2$ [21646-99-1] **Figs. 420, 421A-B**

5. Diethyl diethylpyrophosphonate, $C_8H_{20}O_5P_2$ **Fig. 427**

6. Diisopropyl dimethylpyrophosphonate (**GB Pyroester**), $C_8H_{20}O_5P_2$ **Fig. 426**

7. Bis(Ethyl N,N-Dimethylphosphoramidic) anhydride, [*sym*-bis(dimethylamido) diethyl pyrophosphonate], (**GA Pyro**), $C_8H_{22}N_2O_5P_2$ **Figs. 428, 429**

8. 1-Propanephosphonic acid cyclic anhydride (2,4,6-Tripropyl-1,3,5,2,4,6-Trioxatriphosphorinane 2,4,6-trioxide), $C_9H_{21}O_6P_3$ **Figs. 430, 431, 432**

2.3.18 Other Organophosphorus Compounds of Interest

1. Phosphorus tribromide, Br_3P [7789-60-8] **Figs. 457, 458**

2. **TH**, Phosphorus trichloride, Cl_3P [7719-12-2] **Figs. 455, 456**

3. Phosphorus oxychloride, (phosphoryl chloride), Cl_3OP [10025-87-3] **Fig. 459**

4. Phosphorus sulfochloride, (thiophosphoryl chloride), Cl_3PS [3982-91-0] **Fig. 460**

5. 2-Chloro-2-oxo-1,3,2-dioxaphospholane, $C_2H_4ClO_3P$ [6609-64-9] **Fig. 461**

6. N,N-Dimethylphosphoramidous dichloride, $C_2H_6Cl_2NP$ **Fig. 443**

7. N,N-Dimethylphosphoramidothionic dichloride, $C_2H_6Cl_2NPS$ **Fig. 444**

8. 2-Fluoro-1,3,2-Dioxaphosphorinane-2-oxide, $C_3H_6FO_3P$ **Fig. 435**

9. Morpholinophosphoramidic difluoride, $C_4H_8F_2NO_2P$ **Fig. 436**

10. Isopropyl methylphosphonochloridate (**Chloro GB**), $C_4H_{10}ClO_2P$ **Fig. 437**

11. Isopropyl hydrogenmethylphosphinate (isopropryl methylphosphinate), $C_4H_{11}O_2P$ **Fig. 439**

12. N,N,N',N'-Tetramethylphosphorodiamidic fluoride (**Dimefox**), $C_4H_{12}FNOP$ **Fig. 434**

13. Isopropyl methylphosphonocyanidate (**Cyano GB**), $C_5H_{10}NO_2P$ **Fig. 438**

14. Diethyl S-Methyl phosphorothiolate, (diethyl S-methyl thiophosphate), $C_5H_{13}O_3PS$ **Fig. 448**

15. Phenylphosphonothionic difluoride, $C_6H_5F_2PS$ **Fig. 445**

16. Cyclopentyl hydrogenmethylphosphinate (cyclopentyl methylphosphinate), $C_6H_{13}O_2P$ **Fig. 440**

17. Diisopropyl fluorophosphate (**DFP**), $C_6H_{14}FO_3P$ **Fig. 433**

18. Triethyl phosphorothionate (triethyl thiophosphate), $C_6H_{15}O_3PS$ **Fig. 446**

19. Diethyl S-Ethyl phosphorothiolate (diethyl S-ethyl thiophosphate), $C_6H_{15}O_3PS$ **Fig. 447**

20. Cyclohexyl methylphosphonochloridate, $C_7H_{14}ClO_2P$ **Fig. 441**

21. Pinacolyl methylphosphonofluorothionate (**Thiono GD**), $C_7H_{16}FOPS$ **Fig. 442**

22. Bis(Isopropyl methylphosphonate)barium(II), [the barium(II) salt of **GB acid** or the barium(II) salt of **IMPA**], $C_8H_{20}BaO_6P_2$ **Fig. 451**

23. Bis(Isopropyl methylphosphonate)calcium(II), [the calcium(II) salt of **GB acid** or the calcium(II) salt of **IMPA**], $C_8H_{20}CaO_6P_2$ **Fig. 452**

24. Tris(Ethyl methylphosphonate)iron(III), [the iron(III) salt of ethyl methylphosphonic acid, **EMPA**] $C_9H_{24}FeO_9P_3$ **Fig. 454**

25. 2-Diethylaminoethyl diethyl phosphite, $C_{10}H_{24}NO_3P$ **Fig. 449**

26. Bis(Diisopropyl phosphate)barium(II), $C_{12}H_{28}BaO_8P_2$ **Fig. 453**

27. Tris(Isopropyl methylphosphonate)iron(III), [the iron(III) salt of **GB acid** or the iron(III) salt of **IMPA**], $C_{12}H_{30}FeO_9P_3$ **Fig. 450**

2.3.19 **Inorganic Compounds**

1. Silver hexafluorophosphate, AgF_6P **Fig. 465**

2. Aluminum phosphate, AlO_4P **Fig. 467**

3. Potassium hexafluorophosphate, F_6KP **Fig. 463**

4. Sodium hexafluorophosphate, F_6NaP **Fig. 464**

5. Calcium phosphate dibasic, anhydrous, $HCaO_4P$ **Fig. 473**

6. Potassium phosphate dibasic, anhydrous, HK_2O_4P **Fig. 475**

7. Sodium phosphate dibasic, heptahydrate, HNa_2O_4P **Fig. 474**

8. Potassium phosphate monobasic, anhydrous, H_2KO_4P **Fig. 471**

9. Sodium hypophosphite, hydrate, H_2NaO_2P **Fig. 476**

10. Sodium phosphate, monobasic, H_2NaO_4P **Fig. 470**

11. Sodium phosphate, monobasic, monohydrate, H_2NaO_4P **Fig. 469**

12. Ammonium hexafluorophosphate, H_4F_6NP **Fig. 462**

13. Ammonium dihydrogen phosphate, H_6NO_4P **Fig. 472**

14. Sodium phosphate, tribasic, dodecahydrate, Na_3O_4P **Fig. 468**

15. Tetrabutylammonium hexafluorophosphate, $C_{16}H_{36}F_6NP$ **Fig. 466**

2.4 List of Abbreviations

Band Intensities		Vibrations	
w	weak	ν	stretching
m	medium	as	asymmetric
s	strong	sy	symmetric
v	very	δ	deformation
sh	shoulder	ω	wagging
		τ	twisting
		β	in-plane deformation
		γ	out-of-plane deformation

3. RESULTS AND DISCUSSION

3.1 Phosphines $P(R)_3$

3.1.1 Methoxydichlorophosphine, MD $(CH_3O)P(Cl)_2$

The infrared spectrum of methoxydichlorophosphine (methyl dichlorophosphite), **MD**, was determined previously[c] and is only repeated here for continuity and completeness reasons. The infrared spectrum of liquid **MD** is reproduced in ***Figure 1***. The vapor phase infrared spectrum of MD is reproduced in ***Figure 2.*** The effect of atmospheric moisture on **MD** was to produce methyl hydrogen hydrogenphosphonate $CH_3OP{=}O(H)(OH)$, which was further hydrolyzed to phosphonic acid, $HP{=}O(OH)_2$.. It is also possible that the compound **MD,** might also oxidize to form some **MDO**, methyl dichlorophosphate, $CH_3OP{=}O(Cl)_2$.

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[c] The infrared spectrum of **MD** was presented previously in "Infrared Spectroscopic Observations On The Fate Of Organophosphorus Compounds Exposed To Atmospheric Moisture. Part II. V-Agents And Related Compounds" by Piffath, R.J., 1999.

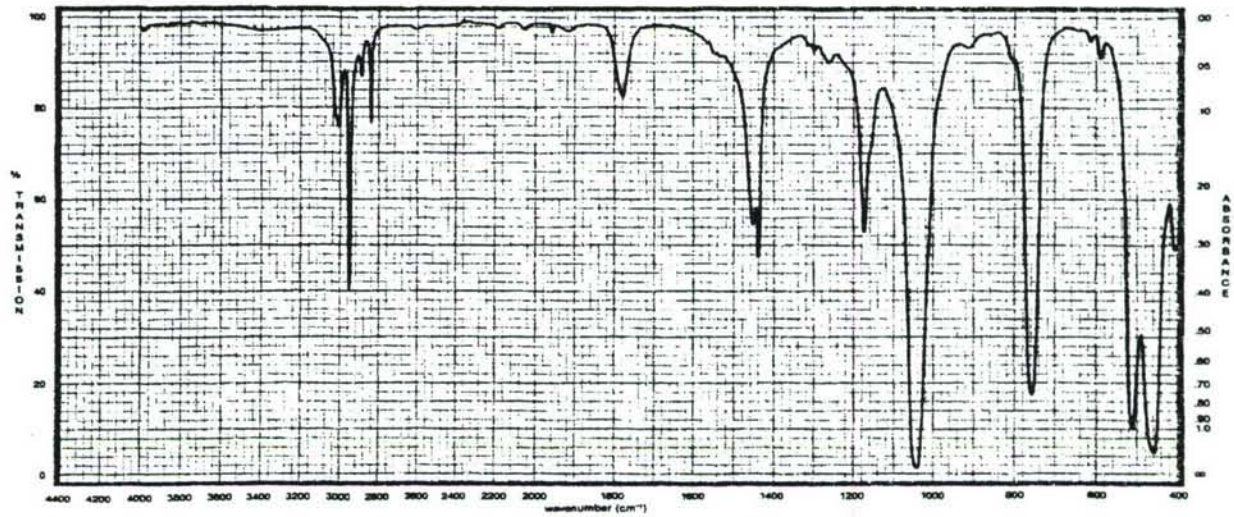

Figure 1 METHOXYDICHLOROPHOSPHINE (MD), LIQUID, CF/KBr

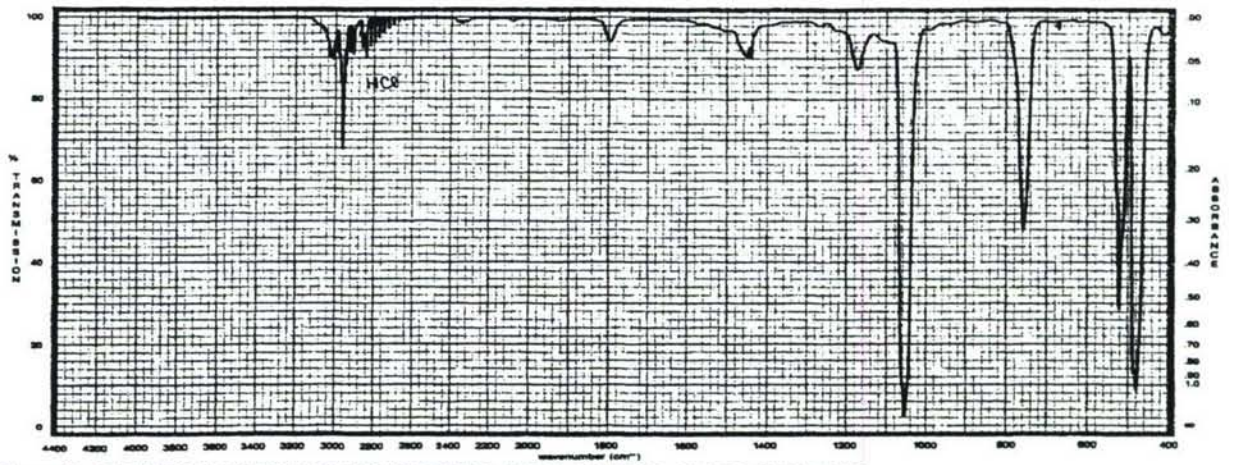

Figure 2 METHOXYDICHLOROPHOSPHINE (MD), VAPOR, 10 CM GAS CELL

3.1.2 Chlorodiphenylphosphine $ClP(C_6H_5)_2$ $C_{12}H_{10}ClP$

The infrared spectrum of chlorodiphenylphosphine is reproduced as ***Figure 3***. The band assignments are as follows: 3072 and 3056 cm^{-1} ms and 3014 and 3002 cm^{-1} m (ν C-H aromatic), 1956 w, 1886 w, 1810 w and 1761 vw cm^{-1} (mono-substituted) aromatic ring summation bands), 1585 m, 1572 w cm^{-1}, and 1478 cm^{-1} ms and 1435 cm^{-1} s (aromatic ring), 1181 w, 1068 w, 1026 m and 998 m cm^{-1} (β C-H aromatic ring), 741 cm^{-1} s (γ C-H mono-substituted aromatic ring), 693 cm^{-1} s (δ mono-substituted aromatic ring), 502 cm^{-1} s (ν P-Cl).

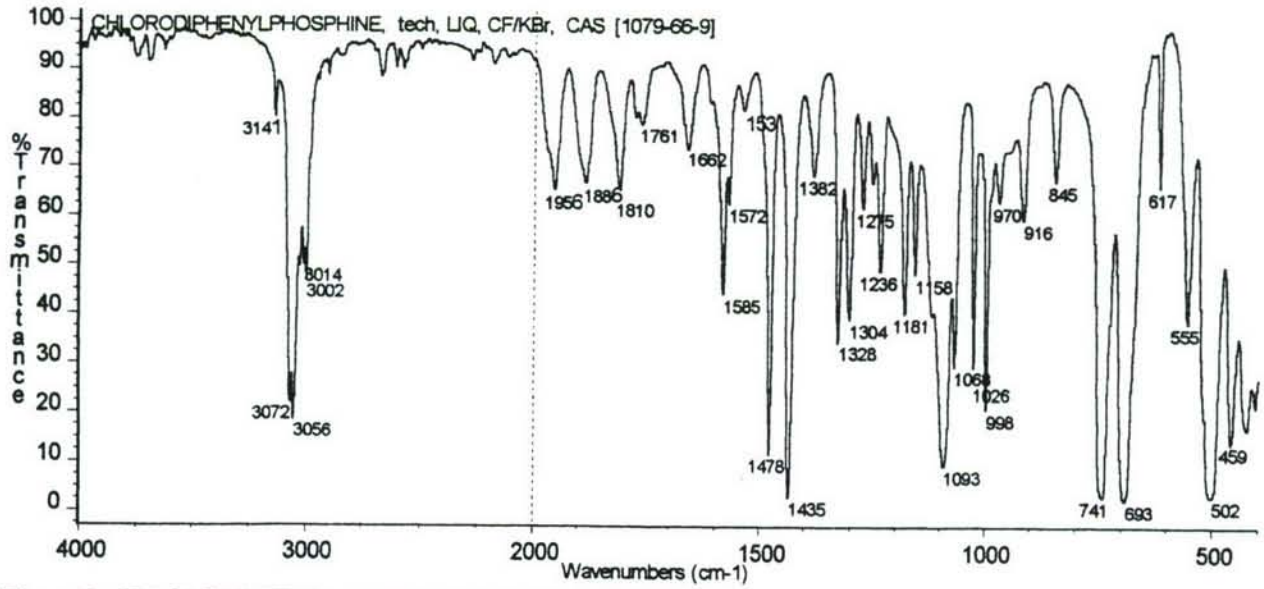

Figure 3 CHLORODIPHENYLPHOSPHINE, LIQUID, CF/KBr

The effect of atmospheric moisture on chlorodiphenylphosphine is shown in ***Figure 4.A-C***. After 2.5 hours of exposure to the atmosphere (***Figure 4A***) the background begins to show a curved shape over the 3000-2000 cm^{-1} range. A new band is just beginning to show near 805 cm^{-1}. After 4 hours a new band appears near 2283 cm^{-1} and is assigned to a P-H stretching vibration. A weak band or shoulder is also beginning to occur near 1200 cm^{-1} (possible ν P=O) and the band near 805 cm^{-1} is also increasing in intensity. These effects continue over the period 47 hours through 8 days (***Figure 4B***). However, now the P-H band near 2284 cm^{-1} seems to have an underlying broadness. A broad band seems to be forming near 2700 cm^{-1}. These "broadenings" could be assigned to the presence of a P-OH moiety. The band forming near 1200 cm^{-1} (ν P=O) is now much stronger after 19 days (***Figure 4C***). A broad band has also been forming near 960 cm^{-1} and may be assigned to a P-OH stretch. The bands indicative of a mono-substituted aromatic ring are still evident in the infrared spectrum. What appears to have happened is that the 2284 cm^{-1} band seems to be due to the P-H stretch from diphenylphosphine, $(C_6H_5)_2P$ (***Figure 5***). The P-acid bands seem to be due to diphenylphosphinic acid, $(C_6H_5)_2P{=}O(OH)$, (***Figure 5***). The end result is a mixture of diphenylphosphine and diphenylphosphinic acid. ***Figure 6*** shows a comparison of the

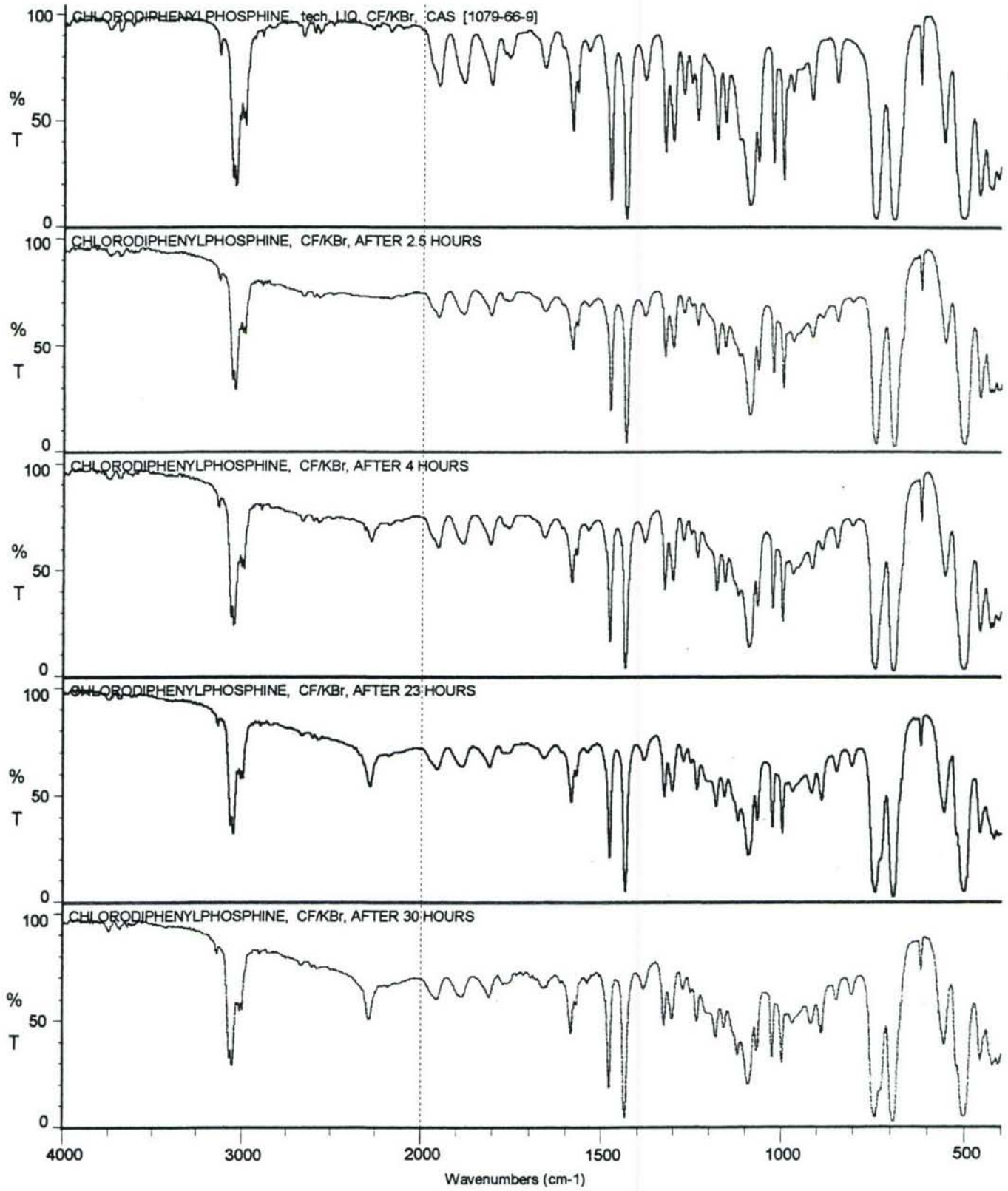

Figure 4 CHLORODIPHENYLPHOSPHINE, LIQUID, CF/KBr, AFTER ATMOSPHERIC EXPOSURE

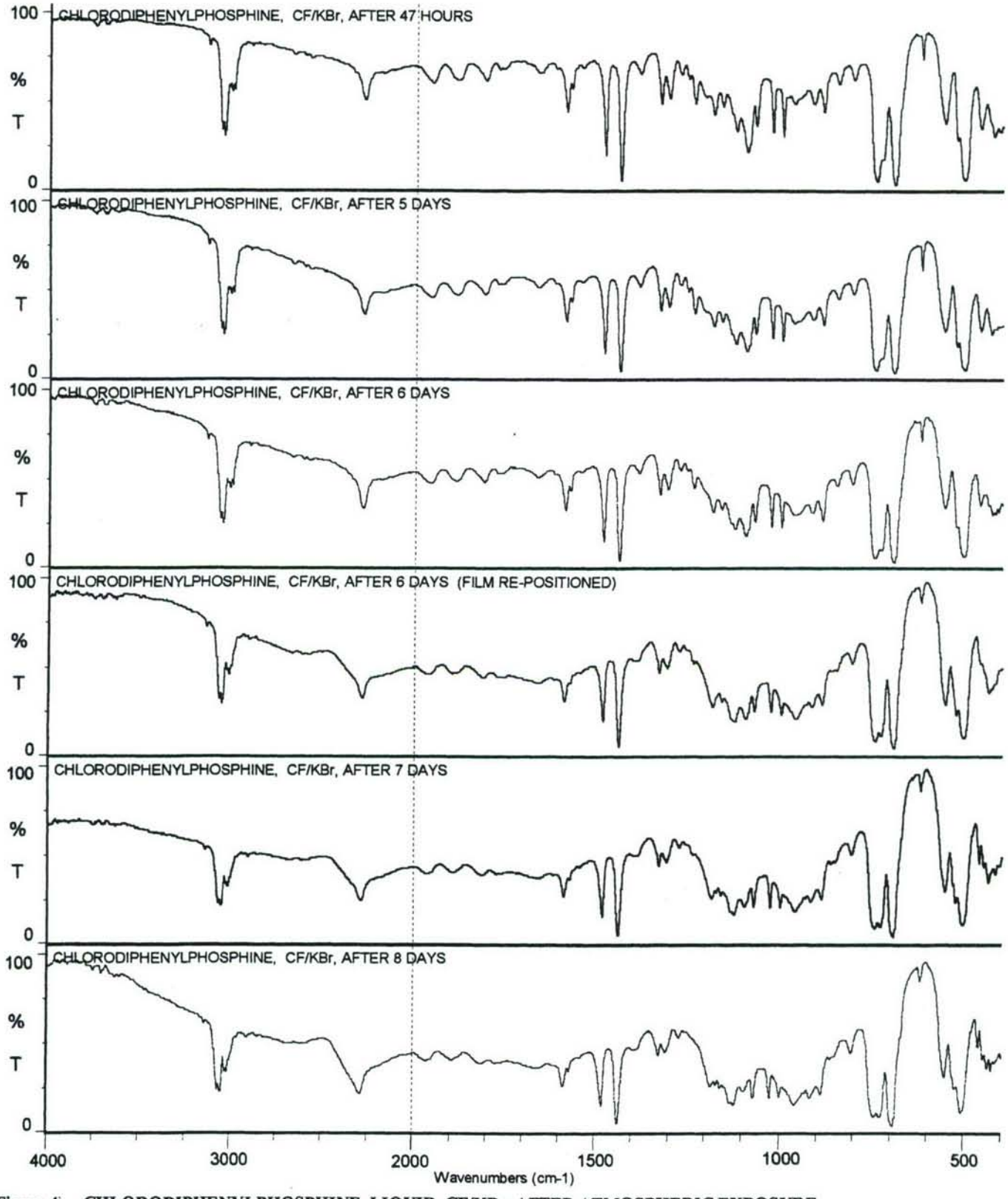

Figure 4 CHLORODIPHENYLPHOSPHINE, LIQUID, CF/KBr, AFTER ATMOSPHERIC EXPOSURE (CONTINUED)

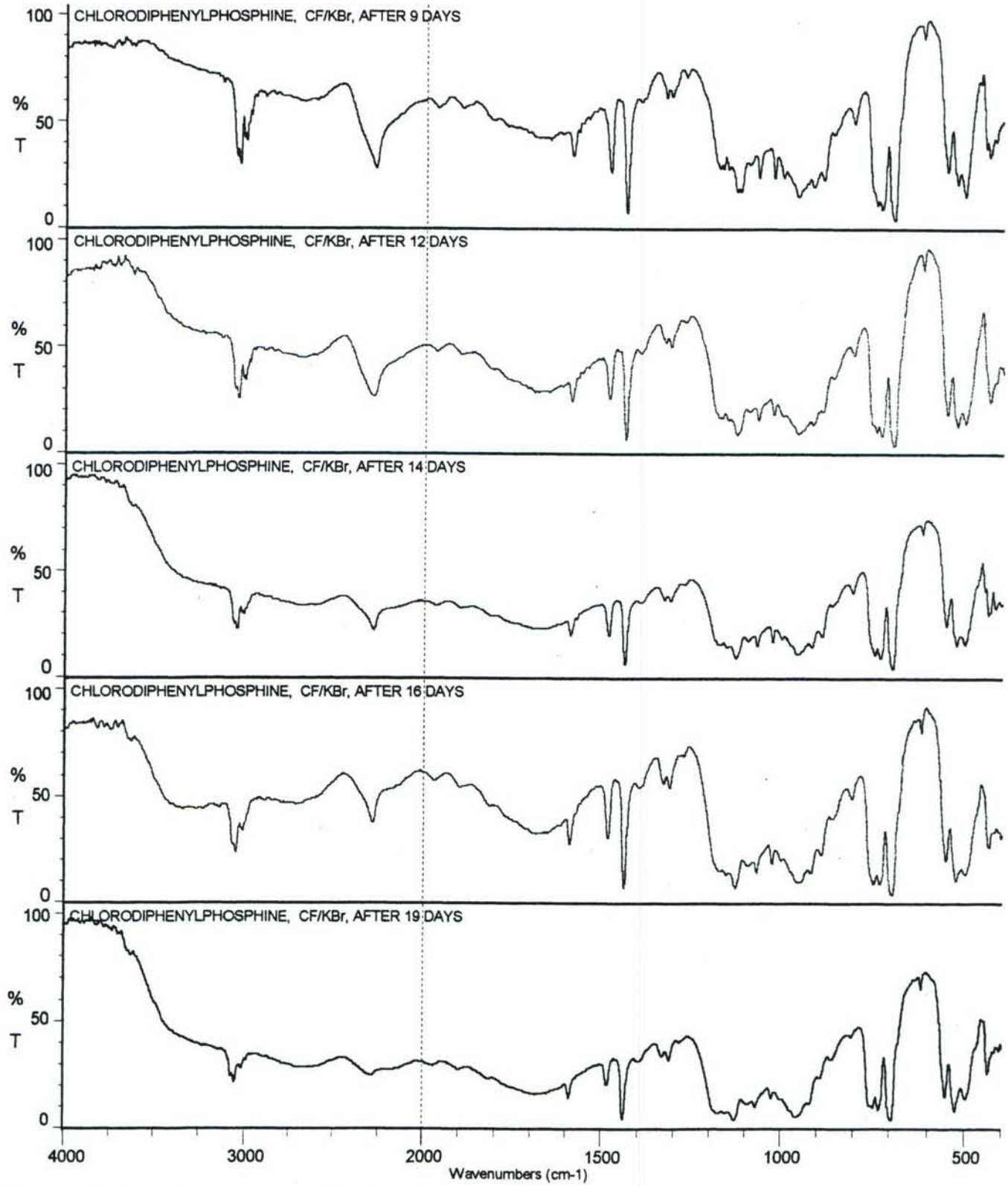

Figure 4 CHLORODIPHENYLPHOSPHINE, LIQUID, CF/KBr, AFTER ATMOSPHERIC EXPOSURE (CONTINUED)

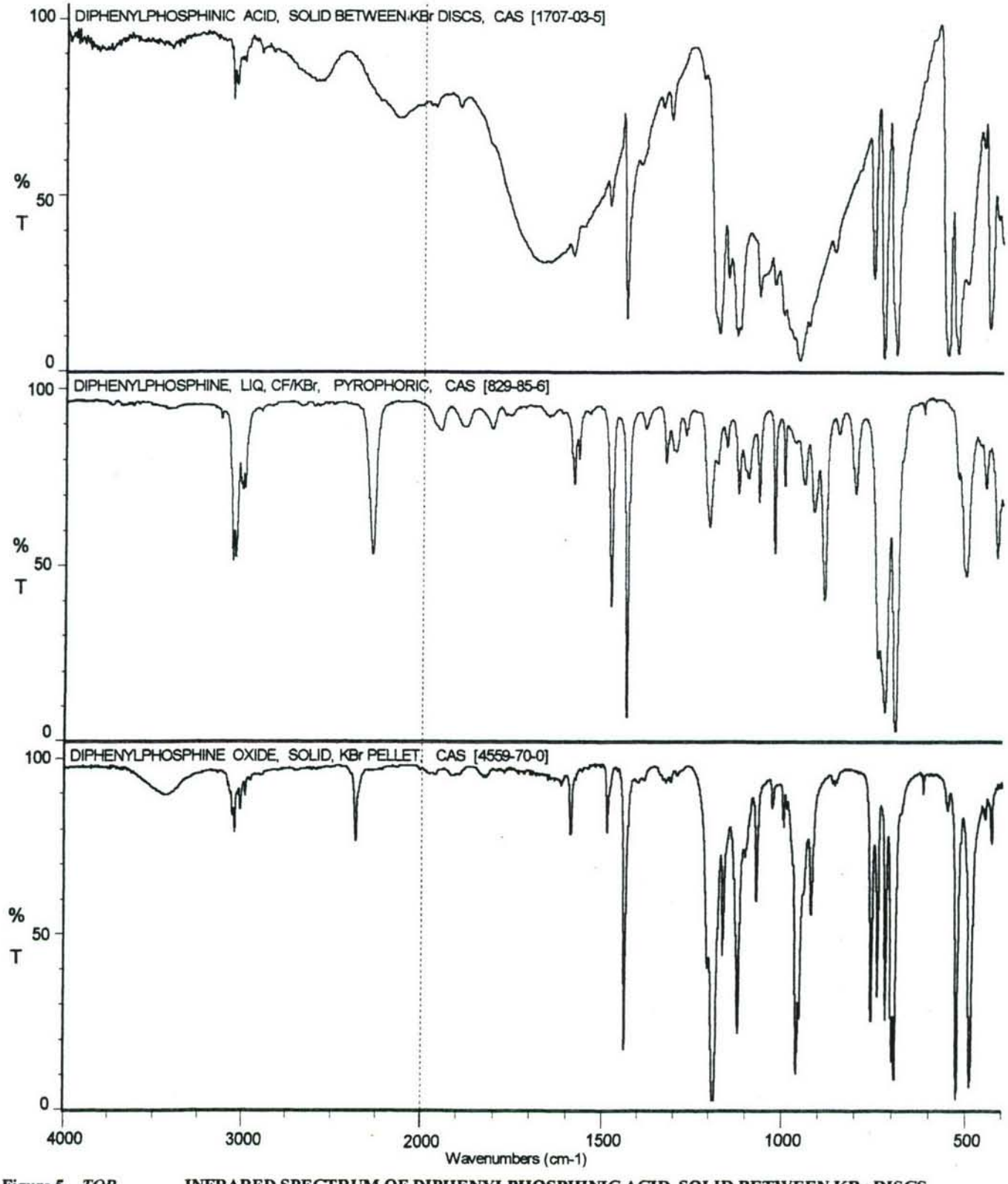

Figure 5 ***TOP*** **INFRARED SPECTRUM OF DIPHENYLPHOSPHINIC ACID, SOLID BETWEEN KBr DISCS**
MIDDLE **INFRARED SPECTRUM OF DIPHENYLPHOSPHINE, LIQUID, CF/KBr**
BOTTOM **INFRARED SPECTRUM OF DIPHENYLPHOSPHINE OXIDE, SOLID KBr PELLET**

spectra of chlorodiphenylphosphine (after an exposure of 12 days) with the computer addition of the individual spectra for diphenylphosphine + diphenylphosphinic acid. One of the expected compounds, diphenylphosphine oxide, $(C_6H_5)_2P{=}O(H)$, has a higher P-H stretch (2369 cm^{-1}) than that observed for the product namely 2282-2284 cm^{-1}. The value for the P-H stretch of diphenylphosphine occurs at 2282 cm^{-1}.

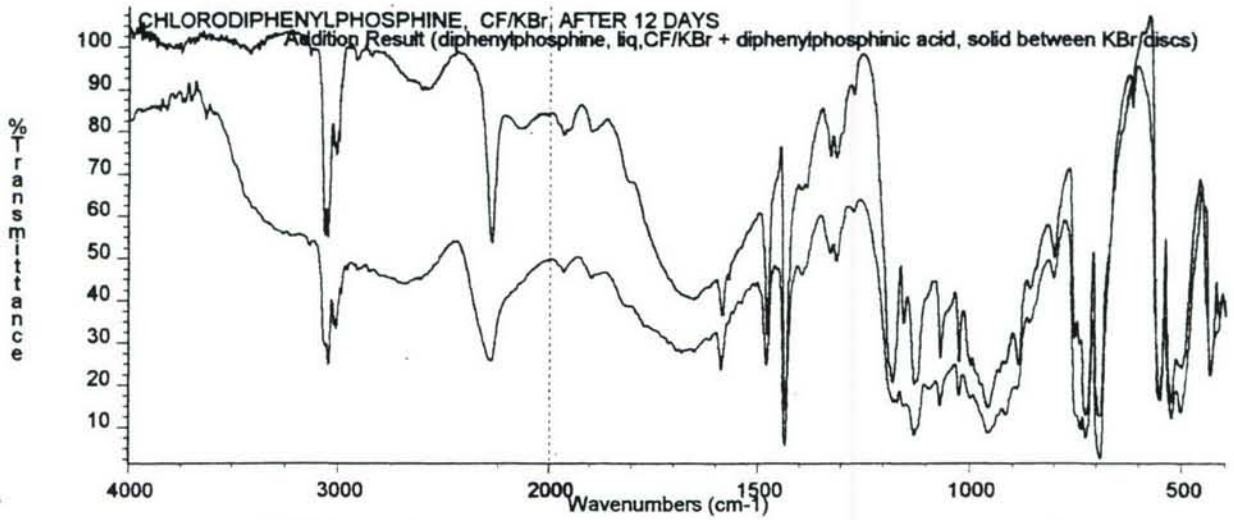

Figure 6 UPPER ADDITION RESULT FROM DIPHENYLPHOSPHINE (LIQ, CF/KBr) + DIPHENYLPHOSPHINIC ACID (SOLID BETWEEN KBR DISCS)
LOWER CHLORODIPHENYLPHOSPHINE, LIQ, CF/KBr, AFTER 12 DAYS OF EXPOSURE TO LAB ATMOSPHERE

3.1.3 Dichlorophenylphosphine (phenylphosphonous dichloride) $C_6H_5PCl_2$

The infrared spectrum of liquid dichlorophenylphosphine is reproduced in ***Figure 7A***, while that of the vapor phase is given in ***Figure 7B*** The band assignments are as follows: 3075 cm^{-1} vw, 3058 cm^{-1} vw and 3005 vvw (ν C-H aromatic), 1585 cm^{-1} vw, 1478 cm^{-1} vw and 1436 cm^{-1} m (aromatic ring), 1384 cm^{-1} vvw (KNO_3 from KBr windows), 1090 cm^{-1} w (phenyl-P), 1067 cm^{-1} vvw, 1026 cm^{-1} vvw and 999 cm^{-1} vw (β C-H aromatic ring), 743 cm^{-1} m (γ C-H mono-substituted aromatic ring), 688 cm^{-1} m (δ aromatic ring), 492 cm^{-1} s ν P-Cl_2. The effect of atmospheric moisture on dichlorophenylphosphine is give in ***Figures 8A*** and ***8B***. The first fifteen days of exposure (***Figure 8A***) show the gradual formation of bands near 2720 and 2288 cm^{-1} (POH), 1230 cm^{-1} (ν P=O). ***Figure 8B*** shows the increase in these bands indicative of the formation of a P-acid moiety, together with the gradual decrease in the PCl_2 band

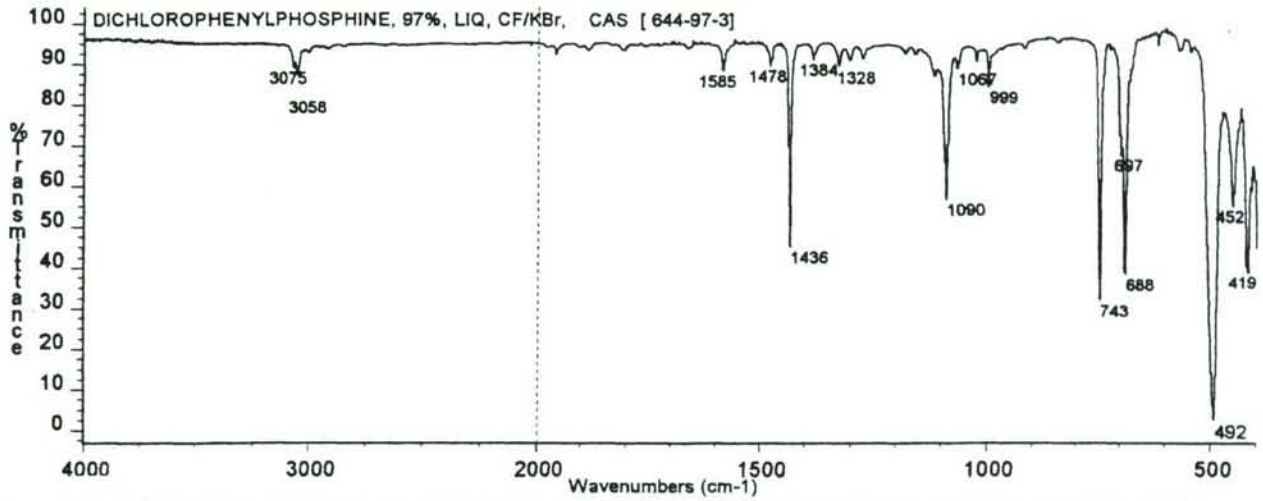

Figure 7A DICHLOROPHENYLPHOSPHINE (PHENYLPHOSPHONOUS DICHLORIDE), 97%, LIQUID, CF/KBr

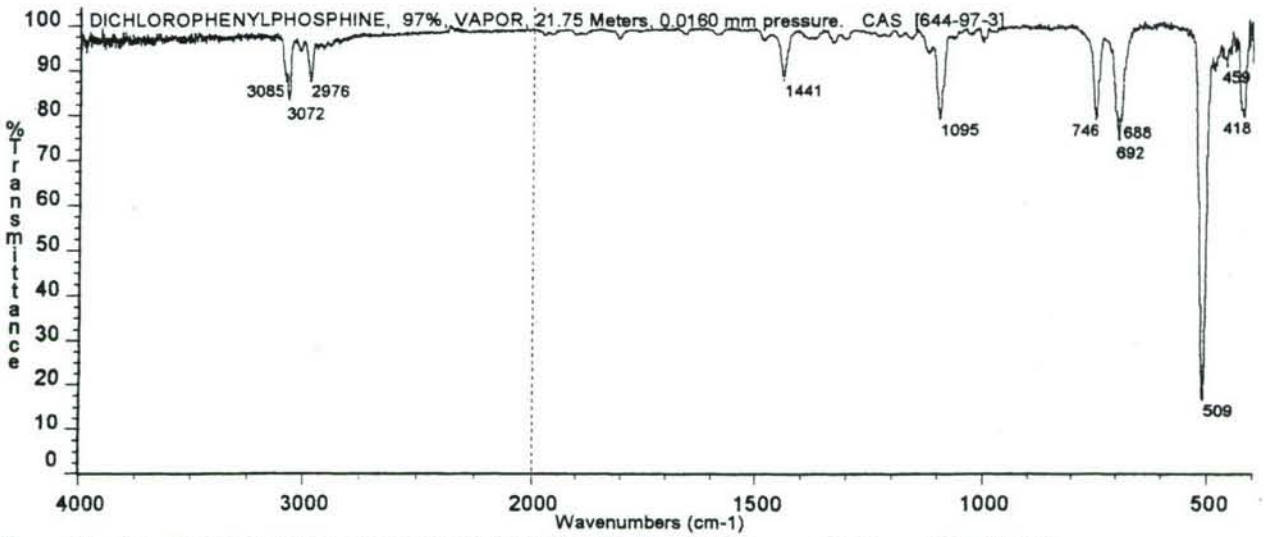

Figure 7B DICHLOROPHENYLPHOSPHINE, 97%, VAPOR, 21.75 Meters, 0.0160 mm PRESSURE

near 492 cm^{-1}. The resultant spectra (***Figure 8A***) take on the appearance of that for phenylphosphonic acid, $C_6H_5P{=}O(OH)_2$, (***Figure 9***). No phenylphosphinic acid, $C_6H_5P{=}O(H)(OH)$, is formed as no P-H bands are apparent in any of the spectra. This would have been the case if the compound had hydrolyzed initially [$C_6H_5PCl_2$ -HOH→ $C_6H_5P{=}O(H)(Cl)$ -HOH→ $C_6H_5P{=}O(H)(OH)$]. Apparently, the compound oxidizes and then hydrolyzes to form the phenylphosphonic acid [$C_6H_5PCl_2$ -[O]→ $C_6H_5P{=}O(Cl)_2$ -HOH→ $C_6H_5P{=}O(Cl)(OH)$ -HOH→ $C_6H_5P{=}O(OH)_2$].

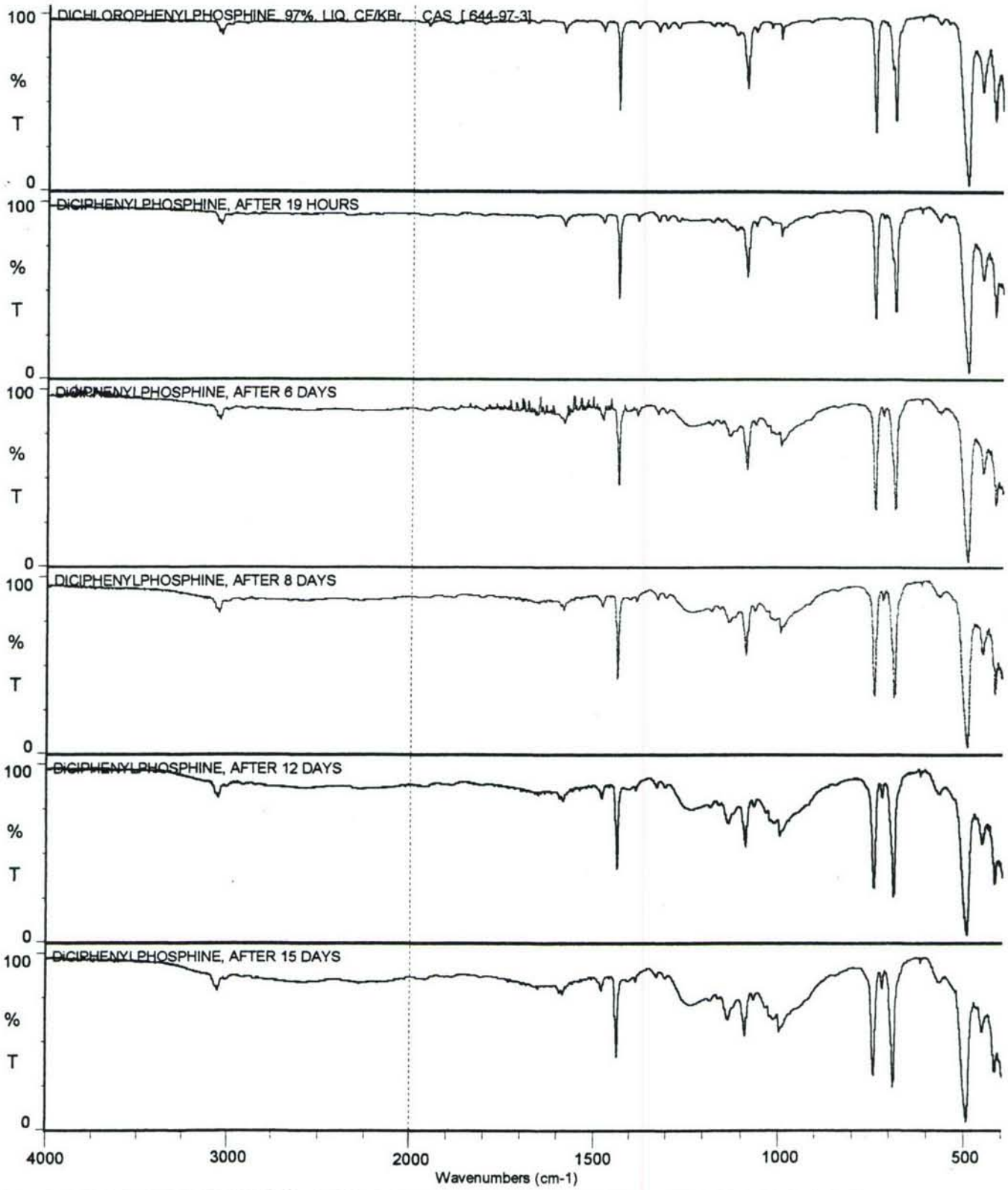

Figure 8A DICHLOROPHENYLPHOSPHINE (PHENYLPHOSPHONOUS DICHLORIDE), 97%, LIQ, CF/KBr, EXPOSED TO ATMOSPHERIC MOISTURE

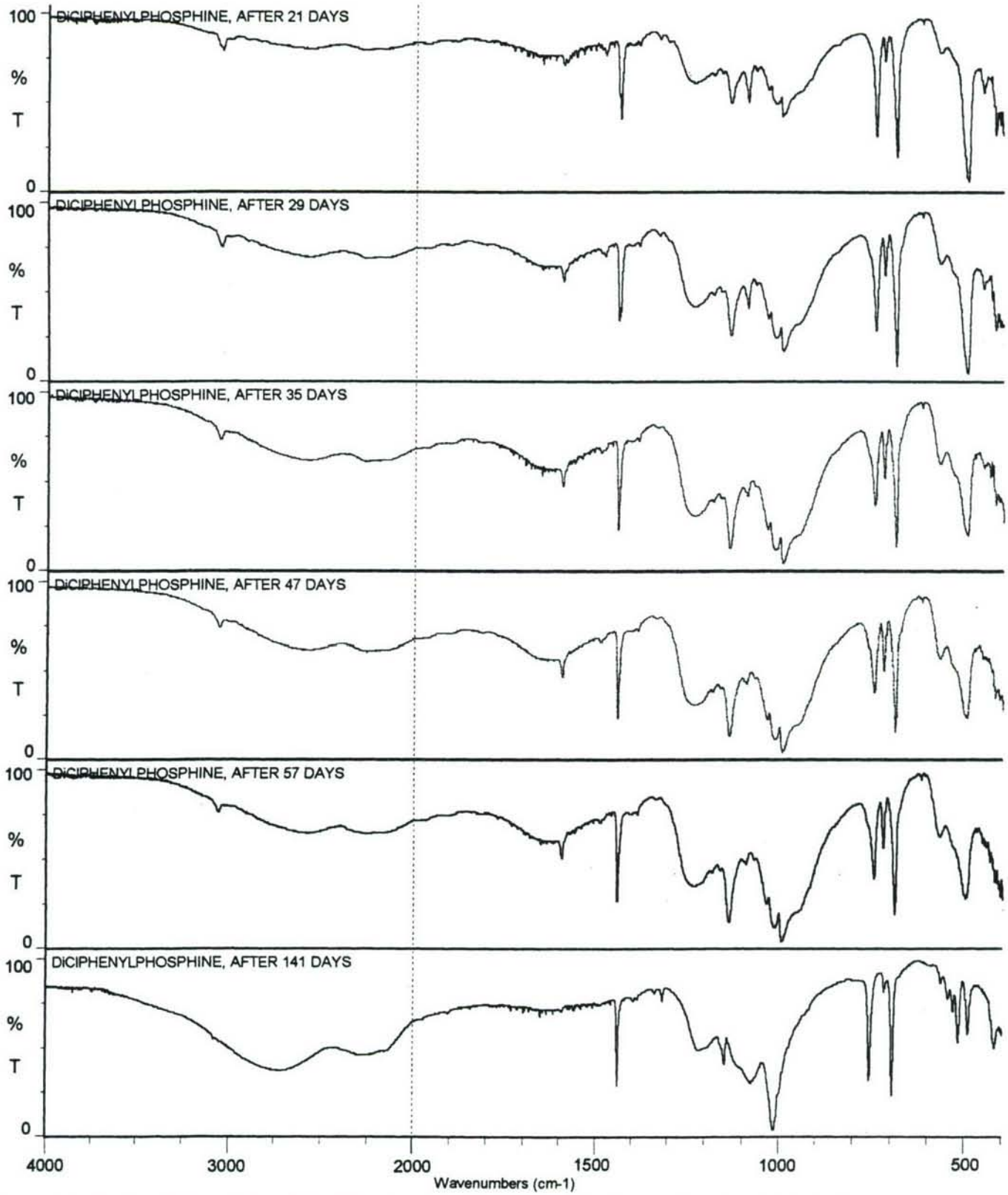

Figure 8B DICHLOROPHENYLPHOSPHINE (PHENYLPHOSPHONOUS DICHLORIDE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

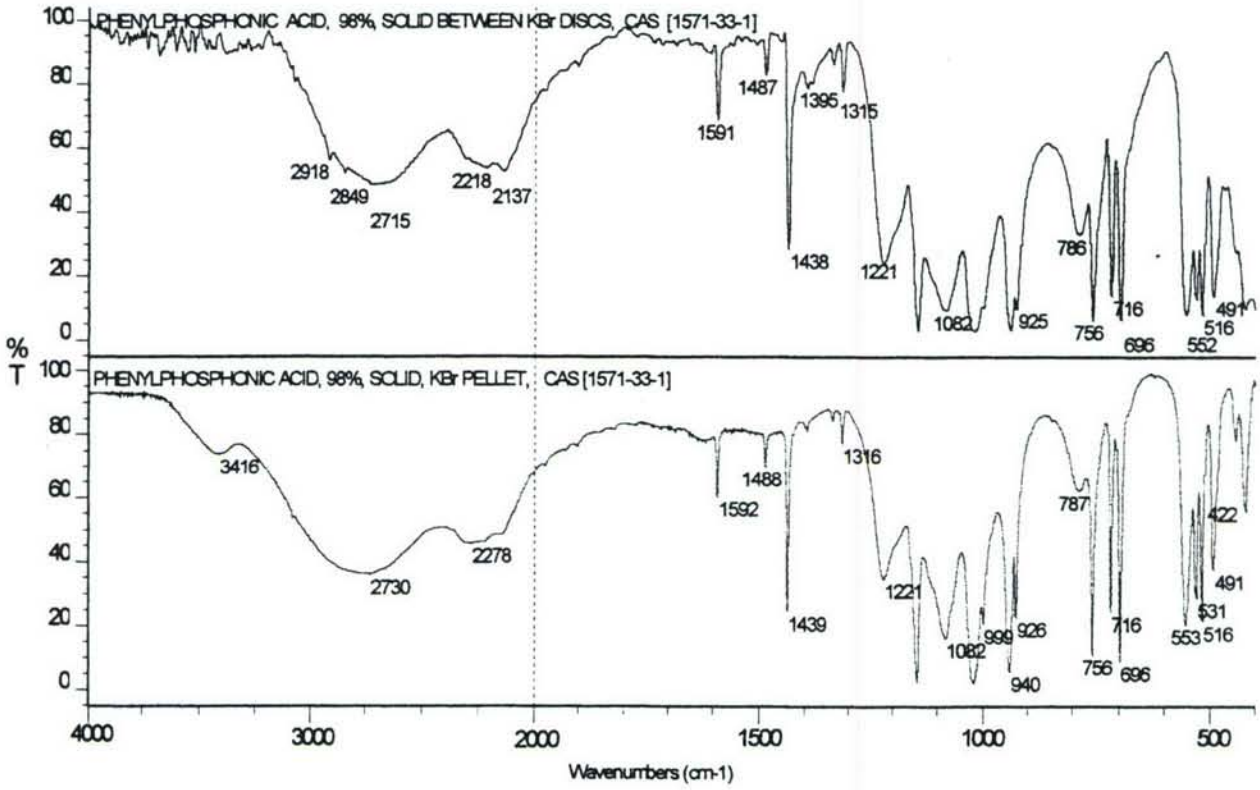

Figure 9 UPPER PHENYLPHOSPHONIC ACID, 98%, SOLID BETWEEN KBr DISCS
LOWER PHENYLPHOSPHONIC ACID, 98%, SOLID, KBr PELLET

3.1.4 Diphenylphosphine $(C_6H_5)_2P\text{-}H$

The infrared spectrum of diphenylphosphine is presented as ***Figure 10***. The infrared spectrum was also presented earlier as part of ***Figure 5***. The band assingments for diphenylphosphine are

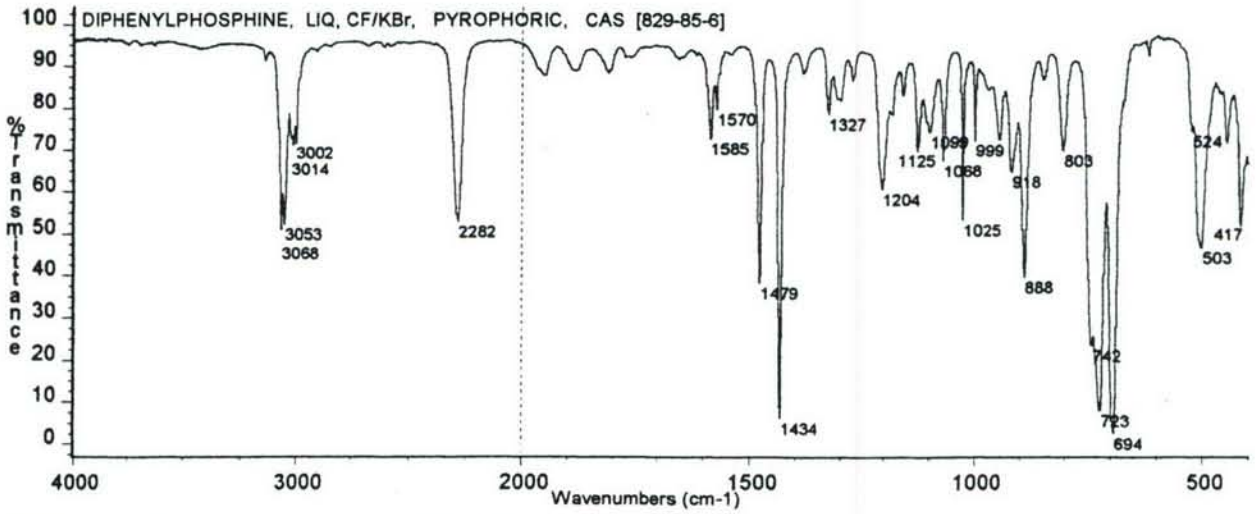

Figure 10 DIPHENYLPHOSPHINE, LIQUID, CF/KBr (PYROPHORIC)

as follows: 3068, 3053 cm^{-1} m and 3014, 3002 cm^{-1} w (ν C-H aromatic), 2282 cm^{-1} m (ν P-H), 1951, 1884 1810 and 1761 cm^{-1} vw (mono-substituted aromatic ring summation bands), 1585 cm^{-1} w, 1570 cm^{-1} vw, 1479 cm^{-1} m and 1434 cm^{-1} s (aromatic ring), 1204 cm^{-1} w (ν P=O ?), 1181, 1068, 1025 and 999 cm^{-1} vw-w (β C-H mono-substituted aromatic ring), 888 cm^{-1} m (P-H deformation ?), 723 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 694 cm^{-1} s (δ mono-substituted aromatic ring). The effect of the ambient environment on diphenylphosphine is illustrated by ***Figures 11A*** and ***11B***. The original sample of diphenylphosphine (top spectrum in ***Figure 11A***) shows a weak band near 1200 cm^{-1} that may be assigned to a P=O stretching vibration. This band continues to increase in intensity through the length of the study. The P-H stretch is still visible in the spectra increasing in frequency to 2324 by the 44th day. A new band near 960 cm^{-1} occurs and may be assigned to the P-H deformation. The new compound appears to be diphenylphosphine oxide, $(C_6H_5)_2P{=}O(H)$, (see ***Figure 5***, Bottom Spectrum).

3.1.5 Dimethylphenylphosphine $C_6H_5\text{-}P(CH_3)_2$

The infrared spectrum of dimethylphenylphosphine is given in ***Figure 12***. The band assignments are as follows: 3070 cm^{-1} m, 3053 cm^{-1} m, and 3013 cm^{-1} w (ν C-H aromatic), 2959 cm^{-1} ms and 2899 cm^{-1} ms (ν_{as} and ν_{sy} CH_3), 2813 cm^{-1} w (2 x δ CH_3), 1948 cm^{-1} vw, 1877 cm^{-1} vw, 1806 cm^{-1} vw and 1751 cm^{-1} vvw (mono-substituted aromatic ring summation bands), 1587 cm^{-1} w, 1571 cm^{-1} vvw, 1484 cm^{-1} m and 1432 cm^{-1} ms (aromatic ring, 1432 cm^{-1} band may also have some contribution from the δ_{as} P-CH_3), 1384 cm^{-1} vvw (possible KNO_3 from the KBr windows),1319 cm^{-1} w, 1303 cm^{-1} w, 1289 cm^{-1} m and 1274 cm^{-1} w (δ_{sy} P-CH_3), 1199 cm^{-1} w, 1070 cm^{-1} w, 1027 cm^{-1} w and 999 cm^{-1} vw (β C-H mono-substituted aromatic ring), 1105 cm^{-1} m (phenyl-P), 941 cm^{-1} ms and 895 cm^{-1} ms (P-CH_3 rock)[d], 740 cm^{-1} s (γ C-H mono-substituted aromatic ring), 695 cm^{-1} s (δ mono-substituted aromatic ring), 664

[d] For P^{+3} compounds, the P-CH_3 rock falls within the range 906-862 cm^{-1} except in compounds with two P-CH_3 groups, where the absorption bands are multiple and fall within the range of comparable P^{+5} compounds (958-835 cm^{-1}). Thomas, L.C., Interpretation of the Infrared Spectra of Organophosphorus Compounds, Heyden and Son, Limited, London, pp. 95,97, 1974.

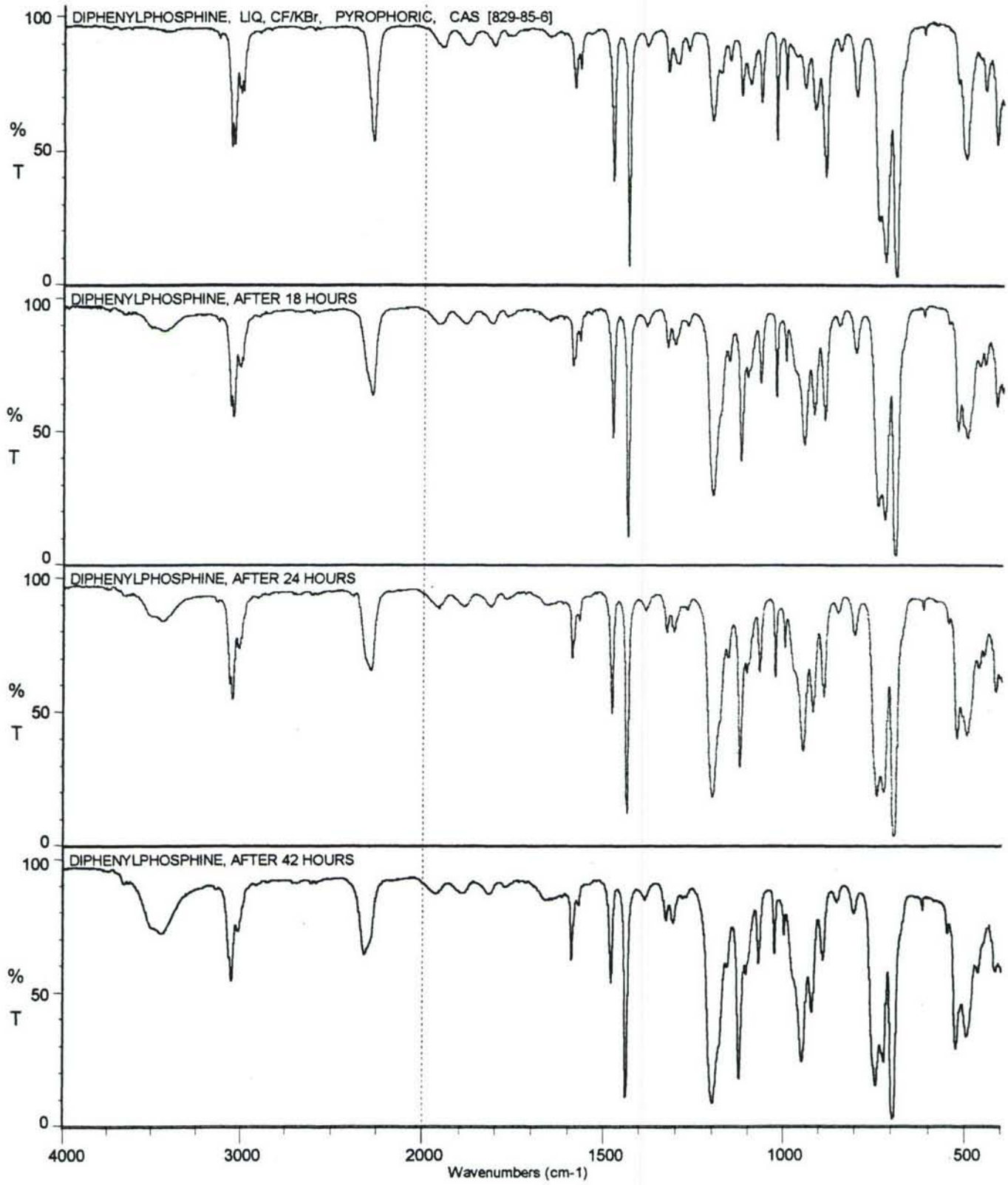

Figure 11A DIPHENYLPHOSPHINE, LIQUID, CF/KBr, AFTER ATMOSPHERIC EXPOSURE

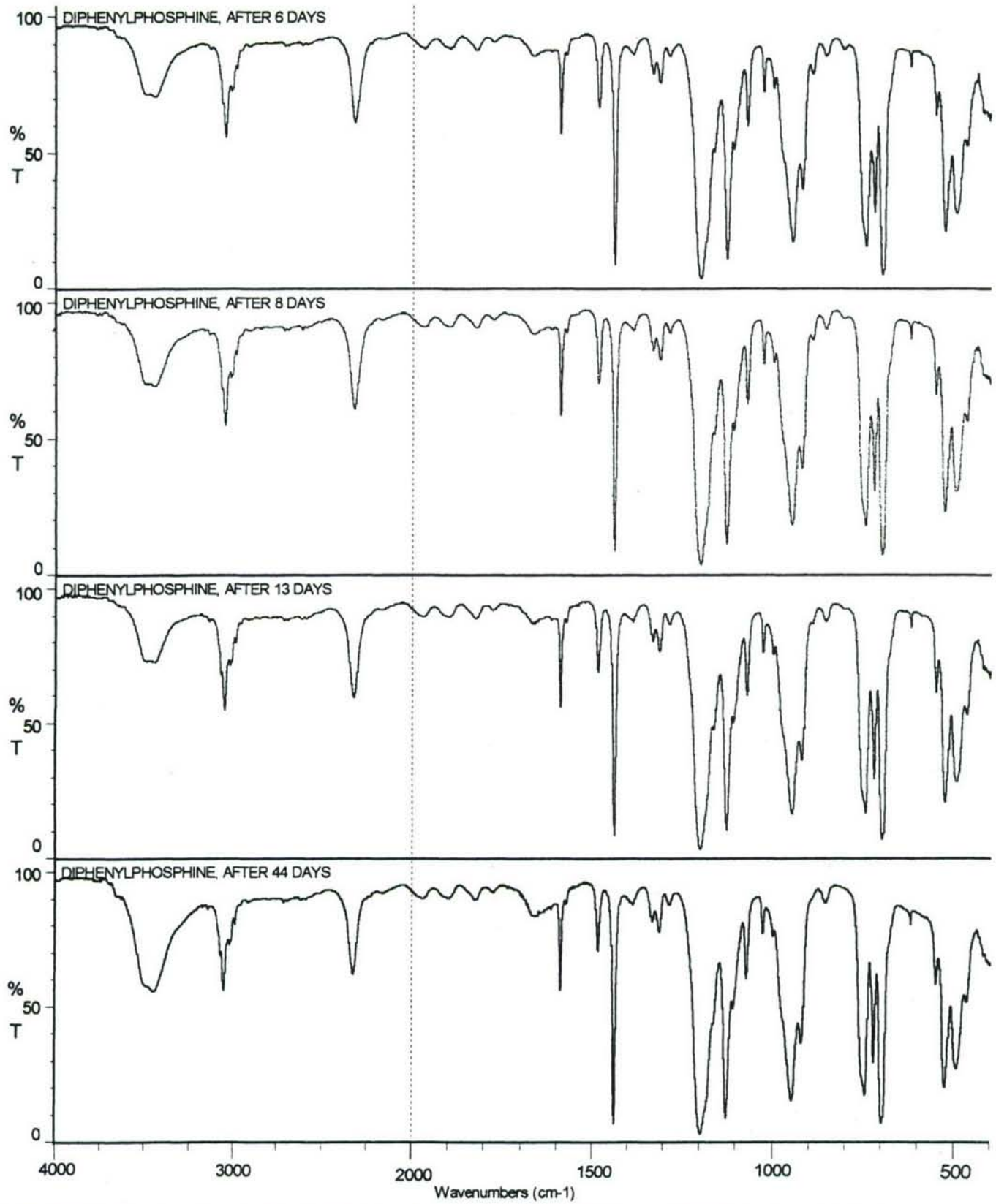

Figure 11B DIPHENYLPHOSPHINE, LIQUID, CF/KBr, AFTER ATMOSPHERIC EXPOSURE (CONTINUED)

cm^{-1} m (ν P-C ?).

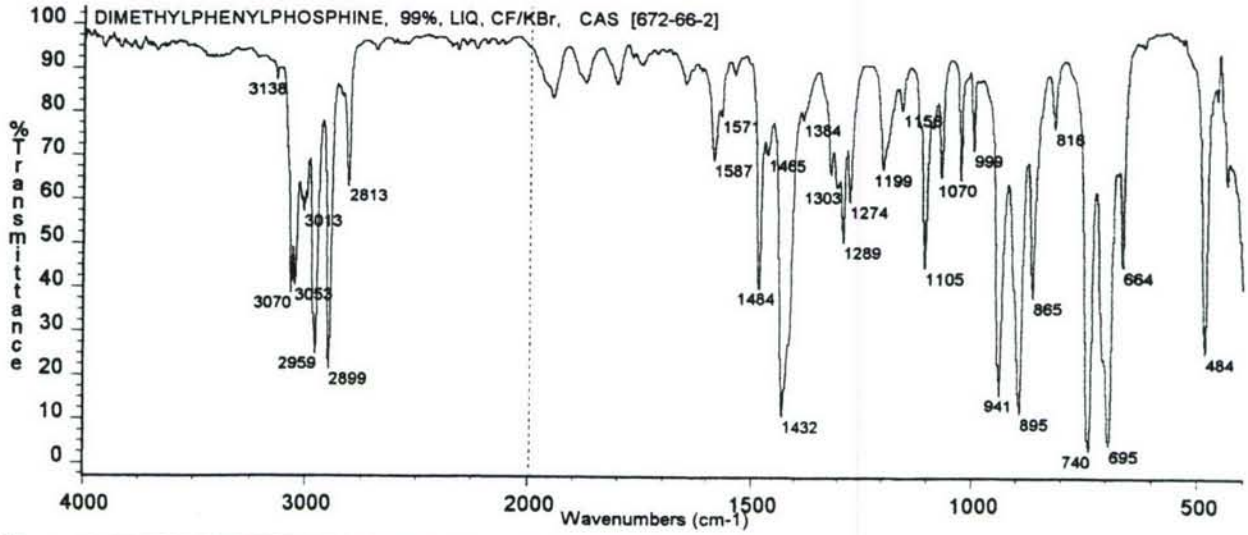

Figure 12 DIMETHYLPHENYLPHOSPHINE, 99%, LIQUID, CF/KBr

The effect of the environment on dimethylphenylphosphine is shown in ***Figure 13***. After 3-4 days of exposure the spectrum shows changes in the regions near 1300 cm^{-1} (δ_{sy} P-CH_3) and 1180-1150 cm^{-1} (ν P=O). The multiple bands due to the P-CH_3 rock are still present near 900 cm^{-1}.(950-860 cm^{-1}). Bands indicative of the mono-substituted aromatic ring are still present. By 17 days of exposure to the atmosphere, the spectrum shows a large amount of water (ca 3400, 1650 and broad background near 700 cm^{-1}) causing the P=O stretching band to decrease in value to 1154 cm^{-1}. The compound has probably been oxidized to dimethylphenylphosphine oxide, C_6H_5-P=O$(CH_3)_2$.

3.1.6 Dimethoxyphenylphosphine (Dimethyl Phenylphosphonite) C_6H_5-P$(OCH_3)_2$

The infrared spectrum of dimethoxyphenylphosphine (dimethyl phenylphosphonite) is given in ***Figure 14***. The band assignments are as follows: 3428 cm^{-1} vw (H_2O), 3073 and 3055 cm^{-1} vw (ν C-H aromatic), 2936 cm^{-1} w and 2831 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1592 cm^{-1} vvw, 1483 cm^{-1} vw and 1436 cm^{-1} w (aromatic ring), 1457 cm^{-1} vw (δ OCH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr discs used to contain the sample), 1238 cm^{-1} vw (possible ν P=O), 1179 cm^{-1} vw (CH_3 rock of $POCH_3$ characteristic), 1103 cm^{-1}

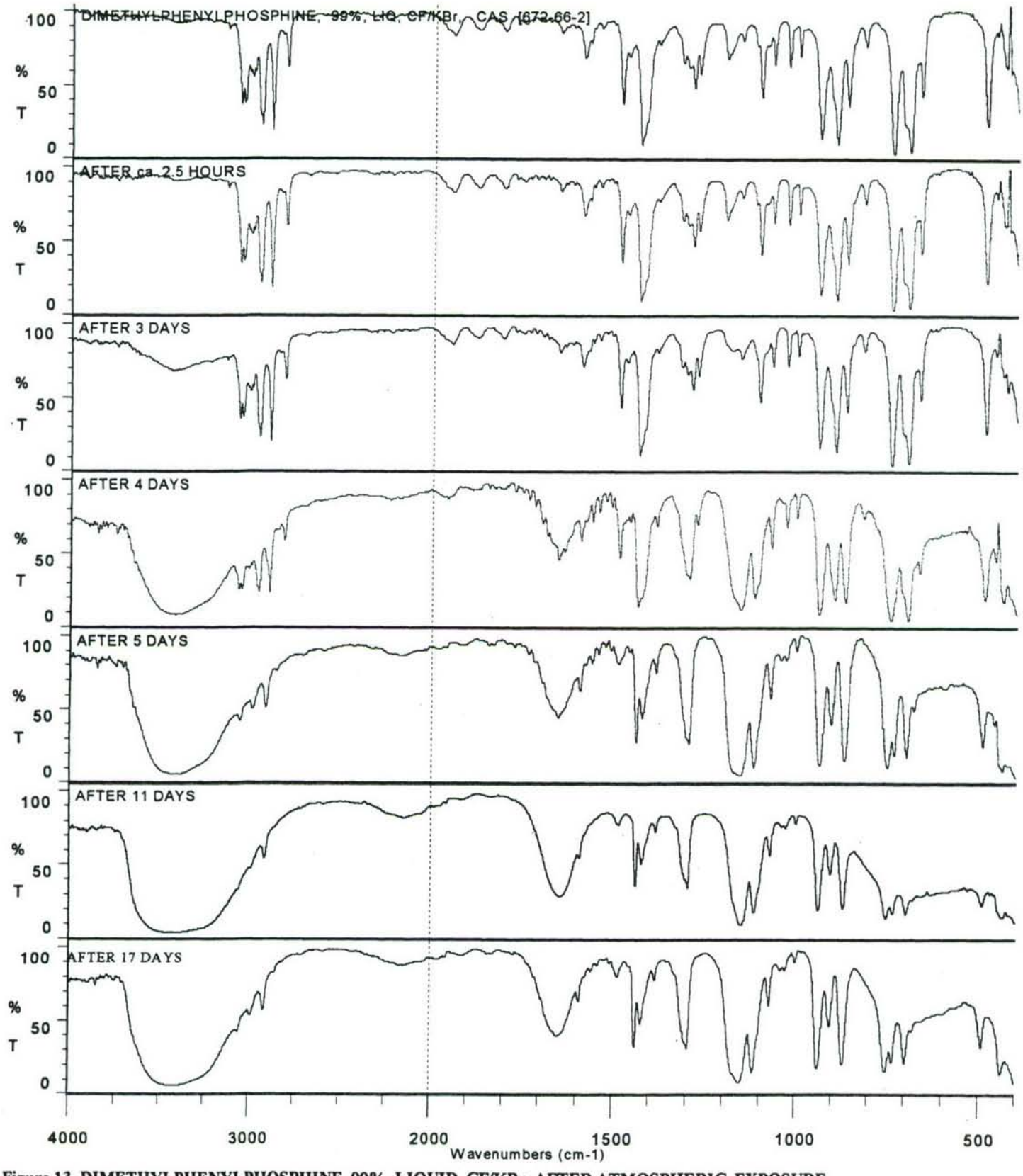

Figure 13 DIMETHYLPHENYLPHOSPHINE, 99%, LIQUID, CF/KBr, AFTER ATMOSPHERIC EXPOSURE

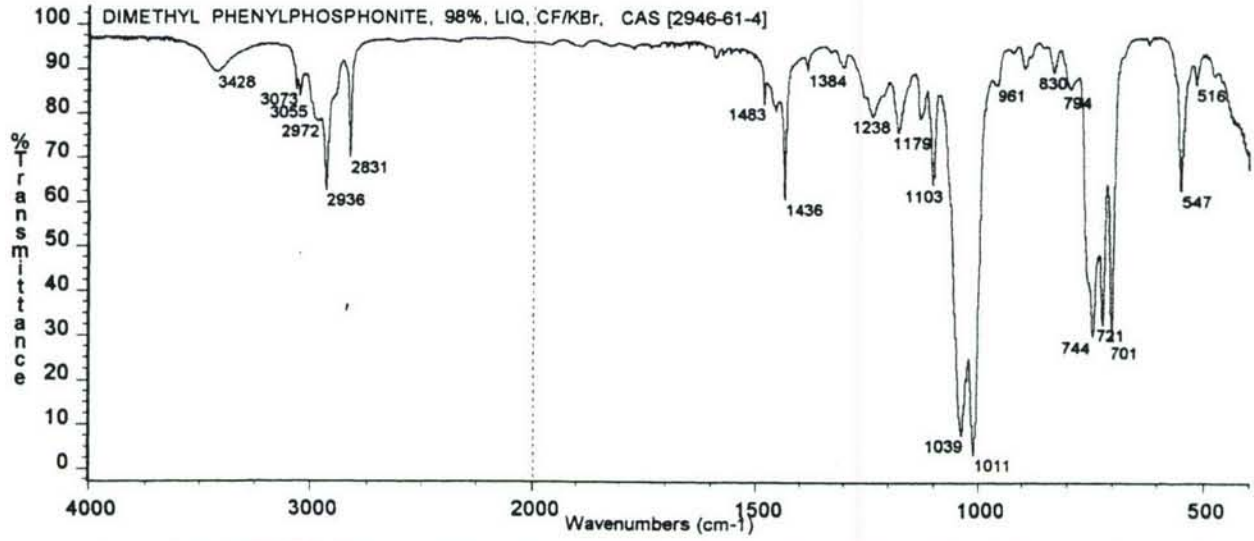

Figure 14 DIMETHOXYPHENYLPHOSPHINE (DIMETHYL PHENYLPHOSPHONITE), 98%, LIQUID, CF/KBr

w (phenyl-P), 1039 cm^{-1} ms and 1011 cm^{-1} (ν P-O-C), 744 cm^{-1} m (γ C-H mono-substituted aromatic ring), 701 cm^{-1} ms (δ mono-substituted aromatic ring).

The effect of atmospheric moisture on dimethoxyphenylphosphine is illustrated by ***Figures 15A*** and ***15B***. After 1 day of exposure to atmospheric moisture the infrared spectrum (***Figure 15A***) shows new bands at 2359 cm^{-1} vw (ν P-H), 1233 cm^{-1} s (ν P=O), 1183 cm^{-1} vw (CH_3 rock of $POCH_3$), 1127 cm^{-1} m (phenyl-P), 1039 cm^{-1} s (ν P-O-C) , 961 cm^{-1} ms (P-H deformation) and 797 cm^{-1} w (POC). Bands indicative of a mono-substituted aromatic ring (751 cm^{-1} m and 706,695 cm^{-1} m) are also present. The original compound, dimethoxyphenylphosphine, appears to have hydrolyzed to methyl phenylphosphinate, C_6H_5-P=O(H)(OCH_3), which has a calculated ν P=O value of 1230 cm^{-1}.[e] By the 5th day the spectrum undergoes further changes. The phosphoryl stretching band at 1233 cm^{-1} decreases in value to 1197 cm^{-1} and a band appears at 972 cm^{-1} (possible ν P-OH). The ν P-H appears to have increased in

[e] The calculation of the phosphoryl stretching frequency (ν P=O) is based on the work of Thomas and Chittenden (Thomas, L.C. and Chittenden, R.A., Spectrochim. Acta, **20**, 467, 1964), who derived the expression $\nu(P=O) = 930 + 40\,\Sigma\pi$. They developed a revised set of values called phosphorus inductive constants denoted by π, which were a measure of the inductive effect of the groups attached to the phosphorus atom. Thomas in Chapter Two of his book, "Interpretation of the Infrared Spectra of Organophosphorus Compounds," Heyden & Son Ltd., 1974, discusses the application of this equation as well as presenting a table of π constants for various substituent groups. Taking the following π constants from this collection for phenyl (2.1), H (2.5), OCH_3 (2.9), the value calculated for the P=O stretching vibration of C_6H_5-P=O(H)(OCH_3), is 1230 cm^{-1} (observed value was 1233 cm^{-1}).

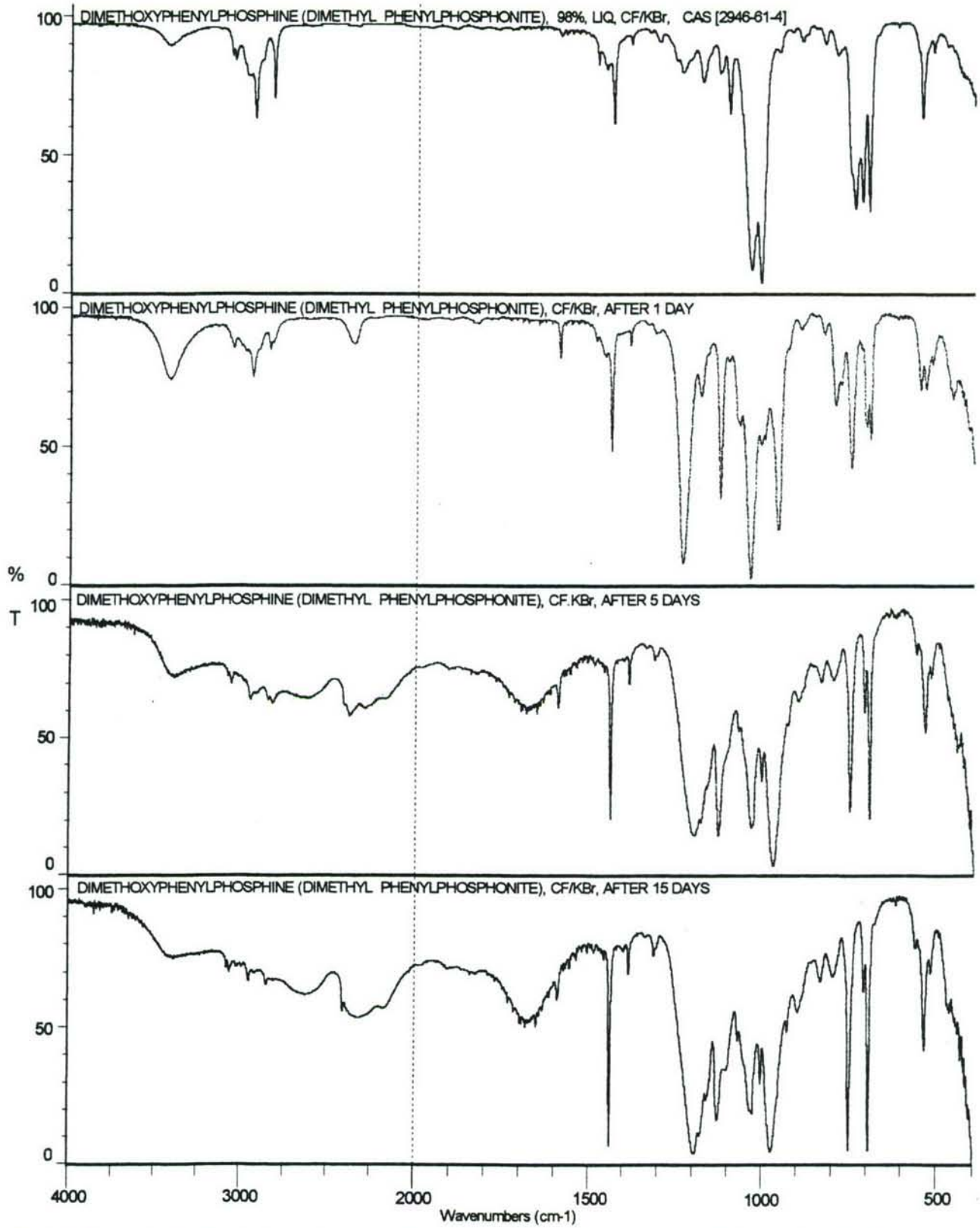

Figure 15A DIMETHOXYPHENYLPHOSPHINE (DIMETHYL PHENYLPHOSPHONITE), CF/KBr, AFTER ATMOSPHERIC EXPOSURE

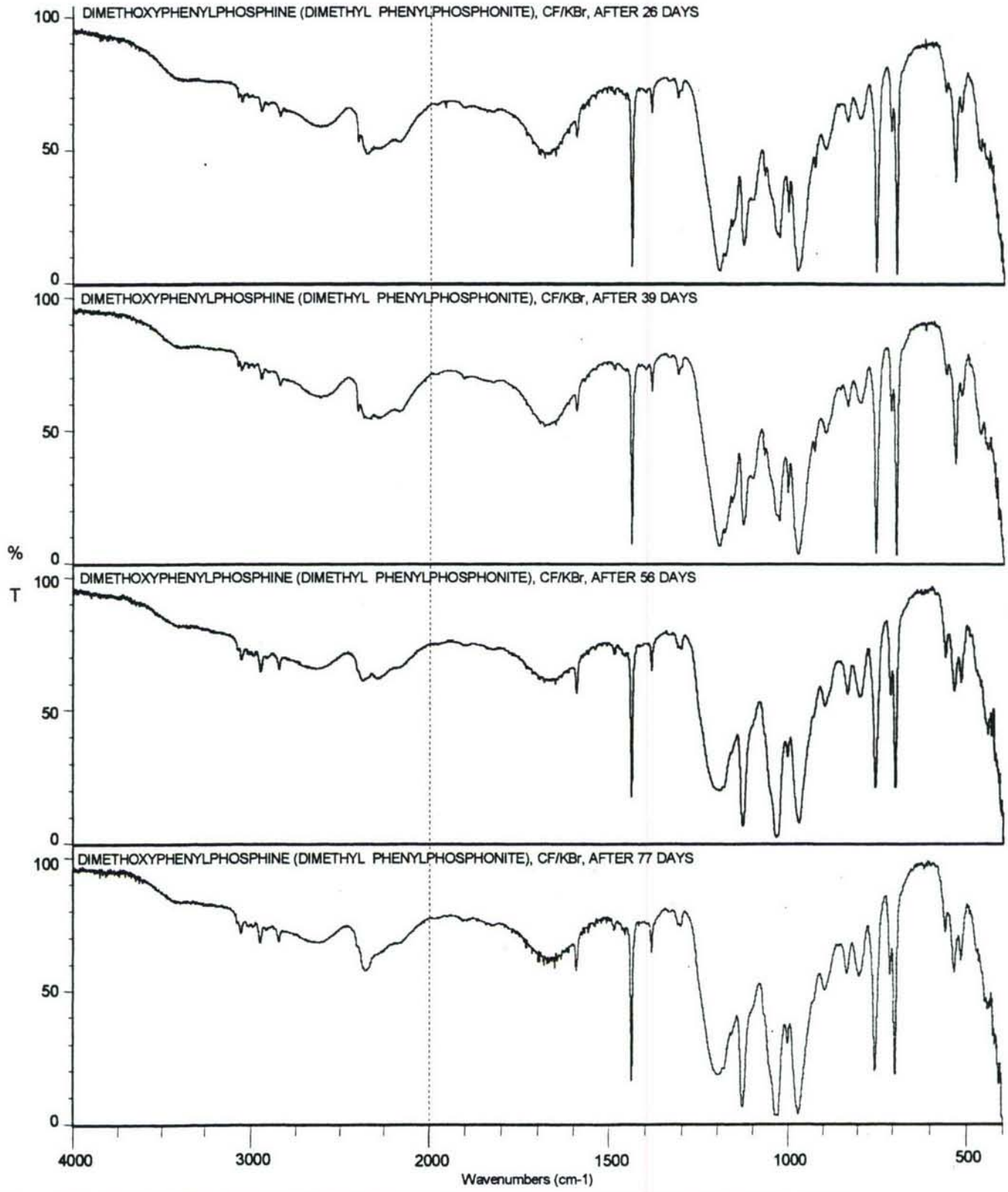

Figure 15B DIMETHOXYPHENYLPHOSPHINE (DIMETHYL PHENYLPHOSPHONITE, CF/KBr, AFTER ATMOSPHERIC EXPOSURE (CONTINUED)

value to 2402 cm^{-1}. Broad bands near 2620 and 2290 cm^{-1} can be assigned to POH. The compound now seems to have undergone further hydrolyis to form C_6H_5-P=O(H)(OH), phenylphosphinic acid (***Figure 16***). This phosphinic acid appears to dominate the spectra over the 77 day period of exposure (***Figure 15B***). The hydrolysis of dimethoxyphenylphosphine may be summarized as follows:

$C_6H_5P(OCH_3)_2$ -HOH→ $C_6H_5P{=}O(H)(OCH_3)$ -HOH → $C_6H_5P{=}O(H)(OH)$ + CH_3OH

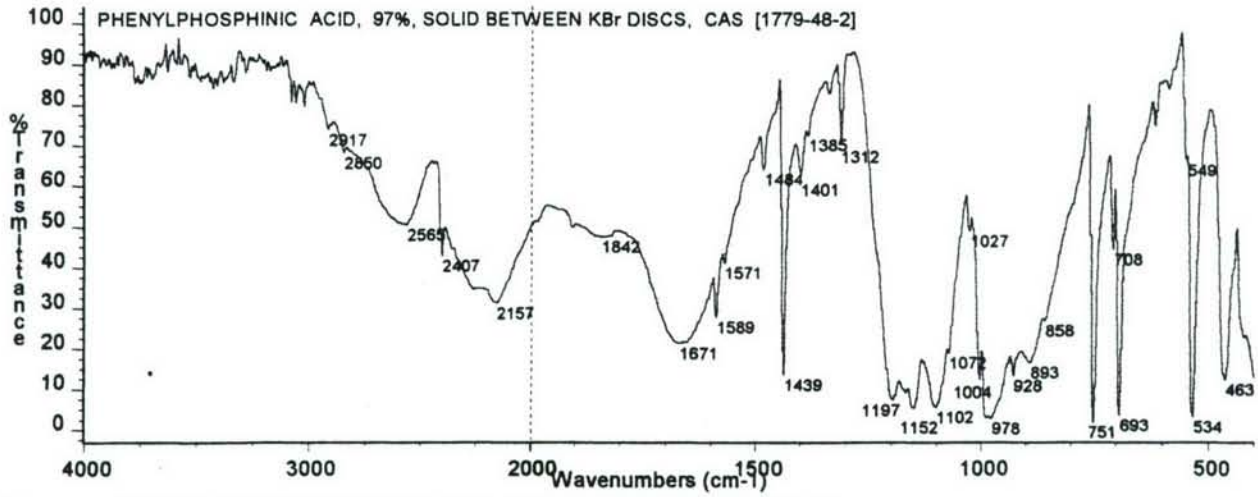

Figure 16 PHENYLPHOSPHINIC ACID, 97%, SOLID BETWEEN KBr DISCS

3.1.7 Diphenylmethoxyphosphine (Methyl Diphenylphosphinite) $(C_6H_5)_2P$-OCH_3

The infrared spectrum of diphenylmethoxyphosphine (methyl diphenylphosphinite) is reproduced as ***Figure 17***. The band assignments are as follows: 3069 and 3053 cm^{-1} m, 3001 cm^{-1} w (ν C-H

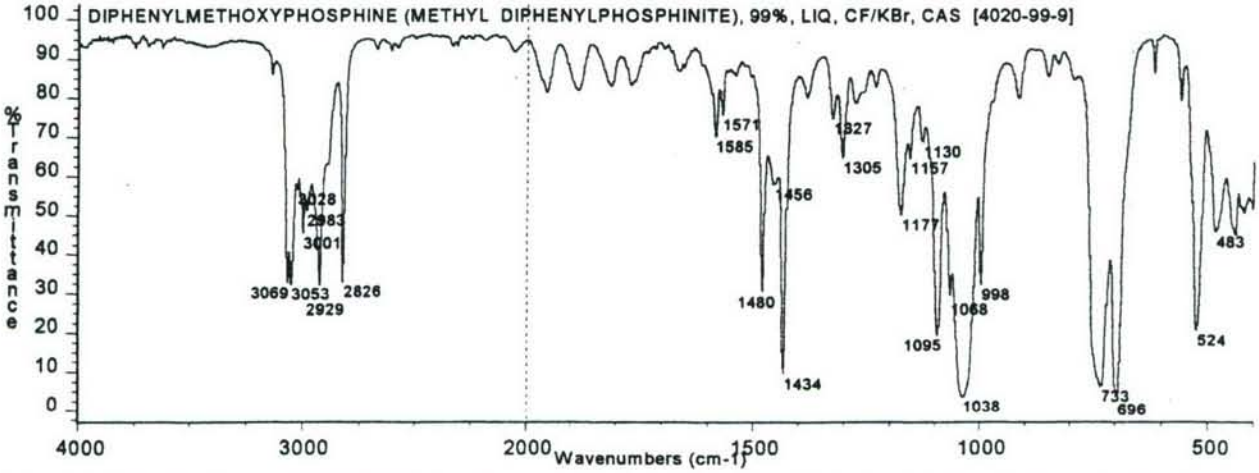

Figure 17 DIPHENYLMETHOXYPHOSPHINE (METHYL DIPHENYLPHOSPHINITE, 99%, LIQUID, CF/KBr

aromatic), 2929 cm^{-1} m and 2826 cm^{-1} m (ν_{as} and ν_{sy} CH_3), 1585 cm^{-1} w, 1571 cm^{-1} vw, 1480 cm^{-1} m and 1434 cm^{-1} ms (aromatic ring), 1456 cm^{-1} vw (δ CH_3), 1177 cm^{-1} w (CH_3 of $POCH_3$, characteristic), 1157 cm^{-1} vw, 1130 cm^{-1} vw, 1068 cm^{-1} w and 998 cm^{-1} m (β C-H mono-substituted aromatic ring), 1095 cm^{-1} ms (phenyl-P), 1038 cm^{-1} s (ν P-O-C), 733 cm^{-1} s (γ C-H mono-substituted aromatic ring), 696 cm^{-1} s (δ aromatic ring), 524 cm^{-1} m (P=O deformation).

The effect of atmospheric moisture on diphenylmethoxyphosphine (methyl diphenylphosphinite) is shown in ***Figures 18A*** and ***18B***. The infrared spectrum of the compound after some 116 days shows the presence of a P-H group near 2327 cm^{-1} (ν P-H) and 950 cm^{-1} (P-H deformation). A strong band near 1195 cm^{-1} can be assigned to a P=O stretching vibration. The P-O-C stretch near 1038 cm^{-1} is gone from the spectrum. The compound has apparently hydrolyzed to diphenylphosphine oxide, $(C_6H_5)_2P{=}O(H)$, (see ***Figure 5*** bottom spectrum).

3.1.8 Methyldiphenylphosphine $CH_3P(C_6H_5)_2$

The infrared spectrum of methyldiphenylphosphine is given in ***Figure 19***. The band assignments are as follows: 3069, 3052 cm^{-1} ms and 3014,3000 cm^{-1} w (ν C-H), 2967 cm^{-1} m and 2904 cm^{-1} m (ν_{as} and ν_{sy} CH_3), 1952 cm^{-1} w, 1884 cm^{-1} w, 1810 cm^{-1} w and 1755 cm^{-1} vw (summation bands mono-substituted aromatic ring), 1584 cm^{-1} m, 1570 cm^{-1} w, 1480 cm^{-1} ms and 1433 cm^{-1} s (aromatic ring), 1421 cm^{-1} sh (δ_{as} P-CH_3), 1305 cm^{-1} w-m (δ_{sy} P-CH_3), 1184 cm^{-1} w, 1156 cm^{-1} w, 1069 cm^{-1} m, 1026 cm^{-1} m and 999 cm^{-1} w-m (β C-H mono-substituted aromatic ring, note: the 1184 cm^{-1} band may also be due to a ν P=O of e.g. a phosphine oxide), 1099 cm^{-1} m (phenyl-P), 879 ms (P-CH_3 rock), 739 cm^{-1} s (γ C-H mono-substituted aromatic ring), 695 cm^{-1} s (δ aromatic ring).

The effect of the ambient atmosphere on the liquid film of methyldiphenylphosphine between KBr windows is illustrated by ***Figures 20A-C***. A gradual change occurs in the spectra over the period up to 7 days as a band begins to grow near 1182 cm^{-1} (***Figure 15A***). This band continues to increase in instensity as time progresses through 47 days (***Figure 20B***), although some splitting of the band is evident (1199 and 1184 cm^{-1}) through 78 days of exposure (***Figure 20C***). Through the period of 168 to 267 days the band becomes a single entity falling between 1187-1180 cm^{-1}. This band is assigned to a

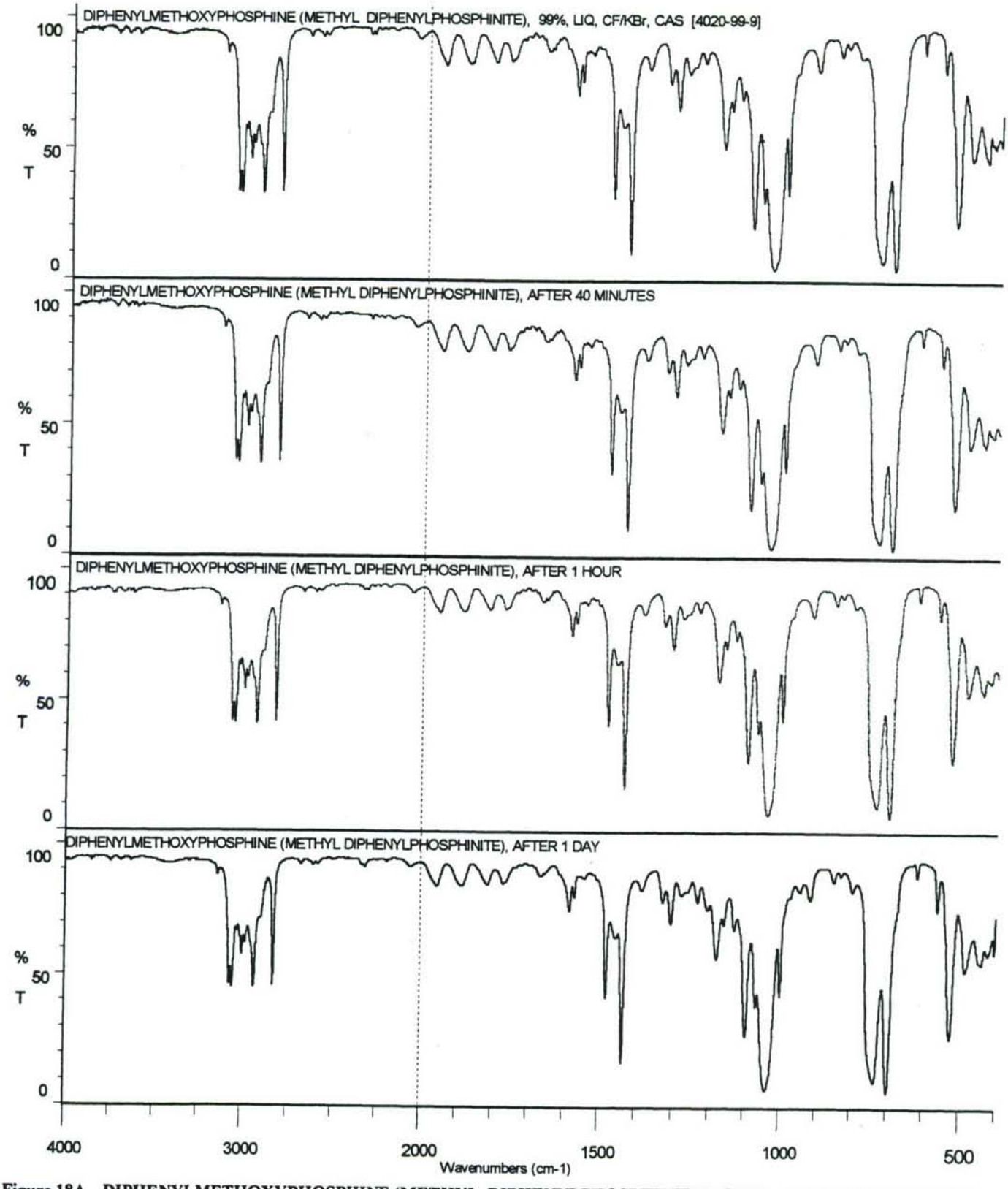

Figure 18A DIPHENYLMETHOXYPHOSPHINE (METHYL DIPHENYLPHOSPHINITE), CFKBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

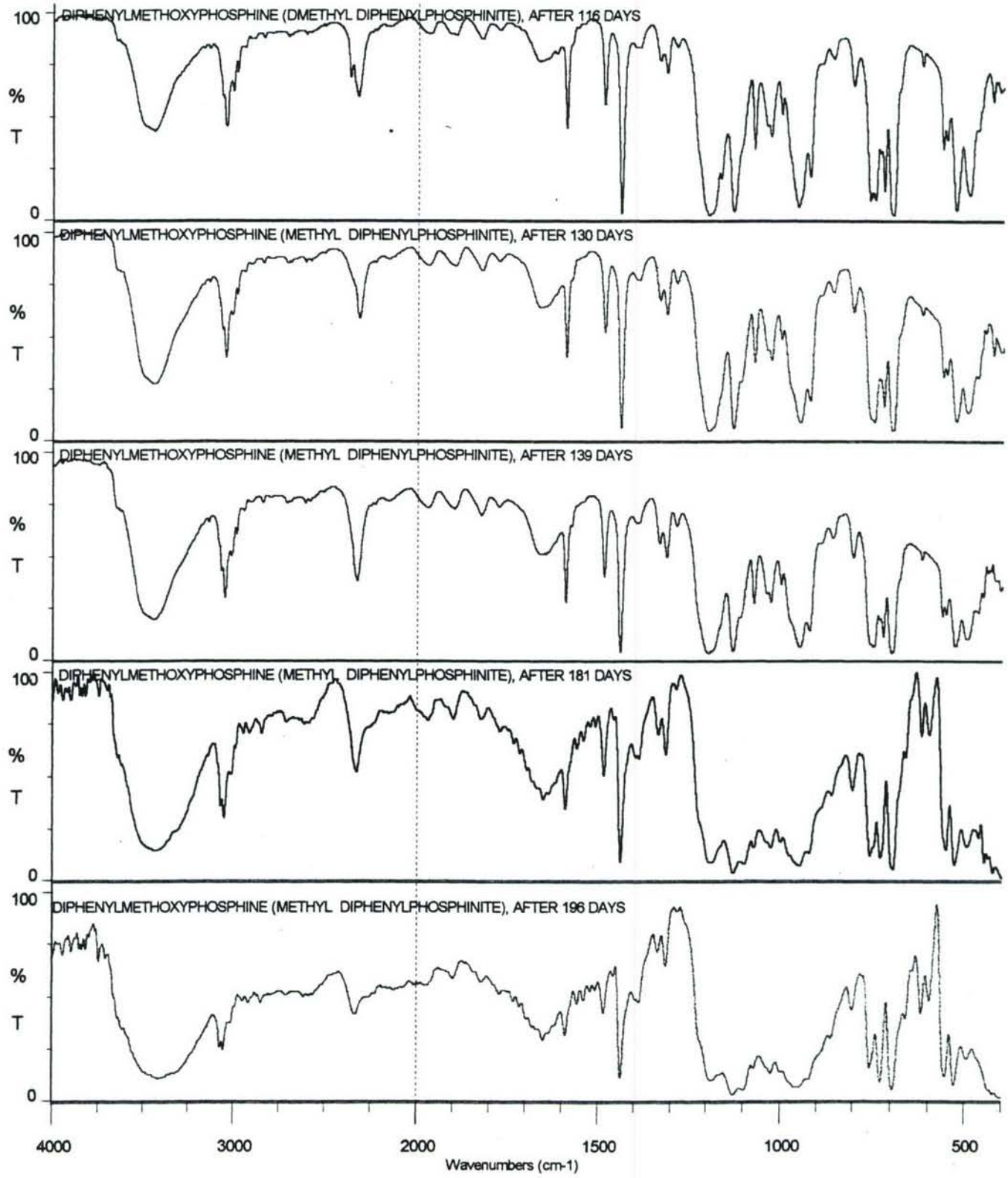

Figure 18B DIPHENYLMETHOXYPHOSPHINE (METHYL DIPHENYLPHOSPHINITE), CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

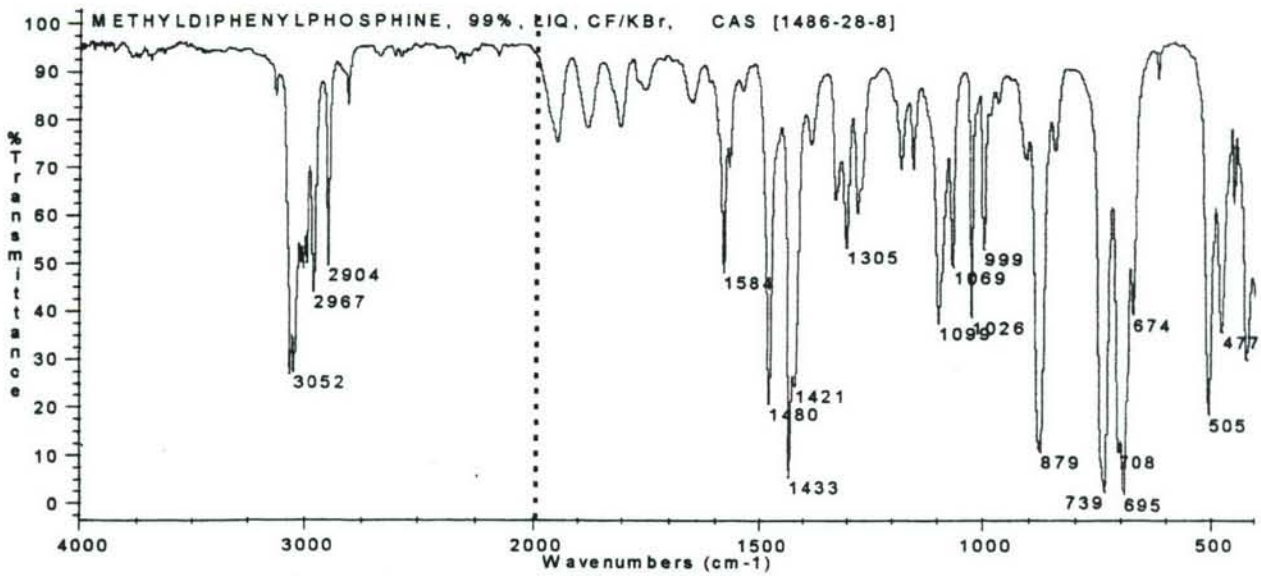

Figure 19 METHYLDIPHENYLPHOSPHINE, 99%, LIQUID, CF/KBr

P=O stretching vibration. Another band near 1123 cm^{-1} has also been growing in intensity and is assigned to a vibration of the phenyl-P moiety. The original compound, methyldiphenylphosphine, appears to have been oxidized to methyldiphenylphosphine oxide, $(C_6H_5)_2$ P=O(CH_3), which would have a calculated ν P=O of 1182.

3.1.9 Diphenyl-2-cyanoethylphosphine $(C_6H_5)_2P(CH_2\text{-}CH_2\text{-}C{\equiv}N)$

The infrared spectrum of diphenyl-2-cyanoethylphosphine as a KBr pellet is reproduced as ***Figure 21***. The band assignments are as follows: 3348 cm^{-1} vw (H_2O), 3070 cm^{-1} vw and 3053 cm^{-1} w (ν C-H aromatic ring), 2961 cm^{-1} vw and 2925 cm^{-1} vw (ν_{as} and ν_{sy} CH_2), 2257 cm^{-1} w and 2236 vw (ν C≡N), 1962 cm^{-1} vw, 1900 cm^{-1} vw, 1829 cm^{-1} vw and 1773 cm^{-1} vw (summation bands of mono-substituted aromatic ring), 1585 cm^{-1} w, 1484 cm^{-1} m and 1432 ms (aromatic ring), 1416 cm^{-1} vvw (δ P-CH_2 ?), 1309 cm^{-1} w (ω CH_2-C≡N), 1151 cm^{-1} w, 1070 cm^{-1} w 1025 cm^{-1} w and 999 cm^{-1} w (β C-H mono-substituted aromatic ring), 932 cm^{-1} w (ν C-C ?, 751 and 734 cm^{-1} s (γ C-H mono-substituted aromatic ring), 703 cm^{-1} s (δ aromatic ring), 513 cm^{-1} ms (mon-substitued aromatic ring ?).

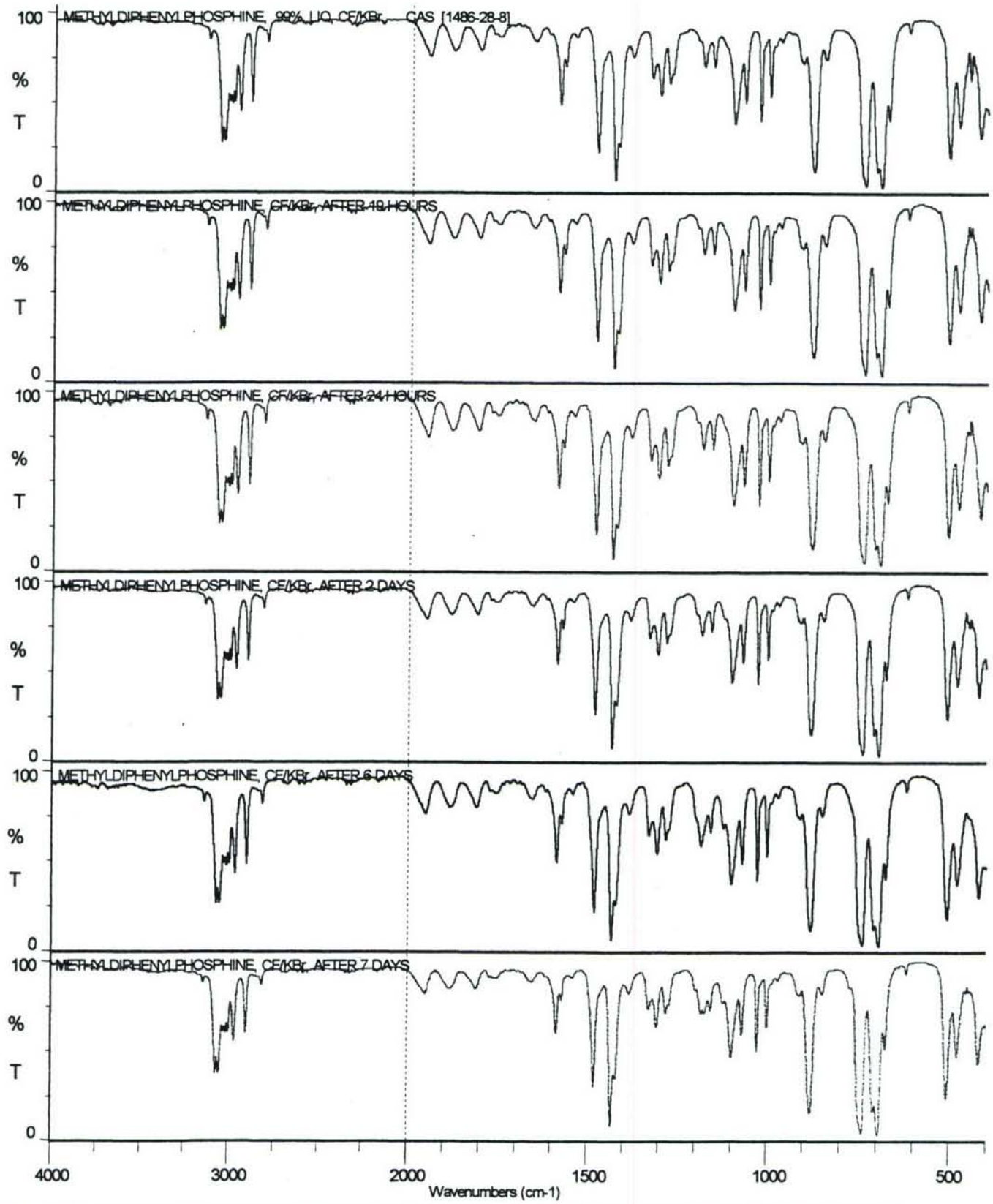

Figure 20A METHYLDIPHENYLPHOSPHINE, CF/KBr, AFTER EXPOSURE TO THE AMBIENT ATMOSPHERE

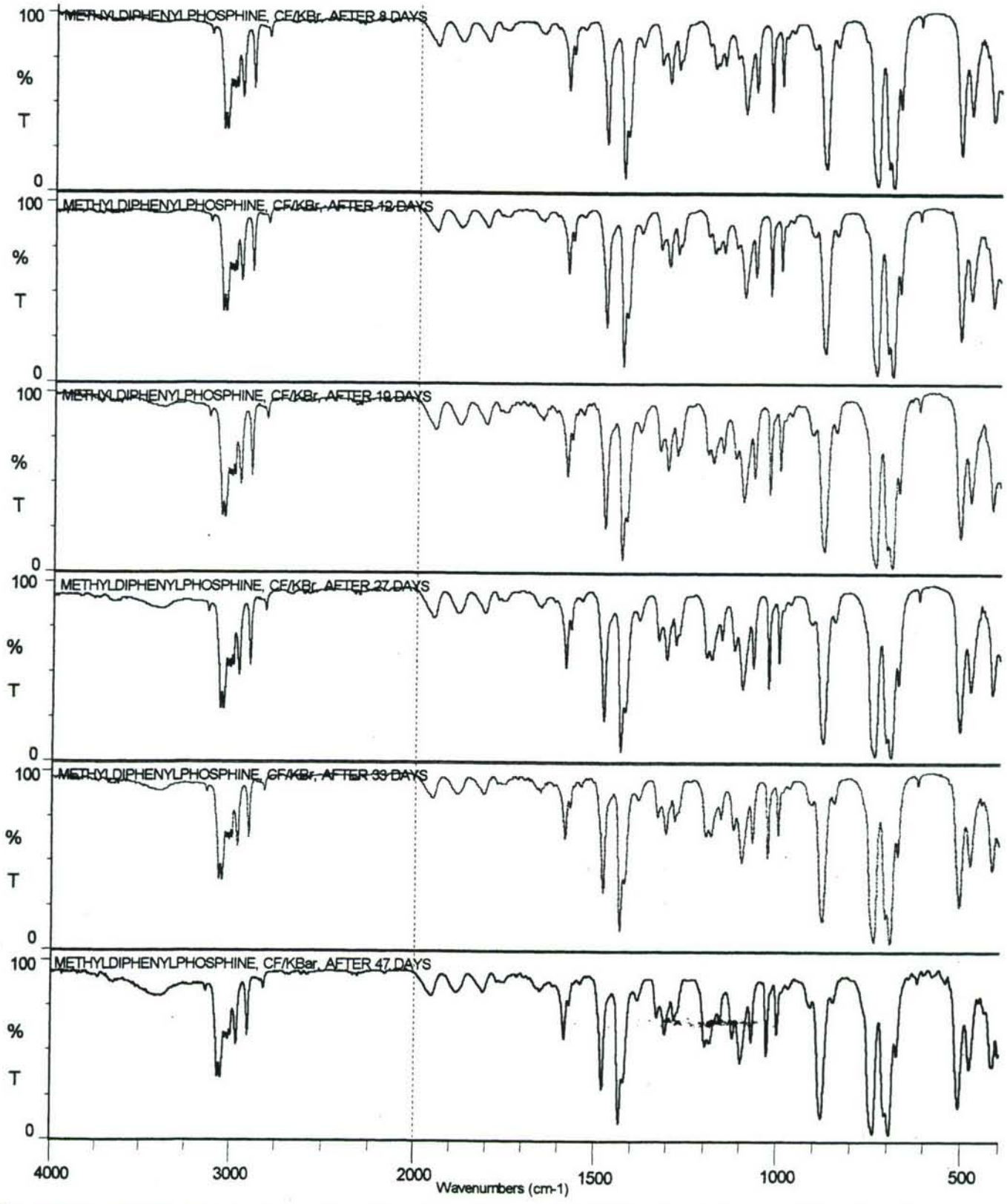

Figure 20B METHYLDIPHENYLPHOSPHINE, CF/KBr, AFTER EXPOSURE TO THE AMBIENT ATMOSPHERE (CONTINUED)

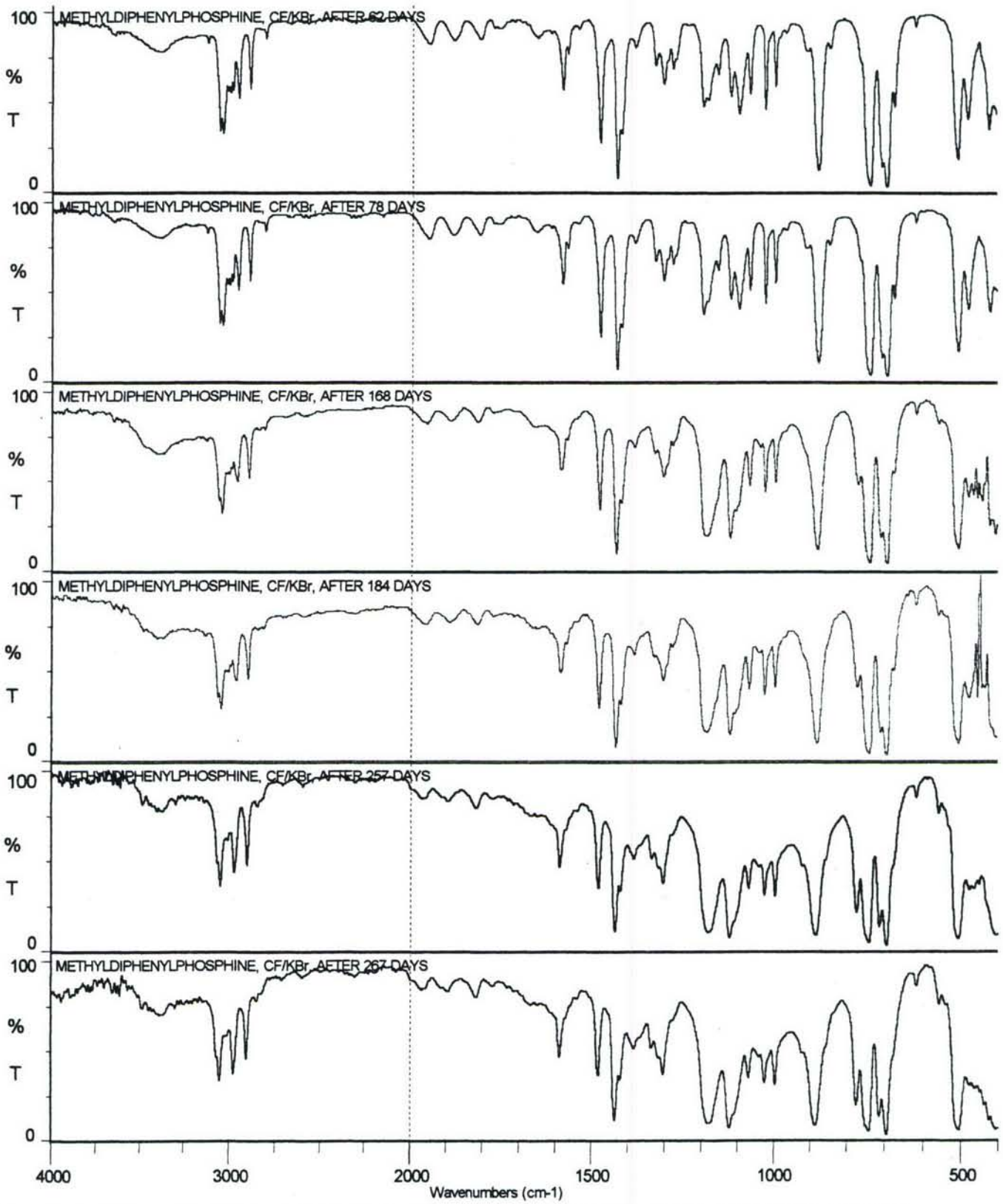

Figure 20C METHYLDIPHENYLPHOSPHINE, CF/KBr, AFTER EXPOSURE TO THE AMBIENT ATMOSPHERE (CONTINUED)

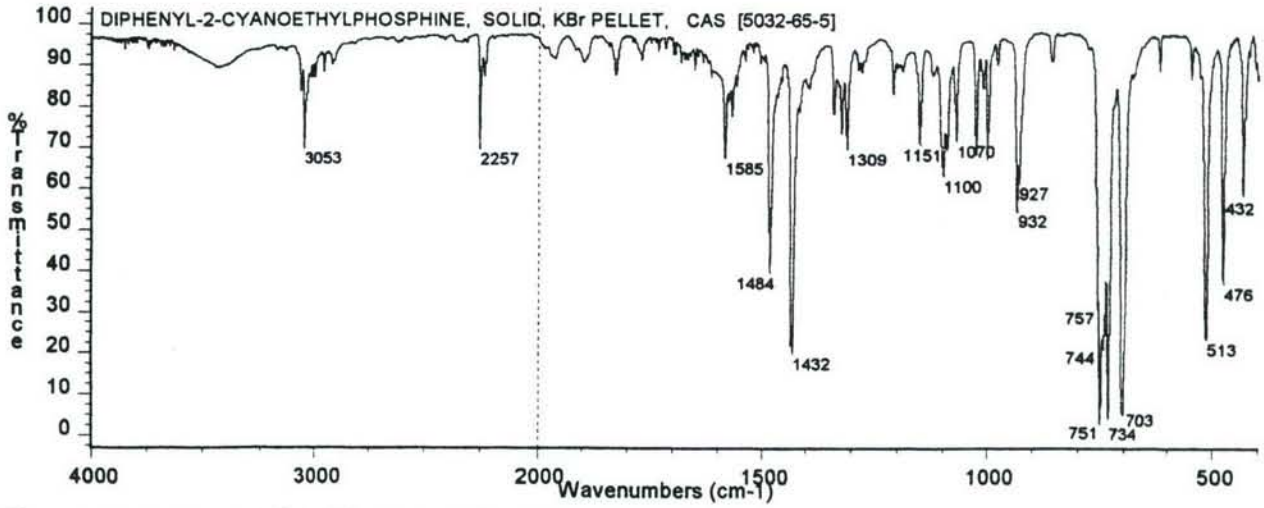

Figure 21 DIPHENYL-2-CYANOETHYLPHOSPHINE, SOLID, KBr PELLET

3.1.10 Triphenylphosphine $(C_6H_5)_3P$

The infrared spectrum of triphenylphosphine is reproduced as ***Figure 22***. The band assignments are as follows: 3423 cm^{-1} vw (H_2O), 3066 cm^{-1} w, 3048 cm^{-1} vw and 3001 cm^{-1} vw (ν C-H aromatic ring), 1961 cm^{-1} vw, 1890 cm^{-1} vw, 1817 cm^{-1} vw and 1768 vvw (summation bands of mono-substituted aromatic ring), 1583 cm^{-1} w, 1570 cm^{-1} vw, 1476 cm^{-1} m, 1435 cm^{-1} and 1430 cm^{-1} m (aromatic ring), 1177 cm^{-1} vw, 1154 cm^{-1} vw, 1025 cm^{-1} w and 995 cm^{-1} vw (β C-H mono-substituted aromatic ring), 1090 cm^{-1} w (phenyl-P), 754 cm^{-1} and 748 cm^{-1} s (γ C-H mono-substituted aromatic ring), 698 cm^{-1} and 692 cm^{-1} s (δ aromatic ring), 513, 499 and 491 cm^{-1} m (mono-substituted ring).

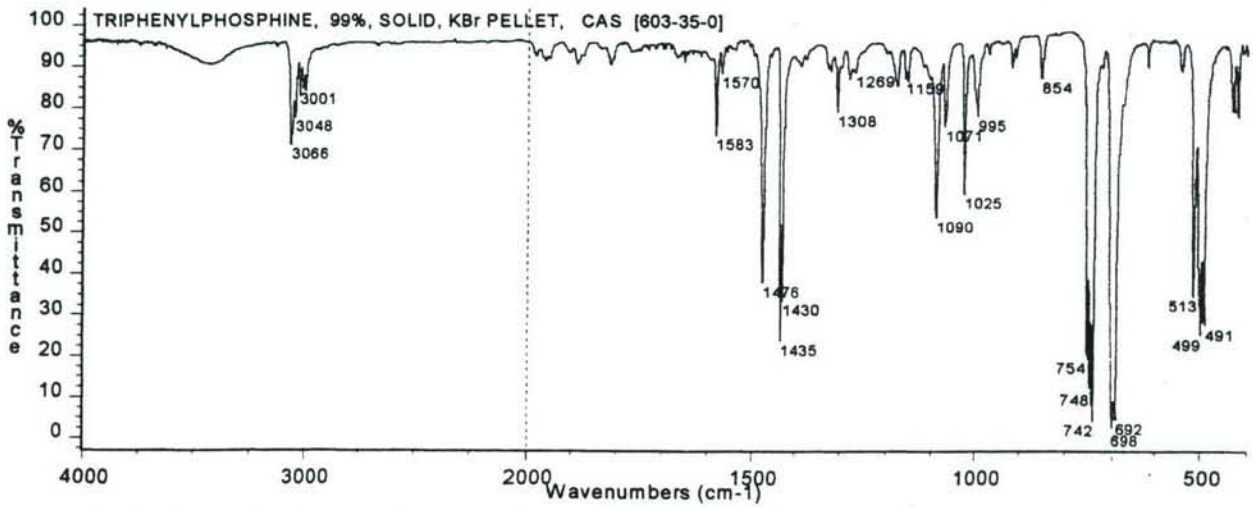

Figure 22 TRIPHENYLPHOSPHINE, 99%, SOLID, KBr PELLET

3.1.11 Isopropyldiphenylphosphine $(C_6H_5)_2P\text{-}CH(CH_3)_2$

The infrared spectrum of isopropyldiphenylphosphine is given in ***Figure 23.*** The band assignments are as follows: 3065 and 3054 cm^{-1} w, 3025 and 3010 cm^{-1} vw (ν C-H aromatic), 2972 and 2956 cm^{-1} m (ν_{as} CH_3), 2878 and 2867 cm^{-1} w (ν_{sy} CH_3), 1961, 1888, 1818 and 1770 cm^{-1} all vw (summation bands mono-substituted aromatic ring), 1599 cm^{-1} vw, 1473, 1467 cm^{-1} w and 1435, 1430 cm^{-1} m (aromatic ring), 1383 w and 1363 vw (δ_{sy} CH_3), 1228 w (isopropyl moiety ?), 1182, 1154, 1073, 1028 and 998 cm^{-1} vw-w (β C-H mono-substituted aromatic ring), 1098, 1089 cm^{-1} w (phenyl-P), 752 and 745 ms (γ C-H mono-substituted aromatic ring), 697 cm^{-1} s (δ mono-substituted aromatic ring).

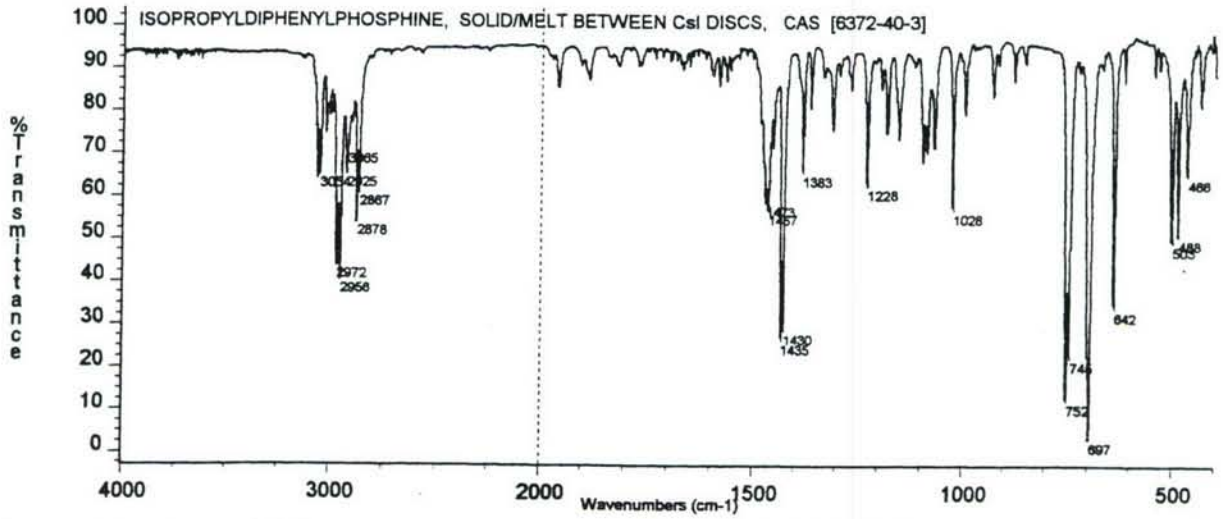

Figure 23 ISOPROPYLDIPHENYLPHOSPHINE, SOLID/MELT BETWEEN CsI DISCS

3.1.12 Diphenylvinylphosphine $(C_6H_5)_2P\text{-}CH{=}CH_2$

The infrared spectrum of diphenylvinylphosphine is reproduced as ***Figure 24***. The band assignments are as follows: 3069, 3053 cm^{-1} m and 3012 cm^{-1} w (ν C-H aromatic and ν_{as} $=CH_2$ and ν_{sy} $=CH_2$ and ν =C-H), 1954, 1886, 1813 and 1773 cm^{-1} vw (summation bands from a mono-substituted aromatic ring: note-the vinyl moiety can have an overtone band, 2 x CH_2 wag, 910-905 cm^{-1}, in the range 1840-1805 cm^{-1}), 1586 cm^{-1} w (ν C=C vinyl, some contribution from the aromatic ring), 1571 cm^{-1} vw, 1480 cm^{-1} m and 1434 cm^{-1} ms (aromatic ring), 1394 cm^{-1} w (δ $=CH_2$), 1182 cm^{-1} vw, 1069 cm^{-1} vw,

1027 cm^{-1} w and 999 cm^{-1} sh (β C-H mono-substituted aromatic ring), 1096 cm^{-1} w (phenyl-P), 985 cm^{-1} m (*trans* C-H wag), 929 cm^{-1} w (=CH_2 wag ?), 743 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 696 cm^{-1} s (δ mono-substituted aromatic ring), 507 cm^{-1} m (mono-substituted aromatic ring ?).

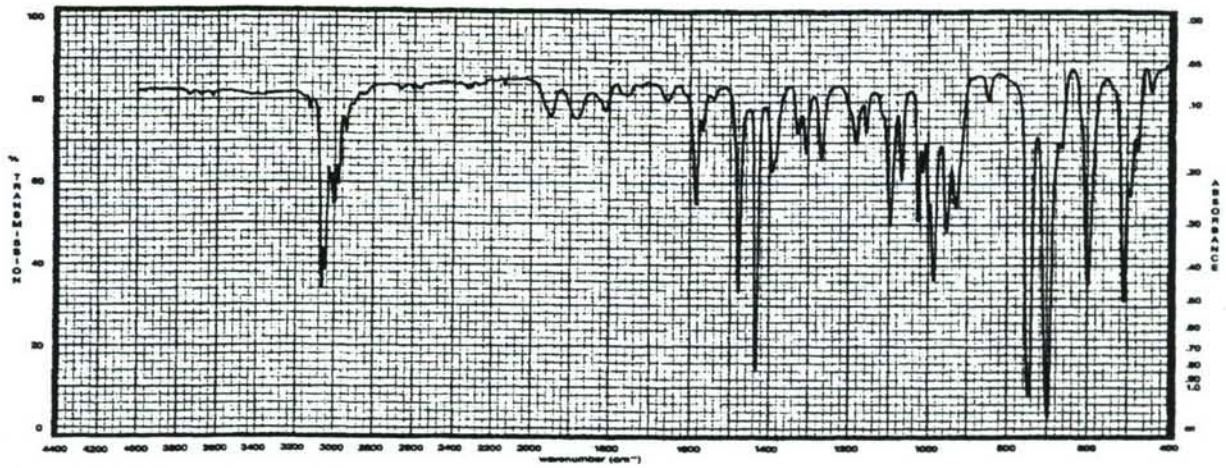

Figure 24 DIPHENYLVINYLPHOSPHINE, LIQUID, CF/CsI

The effect of the environment on a liquid film of diphenylvinylphosphine between CsI windows is illustrated by infrared spectra illustrated in ***Figures 24A*** through ***24D.*** After 6 days of exposure to the environment the infrared spectrum of the compound shows the formation of a new band near 1198cm^{-1}. This new band shows a gradual decrease to 1191 cm^{-1} as the time of exposure approaches 35 days. The band is assigned to a P=O stretching vibration from the oxidation of the original compound to diphenylvinylphosphine oxide, $(C_6H_5)_2P{=}O(CH{=}CH_2)$. This phosphine oxide would have a calculated P=O stetching vibration of 1194 cm^{-1}.

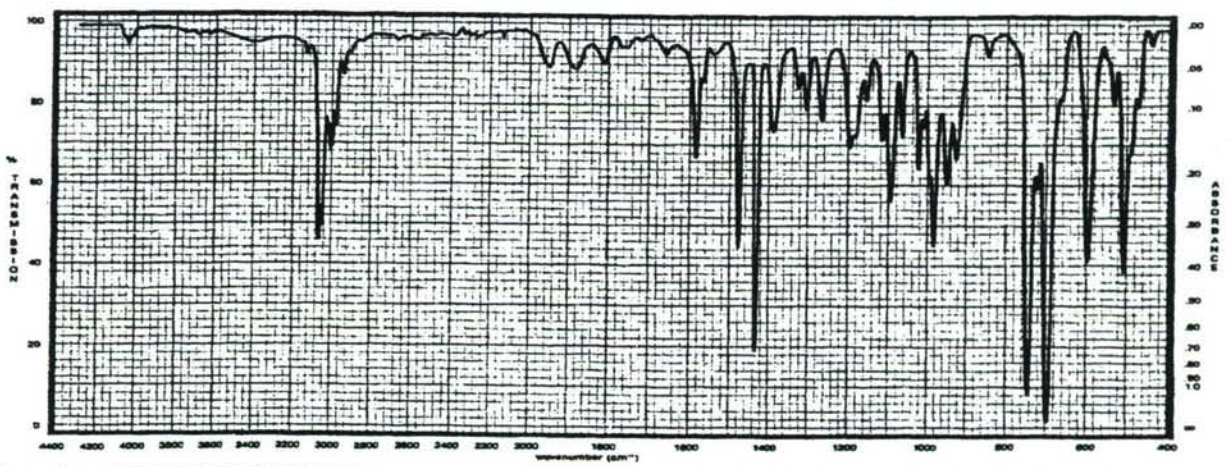

Figure 24A DIPHENYLVINYLPHOSPHINE, LIQ, CF/CsI, AFTER 6 DAYS OF ENVIRONMENTAL EXPOSURE

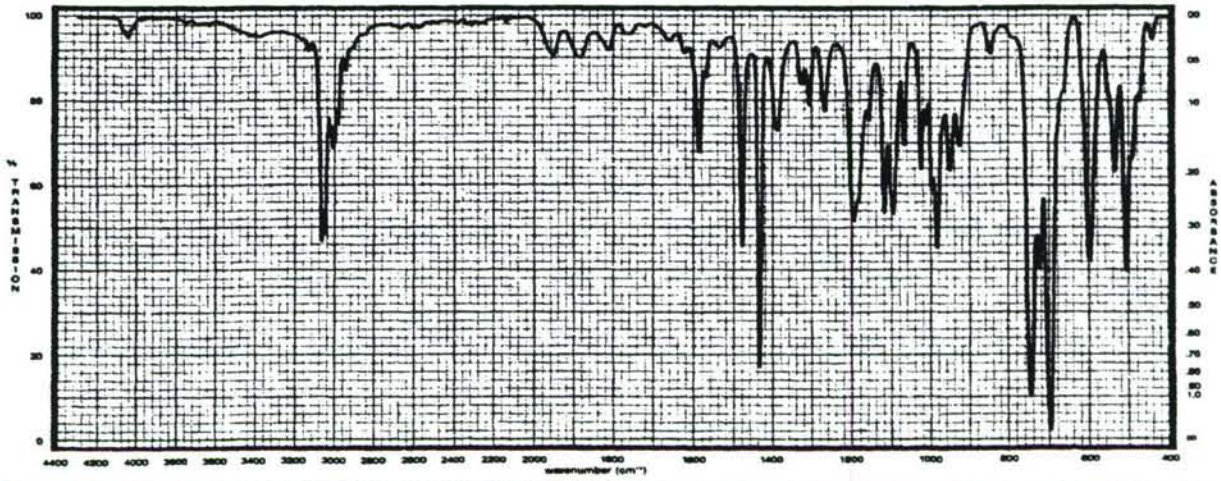

Figure 24B DIPHENYLVINYLPHOSPHINE, LIU, CF/CsI, AFTER 9 DAYS OF ENVIRONMENTAL EXPOSURE

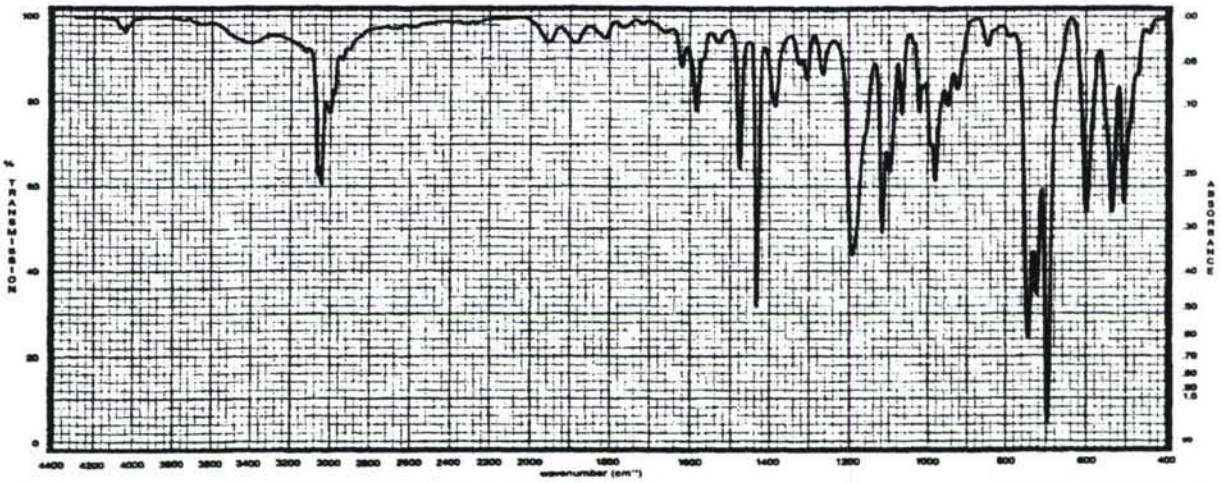

Figure 24C DIPHENYLVINYLPHOSPHINE, LIQ, CF/CsI, AFTER 17 DAYS OF ENVIRONMENTAL EXPOSURE

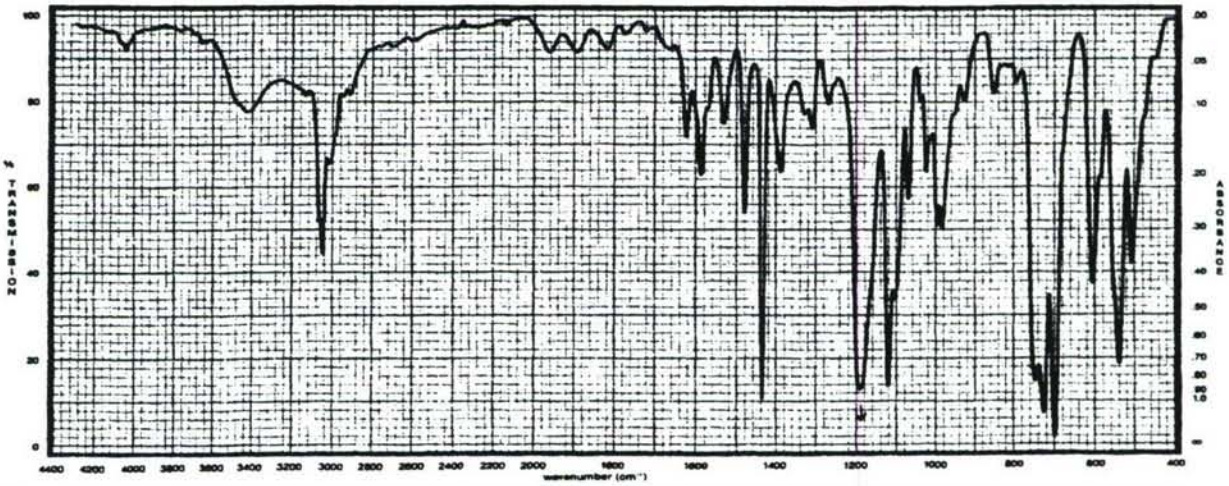

Figure 24D DIPHENYLVINYLPHOSPHINE, LIQ, CF/CsI, AFTER 35 DAYS ENVIRONMENTAL EXPOSURE

3.1.13 Chlorodiethylphosphine (diethylphosphinous chloride) $Cl\text{-}P(CH_2\text{-}CH_3)_2$

The infrared spectrum for a liquid film of chlorodiethylphosphine between CsI discs is given in ***Figure 25***. The band assignments are as follows: 2965 cm^{-1} s (ν_{as} CH_3), 2934 cm^{-1} ms (ν_{as} CH_2), 2908 cm^{-1} vvw (ν_{sy} CH_3), 2877 cm^{-1} ms (ν_{sy} CH_2), 1457 cm^{-1} ms (δ_{as} CH_3), 1406 cm^{-1} w (δ CH_2-P), 1379 cm^{-1} m (δ_{sy} CH_3), ca 1280 cm^{-1} sh and 1237 cm^{-1} vw (P-Ethyl, ω,τ CH_2), 1048 and 1019 cm^{-1} w (ν C-C)m 979 cm^{-1} vw (ν P-OH, from hydrolysis ?), 765 and 755 cm^{-1} m (CH_2 rock), 683 and 666 cm^{-1} m (ν P-C), 482 and 470 cm^{-1} ms (ν P-Cl).

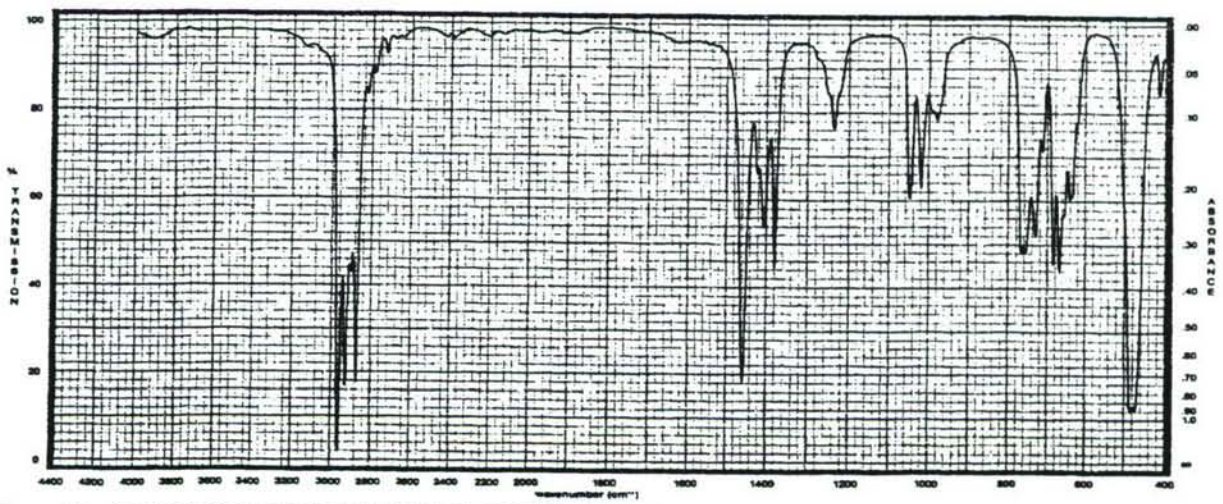

Figure 25 CHLORODIETHYLPHOSPHINE, LIQUID, CF/CsI

The infrared spectra illustrating the effect of atmospheric moisture on chlorodiethylphosphine are reproduced as ***Figures 25A-E***. After 1 hour of exposure the spectrum (***Figure 25A***) shows a split band near 2400 cm^{-1} (2447 and 2389 cm^{-1}) assignable to a P-H stretch. A band at 1218 cm^{-1} may be due to a P=O stretching vibration. Some P-OH may be indicated by the broad underlying band near 2400 and 1620 cm^{-1}. A strong P-Cl band is still evident near 470 cm^{-1}. As exposure time increases to 19 hours (***Figure 25 B***), the band near 1212 cm^{-1} has become stronger as have bands near 2400, 1630 cm^{-1} (POH) and 1170 cm^{-1} (ν P=O, acid). After 43 hours of exposure (***Figure 25C***), the bands due to the formation of a P-acid (ca 2350, 1630, 1159 and 964 cm^{-1}) have become even more intense. The 1300-

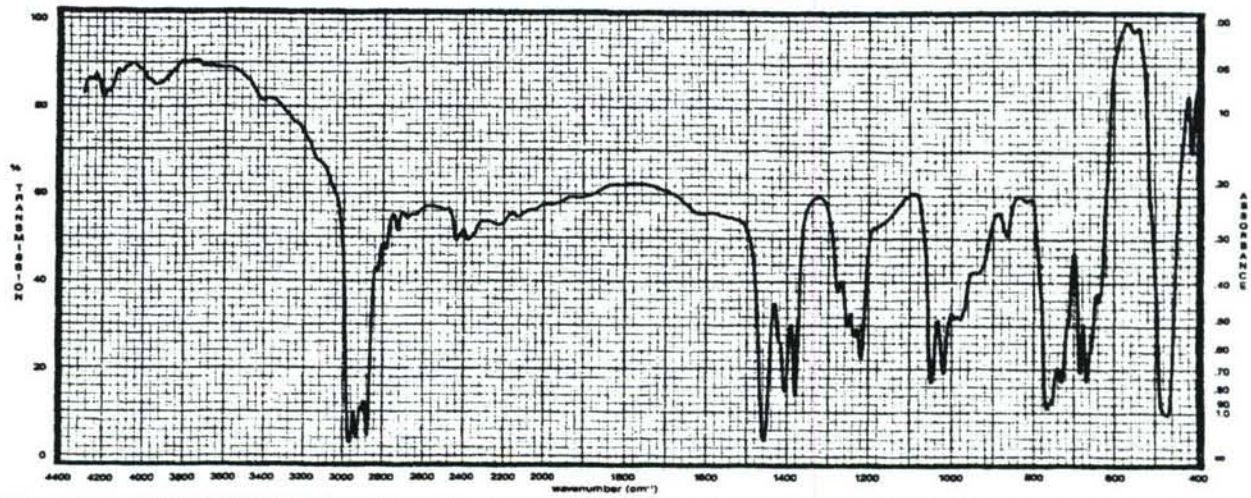

Figure 25A CHLORODIETHYLPHOSPHINE, LIQ, CF/CsI, AFTER 1 HOUR OF ENVIRONMENTAL EXPOSURE

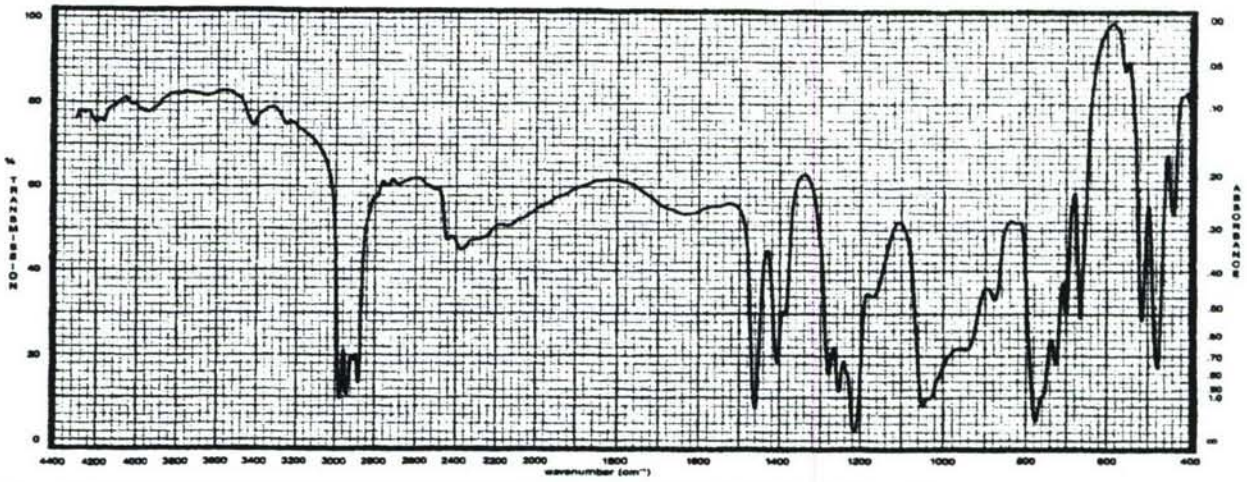

Figure 25B CHLORODIETHYLPHOSPHINE, LIQ, CF/CsI, AFTER 19 HOURS OF ENVIRONMENTAL EXPOSURE

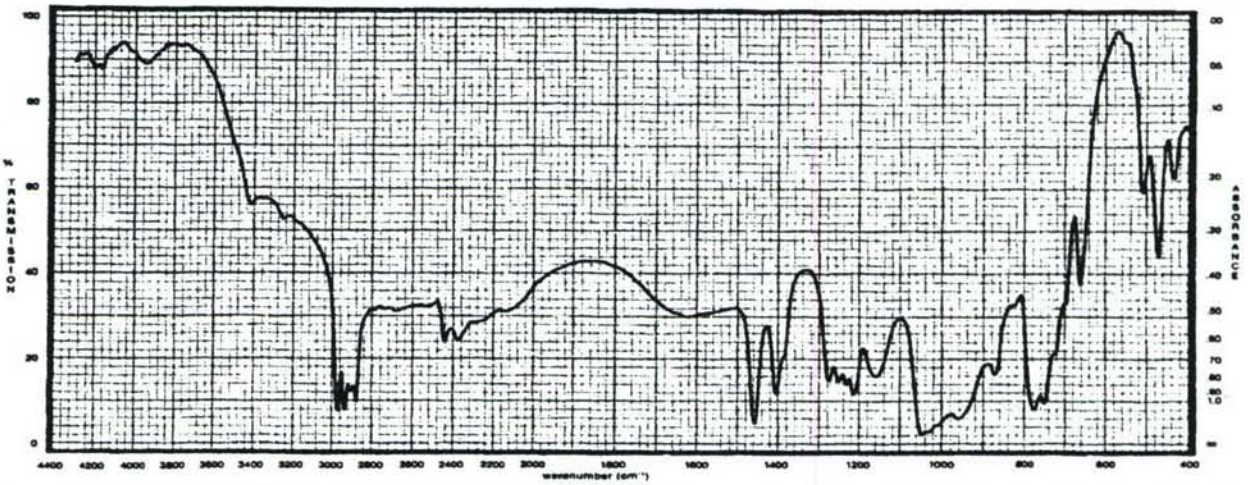

Figure 25C CHLORODIETHYLPHOSPHINE, LIQ, CF/CsI, AFTER 43 HOURS OF ENVIRONMENTAL EXPOSURE

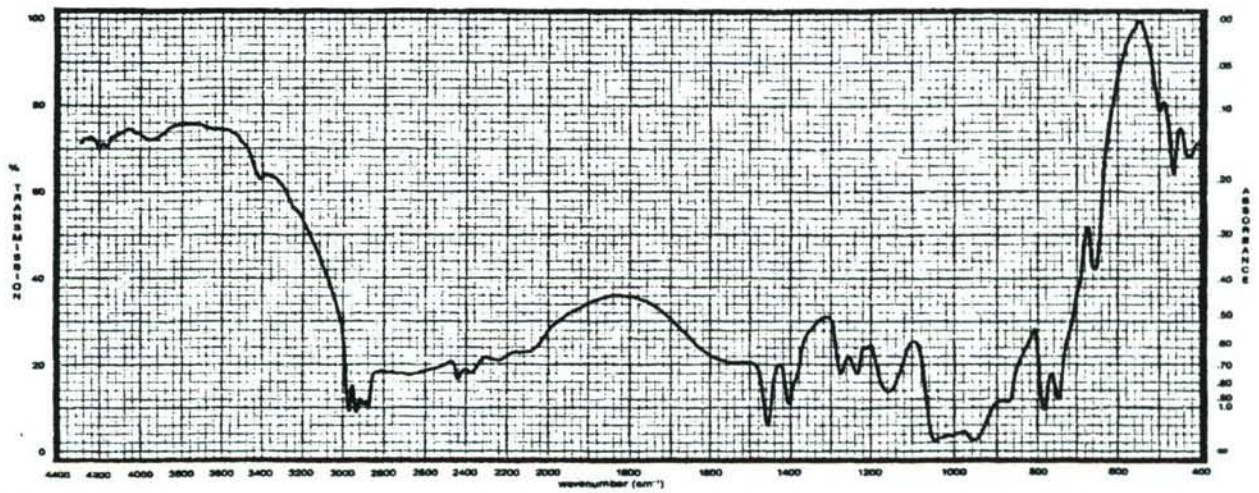

Figure 25D CHLORODIETHYLPHOSPHINE, LIQ, CF/CsI, AFTER 3 DAYS OF ENVIRONMENTAL EXPOSURE

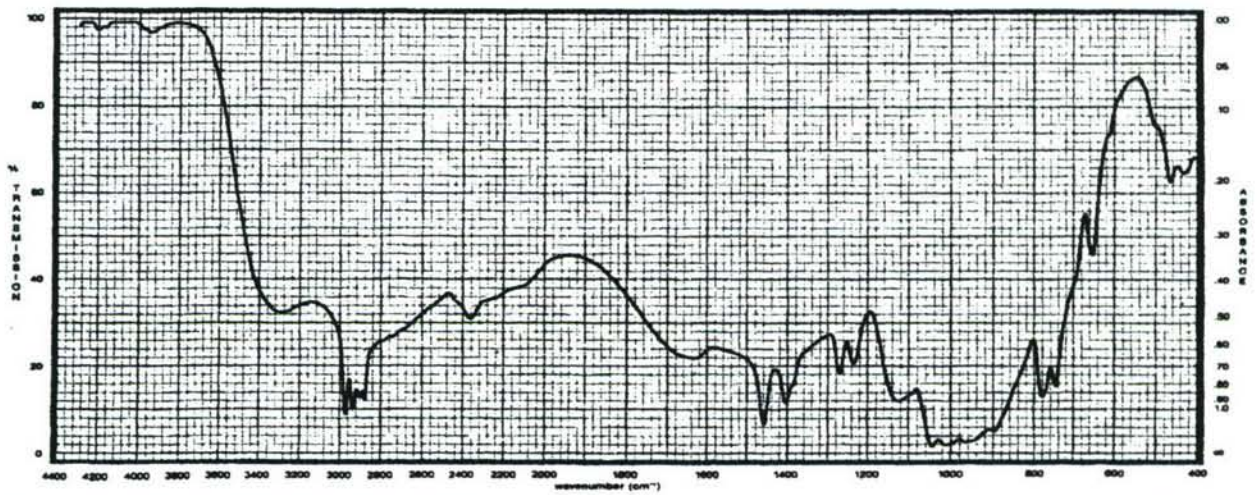

FIgure 25E CHLORODIETHYLPHOSPHINE, LIQ, CF/CsI, AFTER 6 DAYS OF ENVIRONMENTAL EXPOSURE

1200 cm^{-1} region has become complex, now being composed of 4 bands (1277, 1252, 1234 and 1213 cm^{-1}). This region could be composed of bands due to P-Ethyl, P=O (from $ClP{=}OEt_2$, and $Et_2P(=O)$-O-$P(=O)Et_2$, and $HP{=}OEt_2$, which would have calculated ν P=O bands of 1226, 1222 and 1190 cm^{-1} respectively). The compound $Et_2P{=}O(OH)$ might be expected to absorb near 1162 cm^{-1} (ν P=O) and 950 cm^{-1} (ν P-OH). Bands are present at 1159 and 964 cm^{-1}. As the time of exposure increased to 3 days (***Figure 25D***), the bands due to the acid moiety became more predominant. The P-H band near 2400 cm^{-1} was still visible in the spectrum, albeit much weaker. After 6 days of exposure to the environment,

the spectrum (***Figure 25E***) shows mainly the presence of a P-acid, probably $Et_2P{=}O(OH)$, diethylphosphinic acid. A weak band at 2368 cm^{-1} (ν P-H) and a band near 1000 cm^{-1} (P-H deformation) still indicate the presence of some $HP(=O)Et_2$, diethylphosphine oxide. Apparently, hydrolysis and oxidation (followed by hydrolysis) are occuring concurrently. These events may be summarized as follows:

$Cl\text{-}PEt_2$ -HOH→ $HO\text{-}PEt_2$ → $H\text{-}P(=O)Et_2$

$Cl\text{-}PEt_2$ -[O]→ $Cl\text{-}P(=O)Et_2$ -HOH→ $Et_2P(=O)\text{-}O\text{-}P(=O)Et_2$ (?) -HOH→ $HO\text{-}P(=O)Et_2$.

3.1.14 Ethylmethylphenylphosphine $(CH_3CH_2)(CH_3)P\text{-}C_6H_5$

The infrared spectrum of ethylmethylphenylphosphine is give as ***Figure 26***. The band assignments are as follows: 3071and 3053 cm^{-1} m and 3026 cm^{-1} w (ν C-H aromatic), 2961 cm^{-1} s (ν_{as} CH_3), 2929 cm^{-1} m (ν_{as} CH_2), 2901 cm^{-1} ms (ν_{sy} CH_3), 2873 cm^{-1} m (ν_{sy} CH_2), 1587 cm^{-1} vw, 1485 cm^{-1} w, 1433 cm^{-1} ms (aromatic ring), 1456 cm^{-1} m (δ_{as} CH_3), 1376 cm^{-1} w (δ_{sy} CH_3), 1305 cm^{-1} vw (δ_{sy} P-CH_3), 1283 and 1240 cm^{-1} w (P-Ethyl), 1156 cm^{-1} vw, 1070 w (β C-H mono-substituted aromatic ring), 1029 and 1003 cm^{-1} w (ν C-C of P-Ethyl, and β C-H mono-substituted aromatic ring), 875 cm^{-1} ms (P-CH_3 rock), 738 cm^{-1} s (γ C-H mono-substituted aromatic ring), 696 cm^{-1} s (δ mono-substituted aromatic ring), 647 cm^{-1} w (ν P-C).

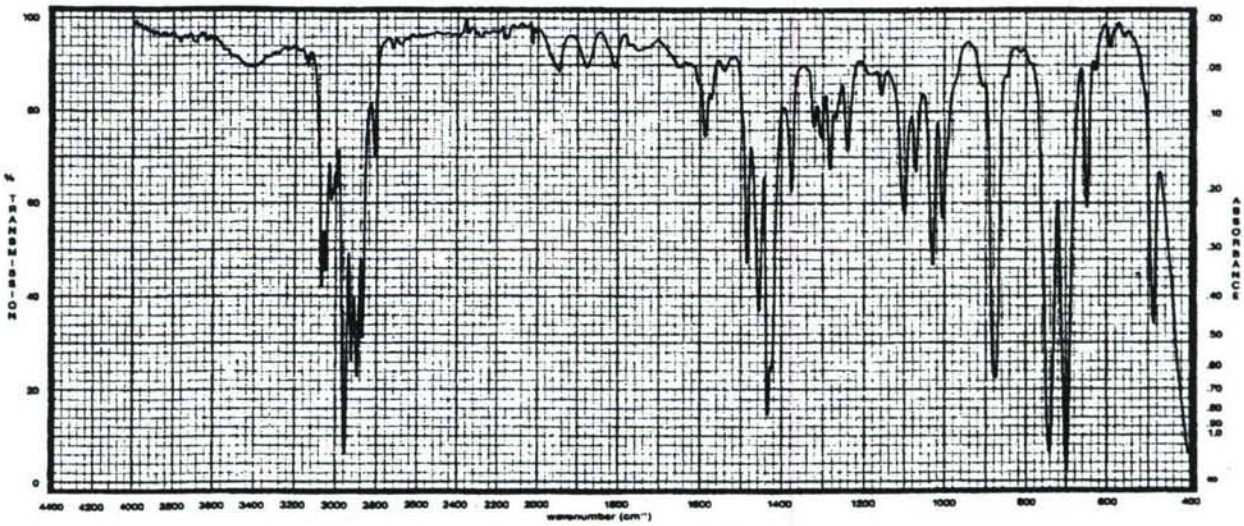

Figure 26 ETHYLMETHYLPHENYLPHOSPHINE, LIQUID, CF/KBr

The exposure of the liquid film of ethylmethylphenylphosphine to the ambient environment resulted in the following results as depicted by ***Figures 26A-C***. After 4 days of exposure the spectrum for the compound (***Figure 26A***) showed the formation of a very weak band near 1190 cm^{-1} (possible ν P=O). This band near 1190 cm^{-1} continues to grow in intensity as the time of exposure increases through 13 days (***Figure 26B***) to 29 days (***Figure 26C***). By 29 days, the band has become quite intense, falling to

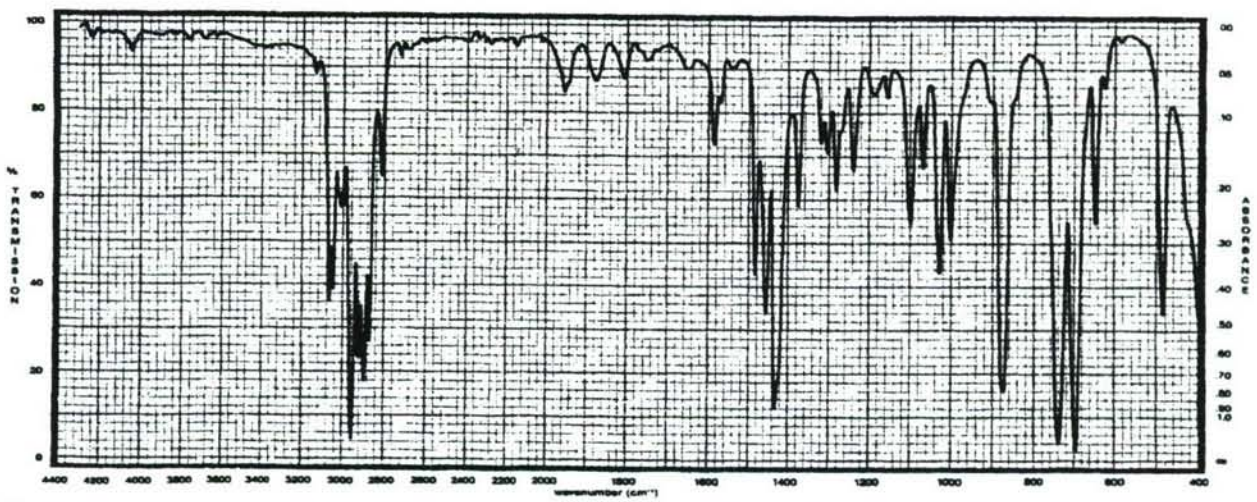

Figure 26A ETHYLMETHYLPHENYLPHOSPHINE, LIQUID, CF/KBr, AFTER 4 DAYS OF ENVIRONMENTAL EXPOSURE

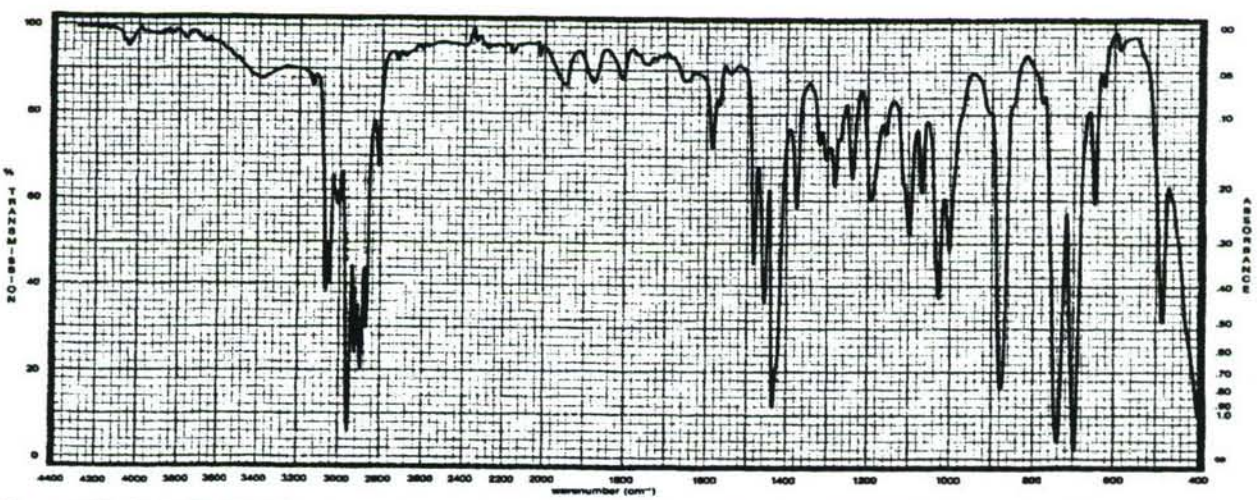

Figure 26B ETHYLMETHYLPHENYLPHOSPHINE, LIQUID, CF/KBr, AFTER 13 DAYS OF ENVIRONMENTAL EXPOSURE

1179 cm^{-1} possibly due to the increase of water as evidenced by the band at 3400 cm^{-1}. This band is assigned to a P=O stretching vibration from the oxidation product ethylmethylphenylphosphine oxide,

(Et)(Me)P=O(C_6H_5). This new compound would have a calculated value of 1178 cm^{-1} for the P=O stretching vibration.

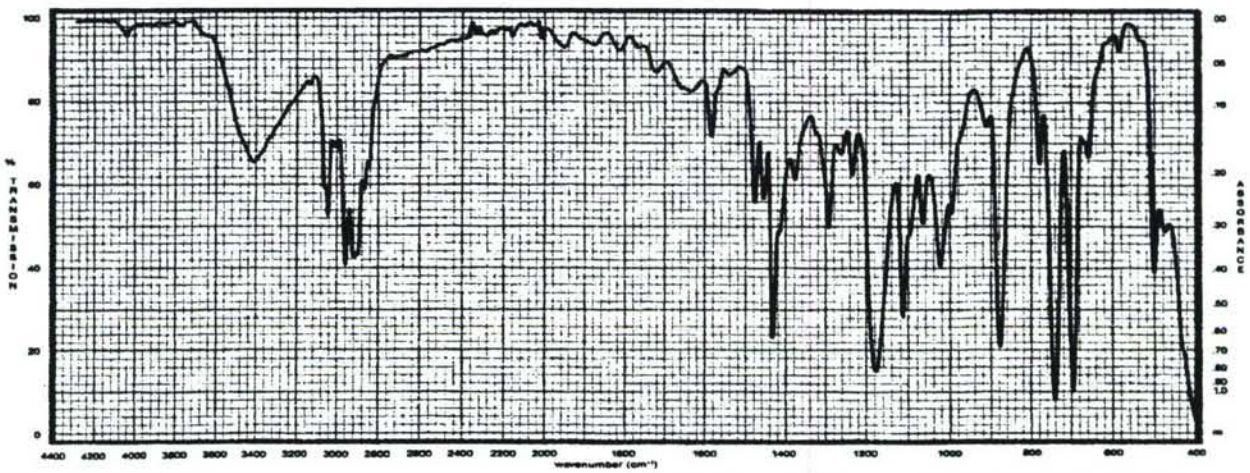

Figure 26C ETHYLMETHYLPHENYLPHOSPHINE, LIQUID, CF/KBr, AFTER 29 DAYS OF ENVIRONMENTAL EXPOSURE

3.1.15 Di-*n*-butylmethylphosphine CH_3-P(n-C_4H_9)$_2$

The infrared spectrum of a liquid film of di-*n*-butylmethylphosphine is given in ***Figure 27***. Band assignments are as follows: 2957 cm^{-1} s (ν_{as} CH_3), 2925 cm^{-1} s (ν_{as} CH_2), 2896 cm^{-1} sh (ν_{sy} CH_3), 2873 cm^{-1} ms (ν_{sy} CH_2), 1463 cm^{-1} ms (δ_{as} CH_3), 1424 cm^{-1} m (δ P-CH_2 and δ_{as} P-CH_3), 1378 cm^{-1} w (δ_{sy} CH_3), 1283 cm^{-1} w (δ_{sy} P-CH_3), 1203 cm^{-1} w (ω CH_2 ?), 1046 cm^{-1} w and 1006 cm^{-1} vw (ν C-C ?), 917 cm^{-1} m (P-CH_3 rock), 720 cm^{-1} w (CH_2 rock, ν P-C).

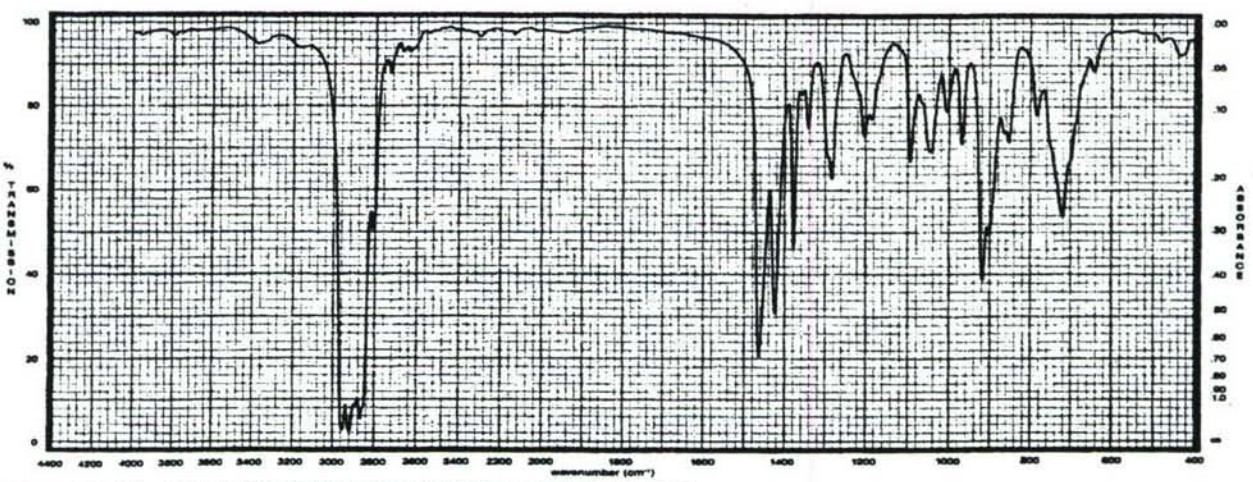

Figure 27 DI-*n*-BUTYLMETHYLPHOSPHINE, LIQUID, CF/CsI

3.1.16 Di-*n*-butylphenylphosphine C_6H_5 -P(n-C_4H_9)$_2$

The infrared spectrum of a liquid film of di-*n*-butylphenylphosphine is reproduced in ***Figure 28***. The band assignments are as follows: 3070 and 3054 cm^{-1} w, 3025 and 3001 cm^{-1} vw (ν C-H aromatic), 2957 cm^{-1} s (ν_{as} CH_3), 2827 cm^{-1} s (ν_{as} CH_2), 2872 cm^{-1} m (ν_{sy} CH_3), 2858 cm^{-1} m (ν_{sy} CH_2), 1587 cm^{-1} vw, 1572 cm^{-1} vvw, 1484 cm^{-1} w and 1434 cm^{-1} m (aromatic ring), 1464 cm^{-1} m (δ_{as} CH_3), 1417 cm^{-1} w (δ CH_2-P), 1378 cm^{-1} w (δ_{sy} CH_3), 1201 cm^{-1} vw (ω CH_2 ?), 1182 cm^{-1} vvw (ν P=O from a phosphine oxide ?), 1096 cm^{-1} w (phenyl-P), 1028 and 1001 cm^{-1} vw (ν C-C from C_4H_9 and/or β C-H mono-substituted aromatic ring), 740 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 697 cm^{-1} ms (δ mono-substituted aromatic ring).

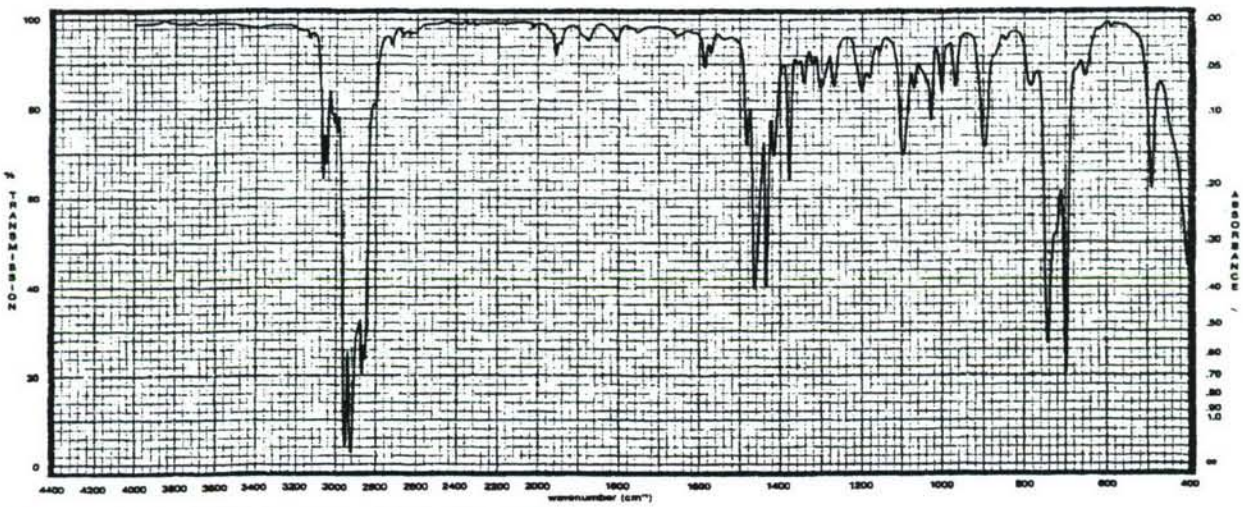

Figure 28 DI-*n*-BUTYLPHENYLPHOSPHINE, LIQUID, CF/KBr

3.1.17 Butyldiphenylphosphine $(C_6H_5)_2P$-C_4H_9

The infrared spectrum of a liquid film of butyldiphenylphosphine is given in ***Figure 29***. The band assignments are as follows: 3070 and 3053 cm^{-1} m, 3015 and 3000 cm^{-1} w (ν C-H aromatic ring), 2957 cm^{-1} ms (ν_{as} CH_3), 2929 cm^{-1} ms (ν_{as} CH_2), 2871 cm^{-1} m (ν_{sy} CH_3), 2858 cm^{-1} m (ν_{sy} CH_2), 1951, 1884, 1810 and 1750 cm^{-1} all vw (summation bands of mono-substituted aromatic ring), 1585 cm^{-1} w, 1571 cm^{-1} vw, 1481 cm^{-1} m 1433 cm^{-1} ms (aromatic ring), 1465 cm^{-1} w (δ_{as} CH_3), 1417 cm^{-1} vw (δ

CH_2 -P), 1378 cm^{-1} w (δ_{sy} CH_3), 1201 cm^{-1} vw (ω CH_2 ?), 1183 cm^{-1} vw, 1157 cm^{-1} vw, 1069 cm^{-1} vw (β C-H mono-substituted aromatic ring), 1093 cm^{-1} w (phenyl-P), 1027 cm^{-1} w and 1000 cm^{-1} vw (ν C-C of butyl moiety, and/or β C-H mono-substituted aromatic ring), 739 cm^{-1} ms (γ C-H mono-substituted ring), 696 cm^{-1} s (δ mono-substituted aromatic ring).

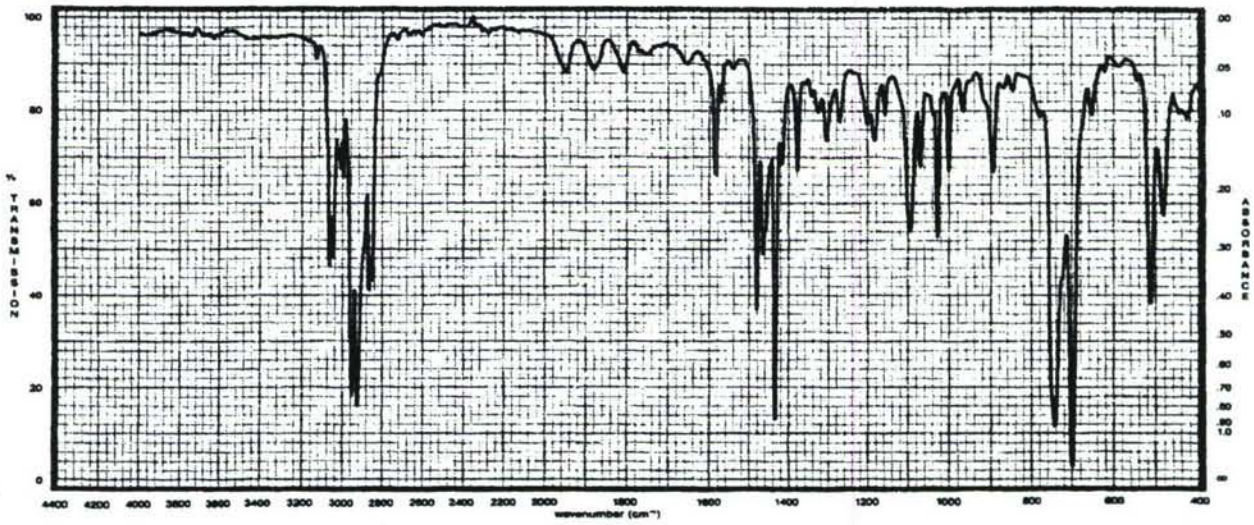

Figure 29 BUTYLDIPHENYLPHOSPHINE, 97%, LIQUID, CF/CsI

3.1.18 Ethyldiphenylphosphine $(C_6H_5)_2P\text{-}CH_2CH_3$

The infrared spectrum of ethyldiphenylphosphine as a liquid film between KBr windows is reproduced as ***Figure 30***. The band assignments are as follows: 3070 and 3053 cm^{-1} m, 3029 cm^{-1} vvw, 3015 and 3001 cm^{-1} vw (ν C-H aromatic ring), 2962 cm^{-1} m (ν_{as} CH_3), 2929 cm^{-1} m (ν_{as} CH_2), 2873 cm^{-1} w and 2823 cm^{-1} vvw (ν_{sy} CH_3 and CH_2), 1958, 1885, 1812 and 1758 cm^{-1} all vw (summation bands of mono-substituted aromatic ring), 1586 cm^{-1} w, 1571 cm^{-1} vvw, 1481 cm^{-1} m and 1434 cm^{-1} ms (aromatic ring), 1455 cm^{-1} w (δ_{as} CH_3), 1377 cm^{-1} vw (δ_{sy} CH_3), 1272 and 1239 cm^{-1} vw (P-Et ω, τ CH_2), 1184 cm^{-1} vw, 1157 cm^{-1} vw, 1070 cm^{-1} w (β C-H mono-substituted aromatic ring), 1095 cm^{-1} w (phenyl-P), 1029 and 999 cm^{-1} w (ν C-C of P-Et and/or β C-H mono-substituted aromatic ring), 738 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 697 cm^{-1} (δ mono-substituted aromatic ring), 660 cm^{-1} w (ν P-C of P-Et), 510 cm^{-1} m (aromatic ring ?).

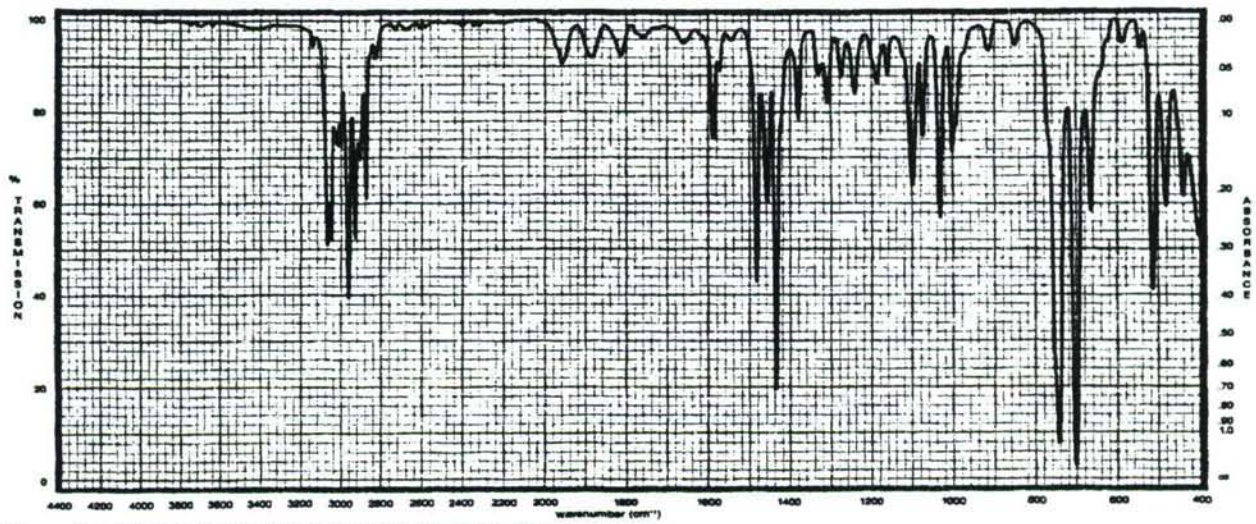

Figure 30 ETHYLDIPHENYLPHOSPHINE, LIQUID, CF/KBr

3.1.19 Dimethylhydroxymethylphosphine $(CH_3)_2P(CH_2OH)$

The infrared spectrum of dimethylhydroxymethylphosphine as a liquid film between CsI windows is given in ***Figure 31***. The band assignments are as follows: 3336 cm^{-1} ms broad (ν OH bonded), 2966 cm^{-1} m, 2898 cm^{-1} ms and 2818 cm^{-1} m (ν CH_3 and CH_2), 1428 cm^{-1} ms (δ_{as} P-CH_3, δ CH_2, and β OH near 1400 cm^{-1}), 1296 cm^{-1} m (δ_{sy} P-CH_3), 1160 and 1141 cm^{-1} m (ω CH_2), 1024 cm^{-1} s (ν C-O), 943 and 892 cm^{-1} ms-m (P-CH_3 asym. and sym. rock), 746 cm^{-1} w and 712 cm^{-1} m (ν P-C), ca 625 cm^{-1} broad and shallow (γ O-H).

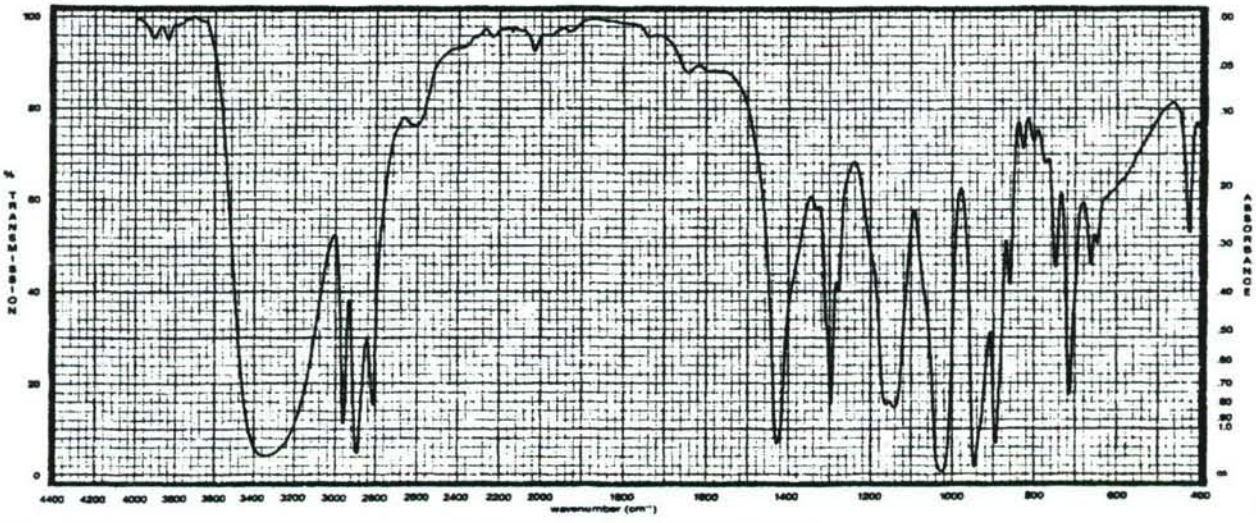

Figure 31 DIMETHYLHYDROXYMETHYLPHOSPHINE, LIQUID, CF/CsI

3.1.20 Bis(hydroxymethyl)methylphosphine $CH_3P(CH_2OH)_2$

The infrared spectrum of bis(hydroxymethyl)methylphosphine as a liquid film between CsI windows is reproduced as ***Figure 32***. The band assignments are as follows: 3322 cm^{-1} s broad (ν OH bonded), 2967 cm^{-1} vw, 2900 cm^{-1} m and 2834 cm^{-1} w (ν CH_3 and CH_2), 1422 cm^{-1} m (δ_{as} P-CH_3 and δ P-CH_2 , and β OH near 1400 cm^{-1}), 1284 cm^{-1} w (δ_{sy} P-CH_3), 1195 cm^{-1} w (ω CH_2), 1013 cm^{-1} s (ν C-O), 900 cm^{-1} m (P-CH_3 rock), 710 cm^{-1} w and 649 cm^{-1} (ν P-C), ca 615 cm^{-1} broad and shallow (γ OH).

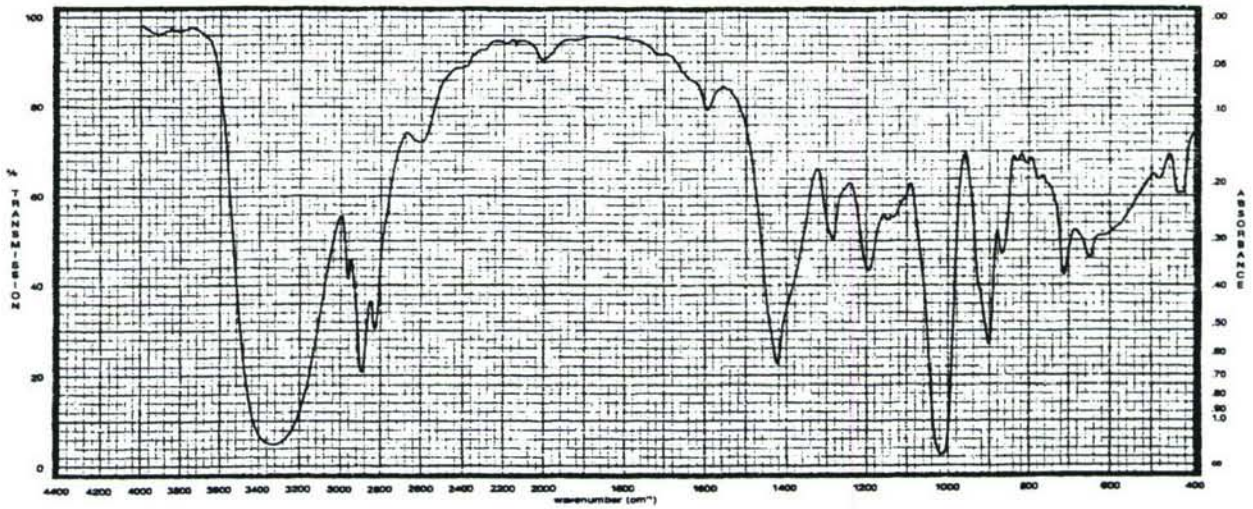

Figure 32 BIS(HYDROXYMETHYL)METHYLPHOSPHINE, LIQUID, CF/CsI

3.1.21 4-(Diisopropylaminomethyl)triphenylphosphine $(C_6H_5)_2P[4\text{-}(i\text{-}C_3H_7)_2N\text{-}CH_2\text{-}C_6H_4]$

The infrared spectrum of 4-(diisopropylaminomethyl)triphenylphosphine as a liquid between KBr windows is given in ***Figure 33***. The band assignments are as follows: 3068 and 3052 cm^{-1} m, 3027 and 3012 cm^{-1} vvw (ν C-H aromatic), 2964 cm^{-1} s (ν_{as} CH_3), 2929 cm^{-1} w (ν_{as} CH_2), 2868 cm^{-1} w (ν_{sy} CH_3), 2811 cm^{-1} w (ν_{sy} CH_2), 2710 and 2609 cm^{-1} vw [characteristic of N(isopropyl)$_2$?][f], 1596 cm^{-1} w, 1585 cm^{-1} w, 1493 cm^{-1} m and 1434 cm^{-1} ms (aromatic ring), 1478 and 1464 cm^{-1} m (δ_{as} CH_3 , δ CH_2), 1381 and 1362 cm^{-1} ms (δ_{sy} CH_3), 1208 and 1178 cm^{-1} ms (ν C-N ?), 1158 and 1139 cm^{-1} w (isopropyl

[f] See "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part II. V-Agents and Related Compounds", R. J. Piffath , 1999.

moiety ?), 1117 and 1090 cm^{-1} m (phenyl-P), 1027 and 1016 cm^{-1} m (β C-H mono- and para- substituted aromatic ring), 831 and 809 cm^{-1} m (γ C-H para-substituted aromatic ring), 743 cm^{-1} s (γ C-H mono-substituted aromatic ring), 696 cm^{-1} s (δ mono-substituted aromatic ring). The mono-substituted aromatic ring may also show β C-H bands as 1178, 1158, 1069, 1027 and 999 cm^{-1}, while the para-substituted aromatic ring may show these bands near 1178, 1117 and 1016 cm^{-1}.

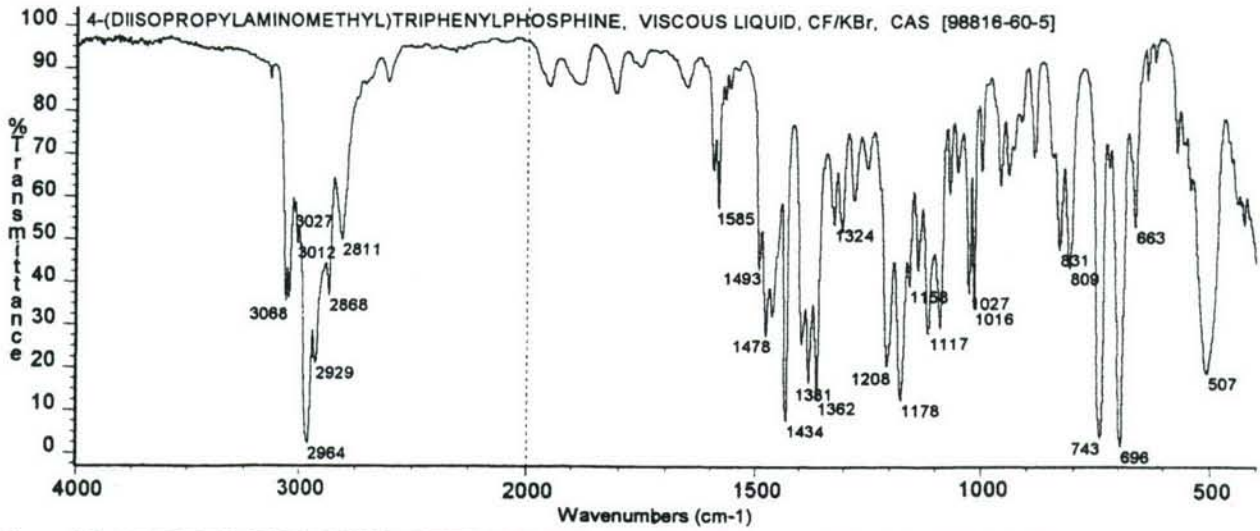

Figure 33 4-(DIISOPROPYLAMINOMETHYL)TRIPHENYLPHOSPHINE, VISCOUS LIQUID, CF/KBr

3.1.22 Tri-*n*-butylphosphine $P(n\text{-}C_4H_9)_3$

The infrared spectrum for a liquid film of tri-*n*-butylphosphine between KBr windows is given in ***Figure 34***. The band assignments are as follows: 2957 cm^{-1} s (ν_{as} CH_3), 2926 cm^{-1} s (ν_{as} CH_2), 2872

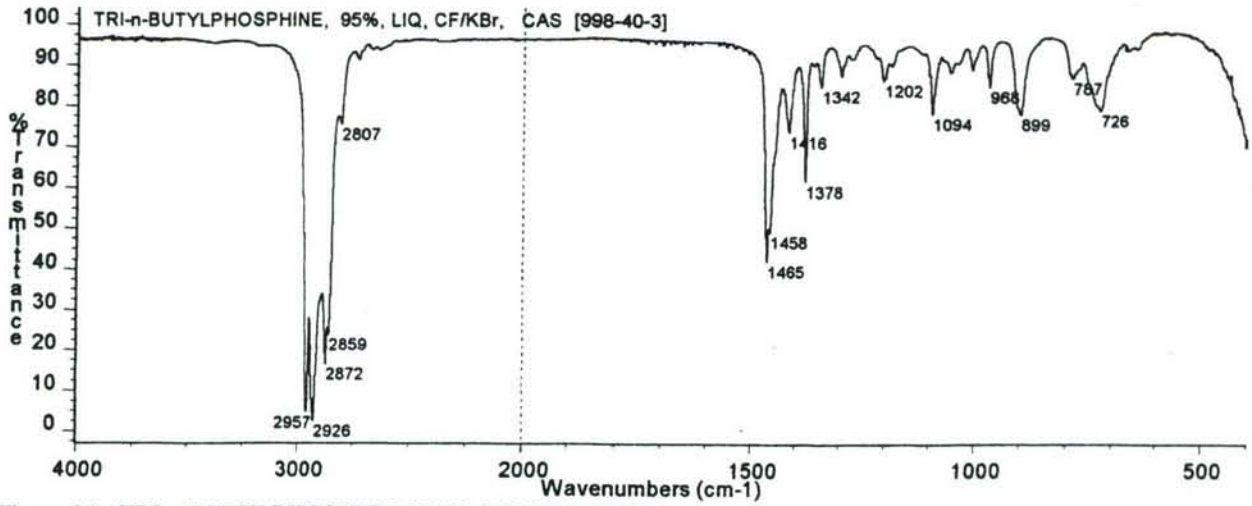

Figure 34 TRI-*n*-BUTYLPHOSPHINE, 95%, LIQUID, CF/KBr

cm^{-1} ms (ν_{sy} CH_3), 2859 cm^{-1} sh (ν_{sy} CH_2), 2807 cm^{-1} vw (1465 + 1342 = 2807 cm^{-1}), 1465 cm^{-1} m and 1458 cm^{-1} sh (δ_{as} CH_3 and δ CH_2), 1416 cm^{-1} vw (δ P-CH_2), 1378 cm^{-1} w (δ_{sy} CH_3), 1202 cm^{-1} vw (ω CH_2), 726 cm^{-1} w (CH_2 rock and ν P-C).

3.1.23 Tri-*n*-octylphosphine $P(n\text{-}C_8H_{17})_3$

The infrared spectrum for a liquid film of tri-*n*-octylphosphine between KBr windows is given in ***Figure 35***. The band assignments are as follows: 2957 cm^{-1} ms (ν_{as} CH_3), 2924 cm^{-1} s (ν_{as} CH_2), 2872 cm^{-1} sh (ν_{sy} CH_3), 2854 cm^{-1} ms (ν_{sy} CH_2), 1465 cm^{-1} m (δ_{as} CH_3 and δ CH_2), 1416 cm^{-1} vw (δ P-CH_2), 1378 cm^{-1} w (δ_{sy} CH_3), 722 cm^{-1} w (CH_2 rock, ν P-C).

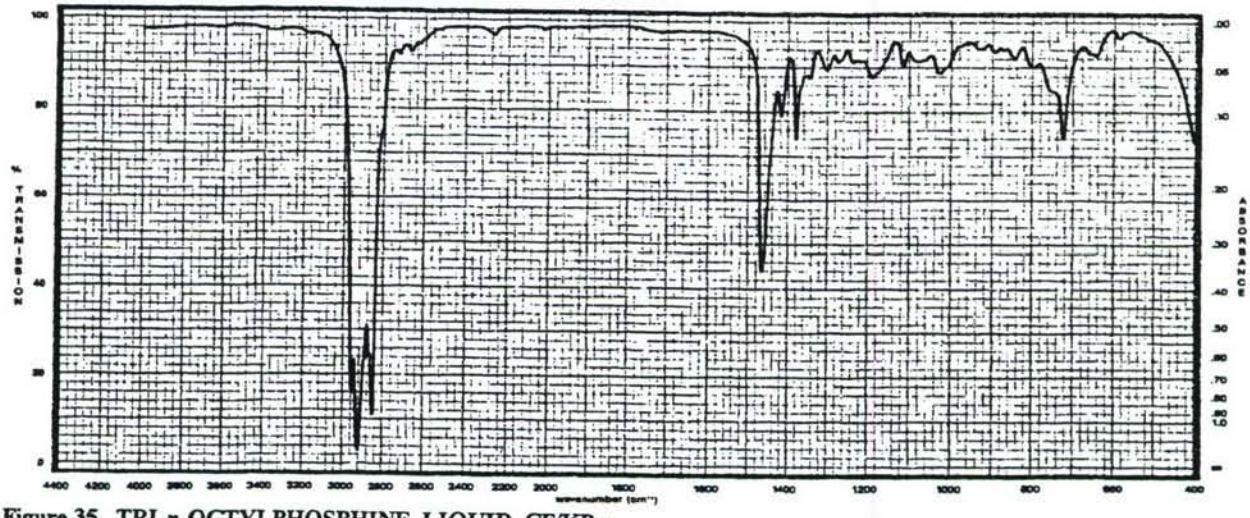

Figure 35 TRI-*n*-OCTYLPHOSPHINE, LIQUID, CF/KBr

3.1.24 Bis(diphenylphosphino)methane, DPM $(C_6H_5)_2P\text{-}CH_2\text{-}P(C_6H_5)_2$

The infrared spectrum of bis(diphenylphosphino)methane (DPM), as a solid between CsI discs (windows), is given as ***Figure 36***. The band assignments are as follows: 3054 cm^{-1} w and 3013 cm^{-1} vw (ν C-H aromatic ring), 2942 cm^{-1} vw (ν_{as} CH_2), 2896 cm^{-1} vvw (ν_{sy} CH_2), 2570 vvw (1479 + 1092 = 2571 cm^{-1} ?), 1955, 1886, 1811 and 1756 cm^{-1} all vw (summation bands of mono-substituted aromatic ring), 1582 cm^{-1} w, 1479 cm^{-1} and 1431 cm^{-1} ms (aromatic ring), 1379 cm^{-1} w (δ P-CH-P ?), 1185 cm^{-1} vw, 1155 cm^{-1} vw, 1069 cm^{-1} w, 1024 cm^{-1} and 999 cm^{-1} w (β C-H mono-substituted aromatic ring), 1092

cm^{-1} m (phenyl-P), 781 and 718 cm^{-1} m (may be due to the ν_{as} and ν_{sy} of the P-CH_2 -P moiety)[g], 743 cm^{-1} s (γ C-H mono-substituted aromatic ring), 693 cm^{-1} (δ mono-substituted aromatic ring).

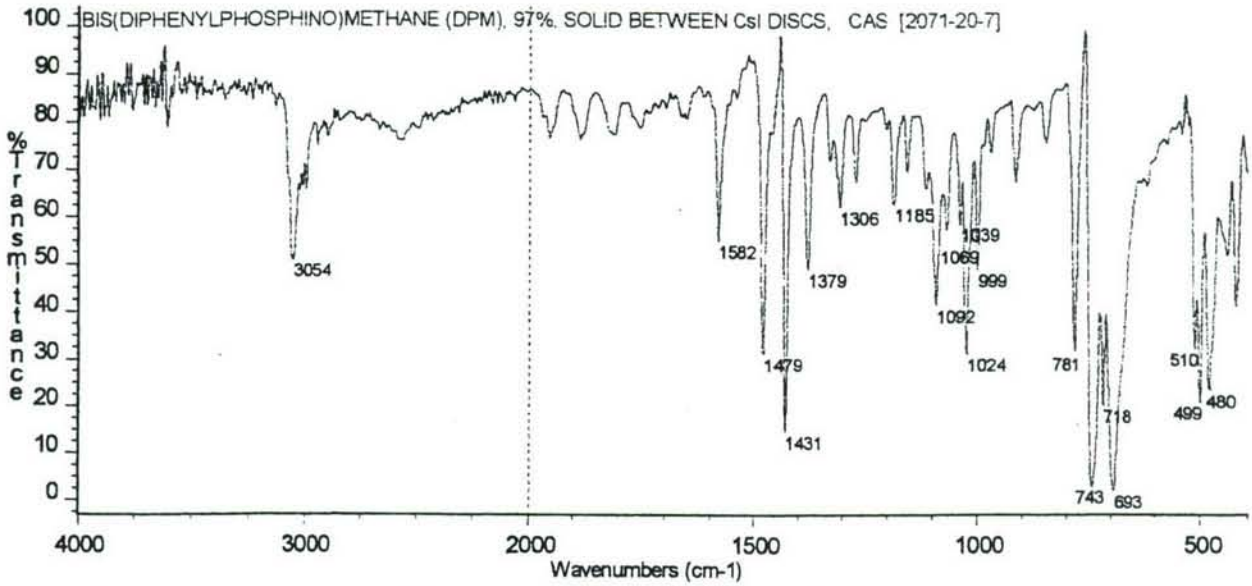

Figure 36 BIS(DIPHENYLPHOSPHINO)METHANE, DPM, 97%, SOLID BETWEEN CsI DISCS

3.1.25 1,2-Bis(diphenylphosphino)ethane **(DIPHOS)** $(C_6H_5)_2P\text{-}CH_2\text{-}CH_2\text{-}P(C_6H_5)_2$

The infrared spectrum of 1,2-bis(diphenylphosphino)ethane, or ethylene bis(diphenylphosphine), as a solid between CsI discs (windows), is reproduced as ***Figure 37***. Band assignments are as follows: 3067, 3047, 3022 and 3001 cm^{-1} all vw (ν C-H aromatic ring), 2928 cm^{-1} vw (ν_{as} CH_2), 2895 cm^{-1} vvw (ν_{sy} CH_2), 1585 vw, 1480 cm^{-1} w and 1432 cm^{-1} m (aromatic ring), 1424 cm^{-1} sh (δ P-CH_2), 1305 and 1274 cm^{-1} vw (ω, τ CH_2), 1186 cm^{-1} vvw, 1161 cm^{-1} vw, 1067 cm^{-1} vw, 1025 cm^{-1} w and 998 cm^{-1} w (β C-H mono-substituted aromatic ring), 1097 cm^{-1} vw (phenyl-P), 752 cm^{-1} w, 741 cm^{-1} m, 727 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 705 cm^{-1} w and 692 cm^{-1} s (δ mono-substituted aromatic ring).

[g] Correlations for the P-CH_2-P group are given as 850-780 cm^{-1} (ν_{as}) and 770-720 cm^{-1} (ν_{sy}) by Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S., "Atlas of IR Spectra of Organophosphorus Compounds, p.4, Kluwer Academic Publishers, Boston, 1990. Thomas, L.C. in "Interpretaton of the Infrared Spectra of Organophosphorus Compounds", p. 98, Heyden & Son Ltd.,1974, lists these ranges as 845-780 cm^{-1} and 770-720 cm^{-1}.

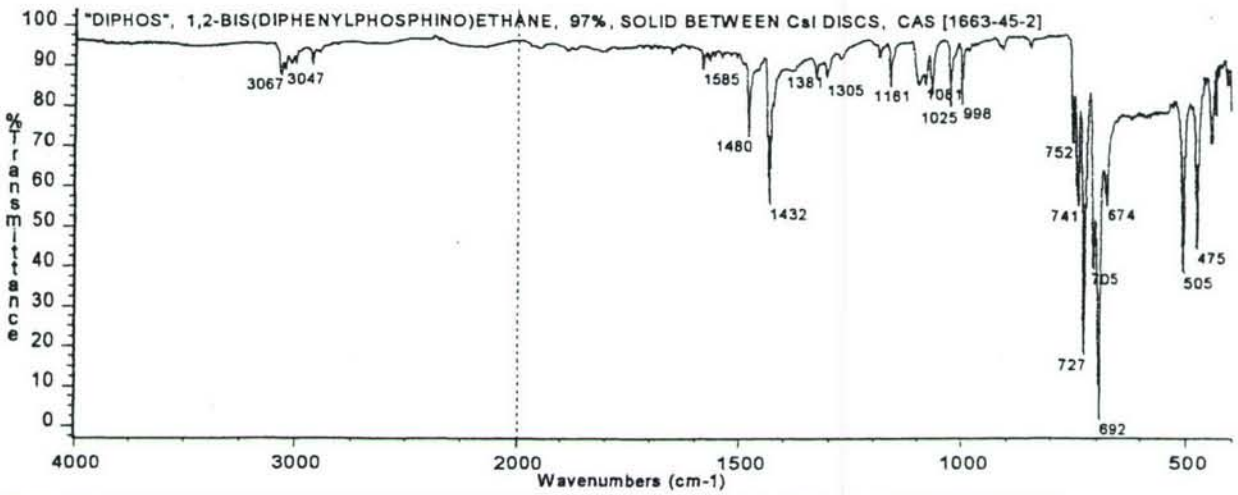

Figure 37 1,2-BIS(DIPHENYLPHOSPHINO)ETHANE, DIPHOS, 97%, SOLID BETWEEN CsI DISCS

3.1.26 1,3-Bis(diphenylphosphino)propane $(C_6H_5)_2P\text{-}CH2\text{-}CH2\text{-}CH_2\text{-}P(C_6H_5)_2$

The infrared spectrum of 1,3-bis(diphenylphosphino)propane as a solid between KBr discs (windows) is given in ***Figure 38***. The band assignments are as follows: 3069 and 3049 cm^{-1} w, 3014 and 2999 cm^{-1} vw (ν C-H aromatic), 2939 and 2925 cm^{-1} w (ν_{as} CH_2), 2893 and 2880 cm^{-1} vw (ν_{sy} CH_2), 1950, 1877, 1807 and 1754 cm^{-1} all vw (summation bands of mono-substituted aromatic ring), 1584 cm^{-1} w, 1481 cm^{-1} ms and 1432 cm^{-1} ms (aromatic ring), 1417 cm^{-1} vw (δ P-CH_2), 1303 cm^{-1} and 1271 cm^{-1} vw (ω, τ CH_2 ?), 1182 cm^{-1} vw, 1151 cm^{-1} vw, 1069 cm^{-1} w, 1026 cm^{-1} w and 999 cm^{-1} w (β C-H mono-substituted aromatic ring), 1094 cm^{-1} m (phenyl-P), 740 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 695 cm^{-1} s (δ mono-substituted ring).

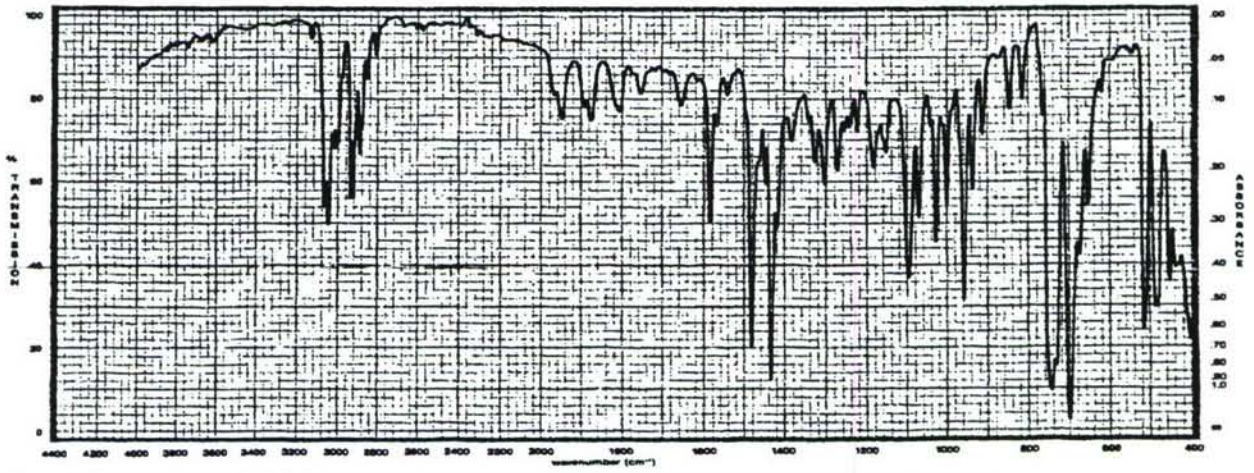

Figure 38 1,3-BIS(DIPHENYLPHOSPHINO)PROPANE, 98%, SOLID BETWEEN KBr DISCS

3.1.27 1,4-Bis(diphenylphosphino)butane $(C_6H_5)_2P\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}P(C_6H_5)_2$

The infrared spectrum of 1,4-bis(diphenylphosphino)butane as a solid between KBr discs (windows) is given in ***Figure 39***. The band assignments are as follows: 3066 and 3050 cm^{-1} w, 3018 cm^{-1} vw (ν C-H aromatic), 2932 cm^{-1} m (ν_{as} CH_2), 2883 cm^{-1} w (ν_{sy} CH_2), 1958, 1888, 1814 and 1757 cm^{-1} all vw (summation bands from mono-substituted aromatic ring), 1584 cm^{-1} w, 1568 cm^{-1} vw, 1479 cm^{-1} m, 1431 cm^{-1} ms (aromatic ring), 1454 cm^{-1} w (δ CH_2 ?), 1411 cm^{-1} w (δ P-CH_2), 1302 cm^{-1} w and 1272 cm^{-1} vw (ω, τ CH_2), 1184 cm^{-1} vw, 1164 cm^{-1} w, 1066 cm^{-1} w, 1027 and 997 cm^{-1} w (β C-H of mono-substituted aromatic ring), 1097 cm^{-1} w (phenyl-P), 744 cm^{-1} ms (γ C-H mono-substituted aromatic ring) 722 cm^{-1} ms (CH_2 rock, ν P-C or perhaps part of γ C-H mono-substituted ring ?), 695 cm^{-1} s (δ mono-substituted aromatic ring).

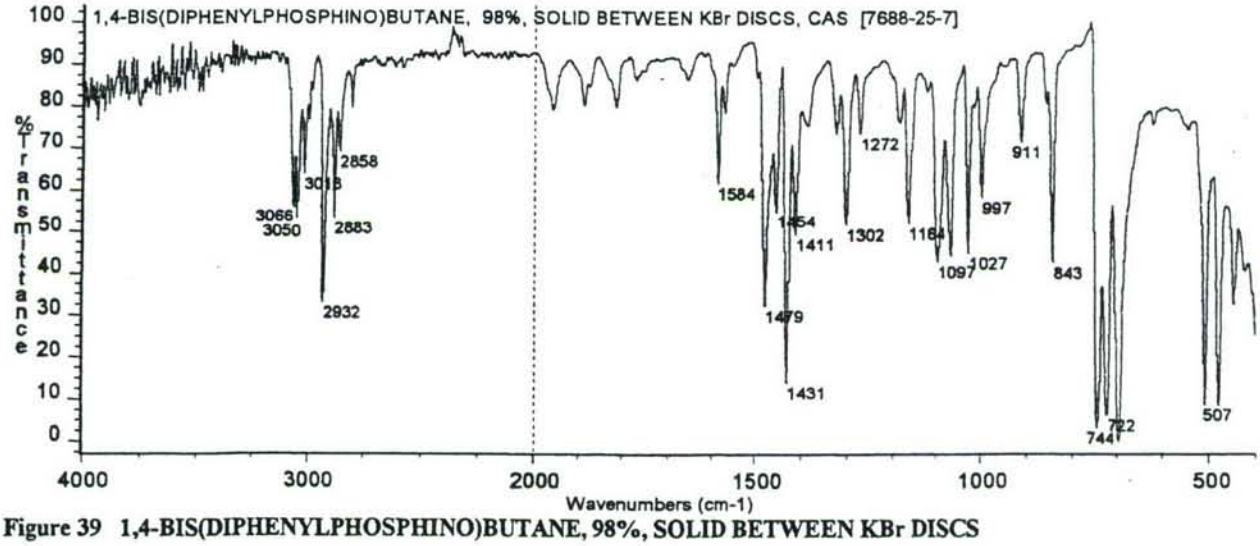

Figure 39 1,4-BIS(DIPHENYLPHOSPHINO)BUTANE, 98%, SOLID BETWEEN KBr DISCS

3.1.28 Bis(2-diphenylphosphinoethyl)phenylphosphine (**TRIPHOS**) $C_6H_5\text{-}P[CH_2CH_2P(C_6H_5)_2]_2$

The infrared spectrum of bis(2-diphenylphosphinoethyl)phenylphosphine (**TRIPHOS**) as a solid between CsI discs (windows) is presented as ***Figure 40***. The band assignments are as follows: 3066 cm^{-1} w, 3046 cm^{-1} vw, 3023 cm^{-1} vw (ν C-H), 2923 cm^{-1} w (ν_{as} CH_2), 2893 cm^{-1} vw (ν_{sy} CH_2), 1583 cm^{-1} vw, 1569 cm^{-1} vvw, 1479 cm^{-1} m, 1430 cm^{-1} ms (aromatic ring), 1304 cm^{-1} w and 1272 cm^{-1} vw (ω, τ CH_2), 1183 cm^{-1} vw, 1163 cm^{-1} w, 1066 cm^{-1} m, 1023 cm^{-1} m and 998 cm^{-1} w (β C-H mono-substituted

aromatic ring), 1091 cm^{-1} w (phenyl-P), 747 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 696 cm^{-1} s (δ mono-substituted aromatic ring).

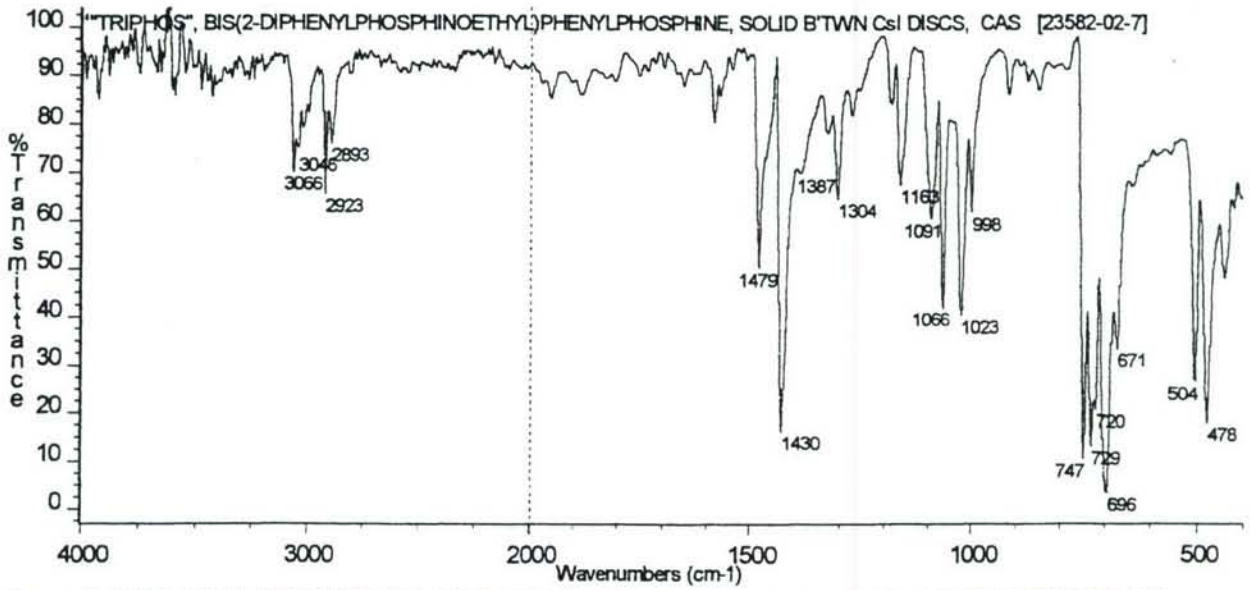

Figure 40 BIS(2-DIPHENYLPHOSPHINOETHYL)PHENYLPHOSPHINE (TRIPHOS), SOLID BETWEEN CsI DISCS

3.1.29 Bis(dimethylamino)methylphosphine, (N, N'-tetramethylmethylphosphonous Diamide)

$CH_3\text{-}P[N(CH_3)_2]_2$

The infrared spectrum for bis(dimethylamino)methylphosphine, or N,N'-tetramethylmethyl-phosphonous diamide, as a liquid film between KBr discs (windows) is presented as ***Figure 41.*** The band assignments are as follows: 2969 cm^{-1} m, 2907 cm^{-1} sh, 2882 cm^{-1} and 2862 cm^{-1} ms, 2832 cm^{-1} w and 2784 cm^{-1} ms [ν_{as} and ν_{sy} CH_3 ; ν_{as} and ν_{sy} $N(CH_3)_2$], 1466 cm^{-1} w and 1447 cm^{-1} m (δ CH_3), 1420 cm^{-1} vw (δ_{as} P-CH_3), 1284 cm^{-1} m (δ_{sy} P-CH_3), 1259 cm^{-1} m [P-$N(CH_3)_2$][h], 1189 cm^{-1} ms and 1058 cm^{-1} w [$PN(CH_3)_2$], 972 cm^{-1} ms and 953 cm^{-1} s (ν_{as} P-N-C), 875 cm^{-1} m (P-CH_3 rock), 711 cm^{-1} m (ν P-C of P-CH_3), 649 cm^{-1} ms (ν_{sy} P-N-C)[i].

[h] The bands assigned to the P-CH_3 and $PN(CH_3)_2$ groups occur in the 1300 cm^{-1} range. The band assigned to the $PN(CH_3)_2$ moiety is somewhat broader than that due to the P-CH_3 moiety. However, the P-CH_3 moiety has a further characteristic band near 900 cm^{-1}, which is not found in the spectra of $PN(CH_3)_2$ containing compounds. (See Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 93,95, Heyden & Son Ltd., 1974.)

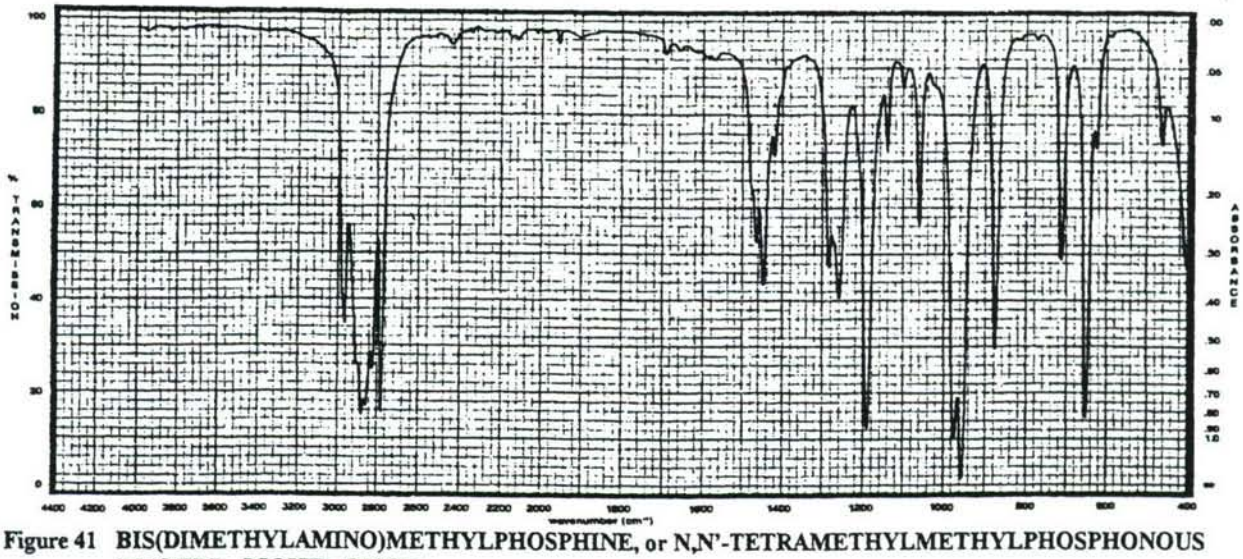

Figure 41 BIS(DIMETHYLAMINO)METHYLPHOSPHINE, or N,N'-TETRAMETHYLMETHYLPHOSPHONOUS DIAMIDE, LIQUID, CF/KBr

P-CH_3), 649 cm^{-1} ms (ν_{sy} P-N-C) [1].

The effect of atmospheric moisture on bis(dimethylamino)methylphosphine is illustrated by the infrared spectra given in ***Figures 42A-D***. The infrared spectrum after 4 hours (***Figure 42A***) shows that the compound has been hydrolyzed. The resulting bands can be assigned as follows: ca 2900 cm^{-1} (overlapping the ν C-H at 3012, 2972 and 2909 cm^{-1}), 2700 cm^{-1} ms and 2446 cm^{-1} ms (ν NH_2^+), 2277 cm^{-1} ms (ν P-H), 1640 cm^{-1} vw (δ NH_2^+), 1471 cm^{-1} w (δ CH_3), 1418 cm^{-1} vw (δ_{as} P-CH_3), 1289 cm^{-1} m (δ_{sy} P-CH_3), 1171 cm^{-1} s (ν_{as} PO_2^-), 1060 cm^{-1} s (ν_{sy} PO_2^-), 974 cm^{-1} w (residual ν_{as} P-N-C ?), 900 cm^{-1} vw or 831 cm^{-1} m (P-CH_3 rock), 715 cm^{-1} w (ν P-C), 477 cm^{-1} m (δ PO_2^-). The bands due to the $PN(CH_3)_2$ moiety have essentially disappeared from the spectrum. By the 4th day of exposure the spectrum (***Figure 42B***) shows only the presence of increased water [3395, ca 1645 (partly H_2O and δ NH_2^+), and near 640 broad and shallow], otherwise the spectrum still indicates the presence of the PO_2 anion. The preceeding analysis also holds for the spectrum (***Figure 42C***) after 14 days of exposure to

[1] L.C. Thomas in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 120-123 lists the $N(CH_3)_2$ as being characterized by absorption bands in the regions of 1300 (1321-1261), 1180 (1205-1155), 1065 (1078-1050) and 975 (1008-935) cm^{-1}. Shagidullin et al ("Atlas of IR Spectra of Organophosphorus Compounds, Interpreted Spectrograms", p 5, Kluwer Academic Publishers, Boston, 1990) lists the $N(CH_3)_2$ as having bands at 1320-1260 cm^{-1} m-s (ν_{as} C-N-C), 1210-1150 cm^{-1} m-s, 1080-1050 m (CH_3 rock), 1010-970 cm^{-1} m-s (ν_{as} P-N-C), 980-940 cm^{-1} s (ν_{as} P^{+3}-N-C) and 700-650 cm^{-1} w-m (ν_{sy} P-N-C).

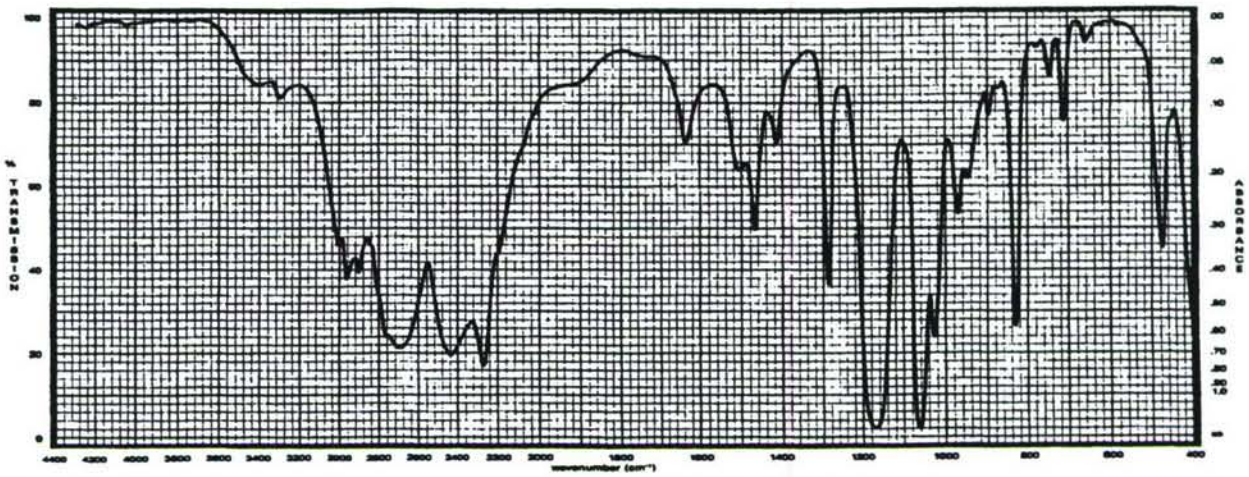

Figure 42A BIS(DIMETHYLAMINO)METHYLPHOSPHINE, LIQUID, CF/KBr AFTER 4 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

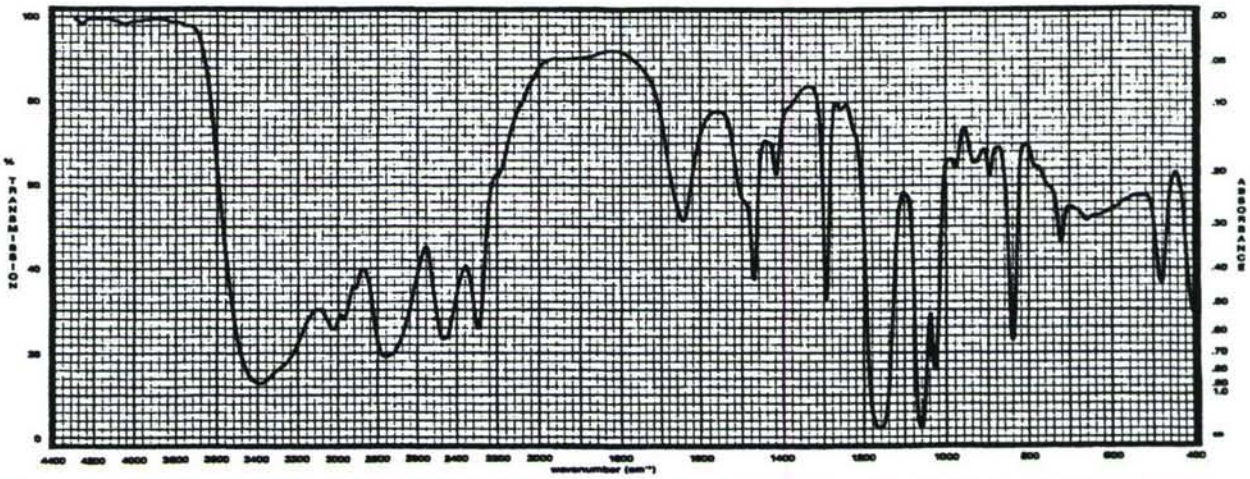

Figure 42B BIS(DIMETHYLAMINO)METHYLPHOSPHINE, LIQUID, CF/KBr, AFTER 4 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

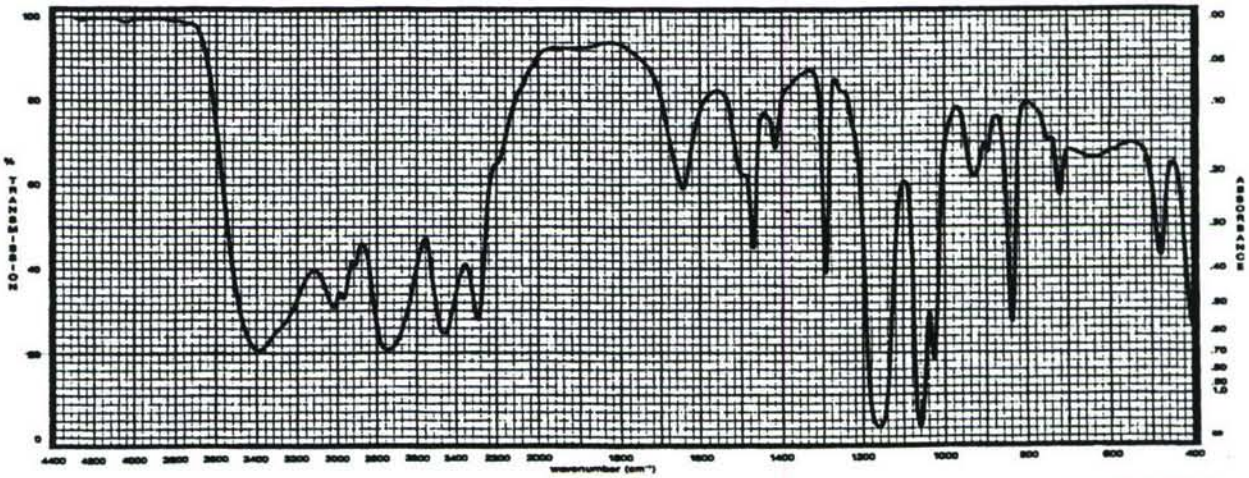

Figure 42C BIS(DIMETHYLAMINO)METHYLPHOSPHINE, LIQUID, CF/KBr, AFTER 14 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

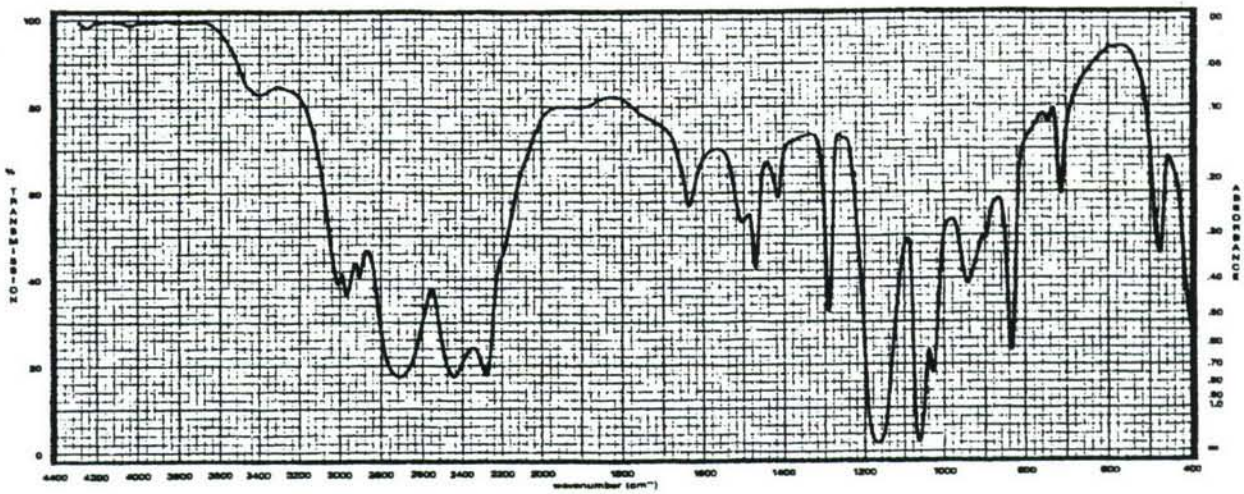

Figure 42D BIS(DIMETHYLAMINO)METHYLPHOSPHINE, LIQUID, CF/KBr, AFTER 22 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE AND 7 DAYS OF DRYING UNDER A NITROGEN PURGE

atmospheric moisture. After 22 days (***Figure 42D***) a much drier spectrum (***Figure 42D***) was obtained by keeping the sample/KBr sandwich under a dry Nitrogen purge for 7 days. This drying produced a much better looking spectrum (***Figure 42D***), that is one showing much less water. The end product of the hydrolysis may be best represented as $[CH_3P(O_2^-)H]H_2N^+(CH_3)_2]$. Therefore, the hydrolysis may be summarized as follows: $CH_3P[N(CH_3)_2]_2$ $\xrightarrow{-HOH}$ $CH_3P(O\text{-}H)[N(CH_3)_2]$ $\rightarrow$ $CH_3P{=}O(H)[N(CH_3)_2]$ $\xrightarrow{HOH}$ $CH_3P{=}O(H)(OH) + N(CH_3)_2 \rightarrow [CH_3P(O_2^-)H]H_2N^+(CH_3)_2]$.

3.1.30 Tris(N,N-diethylamino)phosphine (hexaethylphosphorous triamide) $P[N(CH_2CH_3)]_3$

The infrared spectrum of a liquid film of tris(N,N-diethylamino)phosphine, (hexaethylphosphorous triamide), between KBr windows is given in ***Figure 43***. The band assignments are as follows: 2966 cm^{-1} s (ν_{as} CH_3), 2930 cm^{-1} ms (ν_{as} CH_2), 2865 cm^{-1} and 2852 cm^{-1} ms (ν_{sy} CH_3 and ν_{sy} CH_2), 1461 cm^{-1} m (δ_{as} CH_3 and δ CH_2), 1374 cm^{-1} ms (δ_{sy} CH_3), 1292 and 1231 cm^{-1} w (ω, τ CH_2 ?), 1194 s, 1156 m, 1102 w, 1053 w, 1009 s and 908 m cm^{-1} (characteristic of the $PNEt_2$ group)[j]. The strong band at 1009 cm^{-1} can be assigned to the asymmetric P-N-C stretch. The symmetric P-N-C stretch absorbs at 664 cm^{-1}.

[j] Thomas, L.C. "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 123-125, Heyden & Son Ltd., 1974, lists bands in the vicinity of 1200, 1170, 1060, 1025 and 950 cm^{-1} as being characteristic of the $PNEt_2$ group.

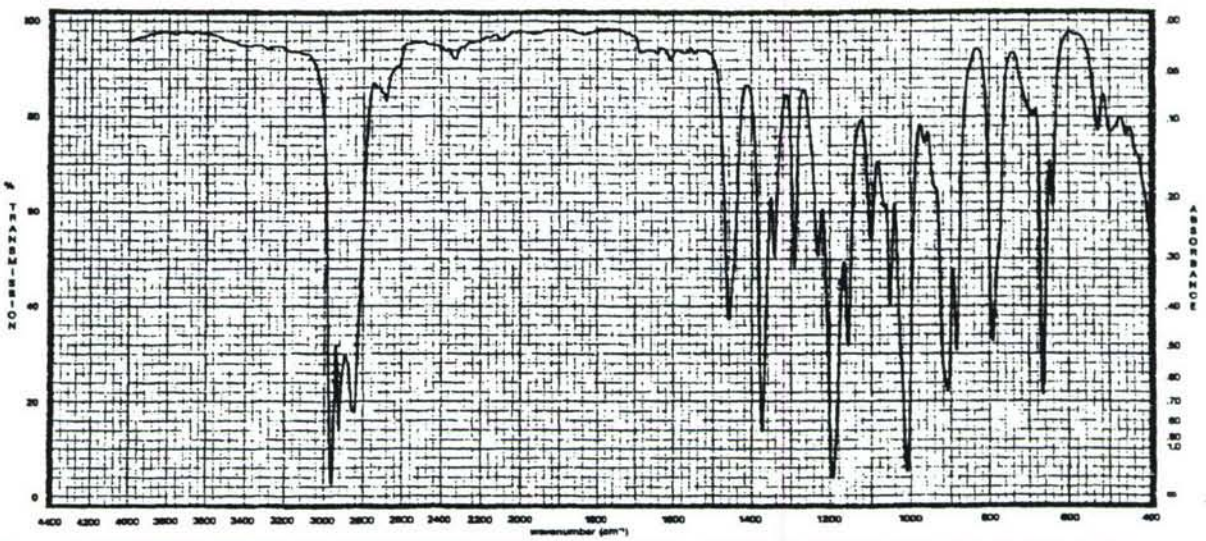

Figure 43 TRIS(N,N-DIETHYLAMINO)PHOSPHINE or HEXAETHYLPHOSPHOROUS TRIAMIDE, LIQUID, CF/KBr

Shagidullin et al[k] list the following bands as being characteristic of the $PNEt_2$ group: 1230-1170 cm^{-1} m (ν_{as} C-N-C), 1190-1150 cm^{-1} m (ω, τ CH_2), 1110-1080 cm^{-1} w, 1080-1050 cm^{-1} w-m (CH_3 rock), 1050-1010 cm^{-1} s (ν_{as} P-N-C), 980-930 cm^{-1} s (ν NC-C), 800-750 cm^{-1} m-s (CH_2 rock), 700-650 cm^{-1} w-m (ν_{sy} P-N-C). ***Figure 43*** shows bands for the compound at 1194, 1156, 1102, 1053, 1009 , 966 (very weak, with much stronger bands at 908 and 886 cm^{-1}), 791 and 664 cm^{-1}.

The infrared spectra illustrating the effect of atmospheric moisture on tris(N,N-diethylamino)-phosphine are given in ***Figures 44A-C***. The spectrum, after 5 hours (***Figure 44A***), shows the formation of a P-H band near 2300 cm^{-1}. Other bands are beginning to show near 2470 cm^{-1} (NH_2^+), 1229 cm^{-1} (this band has increased in intensity, possible ν P=O of $[Et_2N]_2$ P=O(H), which would have a calculated ν P=O of 1222 cm^{-1}) and 982 cm^{-1} (P-H deformation ?). After 3 days of exposure to atmospheric moisture the spectrum shows a strong band near 2800 cm^{-1} with weaker bands near 2490 and 2400 cm^{-1} (NH_2^+). A band at 2294 is assigned to the ν P-H. The strong band near 1200 cm^{-1} can be assigned in part to a ν_{as} PO_2^- and to the $PNEt_2$ group. The band at 1062 cm^{-1} is assigned to a ν_{sy} PO_2^-, while bands at 1026,

[k] Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S. in "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)", p 5, Kluwer Academic Publishers, Boston, 1990.

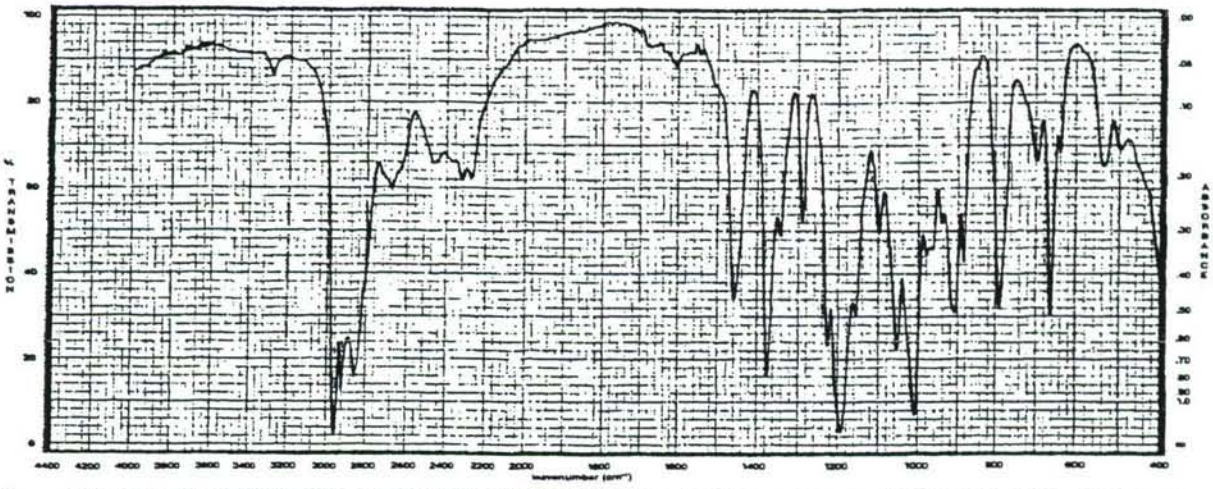

Figure 44A TRIS(N,N-DIETHYLAMINO)PHOSPHINE, LIQUID, CF/KBr, AFTER 5 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

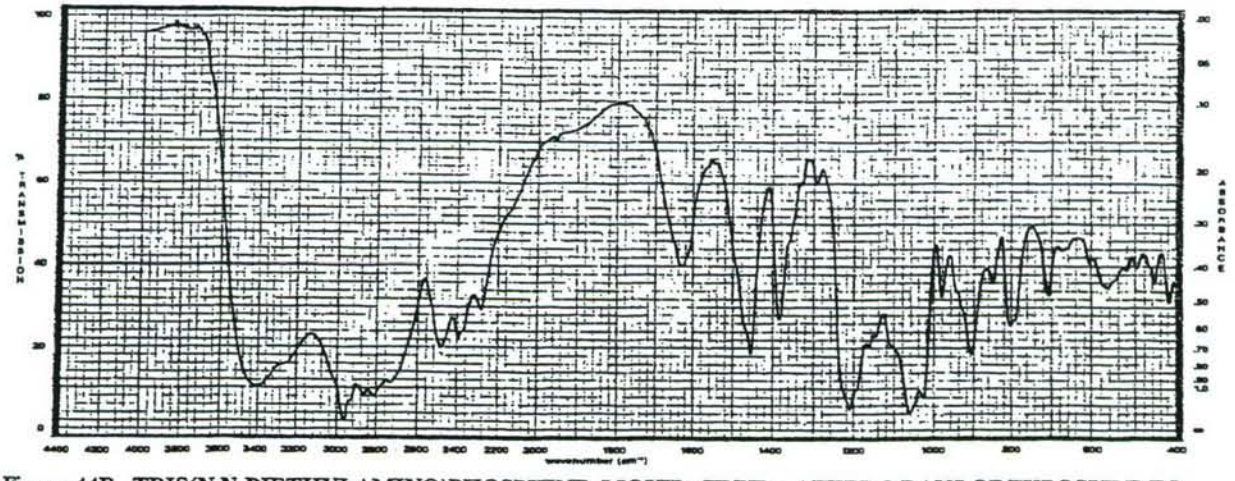

Figure 44B TRIS(N,N-DIETHYLAMINO)PHOSPHINE, LIQUID, CF/KBr, AFTER 3 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

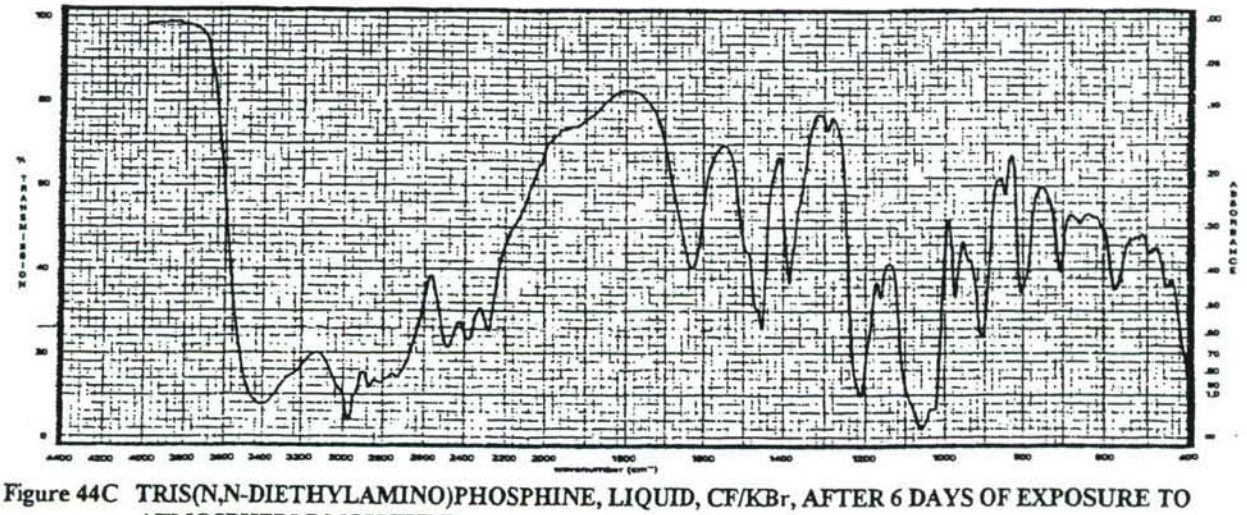

Figure 44C TRIS(N,N-DIETHYLAMINO)PHOSPHINE, LIQUID, CF/KBr, AFTER 6 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

907, 708 cm^{-1} are assignable to the $PNEt_2$ moiety. The spectrum for 6 days of exposure to atmospheric moisture (***Figure 44C***) is similar to that obtained for 3 days (***Figure 44B***). It is believed the compound, tris(N,N-diethylamino)phosphine, has hydrolyzed as follows: $(Et_2N)_2P\text{-}NEt_2$ $\text{-HOH}\rightarrow$ $(Et_2N)_2P{=}O(H)$ $\text{-HOH}\rightarrow$ $E_2N\text{-}P{=}O(OH)(H) + HNEt_2 \rightarrow [Et_2N\text{-}P(O_2^-)H]\ H_2N^+Et_2$.

3.2 Phosphites

3.2.1 Ethyl dichlorophosphite (ethyl phosphorodichloridite) $CH_3\text{-}CH_2\text{-}O\text{-}P(Cl)_2$

The infrared spectrum of ethyl dichlorophosphite (ethyl phosphorodichloridite) is given in ***Figure 45***. The band assignments are as follows: 2992 and 2984 cm^{-1} m (ν_{as} CH_3), 2938 cm^{-1} w (ν_{as} CH_2), 2904 cm^{-1} w (ν_{sy} CH_3), 2869 cm^{-1} vw (ν_{sy} CH_2), 2435 cm^{-1} vvw (ν P-H from hydrolysis product), ca 2300 vvw broad and shallow (ν POH hydrolysis product), 1752 cm^{-1} vw (1024 + 737 = 1761 cm^{-1}), 1699 cm^{-1} vw (963 + 737 = 1700 cm^{-1}), 1472 cm^{-1} w (δ OCH_2), 1442 cm^{-1} w (δ_{as} CH_3), 1387 cm^{-1} w (ω OCH_2 , some δ_{sy} CH_3), 1280 cm^{-1} vw [possible ν P=O from EtO-P=O(H)(Cl), which has a calculated value of 1280 cm^{-1}], 1229 cm^{-1} w (possible ν P=O impurity ?), 1154 and 1097 cm^{-1} w (characteristic of POEt moiety, CH_3 rock), 1024 cm^{-1} s (ν P-O-C), 963 cm^{-1} ms (ν C-C of POEt), 737 cm^{-1} m (POC), 501 and 447 cm^{-1} ms (ν_{sy} and ν_{as} PCl_2).

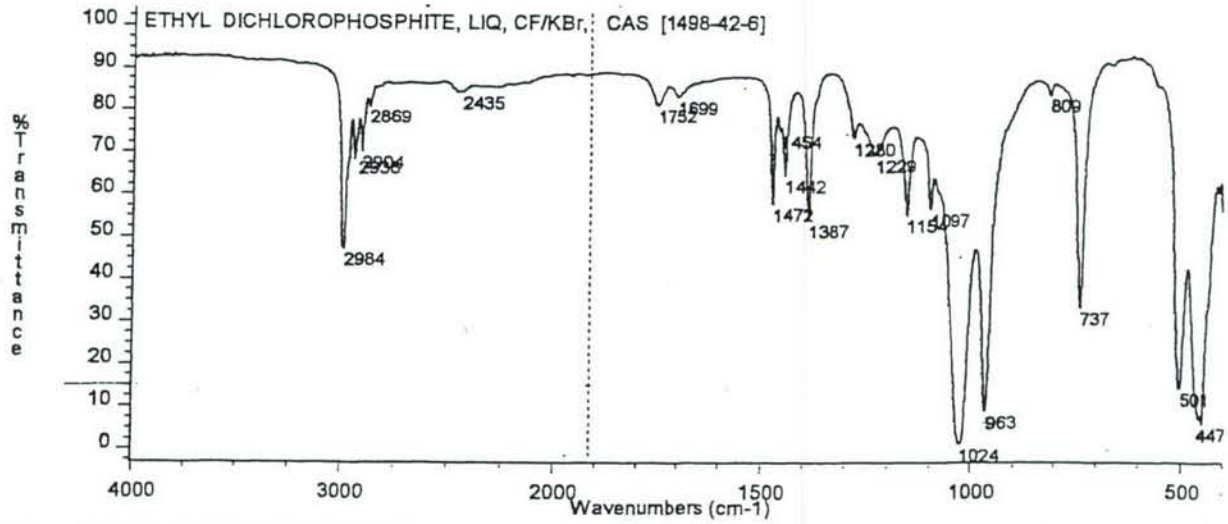

Figure 45 ETHYL DICHLOROPHOSPHITE (ETHYL PHOSPHORODICHLORIDITE), LIQUID, CF/KBr

The effect of atmospheric moisture on ethyl dichlorophosphite is illustrated by the infrared spectra presented in ***Figure 46***. After 2 hours, the infrared spectrum shows the formation of P-acid bands near 2600, 2300 and 1650 cm^{-1} (POH), as well as bands at 1223 cm^{-1} (ν P=O). The ν P-H band is still visible at 2446 cm^{-1}. After 4 hours of exposure of the compound to atmospheric moisture, the spectrum still shows the presence of a P-acid moiety, perhaps EtO-P=O(H)(OH), which should have a calculated ν P=O value near 1216 cm^{-1} (observed value after 4 hours was 1217 cm^{-1}). After 4-5 days the infrared spectrum resembles that of a P-acid with very little contribution from any POEt moiety. A very weak band at 1385 cm^{-1} is probably due to KNO_3 from the KBr windows used to support the liquid film. The spectrum shows POH bands near 2800, 2300, and 1650 (partly due to H_2O) cm^{-1}. The P-H stretch is still visible at 2446. The broad band at 1169 cm^{-1} is due to P=O stretching, while the bands at 1020 and 939 cm^{-1} are assignable to P-OH vibrations. The acid, $HP{=}O(OH)_2$, phosphonic acid should have ν P=O of about 1174 cm^{-1} (observed value of 1169 cm^{-1}). The hydrolysis of ethyl dichlorophosphite may be summarized as follows:

$EtO\text{-}P(Cl)_2$ -HOH→ EtO-P=O(Cl)(H) -HOH→ EtO-P=O(OH)(H) -HOH→ $H\text{-}P{=}O(OH)_2$

3.2.2 Isopropyl dichlorophosphite (isopropyl phosphorodichloridite) $(CH_3)_2CH\text{-}O\text{-}P(Cl)_2$

The infrared spectrum of isopropyl dichlorophosphite as a liquid film between KBr windows is reproduced in ***Figure 47***. The band assignments are as follows: 2982 cm^{-1} m (ν_{as} CH_3), 2940 cm^{-1} w (ν_{sy} CH_3), 2874 cm^{-1} vw (ν -C-H), 1696 cm^{-1} vw (984 + 713 = 1697 cm^{-1}), 1468 cm^{-1} w (δ_{as} CH_3), 1386 cm^{-1} w and 1375 cm^{-1} m (δ_{sy} CH_3), 1346 vw (δ -C-H), 1275 cm^{-1} vvw [ν P=O of (iPrO)P=O(H)(Cl), which has a calculated value of 1276 cm^{-1}], 1227 cm^{-1} vvw [ν P=O of perhaps (iPrO)P=O(H)(OH)], 1179 cm^{-1} w, 1142 cm^{-1} w and 1096 cm^{-1} m (characteristic triplet of POiPr)[1], 984 cm^{-1} s (ν P-O-C), 889 cm^{-1}

[1] The P-O-isopropyl moiety shows three highly characteristic bands in the ranges 1190-1170, 1147-1136 and 1114-1098 cm^{-1}, Thomas, L.C. "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p.54, Heyden & Son Ltd., London, 1974.

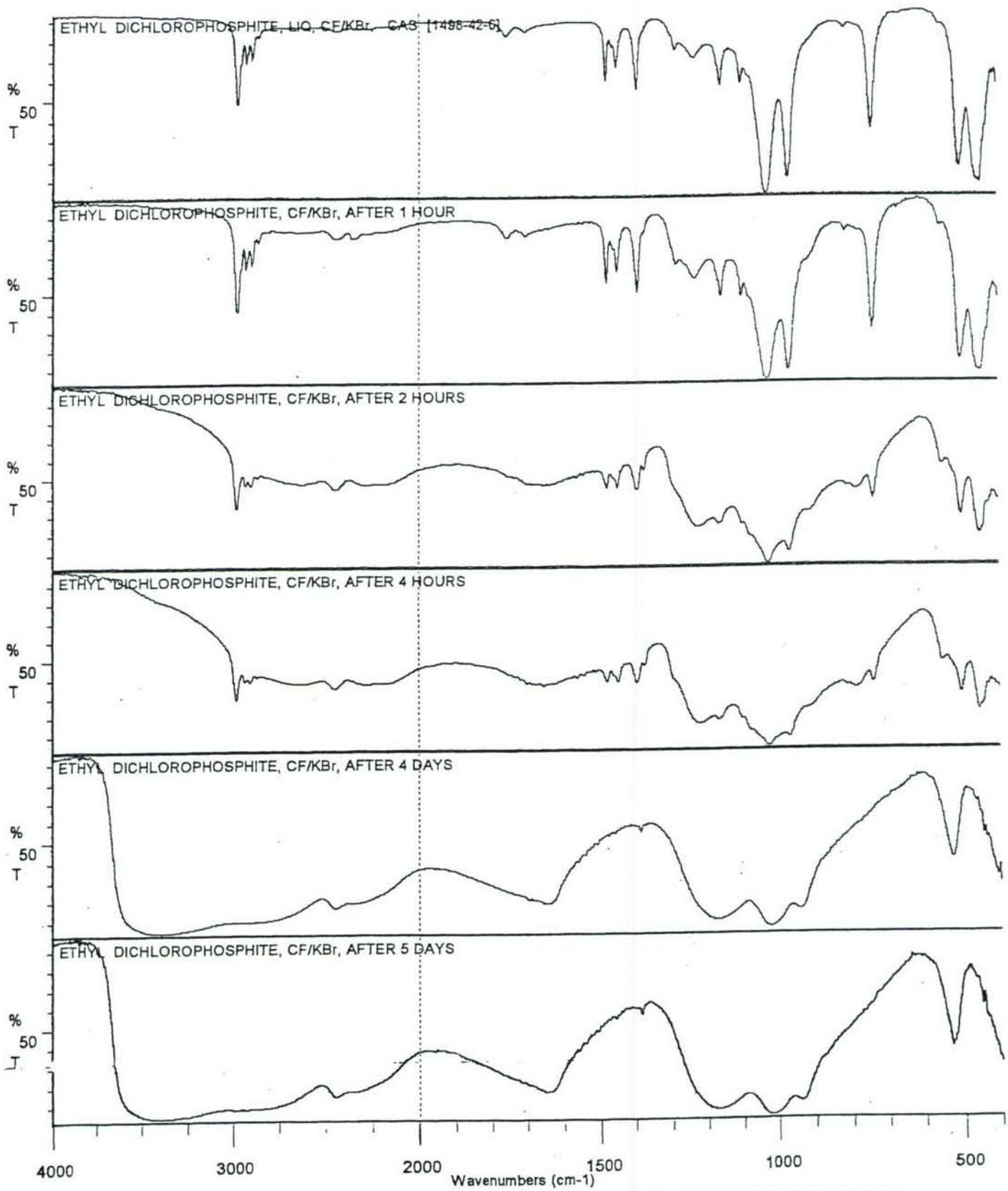

Figure 46 ETHYL DICHLOROPHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

vw (CH_3 rock ?), 713 cm^{-1} w (POC), 502 cm^{-1} m, 463 and 441 cm^{-1} ms (ν_{as} and ν_{sy} PCl_2).[m]

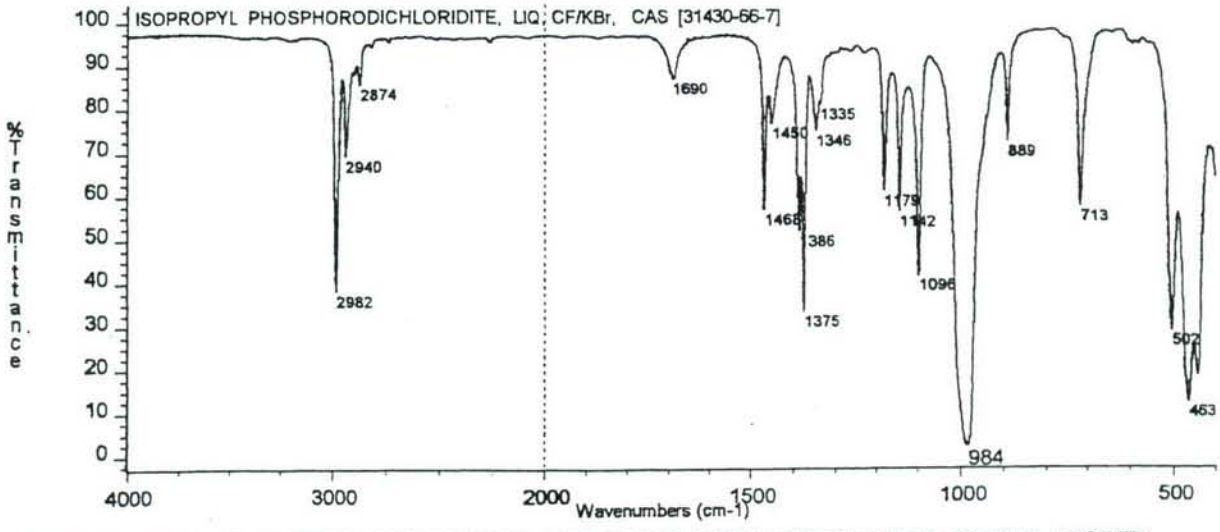

Figure 47 ISOPROPYL DICHLOROPHOSPHITE (ISOPROPYL PHOSPHORODICHLORIDITE), LIQUID, CF/KBr

The effect of atmospheric moisture on isopropyl dichlorophosphite is illustrated in ***Figures 48A-B***. After 1 hour of exposure, the infrared spectrum (***Figure 48A***) shows the formation of very weak bands at 1275 and 1227 cm^{-1}, which could be assigned to the P=O stretches of (iPrO)P=O(H)(Cl) and (iPrO)P=O(H)(OH). Over the period 18 hours to 3 days, the spectra resembles that of a P-acid, such as (iPrO)P=O(OH)(H), isopropyl hydrogen hydrogenphosphonate showing bands near 2650, 2280 and 1650 cm^{-1} (POH), 2440 cm^{-1} (ν P-H), 1215 cm^{-1} (P=O), 1181, 1145 and 1107 cm^{-1} (POiPr), 1007 cm^{-1} (ν P-O-C and ν P-OH). During the period 6 to 31 days, the compound changes by losing the isopropyl group (as evidenced by the lack of isopropyl bands) so that only the acid, $HP{=}O(OH)_2$ is left. The hydrolysis of isopropyl phosphorodichloridite may be represented as follows:

(iPrO)-PCl_2 -HOH→ (iPrO)-P(O-H)(Cl) → (iPrO)-P=O(H)(Cl) -HOH→ (iPrO)-P=O(H)(OH) -HOH→ H-$P{=}O(OH)_2$.

[m] Shagidullin et al in "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)," p. 4, Kluwer Academic Publishers, Boston, 1990, assign the higher band to the symmetric stretch and the lower band to the asymmetric stretch in P^{+3} compounds. Thomas (see general reference 1, p. 81) lists just the opposite for compounds of the type $ROPCl_2$, citing the ranges 508-490 cm^{-1} (ν_{as} PCl_2) and 473-450 cm^{-1} (ν_{sy} PCl_2).

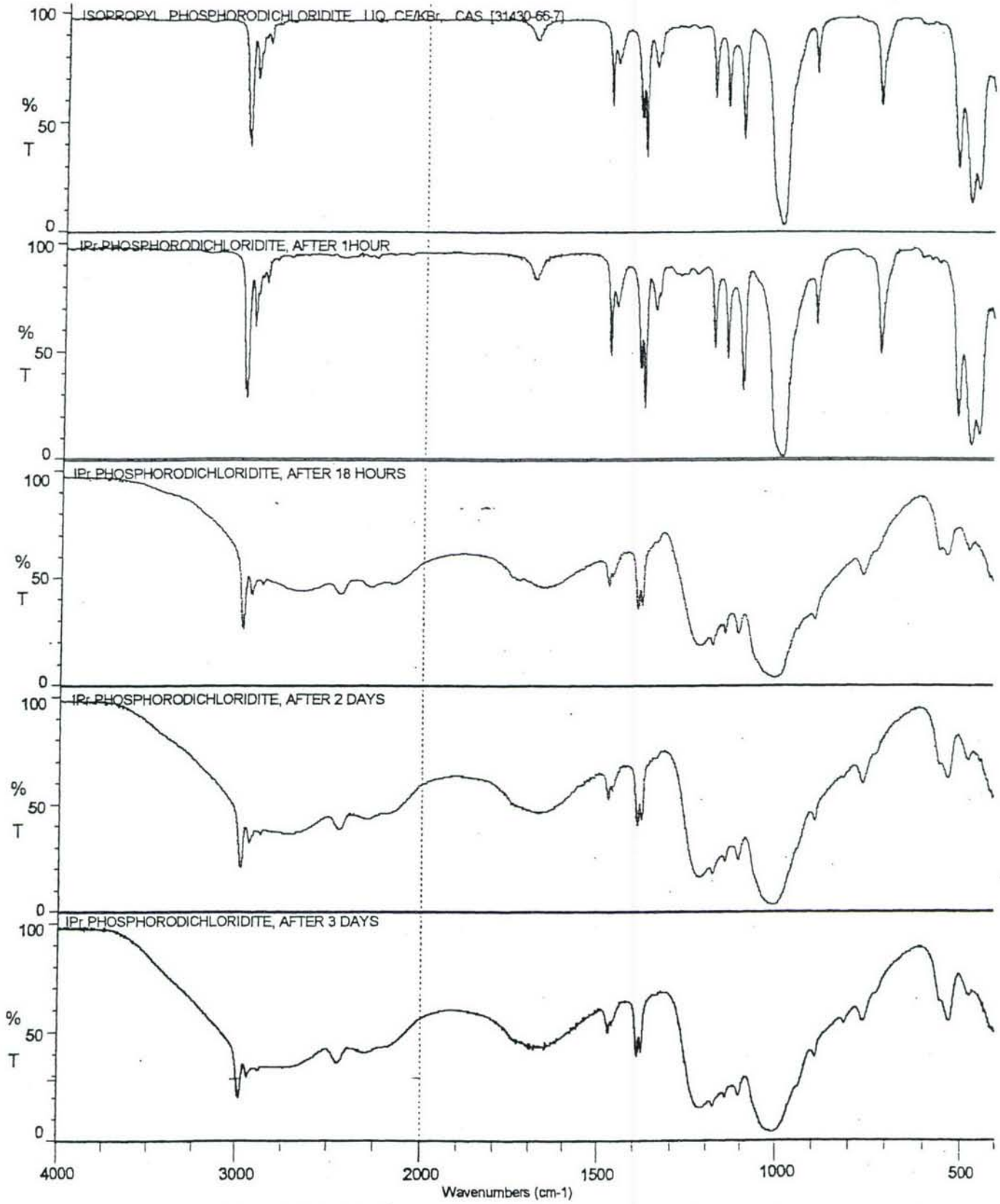

Figure 48A ISOPROPYL PHOSPHORODICHLORIDITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

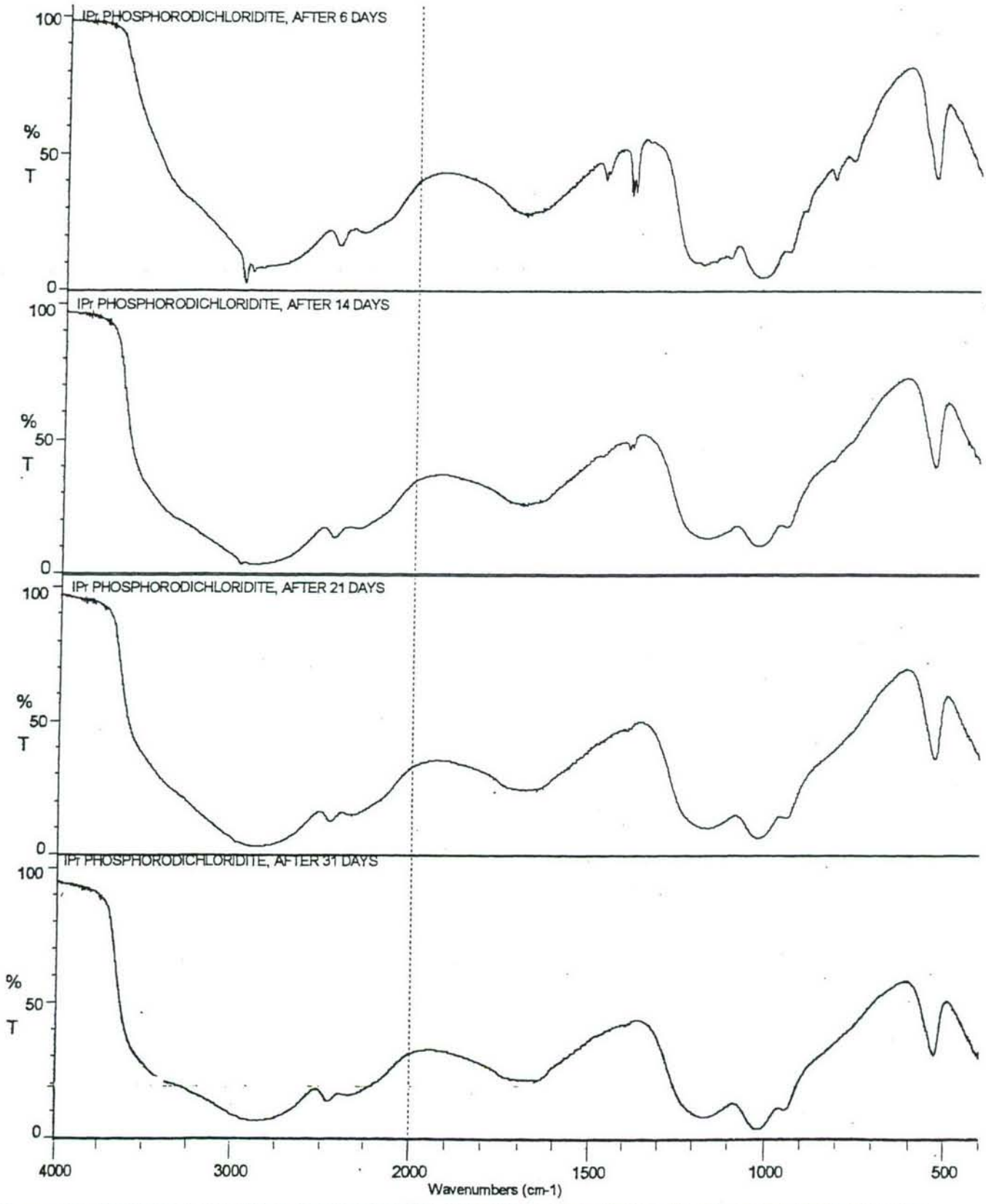

Figure 48B ISOPROPYL PHOSPHORODICHLORIDITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.2.3 *n*-Butyl dichlorophosphite (*n*-butyl phosphorodichloridite) (n-C_4H_9O)-PCl_2

The infrared spectrum of *n*-butyl dichlorophosphite (*n*-butyl phosphorodichloridite) is given in ***Figure 49***. The band assignments are as follows: 2962 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), 2896 cm^{-1} sh (ν_{sy} CH_3), 2875 cm^{-1} m (ν_{sy} CH_2), 1463 cm^{-1} m (δ CH_2), 1437 cm^{-1} vw (δ_{as} CH_3), 1380 cm^{-1} w (δ_{sy} CH_3), 1297 cm^{-1} vw, 1257 cm^{-1} vw and 1230 cm^{-1} vw (ω, τ CH_2), 1145, 1119 cm^{-1} vw (CH_3 rock ?), 1056 m , 1020 and 1002 cm^{-1} s (ν P-O-C), 984 cm^{-1} ms (ν C-C of POC_4H_9), 769 cm^{-1} w (POC), 710 cm^{-1} w (CH_2 rock ?), 506 and 489 cm^{-1} m and 451 cm^{-1} s (ν_{as} and ν_{sy} , see footnote **m**).

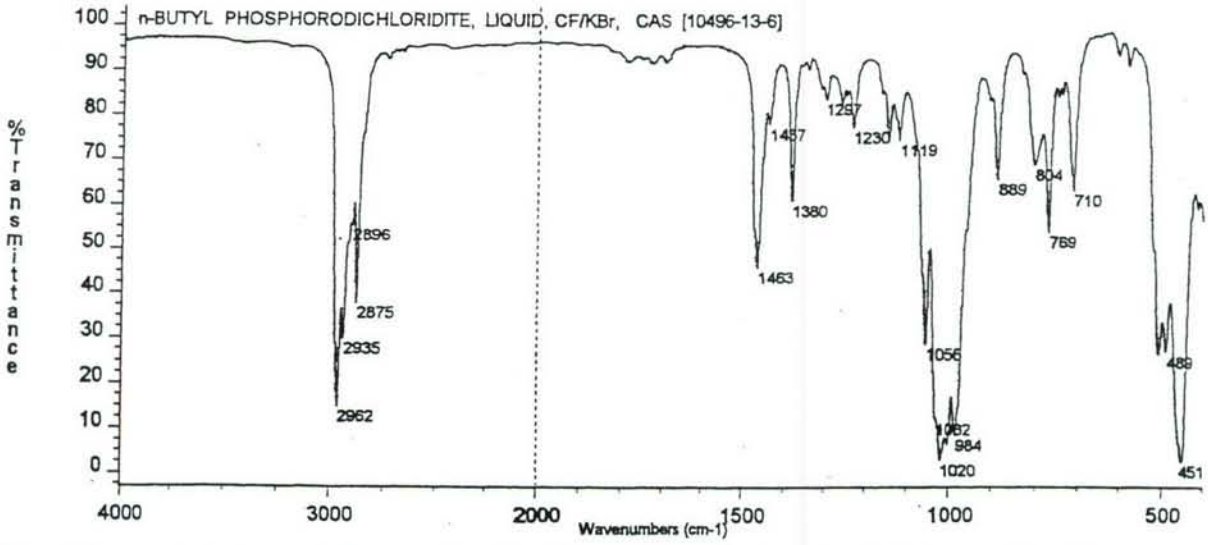

Figure 49 *n*-BUTYL DICHLOROPHOSPHITE (*n*-BUTYL PHOSPHORODICHLORIDITE), LIQUID, CF/KBr

The effect of atmospheric moisture on *n*-butyl dichlorophosphite is shown in ***Figure 50***. After 2.5 hours, a band at 2434 cm^{-1} appears (ν P-H) as does a shoulder near 1275 cm^{-1} [ν P=O of probably n-C_4H_9O-P=O(H)(Cl), which would have a calculated value of 1280 cm^{-1}). Weak and broad bands near 2700, 2300 and 1650 cm^{-1} (POH) are indicative of the formation of a P-acid. After a period of 5 hours, the bands due to the P-acid moiety have become more predominate in the spectrum. By 22-51 hours, the acid bands are very predominant, the PH stretch is still visible at 2445 cm^{-1}, and the P=O stretch has fallen to 1215 cm^{-1}. The strong band at 1006 cm^{-1} can be assigned to the ν P-O-C and ν P-OH. The

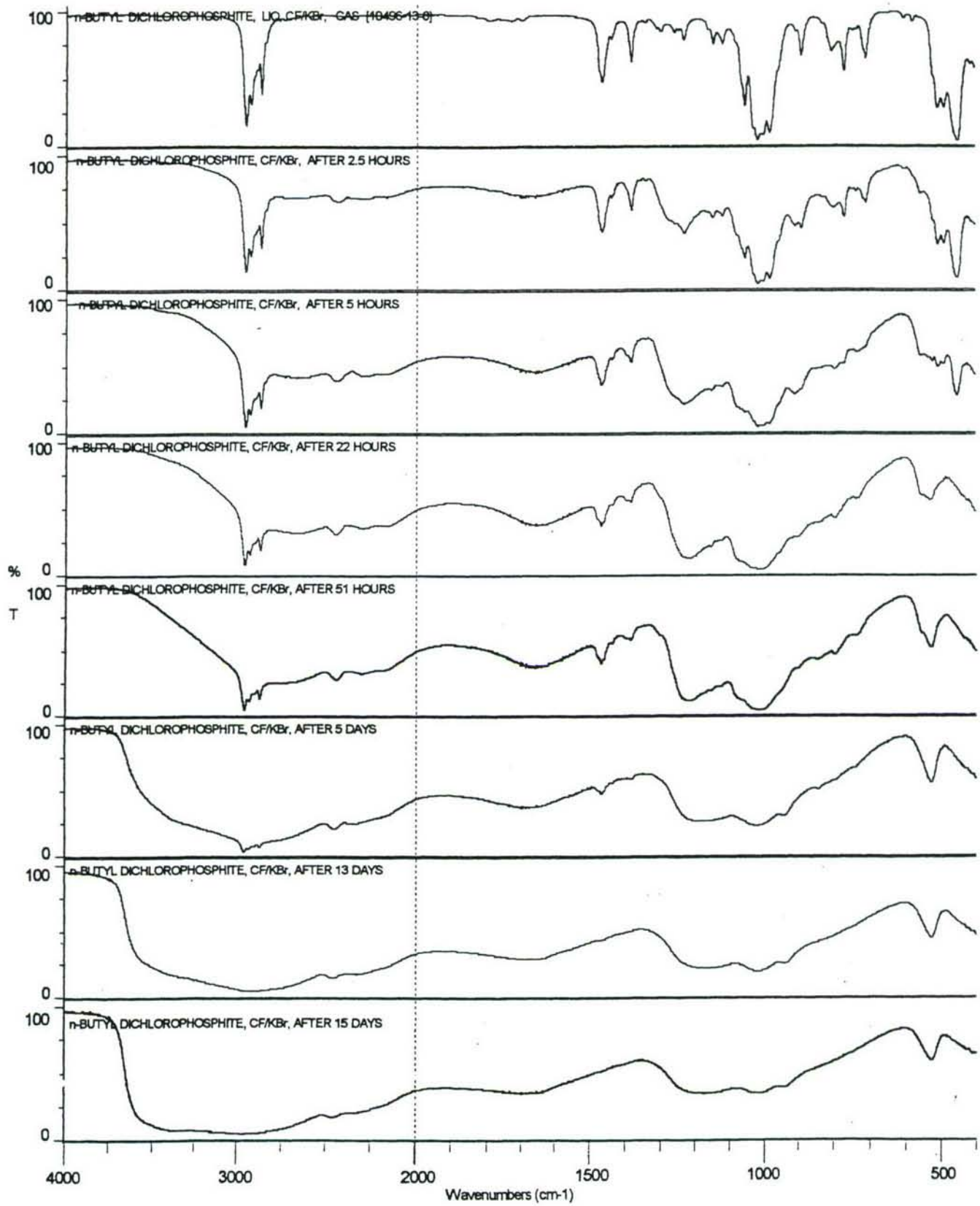

Figure 50 ***n*-BUTYL DICHLOROPHOSPHITE (*n*-BUTYL PHOSPHORODICHLORIDITE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE**

compound fitting these results appears to be $(H_9C_4O)P{=}O(H)(OH)$, which would have a calculated P-OH stretch of 1004 cm^{-1}.[n]

3.2.4 Diethyl chlorophosphite (diethyl phosphorochloridite) $Cl\text{-}P(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of a liquid film of diethyl chlorophosphite (diethyl phosphorochloridite or diethyl chlorophosphonite) between KBr windows is reproduced in ***Figure 51***. The band assignments are as follows: 2982 cm^{-1} ms (ν_{as} CH_3 and ν_{as} CH_2), 2936 cm^{-1} w (ν_{sy} CH_3), 2902 cm^{-1} w (ν_{sy} CH_2), 2428 cm^{-1} vw (ν P-H), 1475 cm^{-1} w (δ OCH_2), 1443 cm^{-1} w (δ_{as} CH_3), 1389 cm^{-1} m (ω OCH_2), ca 1368 cm^{-1} sh (δ_{sy} CH_3), 1260 cm^{-1} w [ν P=O of $HP{=}O(OEt)_2$, which has a calculated value of 1258 cm^{-1}], 1159 cm^{-1} and 1097 cm^{-1} w (Ch_3 rock, characteristic of POEt group), 1020 cm^{-1} s (ν P-O-C), 959 and 933 cm^{-1} ms (ν C-C of POEt), 769 cm^{-1} m and 741 cm^{-1} w (POC), 433 cm^{-1} m (ν P-Cl). There is a shoulder on the 1260 cm^{-1} phosphoryl stretching band at ca 1272 cm^{-}, which may be due to the P=O stretch of the pyro compound $(EtO)(H)P(=O)\text{-}O\text{-}P{=}O(H)(OEt)$. This pyro compound would have a calculated P=O stretch of 1276 cm^{-1}.

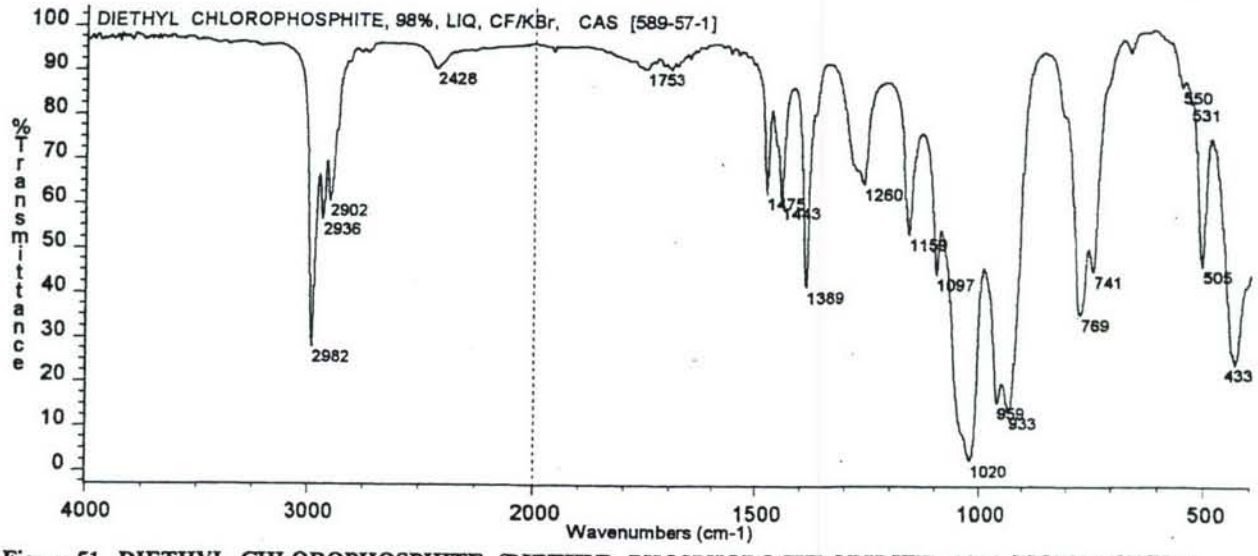

Figure 51 DIETHYL CHLOROPHOSPHITE (DIETHYL PHOSPHOROCHLORIDITE), 98%, LIQUID, CF/KBr

[n] The P-OH stretching vibration may be calculated using the equation , ν P=O $= 650 + 40\sum\pi$, derived by Thomas and Chittenden,. where $\sum\pi$ is the summation of the phosphorus inductive constants of the other groups on the phosphorus. The value for P=O being 3.5 and that for P=S being 2.5. See Thomas, L.C. and Chittenden, R. A., Spectrochim. Acta **20**, 489 (1964) and Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds," Heyden & Son Ltd., 1974.

The effect of atmospheric moisture on diethyl chlorophosphite is illustrated in ***Figure 52***. The original spectrum showed bands at 2428 and 1260 cm^{-1} that were assigned to the P-H and P=O stretching vibrations of H-P=O$(OEt)_2$ (diethyl phosphite or diethyl hydrogenphosphonate, 2426 and 1260 cm^{-1}). As the time of exposure to atmospheric moisture increased (1-3 hours), these bands became more intense. After about 4-6 hours, diffuse and broad bands near 2700 and 2300 cm^{-1} began to become evident in the spectrum. These bands are due to the formation of the POH moiety. After 22 hours, P-acid bands are very evident at 2700, 2300 and 1000 cm^{-1} (POH). The P=O band has fallen to 1223 cm^{-1}, indicative of P-acid formation. Some of the POEt moiety is still present as indicated by the bands in the CH stretching region and the bands at 1166 and 1099 cm^{-1}. The P-H stretch is still visible at 2430 cm^{-1}. The predominant compound may now be HP=O(OH)(OEt). This compond would have a calculated value of 1004 cm^{-1} for the P-OH stretch. The spectrum does show a strong and broad band near 1000 cm^{-1} which could be due in part to the P-H, P-O-C and P-OH moieties. After 5 days, the infrared spectrum shows only bands indicative of a very wet P-acid believed to be $HP{=}O(OH)_2$, phosphonic acid. The hydrolysis of diethyl chlorophosphite may thus be summarized as follows:

$(EtO)_2P\text{-}Cl$ -HOH→ $(EtO)_2$ P-O-H → $(EtO)_2P{=}O(H)$ -HOH→ H(EtO)P(=O)-O-P=O(OEt)H (?) -HOH→ HP=O(OH)(OEt) -HOH→ $HP{=}O(OH)_2$.

3.2.5 Diethyl methyl phosphite (**MP**) $(CH_3)P(OCH_2CH_3)_2$

The infrared spectrum of diethyl methyl phosphite (**MP**) as a liquid film between KBr windows is given in ***Figure 53***. Band assignments are as follows: 2978 cm^{-1} ms, 2935 cm^{-1} m, 2899 cm^{-1} m, 2884 cm^{-1} sh, 2834 cm^{-1} w (ν CH_3 and ν CH_2), 1478 cm^{-1} w (δ OCH_2), 1444 cm^{-1} δas CH_3), 1389 cm^{-1} m (ω OCH_2), ca 1365 cm^{-1} sh (δ_{sy} CH_3), 1292 cm^{-1} vw (?), 1264 cm^{-1} vw [ν P=O from possibly $HP{=}O(OEt)_2$ or HP=O(OMe)(OEt), calculated ν P=O of 1258 and 1260 cm^{-1} respectively-possible hydrolysis products], 1180 cm^{-1} slight shoulder ($POCH_3$), 1163 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1026 cm^{-1} s (slight shoulder near 1060 cm^{-1}, ν P-O-C of both POMe and POEt), 919 cm^{-1}

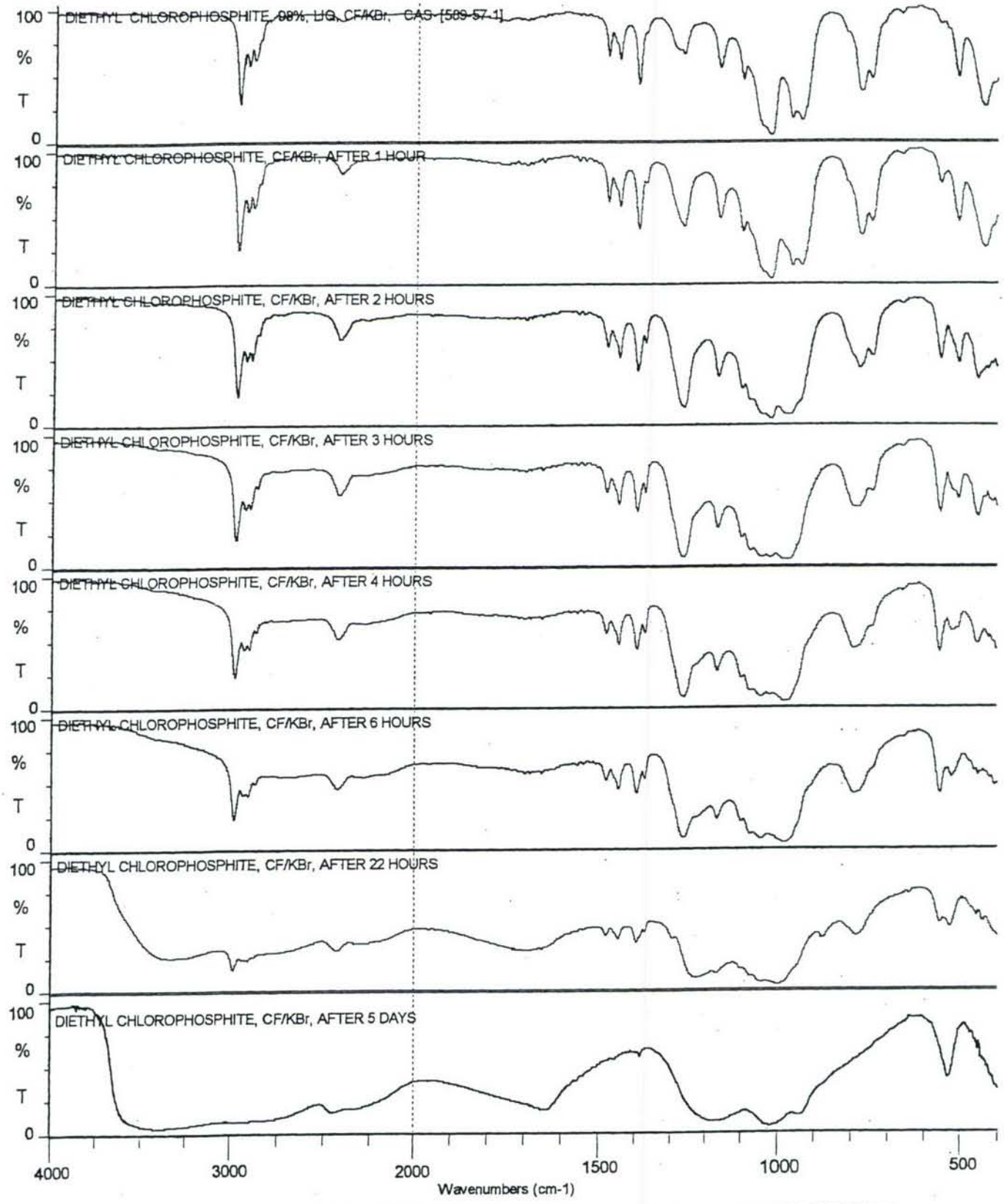

Figure 52 DIETHYL CHLOROPHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

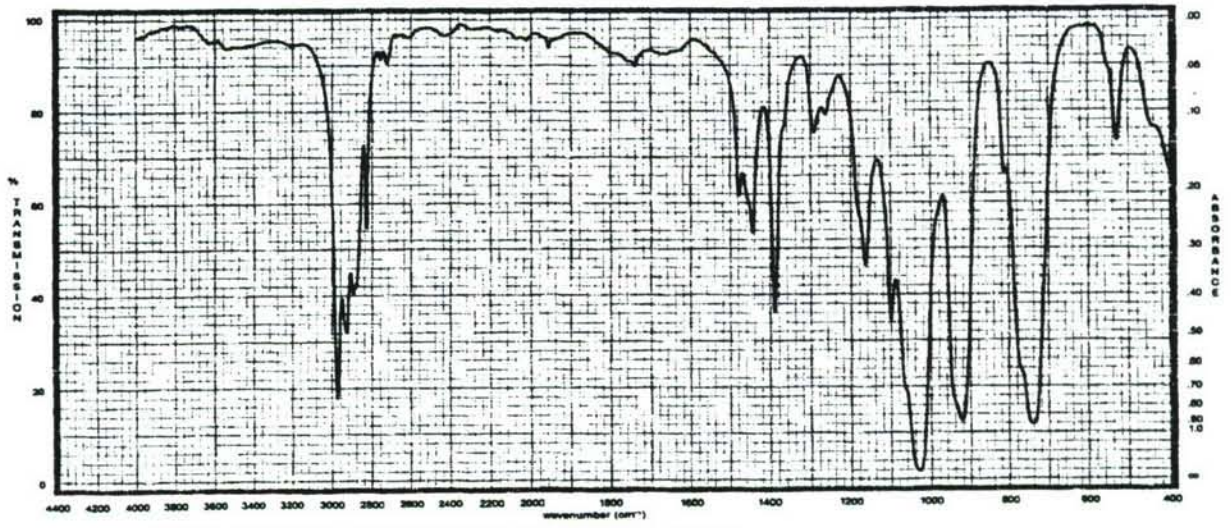

Figure 53 DIETHYL METHYL PHOSPHITE (MP), LIQUID, CF/KBr

ms (ν C-C or POEt, this band is generally lower in the P^{+3} than in the P^{+5} compounds)[o], 809 cm^{-1} sh and 738 cm^{-1} ms (POC).

The effect of atmospheric moisture on diethyl methyl phosphite[p] is illustrated by the spectra given in ***Figures 54A-B***. After 3 hours of exposure to atmospheric moisture, the spectrum (***Figure 54A***) of **MP** shows a very weak band at 2431 cm^{-1} (ν P-H), a weak band at 1262 cm^{-1} (ν P=O) and a very weak band at 981 cm^{-1} (possible P-H deformation). After twenty hours of exposure, the spectrum (***Figure 54B***) shows bands near 3400 cm^{-1} s and 1643 cm^{-1} m (H_2O), 2438 cm^{-1} w (ν P-H), 1480 cm^{-1} w (δ OCH_2), 1447 cm^{-1} w (δ_{as} CH_3), 1395 cm^{-1} w (ω OCH_2), 1371 cm^{-1} vw (δ_{sy} CH_3), 1241 cm^{-1} s (ν P=O), 1166 cm^{-1} w and 1098 cm^{-1} sh (CH_3 rock of POEt, characteristic), 1044 cm^{-1} s (ν P-O-C), 986 cm^{-1} s (P-H deformation and ν C-C of POEt), 772 cm^{-1} w (POC). The compound appears to have hydrolyzed to a phosphonate, such as diethyl hydrogenphosphonate (diethyl phosphite), $HP{=}O(OCH_2CH_3)_2$. Thus the

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[o] According to Thomas, L.C. in "Interpretation of the Infrared Spectra of Organophosphorus Compounds," p. 53, Heyden & Son Ltd., 1974, trivalent esters have a ν C-C band in the region 935-909 cm^{-1}, while pentavalent compounds show this band usually between 982-939 cm^{-1}. Several exceptions have been noted.

[p] Data was also presented in "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part II. V-Agents and Related Compounds," Piffath, R.J., 1999. U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423.

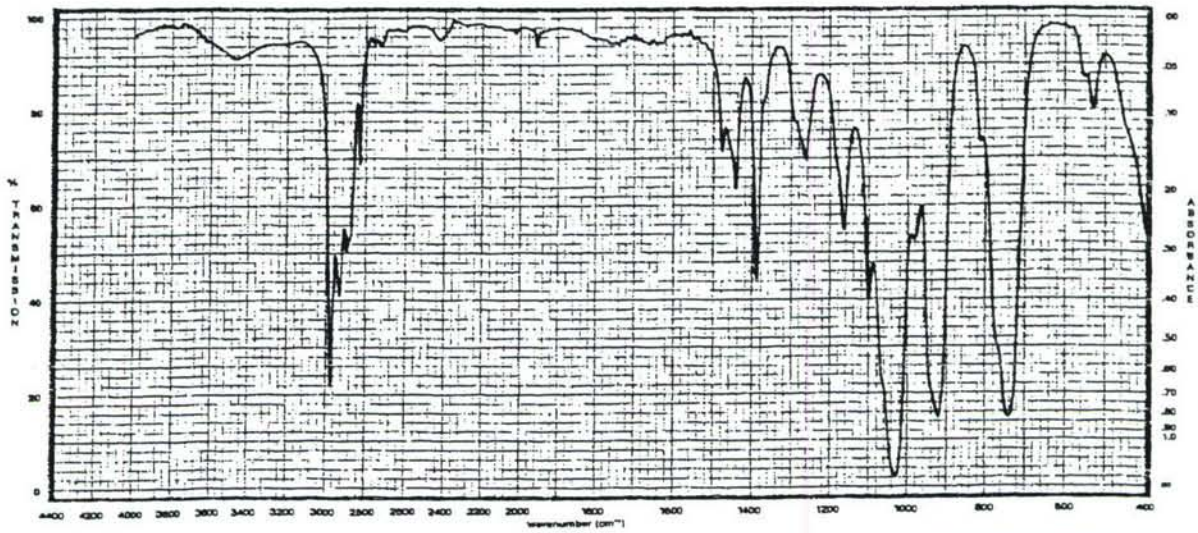


Figure 54A DIETHYL METHYL PHOSPHITE (MP), LIQUID, CF/KBr, AFTER 3 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

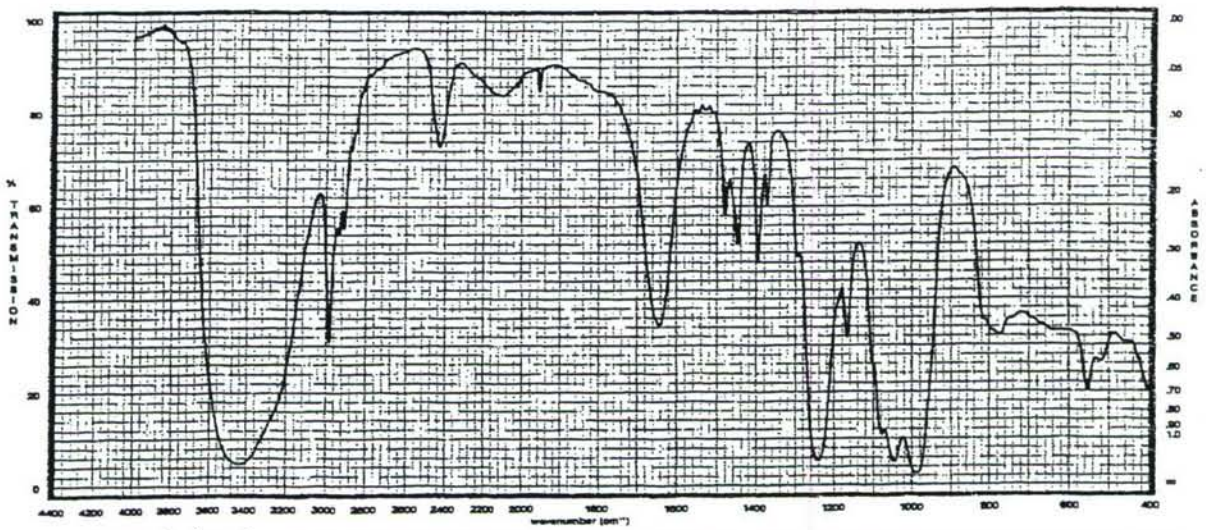


Figure 54B DIETHYL METHYL PHOSPHITE (MP), LIQUID, CF/KBr, AFTER 20 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

hydrolysis of diethyl methyl phosphite may be summarized as follows: $CH_3OP(OEt)_2$ -HOH→ $HP{=}O(OEt)_2$. The hydrolysis may continue to eventually produce $HP{=}O(OH)_2$.

3.2.6 2,2,2-Trichloro-1,1-Dimethylethyl Dichlorophosphite $Cl_2P[0\text{-}C(CH_3)_2\text{-}CCl_3]$

The infrared spectrum of 2,2,2-Trichloro-1,1-dimethylethyl dichlorophosphite as a liquid film between CsI windows is reproduced as ***Figure 55***. The band assignments are as follows: 3005 cm^{-1} w

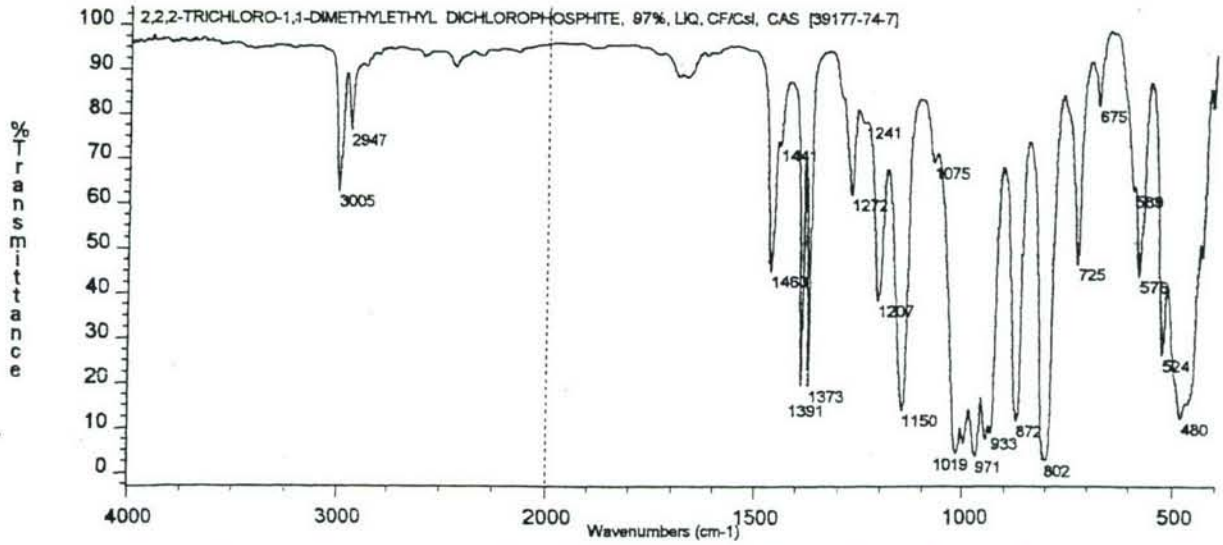


Figure 55 2,2,2-TRICHLORO-1,1-DIMETHYLETHYL DICHLOROPHOSPHITE (2,2,2-TRICHLORO-1,1-DIMETHYLETHYL PHOSPHORODICHLORIDITE), 97%, LIQUID, CF/CsI

(ν_{as} CH_3), 2947 cm^{-1} vw (ν_{sy} CH_3), 2444 cm^{-1} vvw (ν P-H, hydrolysis product), 1463 cm^{-1} m (δ_{as} CH_3), 1391 and 1373 cm^{-1} ms (δ_{sy} CH_3), 1272 cm^{-1} w (ν P=O, impurity-hydrolysis product), 1207 cm^{-1} m and 1150 cm^{-1} ms (*gem*-dimethyl skeletal), 1019, 1000, 971, 947 and 933 cm^{-1} ms-s (ν P-O-C), 872 cm^{-1} ms (ν C-C), 802 cm^{-1} s (ν CCl_3 , ν_{as} ?), 725 cm^{-1} m (POC), 675 cm^{-1} vw (ν_{sy} CCl_3 ?), 524 cm^{-1} m (P=O deformation , or perhaps ν_{sy} PCl_2 ?), 480 cm^{-1} ms (ν PCl_2 , perhaps ν_{as} PCl_2 ? See footnote [m]).

The effect of atmospheric moisture on 2,2,2-trichloro-1,1-dimethylethyl dichlorophosphite is illustrated by the infrared spectra presented in ***Figures 56A-C***. During the period 17-41 hours of exposure the band at 1272 cm^{-1} increases in intensity. This band may be assigned to a P=O stretch from perhaps the hydrolysis product $Cl_3C(CH_3)_2$ CO-P=O((H)(Cl), which would have a calculated P=O stretch of 1278 cm^{-1} (assuming the ester moiety to have a π constant of ca 2.8). The P-H stretch occurs near 2444 cm^{-1}. After 5 days of exposure, the spectrum shows a POH moiety forming, ca 2330 and 1670 cm^{-1} (POH). A band at 1245 cm^{-1} that has been increasing in strength may be due to an acid P=O stretch. This effect continues up to the 14th day where the P-acid moiety becomes more predominant in the spectrum. The P=O stretch decreases to 1211 cm^{-1} , possibly now due to the formation of the hydrolysis product $Cl_3C(CH_3)_2$ CO-P=O(H)(OH). The bands due to the PCl_2 group (480 cm^{-1}) have also disappeared from

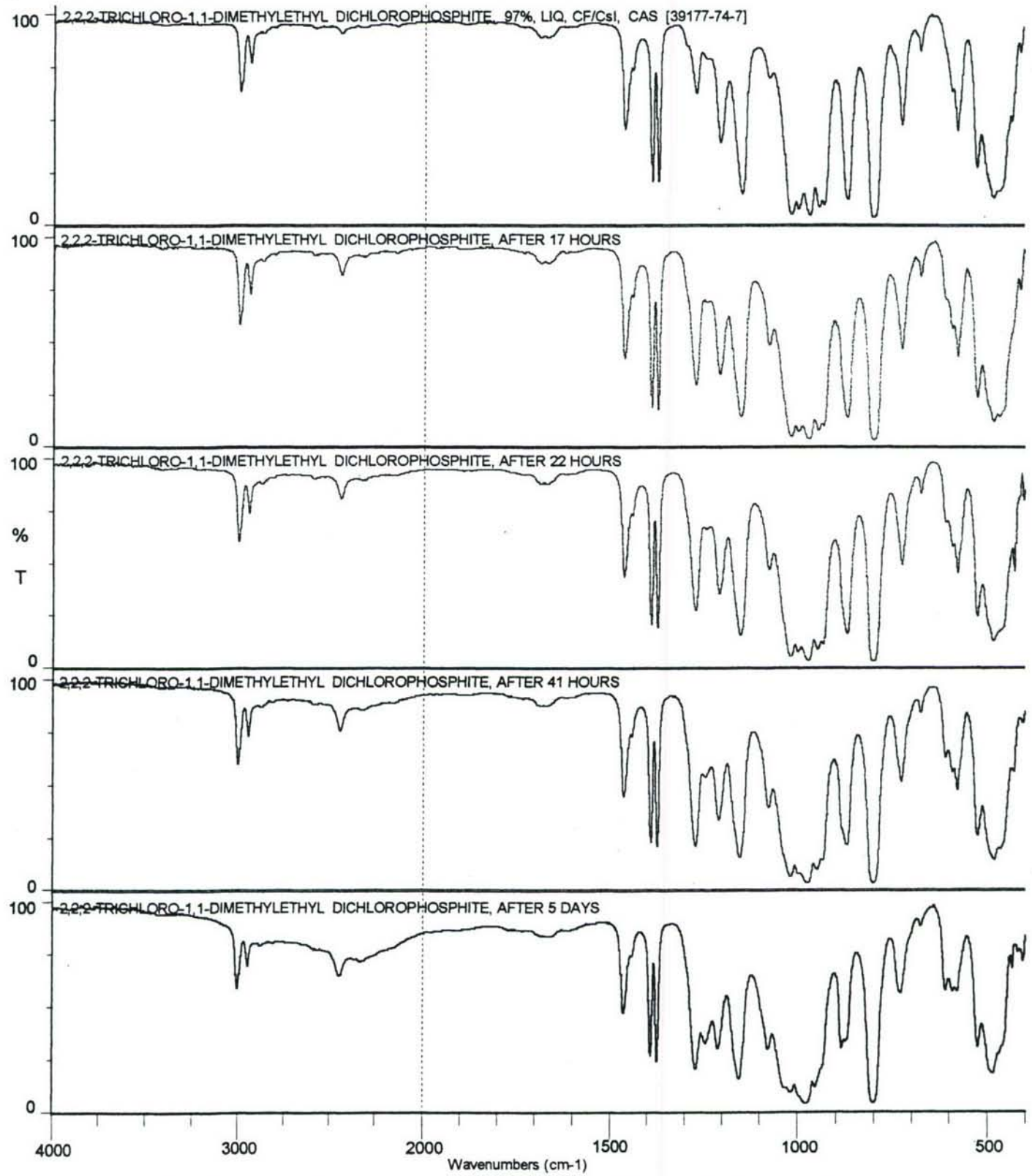


Figure 56A 2,2,2-TRICHLORO-1,1-DIMETHYLETHYL DICHLOROPHOSPHITE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

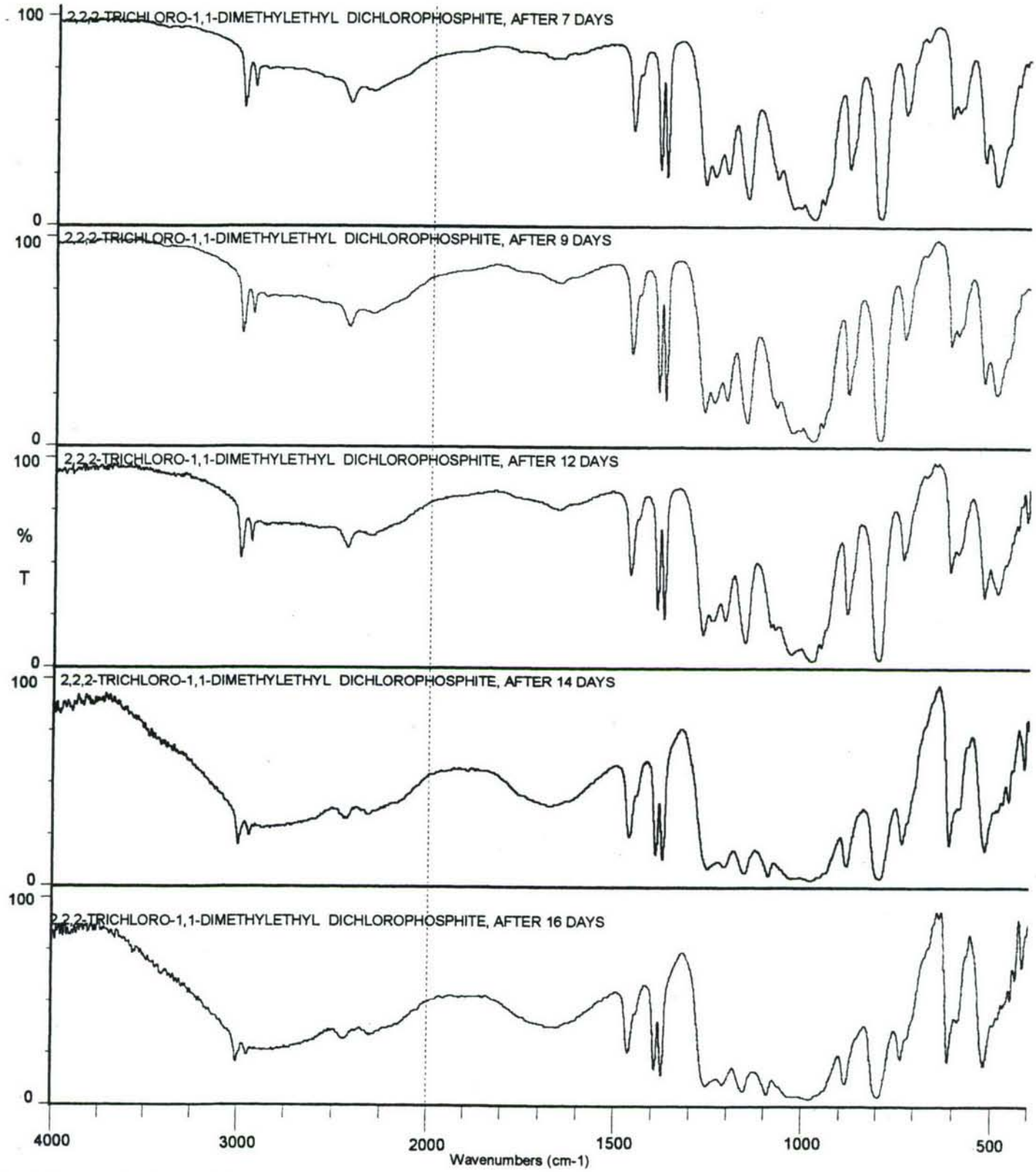


Figure 56B 2,2,2-TRICHLORO-1,1-DIMETHYLETHYL DICHLOROPHOSPHITE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

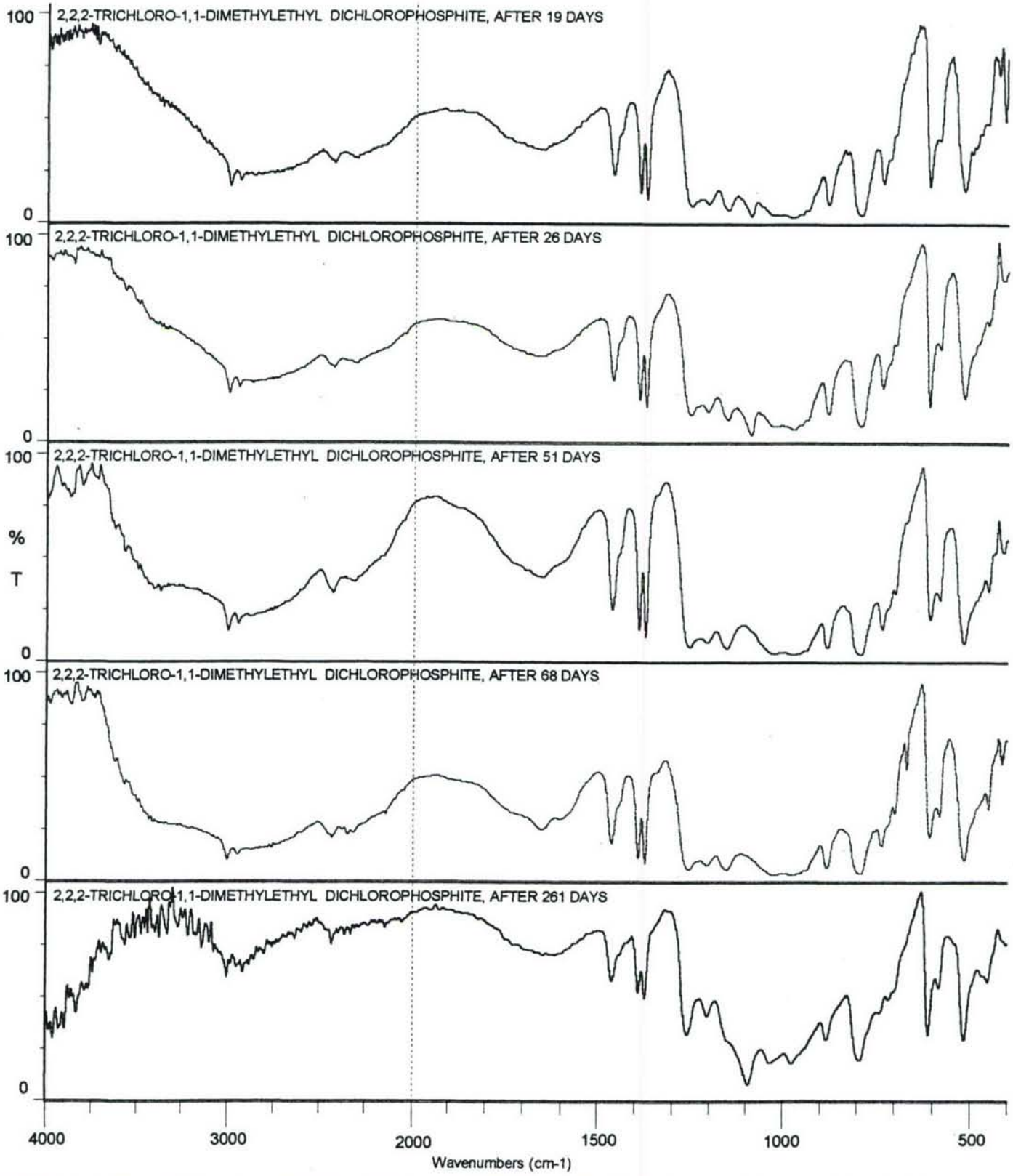


Figure 56C 2,2,2-TRICHLORO-1,1-DIMETHYLETHYL DICHLOROPHOSPHITE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

the spectrum. This appears to be the case even after some 261 days of exposure to atmospheric moisture. Now, bands appear at 1093 and 610 cm^{-1} and are assigned as being due to the formation of cesium sulfate, Cs_2SO_4 from the CsI windows. The hydrolysis of 2,2,2-trichloro-1,1-dimethylethyl dichlorophosphite seems to proceed as follows: $Cl_3C\text{-}C(CH_3)_2O\text{-}PCl_2$ -HOH→ $Cl_3C\text{-}C(CH_3)_2O\text{-}P{=}O(H)(Cl)$ -HOH→ $Cl_3C\text{-}C(CH_3)_2O\text{-}P{=}O(H)(OH)$. However, there may be some contribution from the oxidation of the compound to produce $Cl_3C\text{-}C(CH_3)_2O\text{-}P{=}O(Cl)_2$ (ν P=O calculated as 1294 cm^{-1}), which may hydrolyze to form $Cl_3C\text{-}C(CH_3)_2O\text{-}P{=}O(OH)(Cl)$, which in turn may hydrolyze to form $Cl_3C\text{-}C(CH_3)_2O\text{-}P{=}O(OH)_2$. The compound $Cl_3C\text{-}C(CH_3)_2O\text{-}P{=}O(OH)(Cl)$, could absorb near 1250 cm^{-1} (ν P=O) and 1038 cm^{-1} (ν P-OH). It may be that the two effects, hydrolysis and oxidation, are both occurring.

3.2.7 2-Chlorophenyl dichlorophosphite (2-chlorophenyl phosphorodichloridite)

$2\text{-}Cl\text{-}C_6H_4\text{-}O\text{-}PCl_2$

The infrared spectrum of 2-chlorophenyl dichlorophosphite (2-chlorophenyl phosphorodichloridite) as a liquid film between KBr windows is given in ***Figure 57***. The band assignments are as follows: 3070 cm^{-1} w (ν C-H aromatic), 1581 cm^{-1} m, 1475 cm^{-1} s and 1445 cm^{-1} ms (aromatic ring),

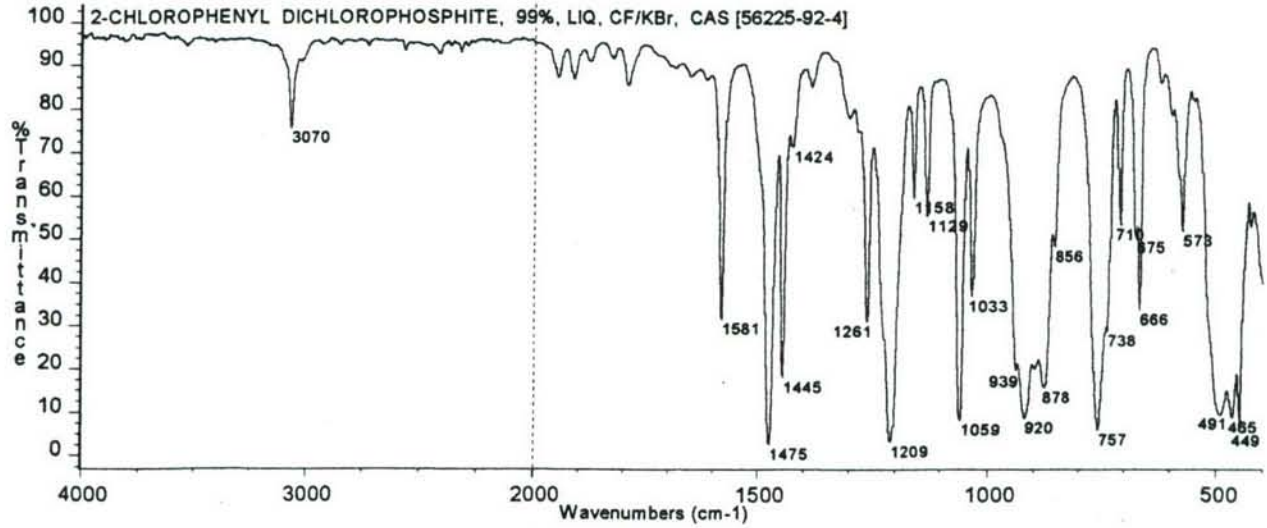


Figure 57 2-CHLOROPHENYL DICHLOROPHOSPHITE (2-CHLOROPHENYL PHOSPHORODICHLORIDITE, 99%, LIQUID, CF/KBr

1301 cm^{-1} vw (ν P=O from possibly $2\text{-}Cl\text{-}C_6H_4\text{-}O\text{-}P{=}OCl_2$, as a result of oxidation), 1261 cm^{-1} m , 1209

cm^{-1} s (ν C-O), 1158 cm^{-1} w, 1129 cm^{-1} w and 1033 cm^{-1} m (β C-H 1,2-disubstituted aromatic ring), 1059 cm^{-1} ms (phenyl-Cl), 920 cm^{-1} ms (ν P-O), 757 cm^{-1} ms (γ C-H 1,2-disubstituted aromatic ring), 491, 465 and 449 ms (ν PCl_2).

Figures 58A and ***58B*** illustrate the effect of atmospheric moisture on the infrared spectra of 2-chlorophenyl dichlorophosphite. After some 19-24 hours of exposure (***Figure 58A***) a very weak band appears near 2470 cm^{-1} (ν P-H) as does a band near 1290 cm^{-1}. These bands may be due to the formation of 2-Cl-C_6H_4 O-P=O(H)(Cl), which would have a calculated P=O stretch of 1290 cm^{-1}. The 24 hour spectrum also shows the appearance of broad absorption in the areas of 2800 and 2300 cm^{-1} which may be assigned to the formation of a POH group. By 43 hours these bands near 2800 and 2300 cm^{-1} are more pronounced as are bands near 1670 and 938 cm^{-1}, all which can be assigned to a POH group. Also, the P=O stretch has decreased in value to 1180 cm^{-1}, and the bands indicative of the 1,2-disubstituted aromatic ring have become much weaker. These trends continue through 68 hours and by the 57^{th} day the aromatic ring is almost completely gone from the spectrum (***Figure 58B***) save for a very weak band at 1481 cm^{-1}. The final spectrum (after 57 days) shows essentially bands due to PH, P=O and POH groups, which may be best represented by the structure H-P=$O(OH)_2$, phosphonic acid [i.e. $P(OH)_3$, phosphorous acid]. Thus, the hydrolysis of 2-chlorophenyl dichlorophosphite may be represented as follows:

2-Cl-C_6H_4 O-PCl_2 -HOH→ 2-Cl-C_6H_4 O-P=O(H)(Cl) -HOH→ 2-Cl-C_6H_4 O-P=O(H)(OH) -HOH→ HP=$O(OH)_2$ + 2-Cl-C_6H_4 OH.

3.2.8 Benzyl diethyl phosphite $(C_6H_5\text{-}CH_2\ O)P(OCH_2CH_3)_2$

The infrared spectrum of benzyl diethyl phosphite as a liquid film between KBr windows is given in ***Figure 59***. The band assignments are as follows: 3089, 3065 and 3032 cm^{-1} vw (ν C-H aromatic), 2977 cm^{-1} m (ν_{as} CH_3), 2931 cm^{-1} w (ν_{as} CH_2), 2896 and 2881 cm^{-1} w (ν_{sy} CH_3) and (ν_{sy} CH_2), 1607 cm^{-1} vvw, 1587 cm^{-1} vvw, 1497 cm^{-1} w and 1454 cm^{-1} w (aromatiac ring), 1477 cm^{-1} vw (δ OCH_2), 1443 cm^{-1} vw (δ_{as} CH_3), 1387 cm^{-1} w (ω OCH_2), ca 1375 cm^{-1} sh (δ_{sy} CH_3), 1276 and 1263 cm^{-1} w (ν

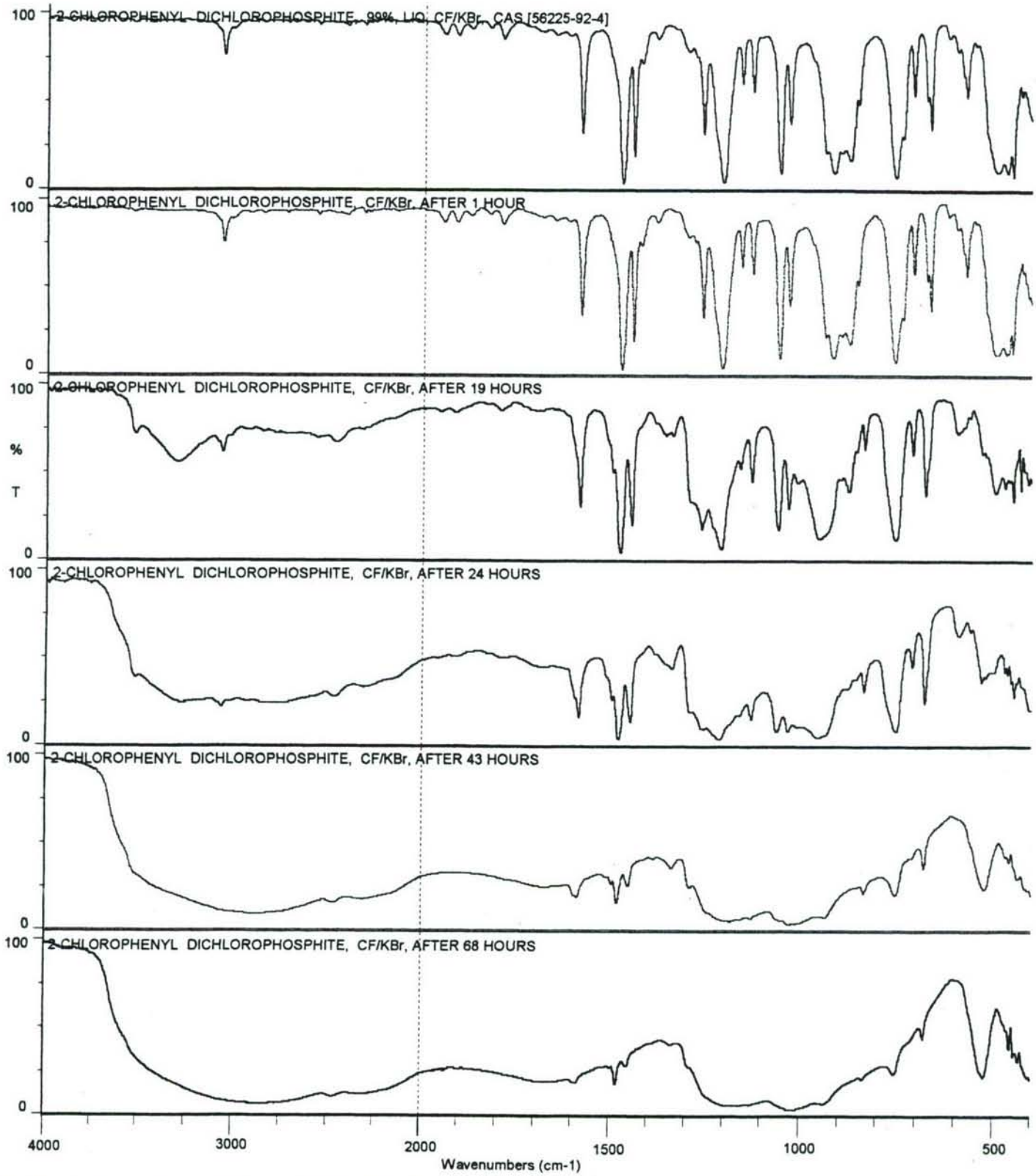


Figure 58A 2-CHLOROPHENYL DICHLOROPHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

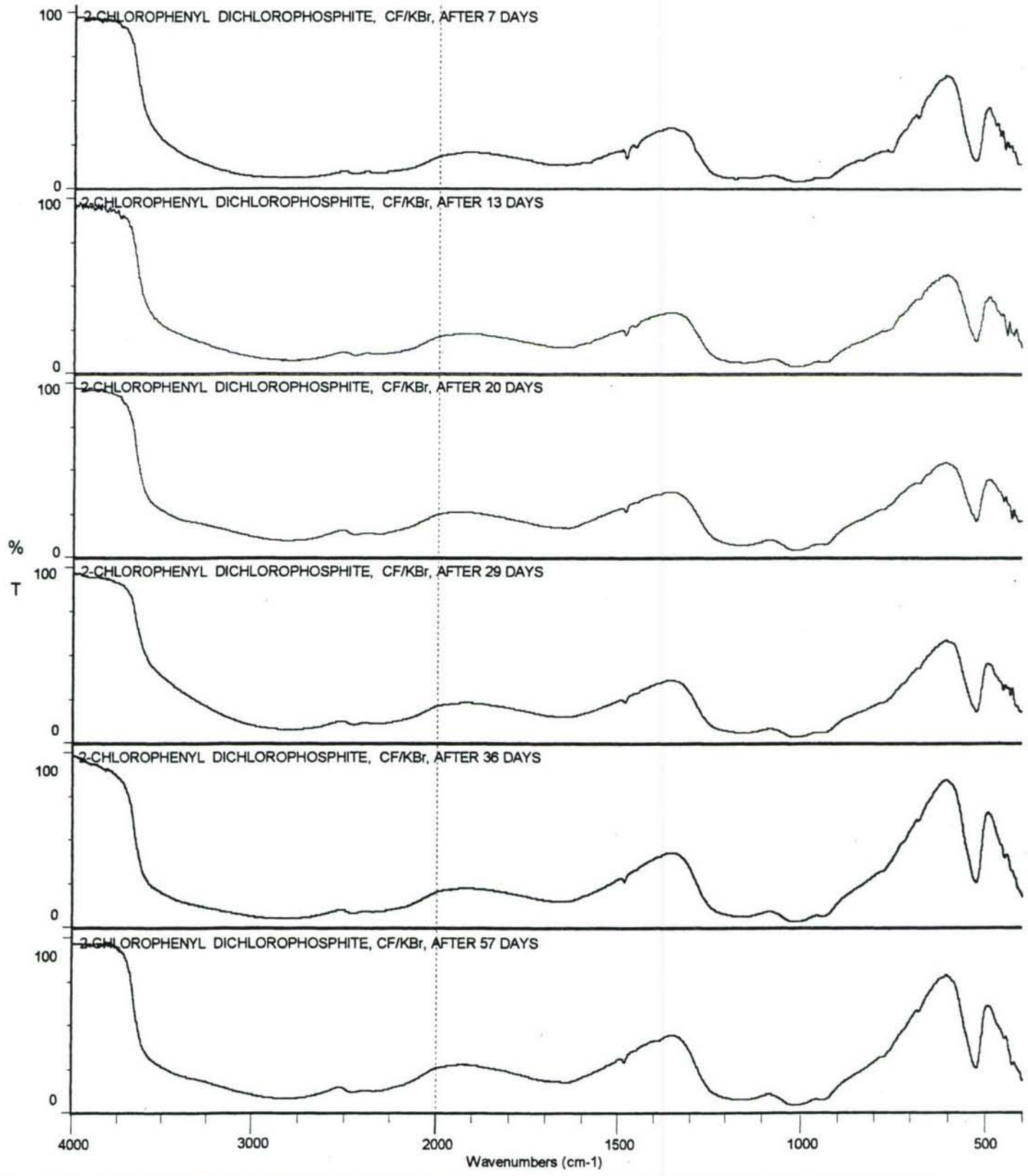


Figure 58B 2-CHLOROPHENYL DICHLOROPHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

P=O from possibly C_6H_5-CH_2-O-P=O$(OEt)_2$, which has a calculated P=O value of 1266 cm^{-1}), 1212 cm^{-1} vw (characteristic of benzyl moiety ?), 1162 and 1097 cm^{-1} w (characteristic of POEt), 1031 cm^{-1} s (ν P-O-C), 918 cm^{-1} ms (ν C-C of POEt), 831 and 808 cm^{-1} vw-w (POC), 734 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 696 cm^{-1} m (δ mono-substituted aromatic ring).

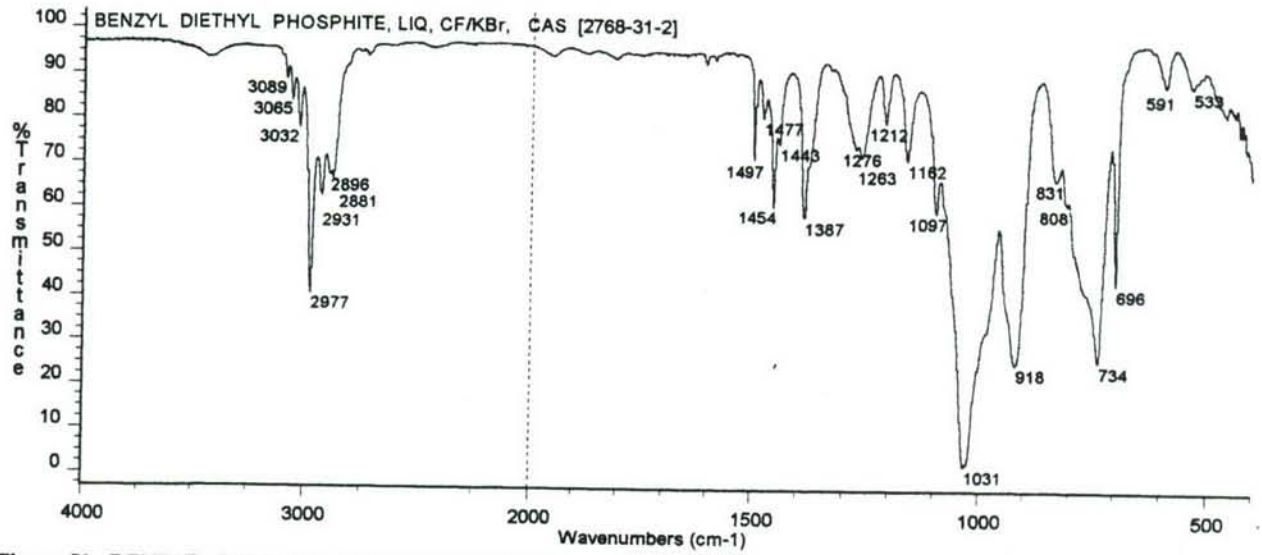


Figure 59 BENZYL DIETHYL PHOSPHITE, LIQUID, CF/KBr

The infrared spectra illustrating the effect of atmospheric moisture on benzyl diethyl phosphite are reproduced in ***Figure 60***. After 4 days the spectrum showed the following: a weak band at 2432 cm^{-1} (ν P-H), 1255 cm^{-1} ms [ν P=O from possibly C_6H_5-CH_2-O-P=O(H)(OEt), which would have a calculated ν P=O of 1252 cm^{-1}], 981 cm^{-1} s (contribution from P-H deformation and ν C-C from P^{+5}OC). After eleven days of exposure the infrared spectrum shows: 2430 cm^{-1} vw (ν PH), ca 2800, 2300 and 1650 cm^{-1} w and broad (POH), 1212 cm^{-1} (partly ν P=O and benzyl moiety), 1024 cm^{-1} s (ν POC, ν P-OH). The bands indicative of the POEt have become very weak in the spectrum. By the 28th day the infrared spectrum resembles that of a P-acid with very little indication of any POEt bands and weak bands from the benzyl moiety. The phosphoryl stretching band now occurs near 1209 cm^{-1} and bands occur near 1020 and 946 (ν P-OH). The hydrolysis may now have progressed to the point where the resultant spectrum is best explained as a mixture of C_6H_5-CH_2-O-P=O(H)(OH) and H-P=O(OH). The hydrolysis of benzyl

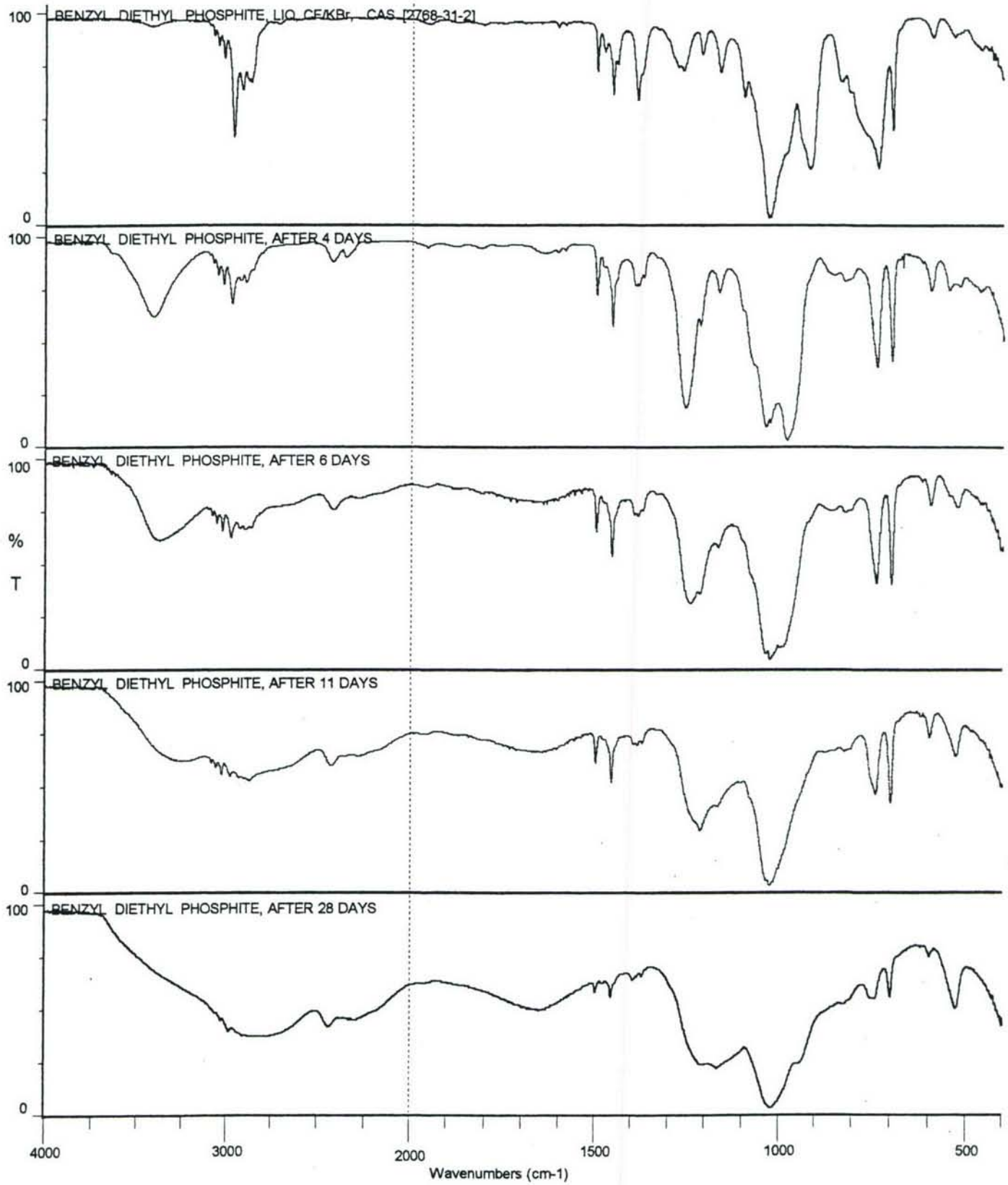


Figure 60 BENZYL DIETHYL PHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

diethyl phosphite may be summarized as follows:

$(C_6H_5\text{-}CH_2\ O)P(OEt)_2$ -HOH→ $(C_6H_5\text{-}CH_2\ O)P{=}O(H)(OEt)$ -HOH→ $(C_6H_5\text{-}CH_2\ O)P{=}O(H)(OH)$ -HOH→ some $H\text{-}P{=}O(OH)_2$.

3.2.9 Trimethyl phosphite (TMP) $P(OCH_3)_3$

The infrared spectrum of a liquid film of trimethyl phosphite (**TMP**) between KBr windows is reproduced in ***Figure 61***. The band assignments are as follows: 2946 cm^{-1} w (ν_{as} CH_3), 2836 cm^{-1} w (ν_{sy} CH_3), 1458 cm^{-1} vw (δ_{as} and δ_{sy} CH_3), 1384 cm^{-1} vvw (KNO_3 from KBr windows), 1181 cm^{-1} w (CH_3 rock from $POCH_3$, characteristic), 1057 cm^{-1} sh and 1013 cm^{-1} s (ν P-O-C), 768 cm^{-1} sh and 729 cm^{-1} ms (POC).[q]

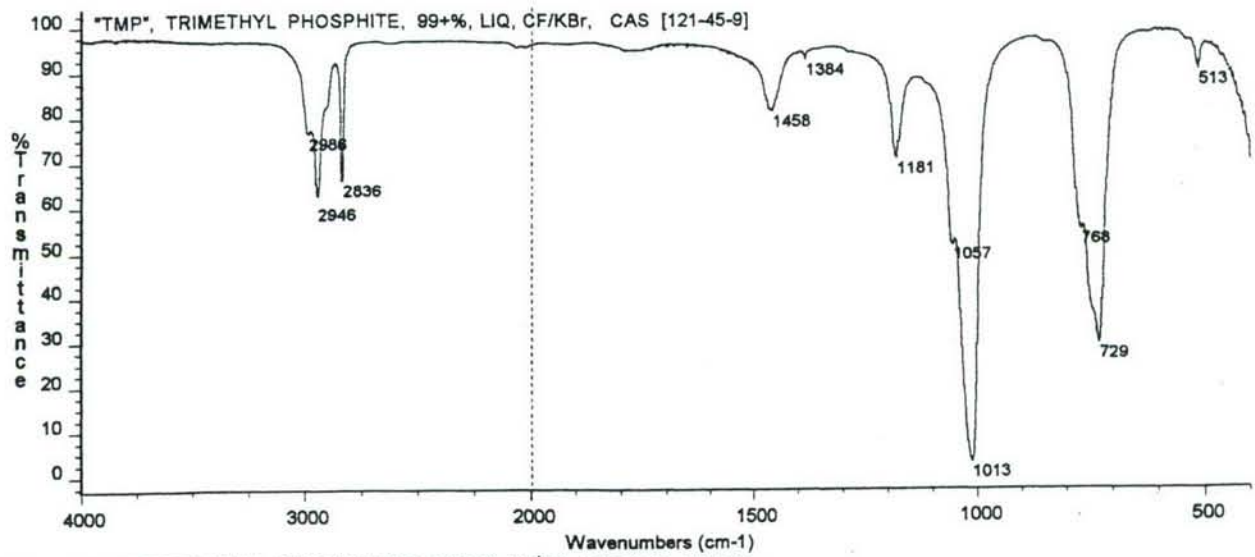


Figure 61 TRIMETHYL PHOSPHITE (TMP), 99⁺%, LIQUID, CF/KBr

The effect of the environment on a liquid film of trimethyl phosphite is shown in ***Figure 62***. After 2.5 hours the infrared spectrum shows the formation of very weak bands near 1280 cm^{-1} (ν P=O) and 850 cm^{-1} (POC). Trimethyl phosphate, $O{=}P(OCH_3)_3$, is probably being formed. The phosphate

[q] Shagidullin R.R, Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S. in "Atlas of IR Spectra of Organophosphorus Compounds (Intrepreted Spectrograms), p 91, IR No. 143, Kluwer Academic Publishers, Boston, 1990, assign these bands as follows: 1013 cm^{-1} (ν PO-C), 768 and 729 cm^{-1} [ν_{sy} and ν_{as} $P(\text{-}O)_3$].

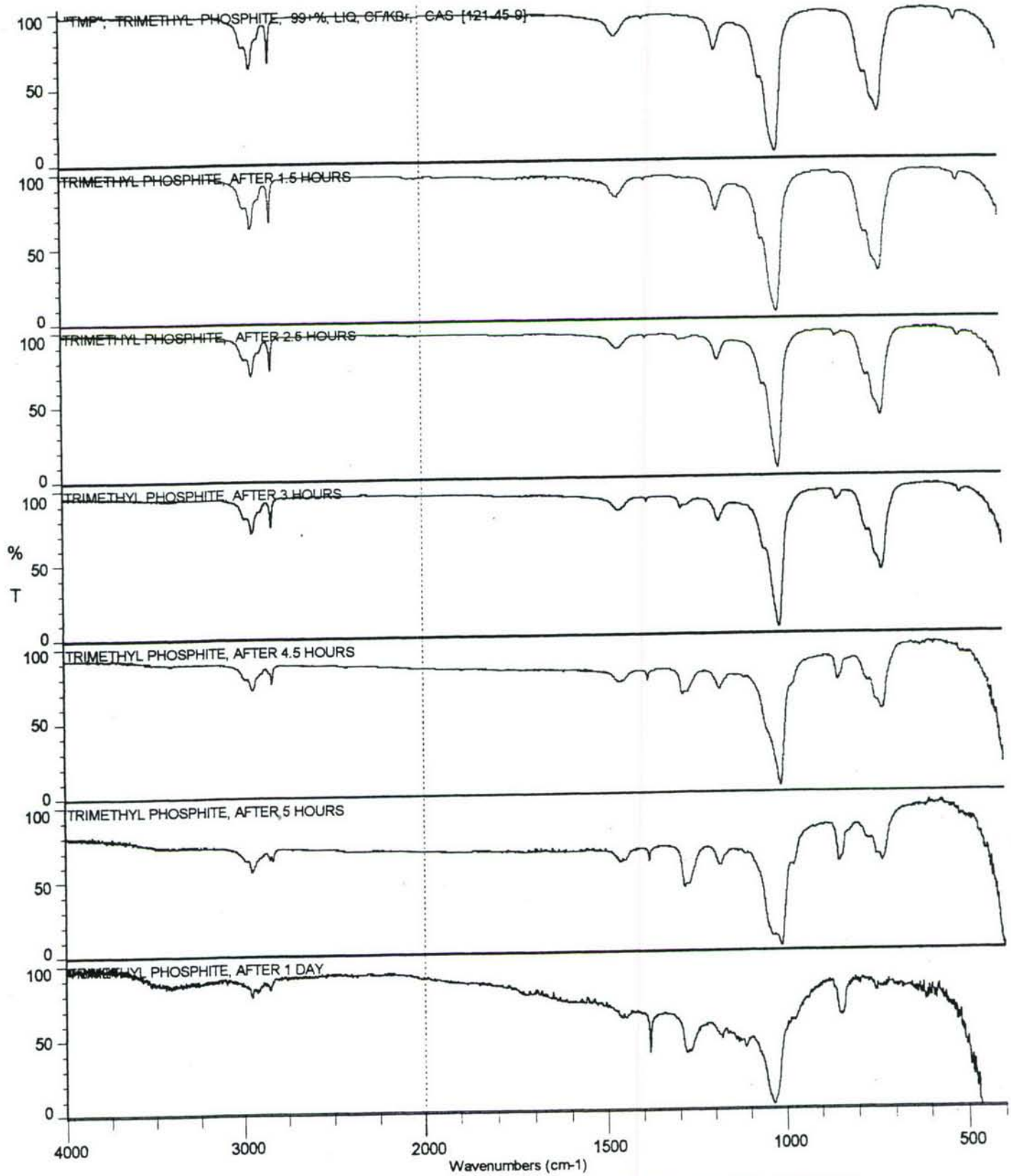


Figure 62 TRIMETHYL PHOSPHITE (TMP), LIQUID, CF/KBr, AFTER EXPOSURE TO THE ENVIRONMENT

compound would have a calculated phosphoryl stretching vibration of 1278 cm^{-1}. This conversion (oxidation) of the P^{+3} to the P^{+5} compound is more predominant after one day. However, the spectrum appears to be getting much weaker (note the increase in background noise) due to evaporation of the sample. This sample evaporation limits the practicality of longer exposure times.

3.2.10 Triethyl phosphite $P(OCH_2CH_3)_3$

The infrared spectrum for a liquid film of triethyl phosphite between KBr windows is given in ***Figure 63***. The band assignments are as follows: 2978 cm^{-1} ms (ν_{as} CH_3), 2930 cm^{-1} m (ν_{as} CH_2), 2899 cm^{-1} m (ν_{sy} CH_3), 2882 cm^{-1} m (ν_{sy} CH_2), 1478 cm^{-1} w (δ OCH_2), 1443 cm^{-1} w (δ_{as} CH_3), 1388 cm^{-1} m (ω OCH_2), 1364 cm^{-1} sh (δ_{sy} CH_3), 1292 and 1263 cm^{-1} vw (ω, τ CH_2, the 1263 cm^{-1} band may be due to the ν P=O of diethyl phosphite, $HP{=}O(OEt)_2$, which would have a calculated value of 1258 cm^{-1}), 1162 and 1097 cm^{-1} w (CH_3 rock, characteristic of POEt), 1028 cm^{-1} s (ν P-O-C), 921 cm^{-1} ms (ν C-C of POEt), 738 cm^{-1} m (POC).

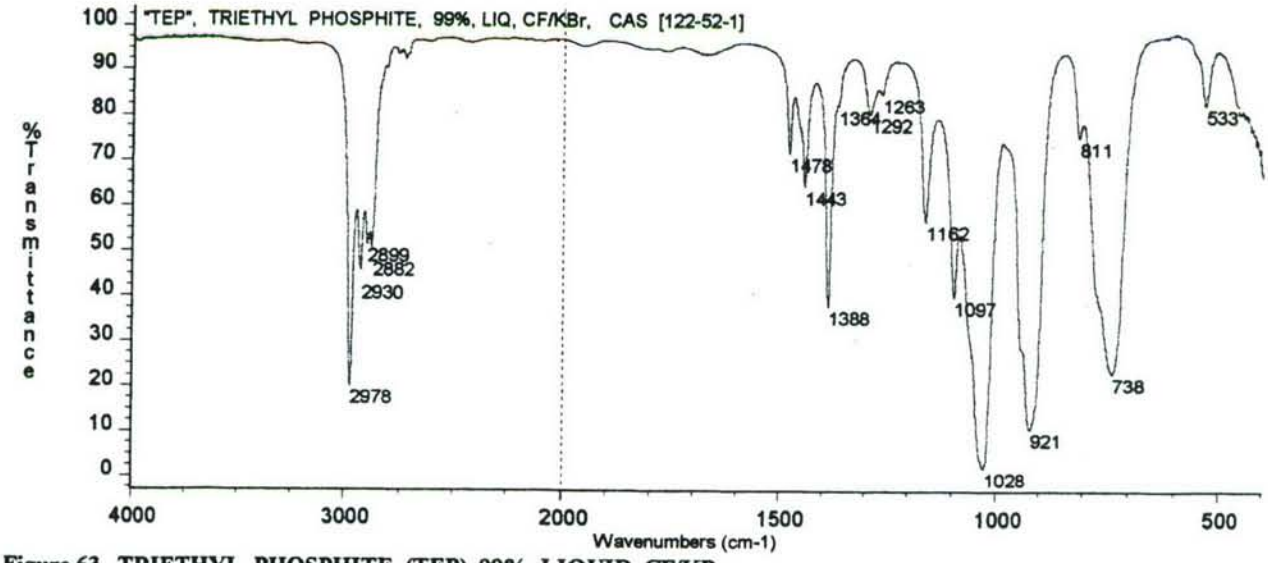


Figure 63 TRIETHYL PHOSPHITE (TEP), 99%, LIQUID, CF/KBr

The effect of atmospheric moisture on a liquid film of triethyl phosphite is illustrated by the infrared spectra given in ***Figure 64***. The infrared spectrum for the initial determination of a sample of triethyl phosphite shows the presence of bands at 2428 and 1262 cm^{-1}, which are assigned to the ν P-H

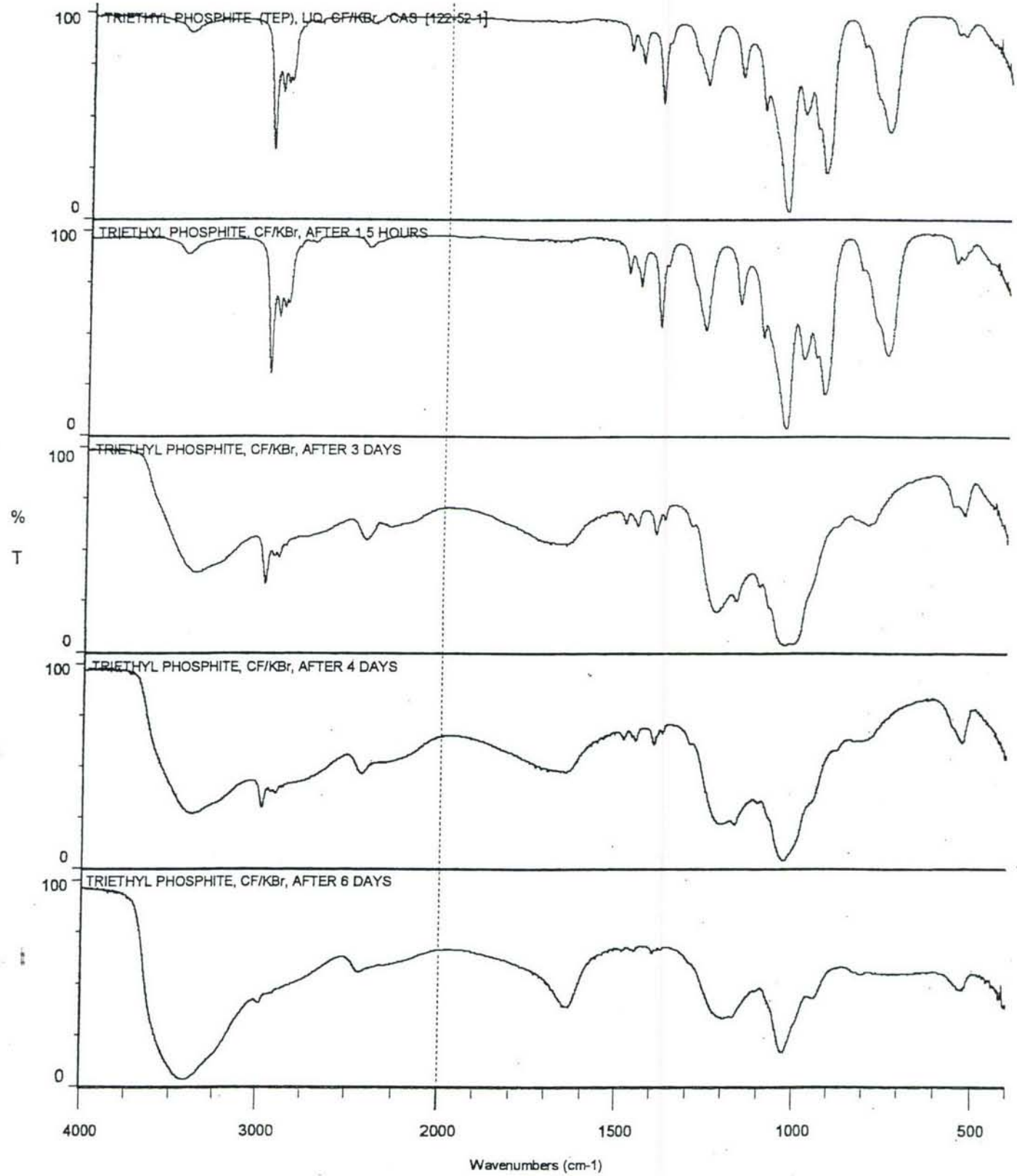


Figure 64 TRIETHYL PHOSPHITE (TEP), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

and ν P=O of diethyl phosphite. Apparently some of the sample has hydrolyzed to the diethyl phosphite. The spectrum after 1.5 hours shows a slight increase in these two bands. By three days the spectrum has dramatically changed, resembling that of a P-acid. The phosphoryl stretch has fallen to 1223 cm^{-1}; POH bands occur near 2800, 2300, 1650 and 1000 cm^{-1}, and the P-H stretch is still visible near 2433 cm^{-1}. The bands indicative of the POEt moiety have become much weaker. After 4 days of exposure the P=O band has fallen to 1206 cm^{-1}, the P-H is at 2433 cm^{-1}, the bands due to the POEt moiety are even weaker and the POH bands are present near 2800, 2300, 1650 and near 1000 cm^{-1}. By the sixth day of exposure the amount of water in the spectrum is quite large as illustrated by the strong band at 3419 cm^{-1}. The acid P=O band has fallen to 1194 cm^{-1} and the bands indicative of the POEt moiety have become extremely weak. The hydrolysis of triethyl phosphite may be summarized as follows:

$P(OEt)_3$ -HOH→ H-P=O$(OEt)_2$ -HOH→ H-P=O(OH)(OEt) -HOH→ H-P=O$(OH)_2$.

3.2.11 Tris(2-chloroethyl) phosphite $P(O\text{-}CH_2\text{-}CH_2\text{-}Cl)_3$

The infrared spectrum for a liquid film of tris(2-chloroethyl) phosphite between KBr windows is given in ***Figure 65***. The band assignments are as follows: 2962 cm^{-1} w (ν_{as} CH_2), 2875 cm^{-1} w (ν_{sy} CH_2), 1454 cm^{-1} w (δ OCH_2), 1429 cm^{-1} w (δ CH_2-Cl), 1383 cm^{-1} w (ω OCH_2), 1304 cm^{-1} m (ω CH_2-Cl),

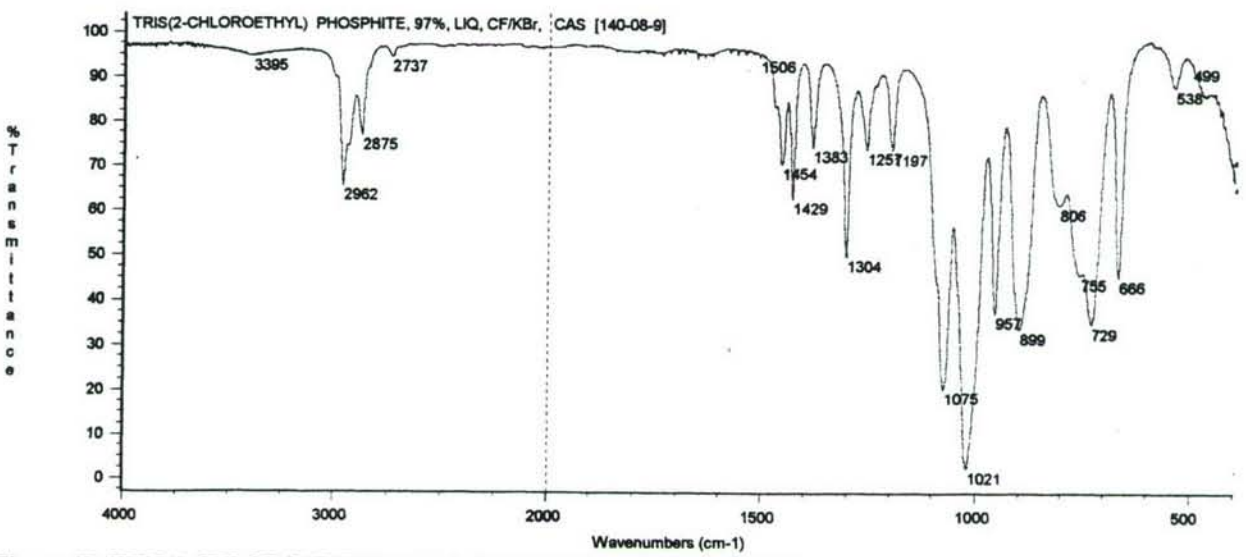


Figure 65 TRIS(2-CHLOROETHYL) PHOSPHITE, 97%, LIQUID, CF/KBr

1257 and 1197 cm^{-1} w, 1075 cm^{-1} ms and 1021 cm^{-1} s (ν P-O-C), 899 cm^{-1} m (ν C-C), 806 cm^{-1} (POC), 729 cm^{-1} m (ν C-Cl *trans* ?), 666 cm^{-1} m (ν C-Cl *cis* ?).

The effect of atmospheric moisture on the liquid film of tris(2-chloroethyl) phosphite is presented in ***Figure 66***. After four days of atmospheric exposure the spectrum shows bands indicative of a POH group (2850, 2300, 1650 cm^{-1}). A P-H group is indicated by the band at 2446 cm^{-1}. The P=O stretch is assigned to a broad band at 1202 cm^{-1}. Some $POCH_2CH_2Cl$ bands are still evident in the spectrum (1457, 1432, 1385, 1306, 1077, 1024 and 665 cm^{-1}). By the 11^{th} to 28^{th} days the bands indicative of the ester moiety are almost completely absent from the spectra, which now are essentially that of a P-acid with a P-H group such as, $H\text{-}P{=}O(OH)_2$. The effect of atmospheric moisture on tris(2-chloroethyl) phosphite can be summarized as follows:

$P(OCH_2CH_2Cl)_3$ -HOH→ $HP{=}O(OCH_2CH_2Cl)_2$ -HOH→ $HP{=}(OH)(OCH_2CH_2Cl)$ -HOH→ $HP{=}O(OH)_2$.

The compound, $HP{=}O(OCH_2CH_2Cl)_2$, should have a calculated P=O stretch of 1270 cm^{-1}, but this was not observed in the spectra since the hydrolysis had already proceeded beyond this compound by the 4^{th} day of exposure.

3.2.12 Tris(2,2,2-trifluoroethyl) phosphite $P(O\text{-}CH_2\text{-}CF_3)_3$

The infrared spectrum of tris(2,2,2-trifluoroethyl) phosphite determined as a liquid film between KBr windows is reproduced as ***Figure 67***. The band assignments are as follows: 2970 cm^{-1} w (ν_{as} CH_2), 2894 cm^{-1} vw (ν_{sy} CH_2), 1456 cm^{-1} m (δ OCH_2), 1414 cm^{-1} m (ω OCH_2), 1384 cm^{-1} vvw (KNO_3 from KBr windows), 1283 cm^{-1} ms and 1169 cm^{-1} s (CF_3), 1061 cm^{-1} ms (ν P-O-C), 964 cm^{-1} ms (ν C-C), 849 cm^{-1} m (POC ?), 799 cm^{-1} m (CF_3 or POC ?).

The effect of atmospheric moisture on a liquid film of tris(2,2,2-trifluoroethyl) phosphite between KBr windows is illustrated by the infrared spectra reproduced in ***Figure 68***. After one day of exposure to atmospheric moisture the infrared spectrum for the compound shows a P-H band at 2459, and POH bands near 2850, 2300 and 1650 cm^{-1}. A band at 1280 cm^{-1} can be assigned to a P=O stretching

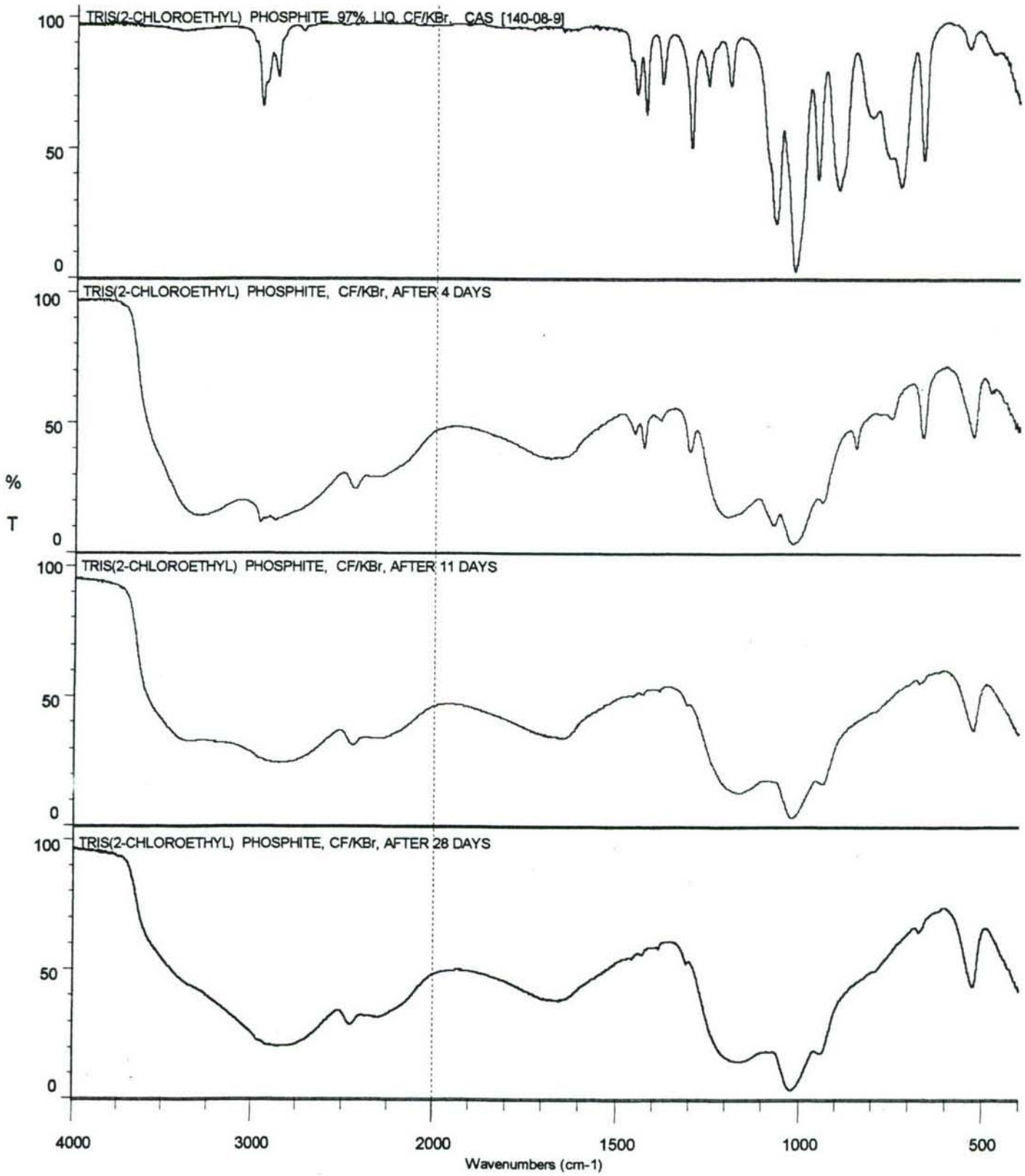


Figure 66 TRIS(2-CHLOROETHYL) PHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

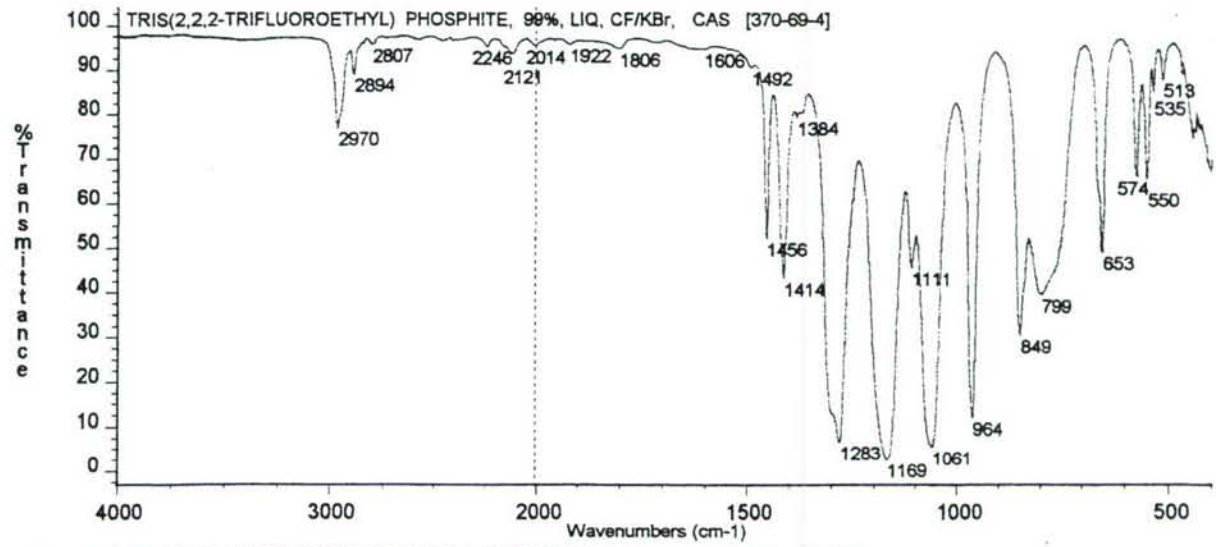


Fig:ure 67 TRIS(2,2,2-TRIFLUOROETHYL) PHOSPHITE, 99%, LIQUID, CF/KBr

vibration from possibly H-P=O$(OCH_2CF_3)_2$, which would have a calculated value of 1286 cm^{-1}. The strong band at 1165 cm^{-1} could be assigned to the P=O stretch from a P-acid compound. Very little absorption appears to be present from the ester moiety. Over the period of 6-38 days, the spectra resemble that for phosphonic acid, H-P=O$(OH)_2$. No bands indicative of the ester moiety are apparent in these remaining spectra. No indication of the formation of the compound, HP=O(OH)(OCH_2CF_3), was evident, although this compound may have been formed somewhere in the time period between the 1 to 6 days of exposure.

3.2.13 Triisopropyl phosphite $P[O\text{-}CH(CH_3)_2]_3$

The infrared spectrum of triisopropyl phosphite as a liquid film between KBr windows is given in ***Figure 69***. The band assignments are as follows: 2974 cm^{-1} ms (ν_{as} CH_3), 2932 cm^{-1} m (ν -CH), 2876 cm^{-1} w (ν_{sy} CH_3), 1466 and 1454 cm^{-1} w (δ_{as} CH_3), 1383 and 1371 cm^{-1} m (δ_{sy} CH_3), 1351 cm^{-1} w (δ -C-H), 1280 and 1263 cm^{-1} vw (possible P=O stretching vibrations from O=P$(OiPr)_3$ and HP=O$(OiPr)_2$,, which have calculated values of 1260 and 1250 cm^{-1} respectively. The compound (H)(OiPr)P(=O)-O-P=O(OiPr)(H) would have a caculated P=O stretch of 1272 cm^{-1}.), 1176, 1138 and

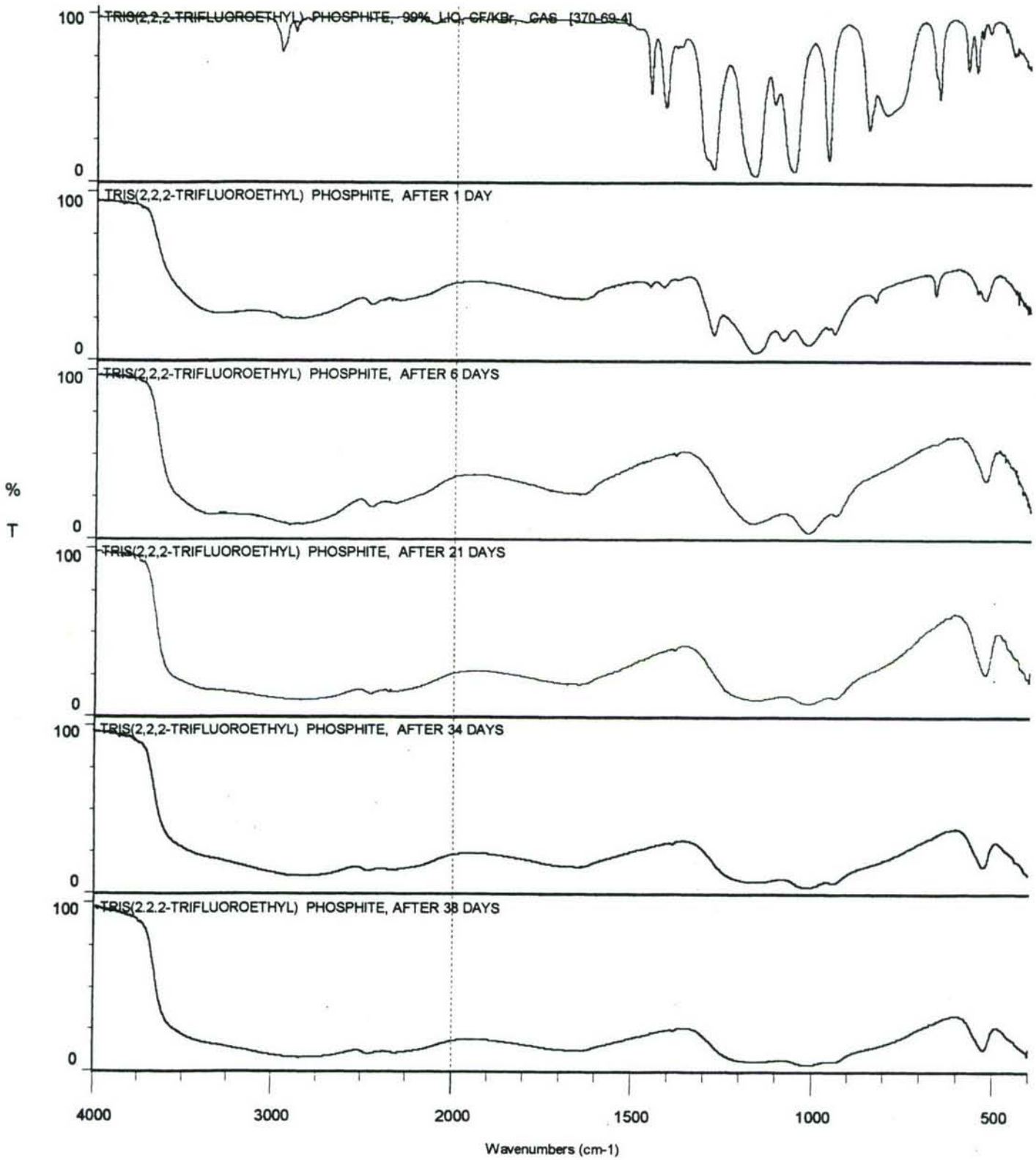


Figure 68 TRIS(2,2,2-TRIFLUOROETHYL) PHOSPHITE, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

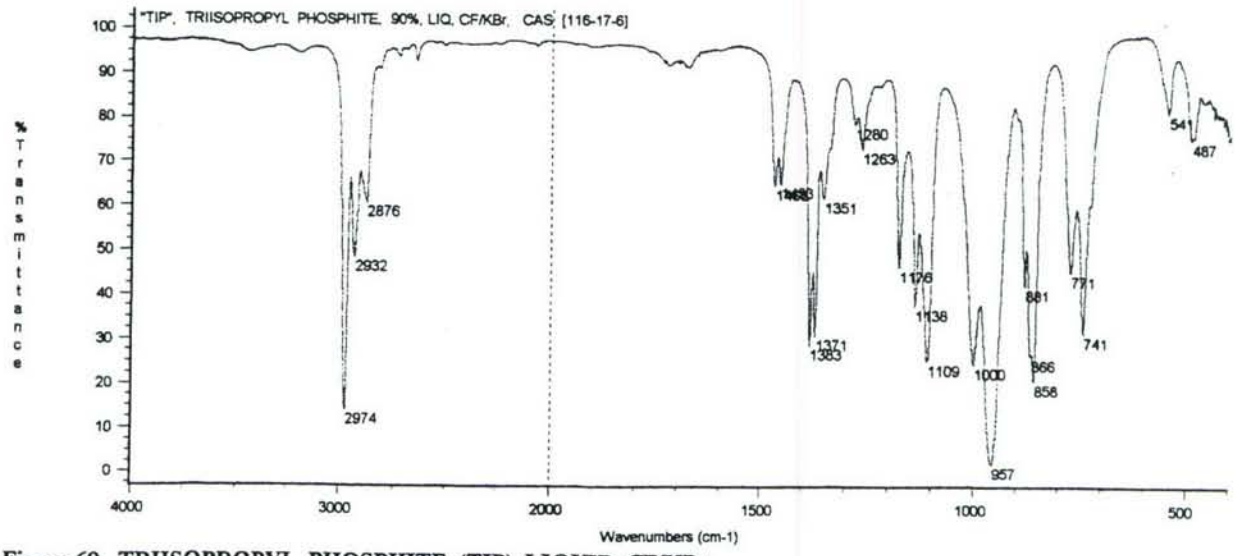


Figure 69 TRIISOPROPYL PHOSPHITE (TIP), LIQUID, CF/KBr

1109 cm^{-1} m (triplet of bands characteristics of POiPr), 1000 cm^{-1} m and 957 cm^{-1} s (ν P-O-C), 881 cm^{-1} sh and 858 cm^{-1} m (CH_3 rock isopropyl), 771 and 741 cm^{-1} m (POC).

The effect of the environment on a thin film of triisopropyl phosphite is shown in ***Figure 70***. After some twenty five hours of environmental exposure the infrared spectrum shows an increase in the bands near 1277 and 1262 cm^{-1}. These two bands were assigned as being possibly due to phosphoryl stretching vibrations. A weak band also occurs near 2425 cm^{-1} and is a possible P-H stretching vibration. After 4 days the P=O band at 1261cm^{-1} appears to have reached its maximum intensity. Then the intensity decreases and the band becomes more of a doublet again. The P-H band near 2424 also appears to diminish in intensity after the fourth day. The sample may be evaporating. Two effects may be occurring, namely oxidation to produce triisopropyl phosphate (the P=O band near 1277 cm^{-1}) and hydrolysis to produce diisopropyl phosphite (the P=O band near 1262 cm^{-1}).

3.2.14 Tributyl phosphite $P(OC_4H_9)_3$

The infrared spectrum of a liquid film of tributyl phosphite between KBr windows (discs) is reproduced as ***Figure 71***. The band assignments are as follows: 2960 cm^{-1} s (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), ca 2910 sh (ν_{sy} CH_3), 2874 cm^{-1} ms (ν_{sy} CH_2), 1466 cm^{-1} m (δ CH_2), 1432 cm^{-1} vw (δ_{as} CH_3), 1380 cm^{-1} m (δ_{sy} CH_3), 1263 cm^{-1} vw [possible ν P=O from $HP{=}O(O\text{-}C_4H_9)_2$, which has a calculated value of

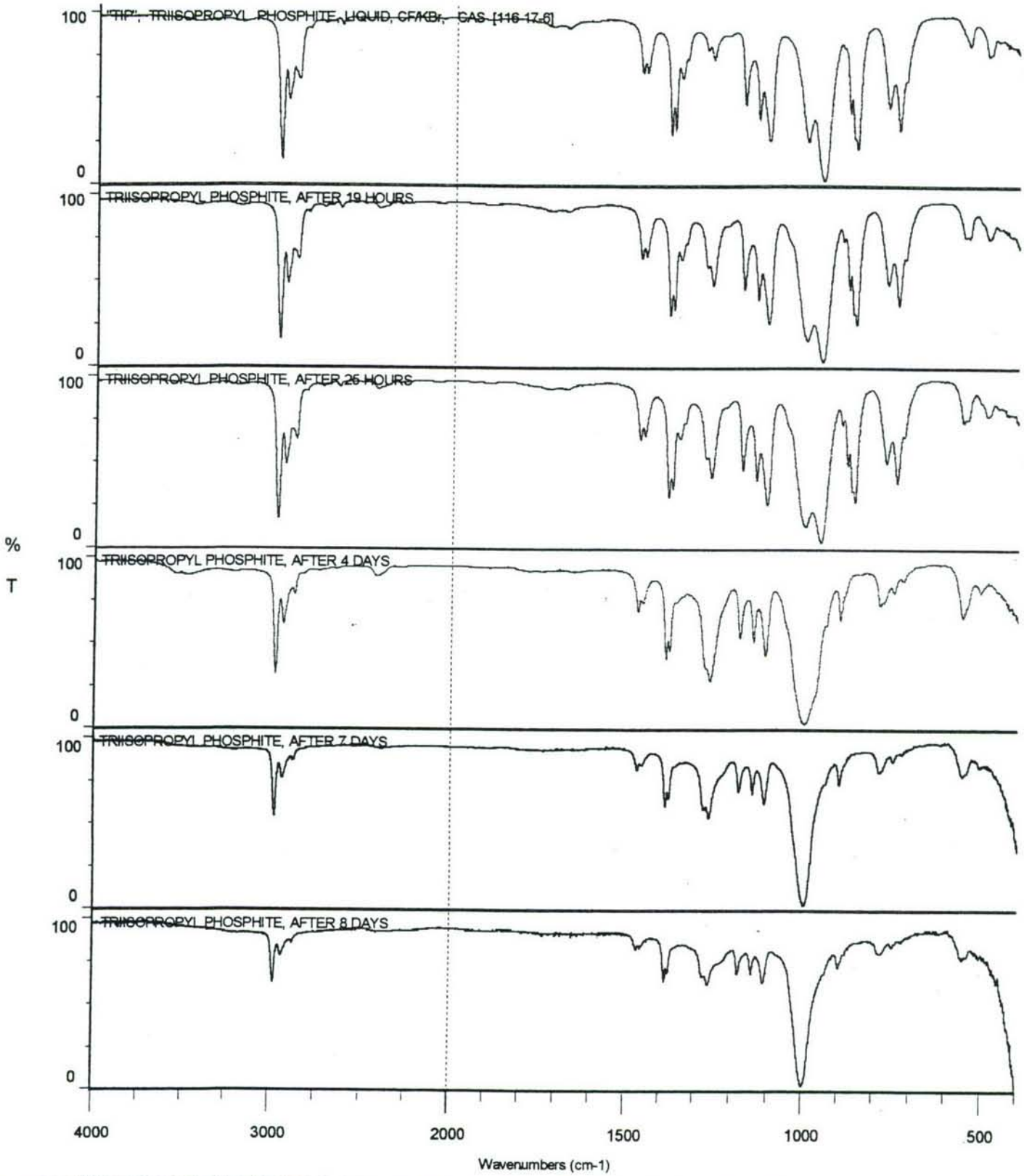


Figure 70 TRIISOPROPYL PHOSPHITE, LIQUID, CF/KBr, AFTER ENVIRONMENTAL EXPOSURE

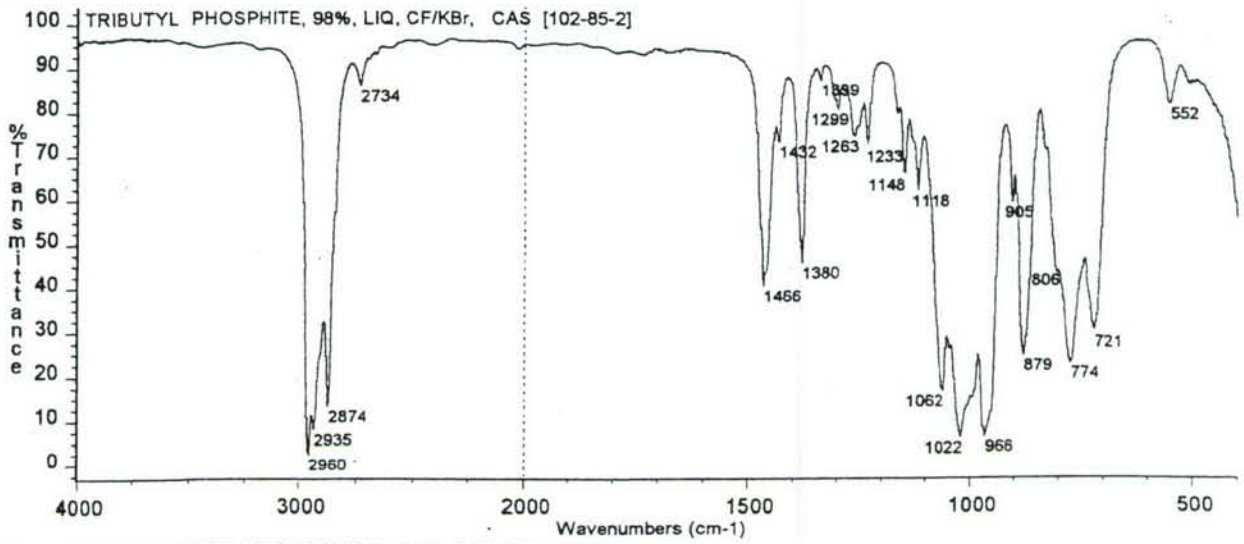


Figure 71 TRIBUTYL PHOSPHITE, 98%, LIQUID, CF/KBr

1258 cm^{-1}], 1164 cm^{-1} sh, 1148 cm^{-1} w and 1118 cm^{-1} w (CH_3 rock from P-O-*n*-C_4H_9), 1062 cm^{-1} ms, 1022 cm^{-1} s and 966 cm^{-1} s (ν P-O-C), 879 cm^{-1} m (ν C-C), 774 cm^{-1} m (POC), 721 cm^{-1} m (CH_2 rock ?).

The effect of atmospheric moisture on a liquid film of tributyl phosphite is illustrated by the infrared spectra reproduced in ***Figure 72***. The infrared spectrum, after one day of exposure, shows a very weak band at 2426 cm^{-1} (ν P-H) and a weak to medium band at 1263 cm^{-1} (ν P=O) probably from the formation of the compound dibutyl phosphite (i.e., dibutyl hydrogenphosphonate). This phosphonate would have a calculated value of 1258 cm^{-1} for the phosphoryl stretch. After nine days the spectrum shows the presence of bands indicative of a P-acid (2670, 2300, 1650 and 1005 cm^{-1}). The phosphoryl stretch has fallen to 1224 cm^{-1} and the bands from the ester moiety are greatly reduced in intensity. By the 13th through 27th days the bands from the ester moiety are almost completely gone from the spectrum and the phosphoryl stretching band further decreases to 1149 cm^{-1}. The POH bands are visible near 2800, 2300, 1650, 1020 and 943 cm^{-1}. The P-H stretch is also visible near 2450 cm^{-1}. It appears the compound has hydrolyzed to the phosphonic acid, H-P=O$(OH)_2$. The hydrolysis may be summarized as follows:

$P(O\text{-}C_4H_9)_3$ -HOH→ H-P=O$(OC_4H_9)_2$ -HOH→ H-P=O(OH)(OC_4H_9) -HOH→ H-P=O$(OH)_2$.

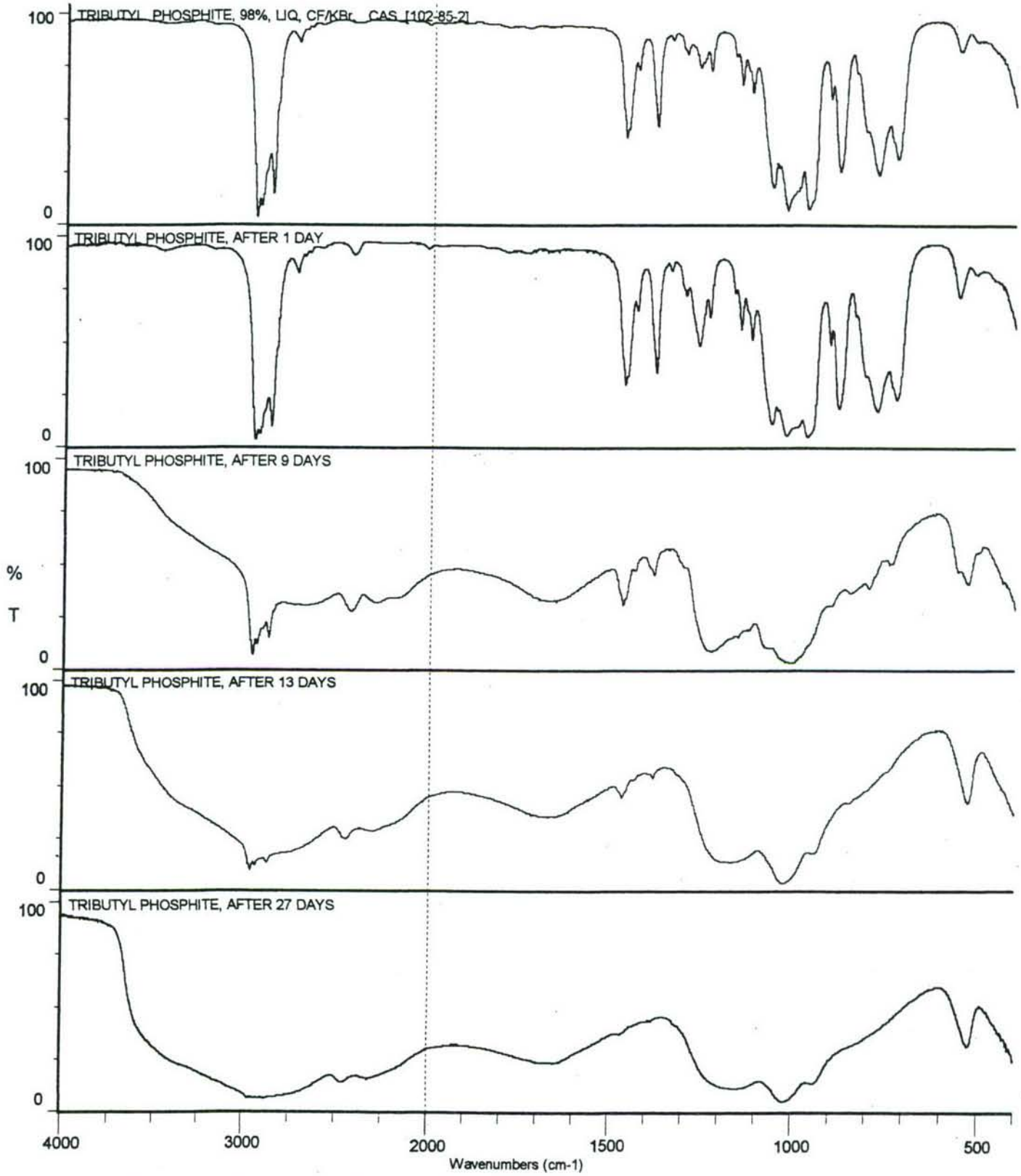


Figure 72 TRIBUTYL PHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.2.15 Triallyl phosphite $P(O\text{-}CH_2\text{-}CH{=}CH_2)_3$

The infrared spectrum of trially phosphite as a liquid film between KBr windows is given as *Figure 73*. The band assignments are as follows: 3084 cm^{-1} vw (ν_{as} $=CH_2$), 3017 cm^{-1} vw (ν =CH and ν_{sy} $=CH_2$), 2925 cm^{-1} w (ν_{as} CH_2), 2869 cm^{-1} w (ν_{sy} CH_2), 1859 cm^{-1} vvw (2 x $=CH_2$ wag), 1648 cm^{-1} w (ν C=C), 1456 cm^{-1} w (δ OCH_2), 1423 cm^{-1} w (δ $=CH_2$), 1408 cm^{-1} vw (ω OCH_2), 1264 cm^{-1} w [ν P=O possibly from diallyl phosphite, $H\text{-}P{=}O(OCH_2\text{-}CH{=}CH_2)_2$, which has an observed value of 1262 cm^{-1}], 988 cm^{-1} s (ν P-O-C, possibly some contribution from the *trans* CH wag), 922 cm^{-1} ms (ν C-C ?, possibly some contribution from $=CH_2$ wag), 801 cm^{-1} m (POC).

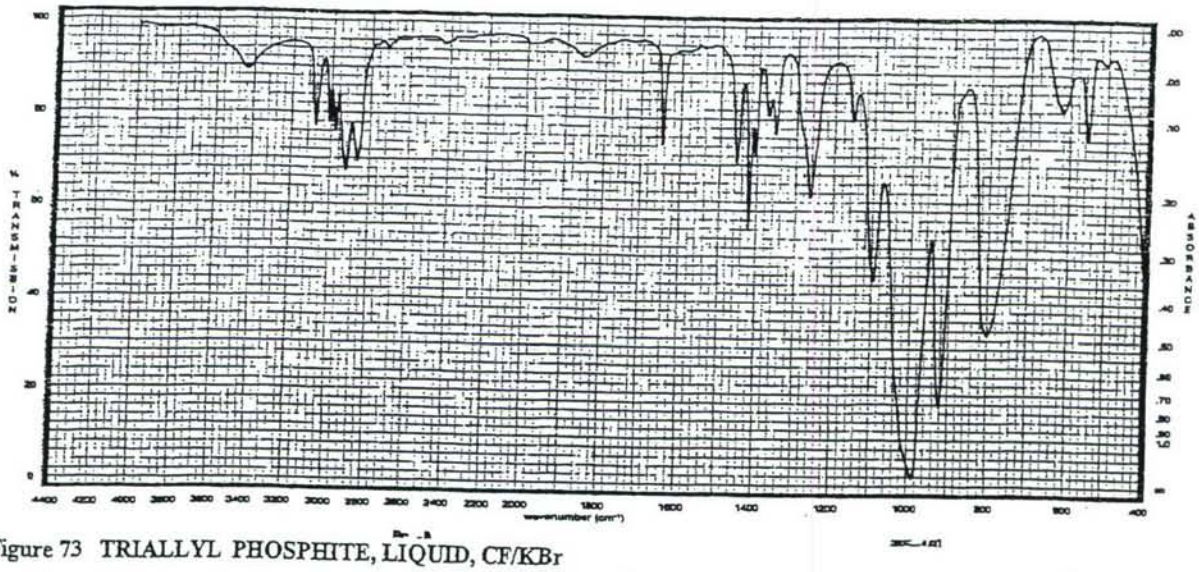


Figure 73 TRIALLYL PHOSPHITE, LIQUID, CF/KBr

The effect of atmospheric moisture on a liquid film of triallyl phosphite is illustrated by the infrared spectra given in *Figures 74* and *75*. The infrared spectrum, after three days of exposure (*Figure 74*), is very similar to the initial scan (*Figure 73*) except for a slight increase in the intensity of the phosphoryl band at 1264 cm^{-1}. After six days, the phosphoryl band is very prominant at 1261 cm^{-1}. The ν C=C is still present at 1647 cm^{-1}. The P-H band at 2433 cm^{-1} is slightly stronger, but still quite weak. The spectum has become somewhat distorted perhaps due to evaporation of the sample. It is probable that both hydrolysis and oxidation are taking place to produce diallyl phosphite and triallyl phosphate respectively.

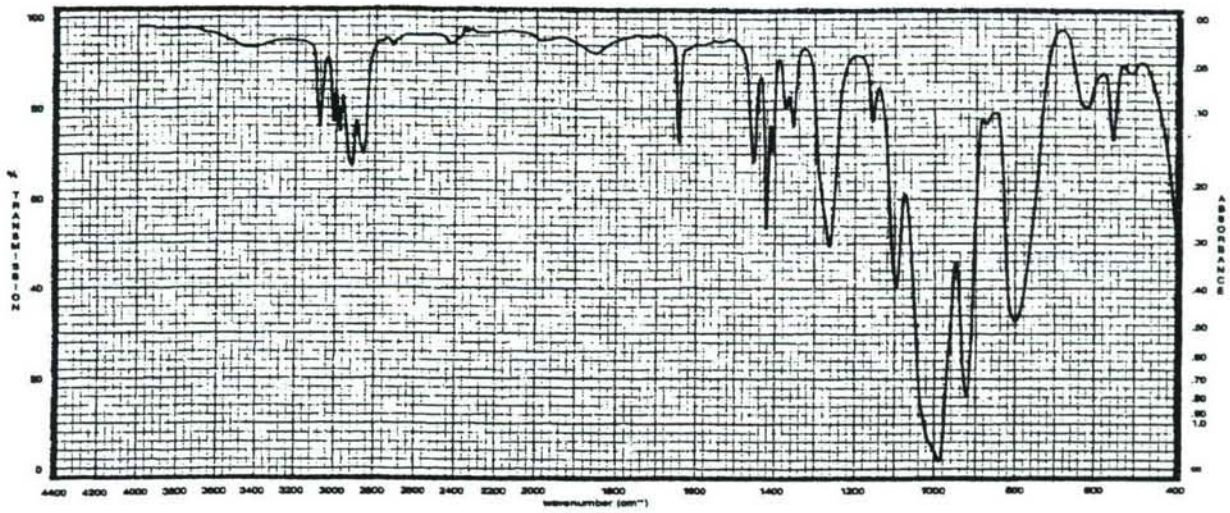


Figure 74 TRIALLYL PHOSPHITE, LIQUID, CF/KBr, AFTER 3 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

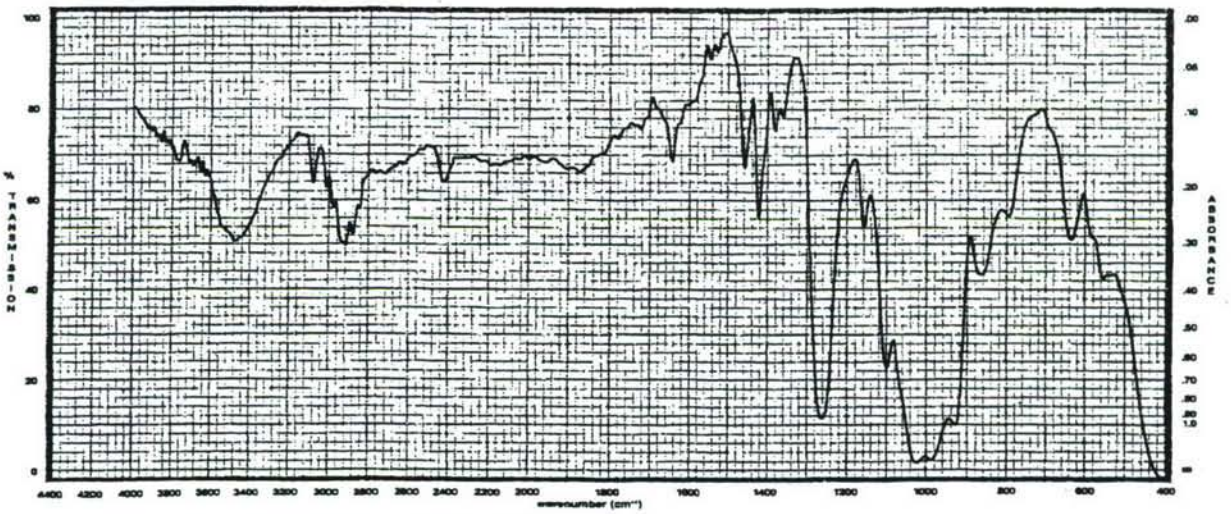


Figure 75 TRIALLYL PHOSPHITE, LIQUID, CF/KBr, AFTER 6 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

3.2.16 Dimethyl trimethylsilyl phosphite $(CH_3\text{-}O)_2P\text{-}O\text{-}Si(CH_3)_3$

The infrared spectrum of a liquid sample of dimethyl trimethylsilyl phosphite between KBr windows is reproduced as ***Figure 76***. The band assignments are as follows: 2960 cm^{-1} m (ν_{as} CH_3), 2901 cm^{-1} w (ν_{sy} CH_3), 2833 cm^{-1} w (ν CH_3O), 1460 cm^{-1} w (δ CH_3O), 1417 cm^{-1} vw (δ_{as} CH_3-Si), 1255 cm^{-1} ms (δ_{sy} CH_3-Si), 1180 cm^{-1} w (CH_3 rock of $POCH_3$, characteristic), 1056 cm^{-1} m and 1020 cm^{-1} s (ν

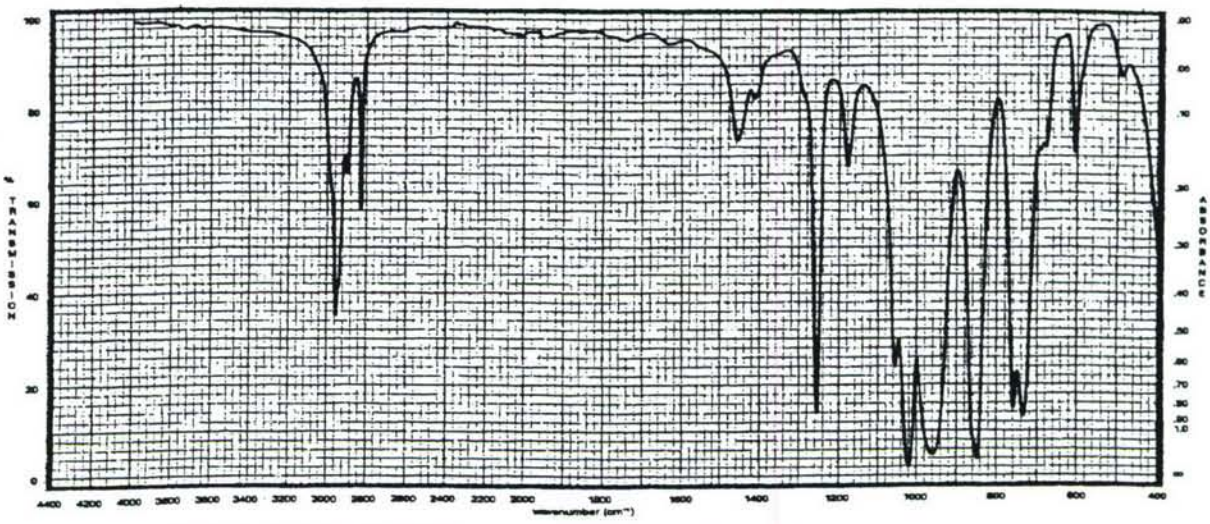


Figure 76 DIMETHYL TRIMETHYLSILYL PHOSPHITE, 98%, LIQUID, CF/KBr

P-O-C), 961 cm^{-1} ms (ν P-O-Si), 848 cm^{-1} s [$Si(CH_3)_3$ CH_3 rock + some ν Si-C], 759 and 734 cm^{-1} ms [$Si(CH_3)_3$ and POC].

The effect of atmospheric moisture of a liquid film of dimethyl trimethylsilyl phosphite is shown in ***Figures 77A-C***. The infrared spectrum of the sample after 3 hours ***(Figure 77A)*** shows the formation of a new band at 2431 cm^{-1} (ν P-H) and a change in the appearance of the 1256 cm^{-1} band. These changes are more prevalent after 5 hours of exposure and the spectrum (***Figure 77B***) shows the conversion (hydrolysis) of the original compound to dimethyl phosphite (dimethyl hydrogenphosphonate, $H\text{-}P{=}O(OCH_3)_2$). The P-H stretch occurs at 2432 cm^{-1} and the phosphoryl stretch occurs at 1257 cm^{-1} (calculated value is 1262 cm^{-1}). Other groups present are OCH_3 (2835 and 1187 cm^{-1}), POC (1049 and 826 cm^{-1} and P-H (979 cm^{-1} deformation). The spectrum after 5 days of exposure (***Figure 77C***) shows the hydrolysis of the dimethyl phosphite to phosphonic acid, $H\text{-}P{=}O(OH)_2$. The following bands are now present, POH (2800, 2300, 1650, 1015 and 941 cm^{-1}), P-H (2452 cm^{-1}), and P=O (ca 1160 cm^{-1}). The hydrolysis of dimethyl trimethylsilyl phosphite may thus be summarized as follows:

$(CH_3O)_2P\text{-}O\text{-}Si(CH_3)_3$ $\text{-HOH}\rightarrow$ $(CH_3O)_2P\text{-}O\text{-}H \rightarrow (CH_3O)_2P{=}O(H)$ $\text{-HOH}\rightarrow$ $H\text{-}P{=}O(OH)_2$.

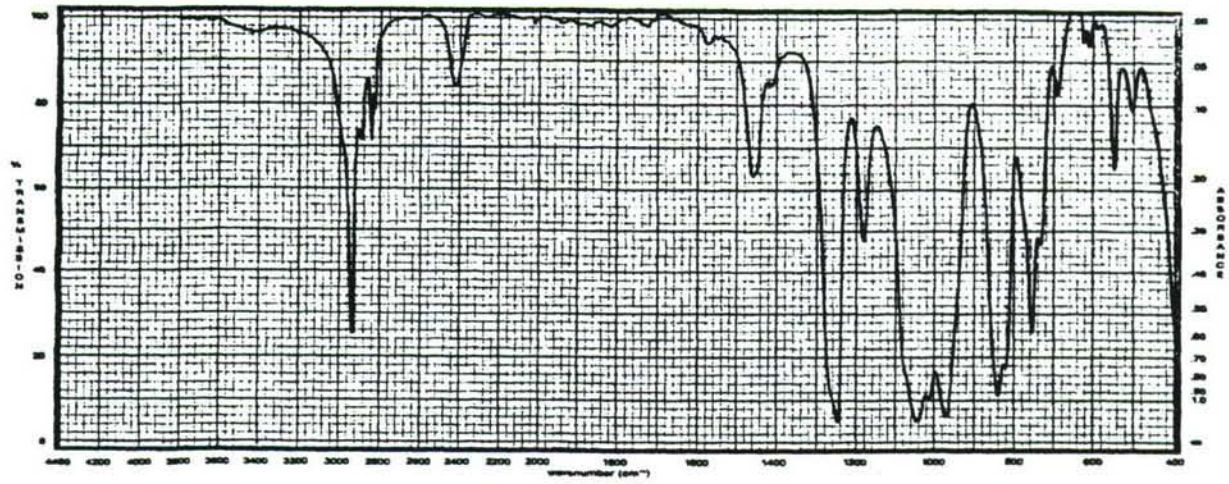


Figure 77A DIMETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr, AFTER 3 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

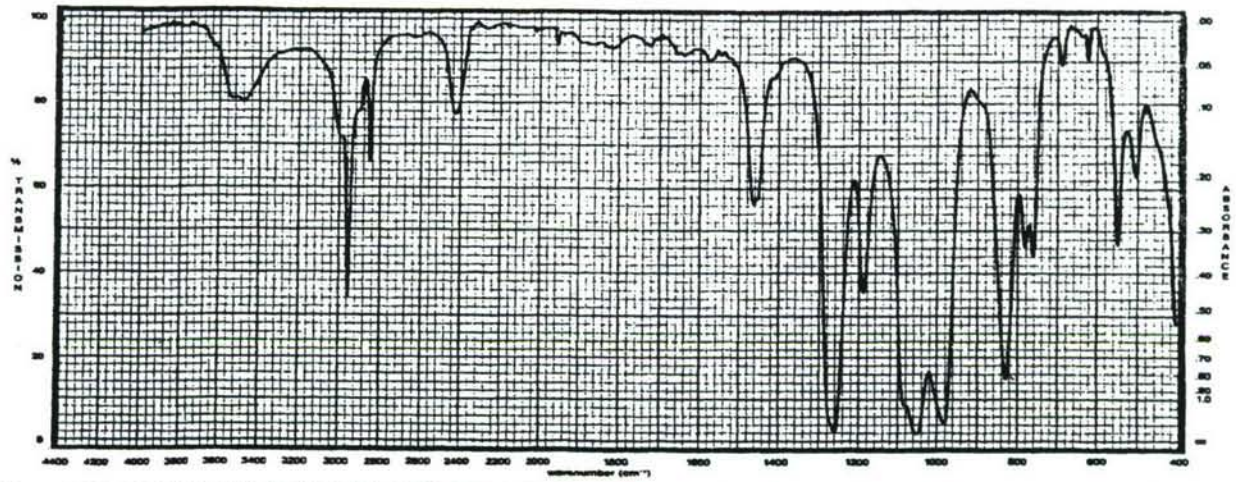


Figure 77B DIMETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr, AFTER 5 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

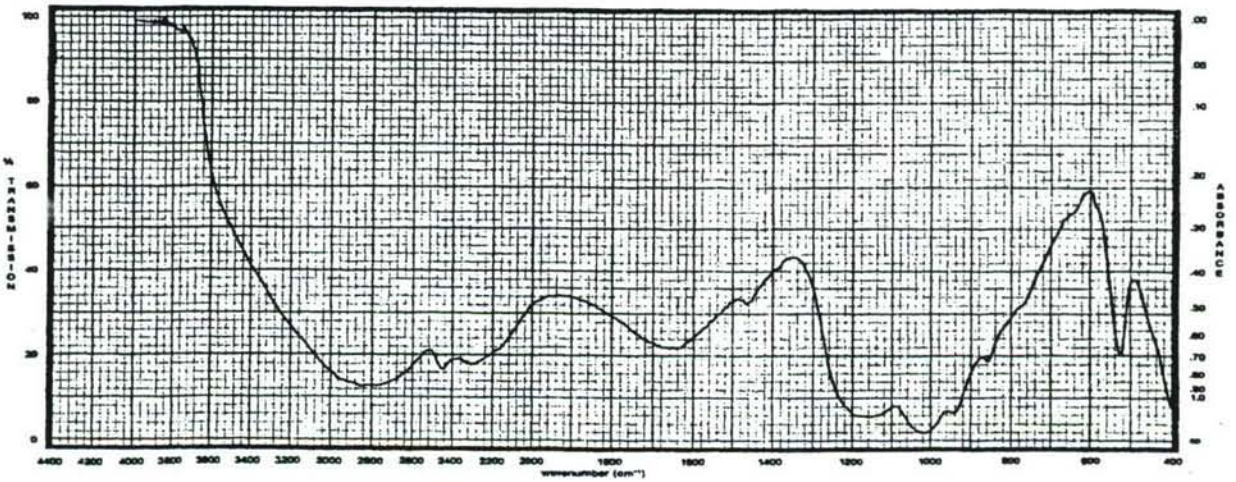


Figure 77C DIMETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr, AFTER 5 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

3.2.17 Diethyl trimethylsilyl phosphite $(CH_3\text{-}CH_2\text{-}O)_2P\text{-}O\text{-}Si(CH_3)_3$

The infrared spectrum of a liquid film of diethyl trimethylsilyl phosphite between KBr windows is reproduced as ***Figure 78***. The band assignments are as follows: 2977 cm^{-1} m (ν_{as} CH_3), 2931 cm^{-1} w (ν_{as} CH_2), 2900 cm^{-1} w (ν_{sy} CH_3), 2881 cm^{-1} sh (ν_{sy} CH_2), 1478 cm^{-1} vw (δ OCH_2), 1444 cm^{-1} w (δ_{as} CH_3), 1387 cm^{-1} m (ω OCH_2), ca 1363 cm^{-1} sh (δ_{sy} CH_3), 1254 cm^{-1} ms (δ_{sy} CH_3-Si), 1162 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1059 cm^{-1} sh and 1032 cm^{-1} s (ν P-O-C), 977 cm^{-1} s (ν P-O-Si), 927 cm^{-1} s (ν C-C of POEt), 848 cm^{-1} s [$Si(CH_3)_3$ rock and some ν Si-C], 759 cm^{-1} ms and 741 cm^{-1} sh [$Si(CH_3)_3$ and POC].

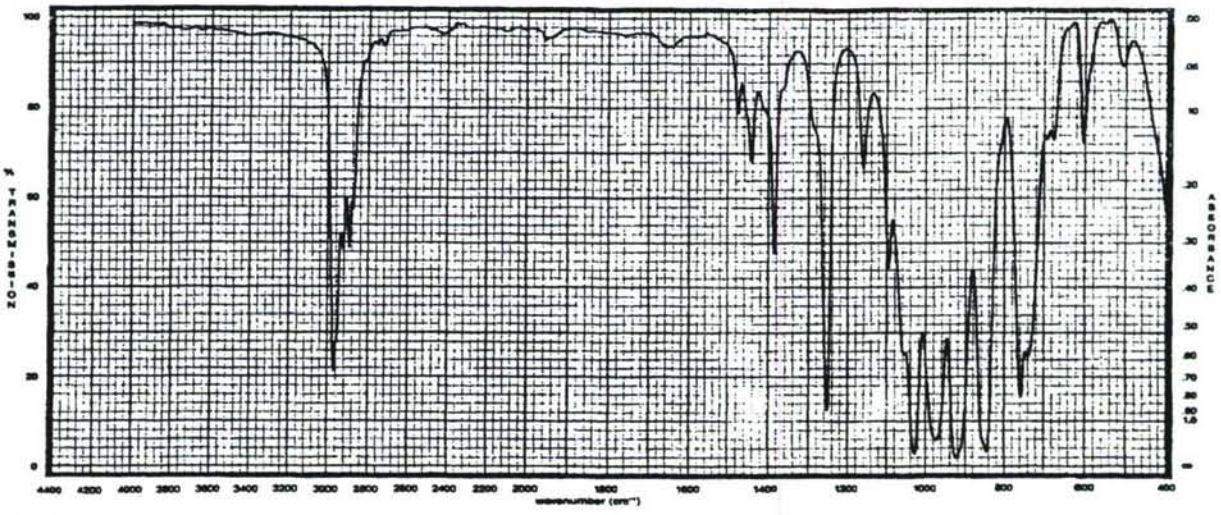


Figure 78 DIETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr

The effect of atmospheric moisture on diethyl trimethylsilyl phosphite is illustrated by the infrared spectra reproduced in ***Figures 79A-F***. The infrared spectrum after 1 hour of exposure (***Figure 79A***) shows the bands at 2430 cm^{-1} (ν P-H) and 1255 cm^{-1} (ν P=O) due to the formation of diethyl phosphite, H-P=O$(OEt)_2$ (calculated ν P=O is 1258 cm^{-1}). After 19 hours of exposure (***Figure 79B***), weak diffuse bands begin to appear near 2800, 2300 and 1650 cm^{-1} due to the formation of the POH group. After 5 days of exposure to atmospheric moisture (***Figure 79C***), the spectrum is that of a P-Acid with bands near 2800, 2300 and 1650 cm^{-1} (POH), 2448 cm^{-1} (ν P-H), 1191 cm^{-1} (ν P=O), 1021 and ca 940 cm^{-1} (ν P-OH). Some weak residual bands due to the POEt group are still visible in the spectrum.

Figure 79A DIETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr AFTER 1 HOUR OF EXPOSURE TO ATMOSPHERIC MOISTURE

Figure 79B DIETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBrM, AFTER 19 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

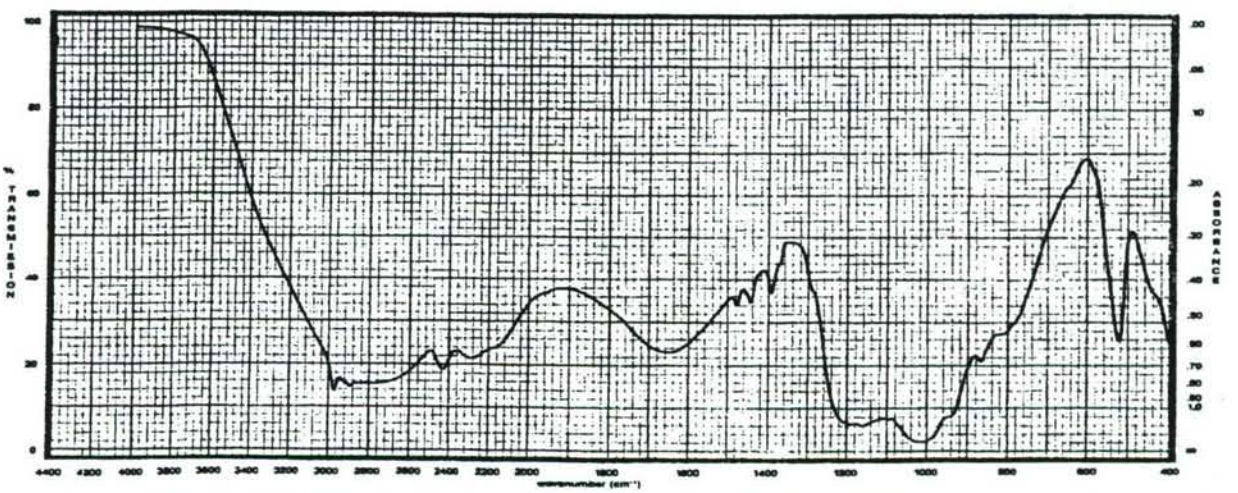


Figure 79C DIETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr, AFTER 5 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

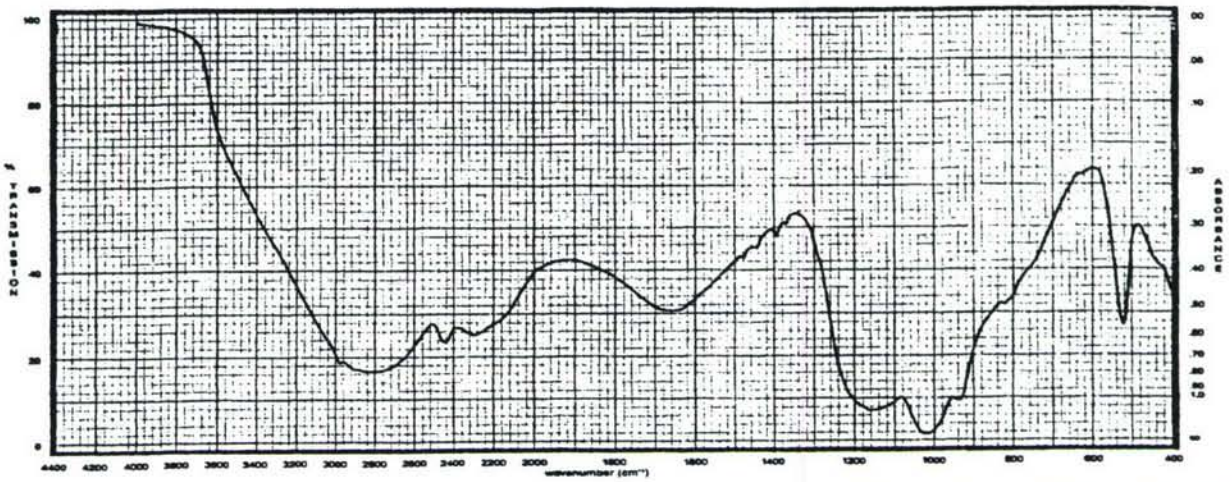


Figure 79D DIETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr, AFTER 12 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

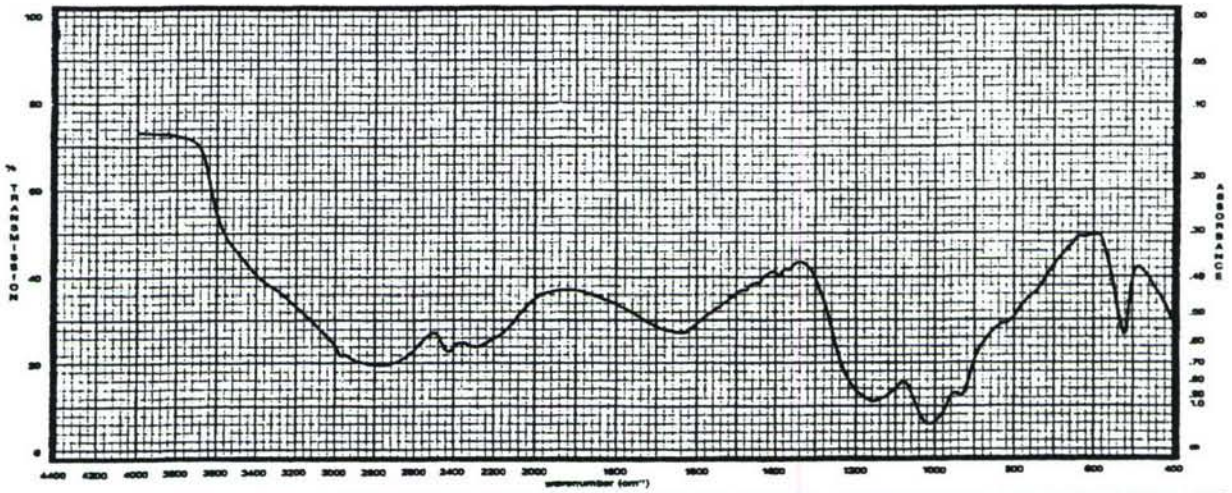


Figure 79E DIETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr, AFTER 35 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

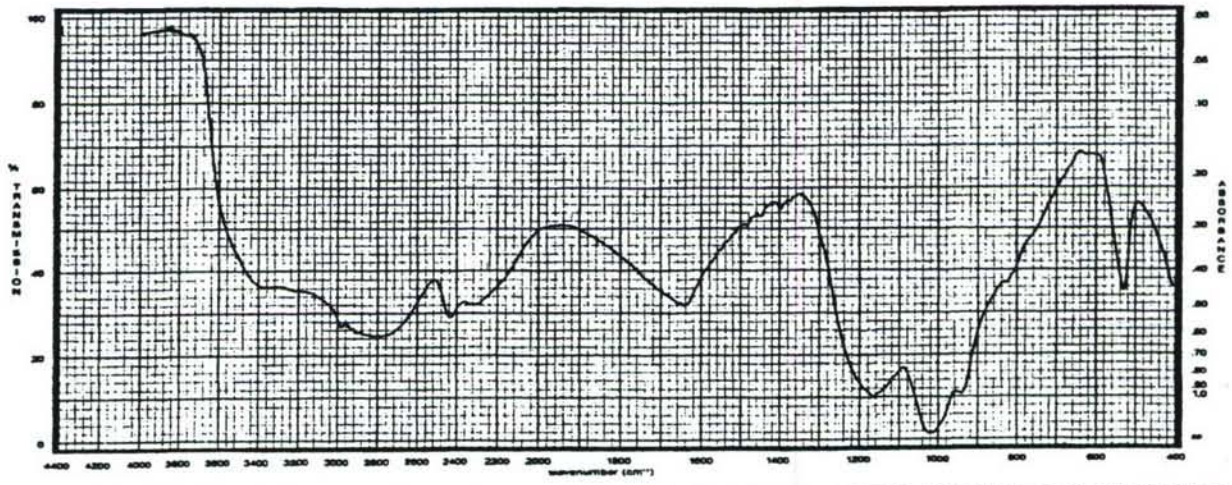


Figure 79F DIETHYL TRIMETHYLSILYL PHOSPHITE, LIQUID, CF/KBr, AFTER 62 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

As the time of exposure to atmospheric moisture increases through 12, 35 and 62 days (Figures 79D, 79E and 79F) the traces of the POEt moiety become increasingly faint leading to a final spectrum of mainly phosphonic acid, $H\text{-}P{=}O(OH)_2$. The hydrolysis of diethyl trimethylsilyl phosphite may thus be summarized as follows:

$(EtO)_2P\text{-}OSi(CH_3)_3$ -HOH→ $H\text{-}P{=}O(OEt)_2$ -HOH→ $H\text{-}P{=}O(OH)(OEt)$ -HOH→ $H\text{-}P{=}O(OH)_2$.

The compound $H\text{-}P{=}O(OH)(OEt)$ was not seen probably because it was formed sometime during the time period between 19 hours and 5 days when no spectra were determined.

3.3 Phosphonites

3.3.1 Methyl ethyl methylphosphonite (MR) $CH_3\text{-}P(OCH_3)(OCH_2CH_3)$

The infrared spectrum of methyl ethyl methylphosphonite (**MR**) as a liquid film between KBr windows is given as ***Figure 80***. The band assignments are as follows: 3433 cm^{-1} w and 1646 cm^{-1} vw (H_2O), 2877 cm^{-1} ms, 2934 cm^{-1} m, 2909 cm^{-1} vw, 2879 cm^{-1} vw and 2830 cm^{-1} w (ν CH_3 and CH_2), 2348 cm^{-1} vw (ν P-H from the hydrolysis of **MR**), 1475 cm^{-1} w (δ OCH_2), 1456 cm^{-1} sh and 1445 cm^{-1} w (δ_{as} CH_3), 1415 cm^{-1} w (δ_{as} P-CH_3), 1387 cm^{-1} m (ω OCH_2), 1304 cm^{-1} w (δ_{sy} P^{+5}-CH_3), 1280 cm^{-1} m (δ_{sy} P^{+3}-CH_3), 1235 cm^{-1} m [ν P=O of perhaps $CH_3P{=}O(H)(OCH_3)$ or $CH_3P{=}O(H)(OEt)$], 1180 cm^{-1} sh

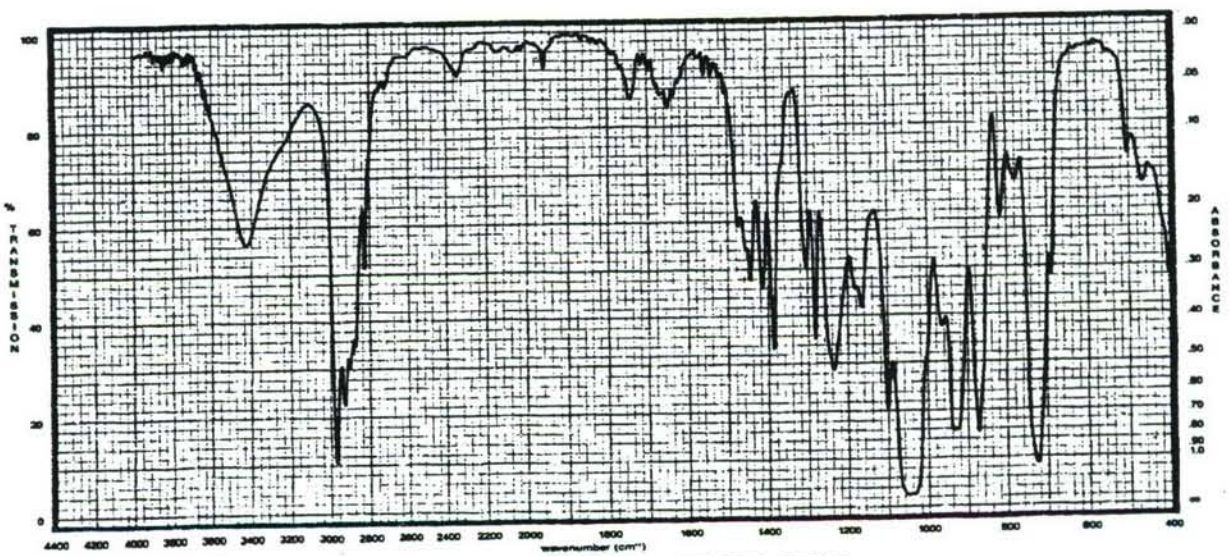


Figure 80 METHYL ETHYL METHYLPHOSPHONITE (MR), LIQUID, CF/KBr

(CH_3 rock of $POCH_3$), 1163 cm^{-1} w and 1099 cm^{-1} m (CH_3 rock of POEt), 1049 and 1033 cm^{-1} s (ν P-O-C), 963 cm^{-1} w (ν C-C of P^{+5}-OEt), 934 cm^{-1} ms (ν C-C of P^{+3}-OEt), 870 cm^{-1} ms (P-CH_3 rock), 814 cm^{-1} w and 778 cm^{-1} vw (POC), 722 cm^{-1} ms (ν P-C). This initial infrared spectrum shows that the sample already contained some hydrolysis product(s).

The effect of atmospheric moisture on ethyl methyl methylphosphonite (**MR**) is illustrated by the spectra reproduced in ***Figures 81A-C***. The infrared spectrum after 1 hour of exposure to atmospheric moisture (***Figure 81A***) shows as increase in the intensities of the P-H and the P=O stretching bands at 2349 cm^{-1} and 1231 cm^{-1} respectively. The relative intensities of the 1303 cm^{-1} (δ_{as} P^{+5}-CH_3) and the 1281 cm^{-1} (δ_{sy} P^{+3}-CH_3) bands are reversed, the 1303 cm^{-1} band becoming the stronger of the two bands. A new band appears at 1000 cm^{-1} assignable to a P-H deformation. The 962 cm^{-1} band (ν C-C of P^{+5}OEt) is becoming stronger, while the band at 934 cm^{-1} (ν C-C of P^{+3}OEt) is decreasing in intensity.

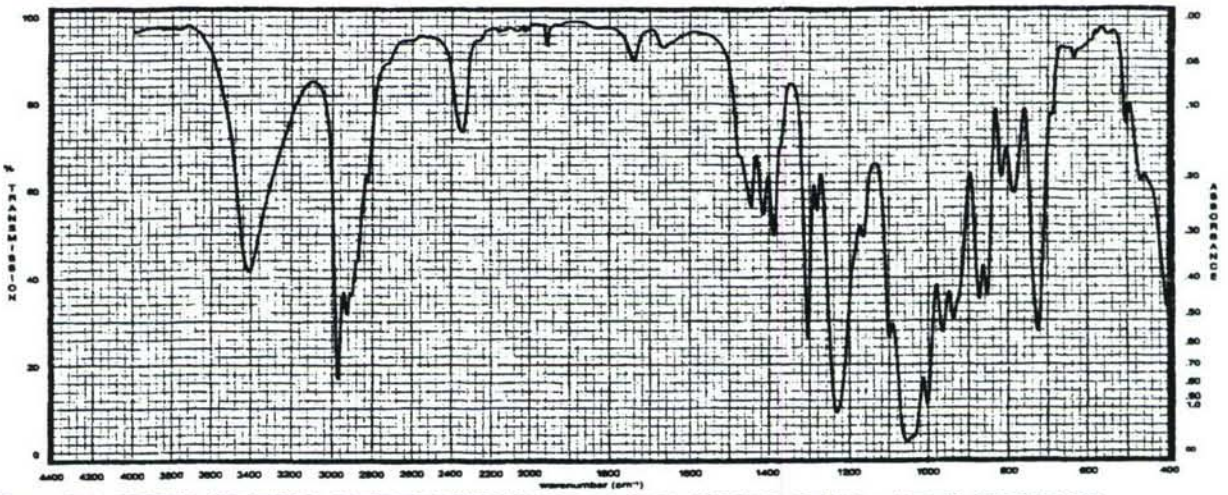


Figure 81A ETHYL METHYL METHYLPHOSPHONITE (MR), LIQUID, CF/KBr, AFTER 1 HOUR OF EXPOSURE TO ATMOSPHERIC MOISTURE

By 4 hours of exposure, the spectrum (***Figure 81B***) is essentially that of a wet sample of ethyl hydrogen-methylphosphinate, CH_3P=O(H)(OEt), also known as **YL**. After 70 hours of exposure to atmospheric moisture, the infrared spectrum (***Figure 81C***) show s that the compound **YL** has undergone further hydrolysis to form a P-acid. The following bands are now evident: 2987 cm^{-1} w, 2919 cm^{-1} w and 2853

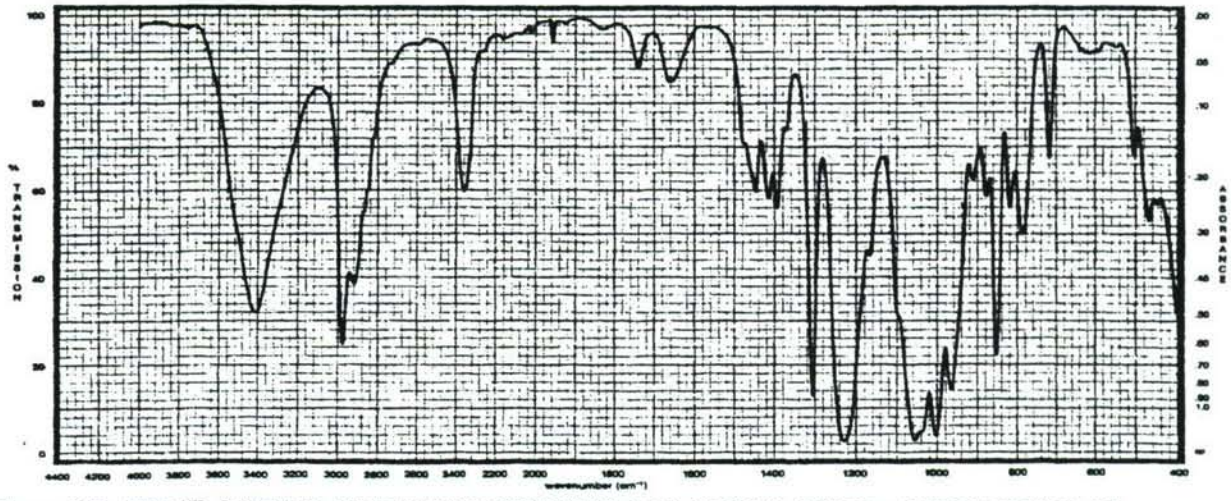


Figure 81B ETHYL METHYL METHYLPHOSPHONITE (MR), LIQUID, CF/KBr, AFTER 4 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

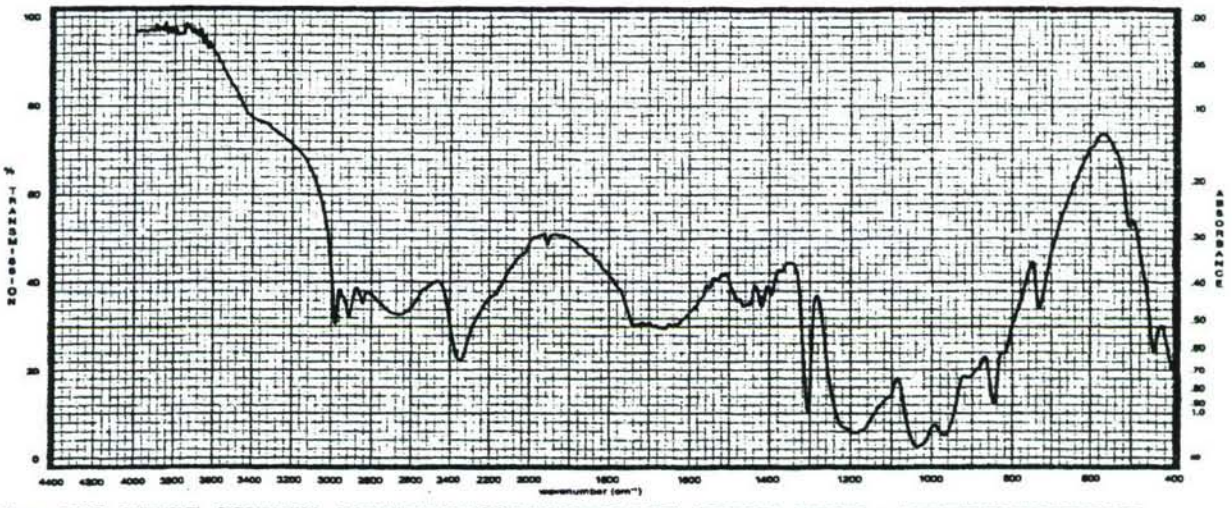


Figure 81C ETHYL METHYL METHYLPHOSPHONITE (MR), LIQUID, CF/KBr, AFTER 70 HOURS OF EXPOSUTE TO ATMOSPHERIC MOISTURE

cm^{-1} vw (ν CH_3 and ν CH_2), 2650 cm^{-1} w and broad (POH), 2351 cm^{-1} w (ν P-H, some POH also absorbs here, thus accounting for the broadness of the band), ca 1650 cm^{-1} w broad (POH), 1303 cm^{-1} m (δ_{sy} P-CH_3), 1189 cm^{-1} ms (ν P=O), 1034 and 968 cm^{-1} (ν P-H, ν P-OH, possibly some POC from **YL**), 843 cm^{-1} w (P-CH_3 rock). Thus, the hydrolysis of ethyl methyl methylphosphonite (**MR**) may be summarized as follows:

$CH_3P(OCH_3)(OEt)$ -HOH→ $CH_3P{=}O(H)(OEt)$ -HOH→ $CH_3P{=}O(H)(OH)$.

3.3.2 Dimethyl ethylphosphonite $CH_3CH_2\text{-}P(OCH_3)_2$

The infrared spectrum of dimethyl ethylphosphonite as a liquid film between KBr windows is given in ***Figure 82***. The band assignments are as follows: 3422 cm^{-1} w (H_2O), 2966 cm^{-1} ms, 2937 cm^{-1} ms, 2913 cm^{-1} sh, 2881 cm^{-1} w, 2831 cm^{-1} m (ν_{as} CH_3 and CH_2, ν_{sy} CH_3 and CH_2, ν OCH_3 2831 cm^{-1}), 2337 cm^{-1} vw (ν P-H), 1461 cm^{-1} m (δ_{as} CH_3), 1412 cm^{-1} w (δ CH_2-P), 1382 cm^{-1} vw (δ_{sy} CH_3), 1281 cm^{-1} w and 1249 cm^{-1} m (ω, τ CH_2 of P-Ethyl), 1220 cm^{-1} m [ν P=O, from hydrolysis-when taken together with P-H band at 2337 cm^{-1} could be due to Et-P=O(H)(OCH_3), which would have a calculated value of 1226 cm^{-1}], 1191 cm^{-1} m (CH_3 rock of $POCH_3$), 1048 and 1021 cm^{-1} s (ν P-O-C), 800 cm^{-1} m (POC), 741 cm^{-1} ms (CH_3 rock of P-Et ?), 714 cm^{-1} m (ν P-C ?).

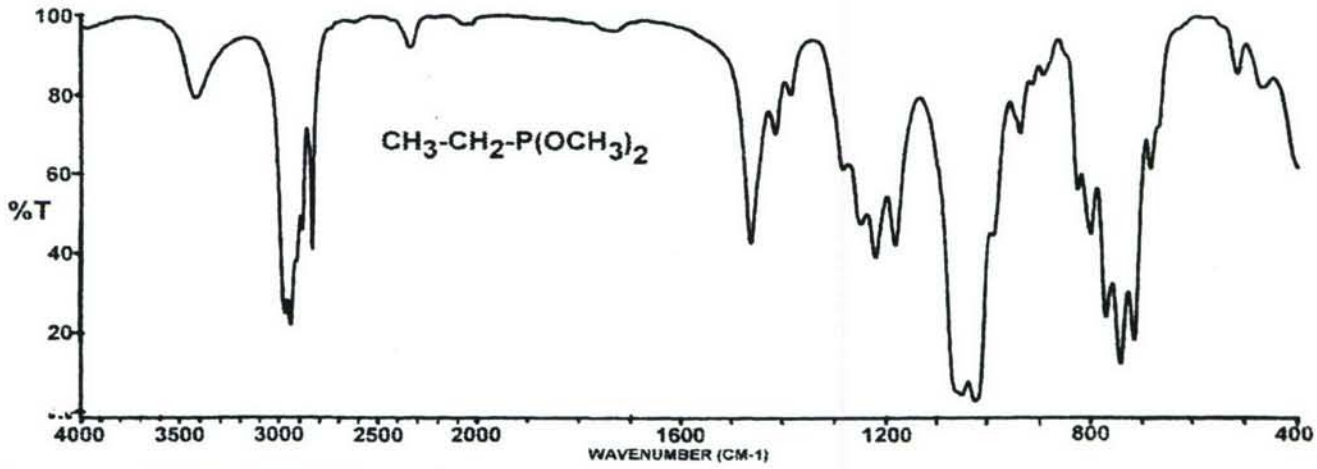


Figure 82 DIMETHYL ETHYLPHOSPHONITE, LIQUID, CF/KBr

The effect of atmospheric moisture on the liquid film of dimethyl ethylphosphonite is shown in ***Figures 83A-E***. After 3 hours of exposure to atmospheric moisture, the infrared spectrum (***Figure 83A***) shows an increase in the intensities of the bands due to the PH (2345 cm^{-1}) and P=O (1218 cm^{-1}). By 20 hours of exposure (***Figure 83B***) the bands due to the P-H (2348 cm^{-1}), P=O (1212 cm^{-1}) and P-O-C (1057 and 1027 cm^{-1} are still predominant in the spectrum as are bands due to water (3455 and 1650 cm^{-1}). After 45 hours of atmospheric exposure have passed, the spectrum (***Figure 83C***) shows the beginnings of absorption due to POH (2700, 2150 cm^{-1}). The P-Et group is still evident by the bands at 1277 and 1247 cm^{-1}. The P=O stretching band near 1206 cm^{-1} has become somewhat broader. By the 6th day (***Figure 83D***) the presence of the POH moiety is

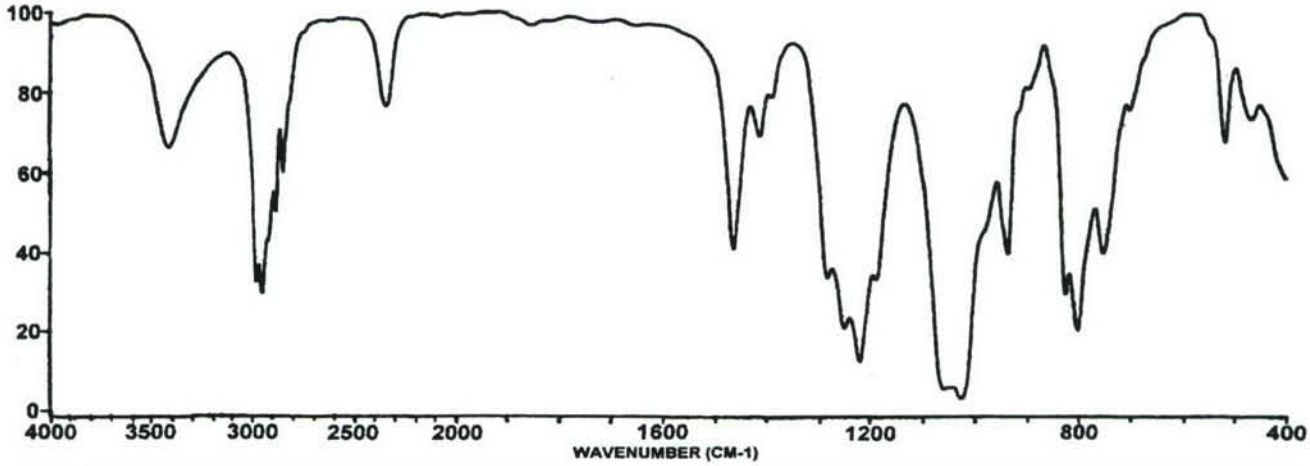


Figure 83A DIMETHYL ETHYLPHOSPHONITE, LIQUID, CF/KBr, AFTER 3 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

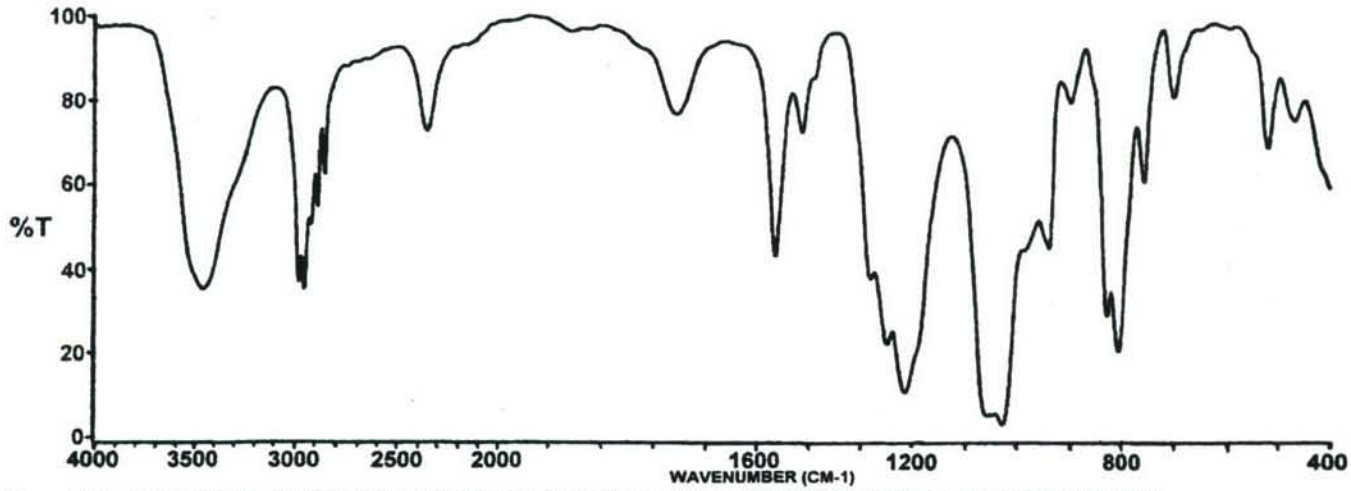


Figure 83B DIMETHYL ETHYLPHOSPHONITE, LIQUID, CF/KBr, AFTER 20 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

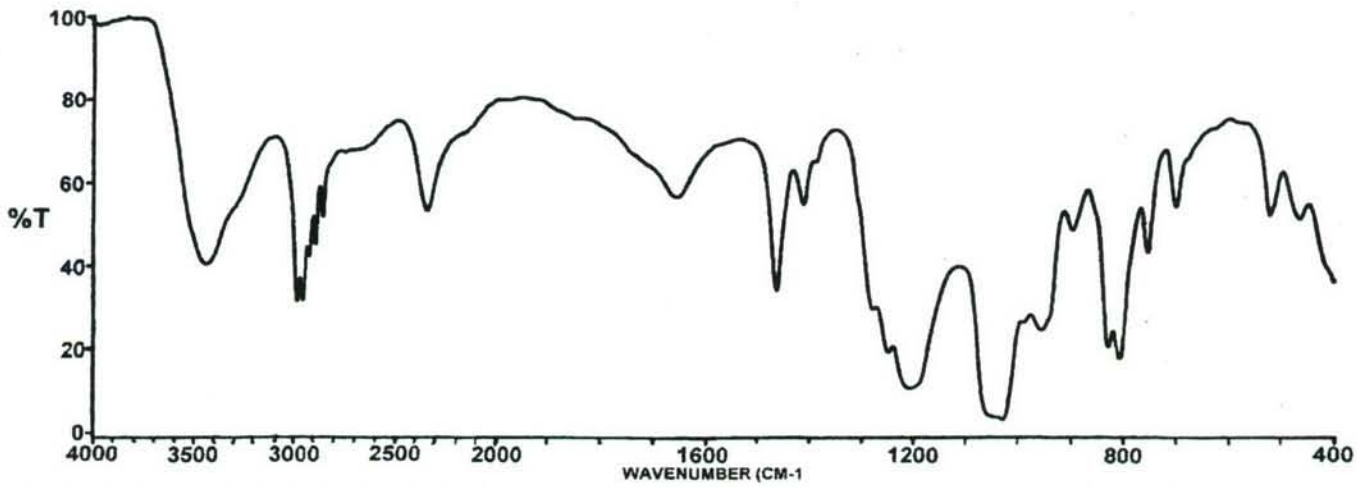


Figure 83C DIMETHYL ETHYLPHOSPHONITE, LIQUID, CF/KBr, AFTER 45 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

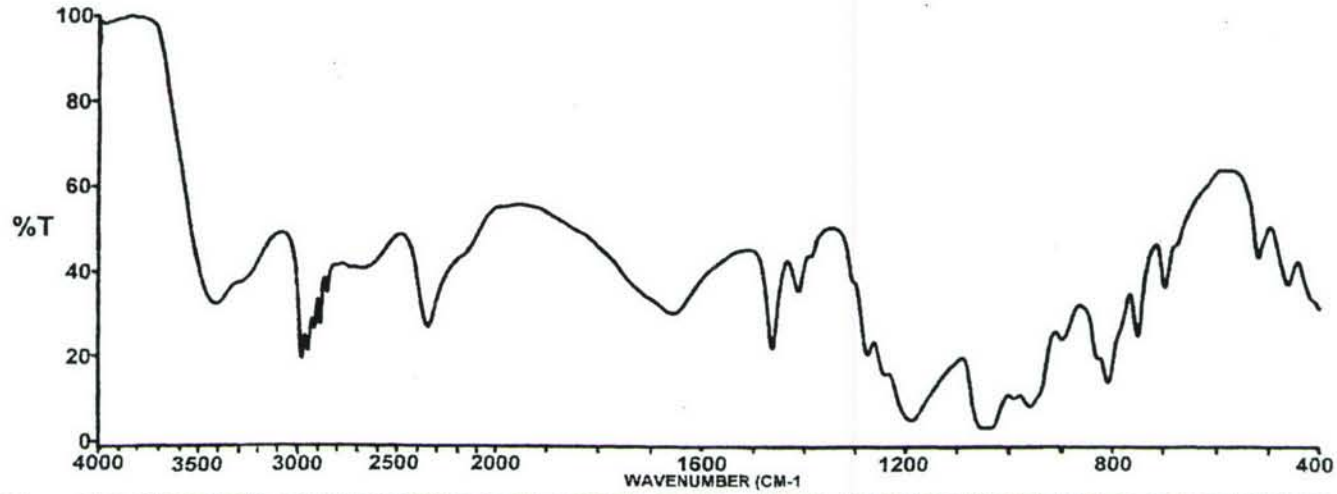


Figure 83D DIMETHYL ETHYLPHOSPHONITE, LIQUID, CF/KBr, AFTER 6 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

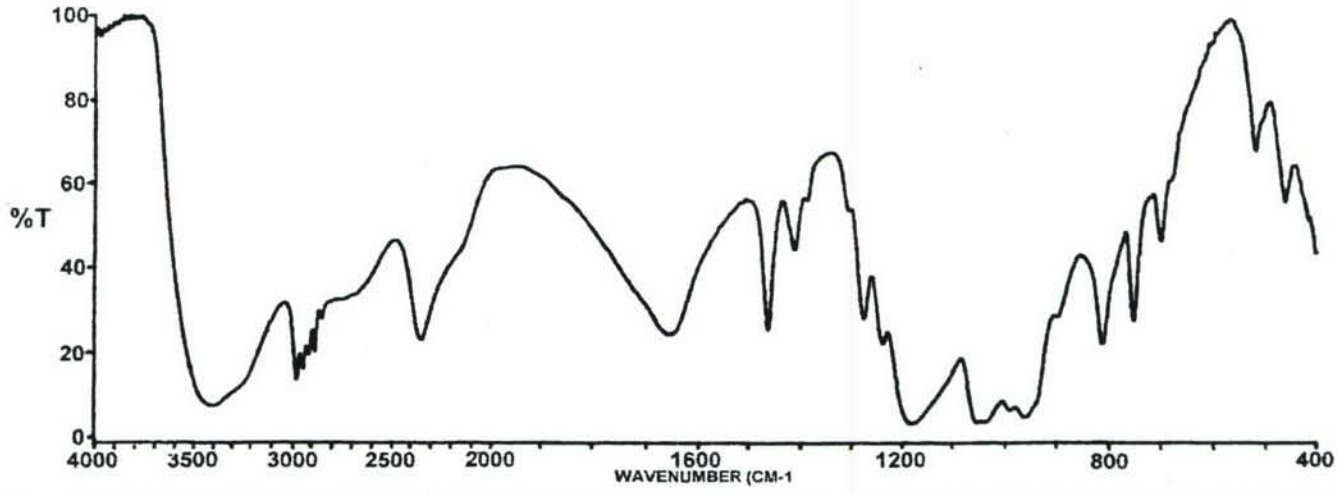


Fig:ure 83E DIMETHYL ETHYLPHOSPHONITE, LIQUID, CF/KBr, AFTER 27 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

more evident at 2700, 2150, 1650 (partly due to water) and 956 cm^{-1}. The P-H is still evident at 2345 cm^{-1} (ν P-H) and 990 cm^{-1} (P-H deformation). By the 27th day of exposure to atmospheric moisture, the spectrum (***Figure 83E***) shows lots of water (3413 and 1650 cm^{-1}), POH [(2700, 2150 (partly P-H, 2345 cm^{-1}), 1650 (partly water) and 962 cm^{-1}]. Other bands are 1276 and 1237 cm^{-1} m (PEt), 1182 cm^{-1} s and broad (ν P=O), 1054 and 1040 cm^{-1} (some residual $POCH_3$, and some contribution from ν C-C of PEt), 990 cm^{-1} (P-H deformation), 751 and 700 cm^{-1} w-m (P-Et, CH_2 rock and ν P-C). The hydrolysis of dimethyl ethylphosphonite may be summarized as follows:

$Et\text{-}P(OCH_3)_2$ -HOH→ $Et\text{-}P{=}O(H)(OCH_3)$ -HOH→ $Et\text{-}P{=}O(H)(OH)$.

3.3.3 Diethyl methylphosphonite (**TR**) $CH_3\text{-}P(OCH_2CH_3)_2$

The infrared spectrum of a liquid film of diethyl methylphosphonite (**TR**) between KBr windows is given as ***Figure 84***. The band assignments are as follows: 2977 cm^{-1} ms, 2931 cm^{-1} m, 2909 cm^{-1} w and 2878 cm^{-1} m (ν_{as} and ν_{sy} CH_3 and CH_2), 1477 cm^{-1} w (δ OCH_2), 1443 cm^{-1} w (δ_{as} CH_3), 1413 cm^{-1} w (δ_{as} P-CH_3), 1386 cm^{-1} m (ϖ OCH_2), 1362 cm^{-1} vw (δ_{sy} CH_3), 1279 cm^{-1} m (δ_{sy} P-CH_3), 1249 cm^{-1} vw [ν P=O of **TRO**, $CH_3P{=}O(OEt)_2$?], 1161 and 1099 cm^{-1} w (Ch_3 rock of POEt, characteristic), 1052 and 1033 cm^{-1} s (ν P-O-C), 934 and 921 cm^{-1} ms (ν C-C of POEt), 869 cm^{-1} ms (P-CH_3 rock), 733 cm^{-1} m (POC), 688 cm^{-1} sh (ν P-C ?).

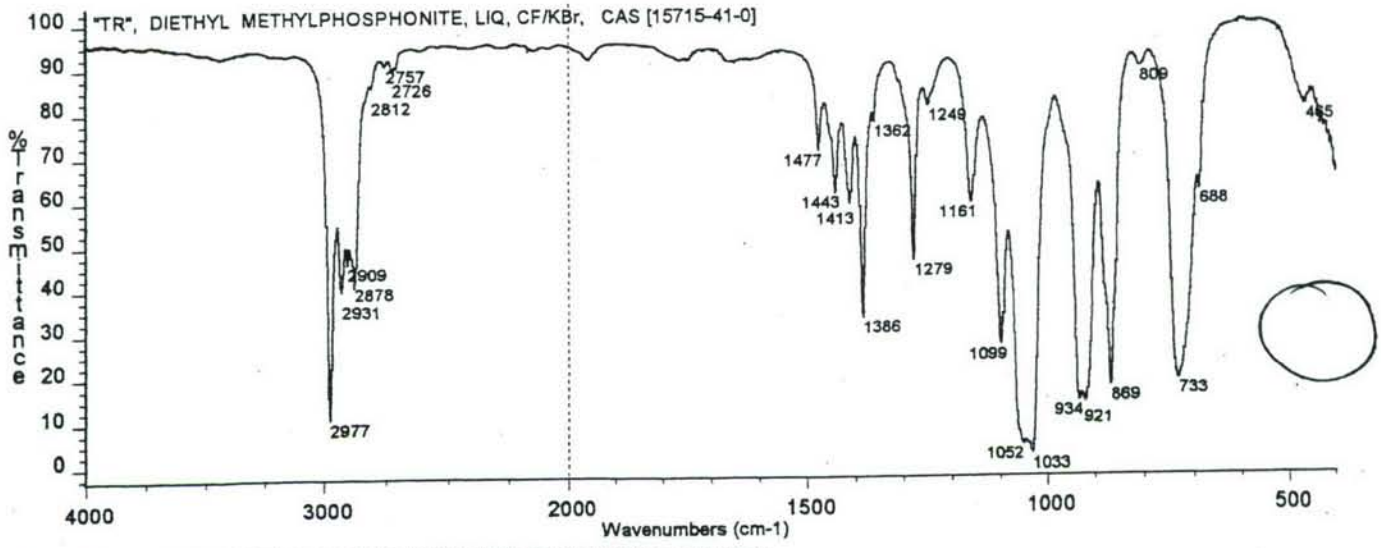
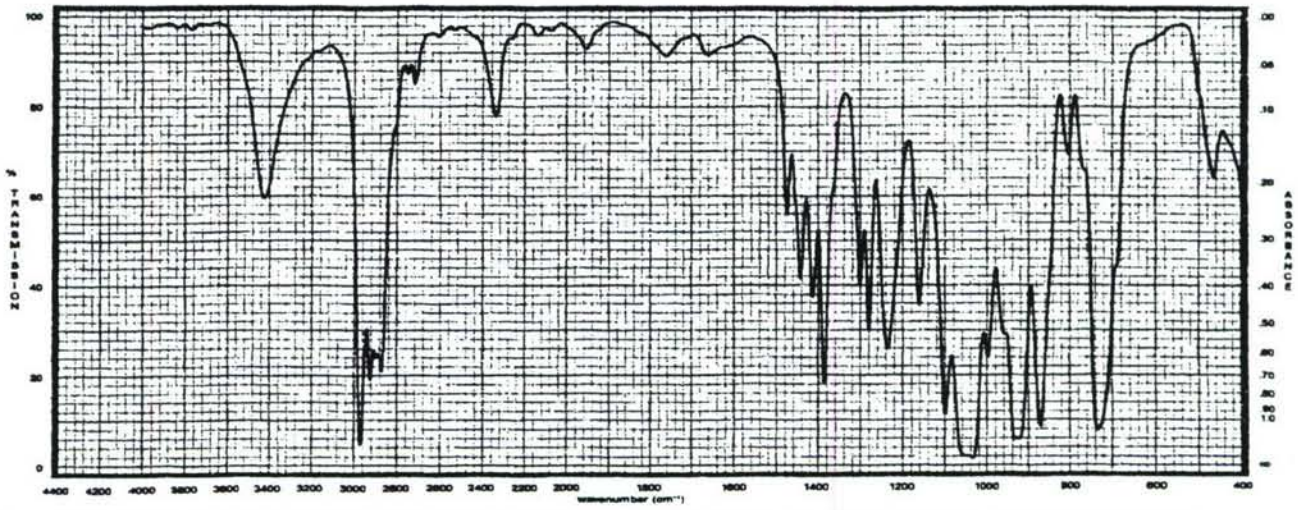


Figure 84 DIETHYL METHYLPHOSPHONITE (TR), LIQUID, CF/KBr

The infrared spectra showing the effect of atmospheric moisture on **TR** are reproduced in ***Figures 85A*** through ***85E***. The infrared spectrum of **TR** after 30 minutes of exposure to atmospheric moisture (***Figure 85A***) shows the following: 3433 cm^{-1} w (H_2O), 2977 cm^{-1} ms, 2932 cm^{-1} m, 2909 cm^{-1} vw, 2879 cm^{-1} m (ν CH_3 and ν CH_2), 2348 cm^{-1} vw (ν P-H), 1766 cm^{-1} vvw (1033 + 734 = 1767 cm^{-1}), 1477 cm^{-1} w (δ OCH_2), 1444 cm^{-1} w (δ_{as} CH_3), 1414 cm^{-1} w (δ_{as} P-CH_3), 1387 cm^{-1} m (ω OCH_2), ca 1365 cm^{-1} sh (δ_{sy} CH_3), 1302 cm^{-1} w (δ_{sy} P^{+5}-CH_3), 1280 cm^{-1} m (δ_{sy} P^{+3}-CH_3), 1237 cm^{-1} m [probably composed of ν P=O from **TRO** and ν P=O of **YL**, $CH_3P{=}O(H)(OC_2H_5)$],1162 cm^{-1} w and 1099 cm^{-1} m (CH_3 rock of POEt, characteristic), 1052 and 1033 cm^{-1} s (ν P-O-C), 998 cm^{-1} w (P-H deformation), 959 cm^{-1} sh (ν C-C of P^{+5}-OEt), 933 cm^{-1} ms (ν C-C of P^{+3}-OEt), 870



Figu;re 85A DIETHYL METHYLPHOSPHONITE (TR), LIQUID, CF/KBr, AFTER 30 MINUTES OF EXPOSURE TO ATMOSPHERIC MOISTURE

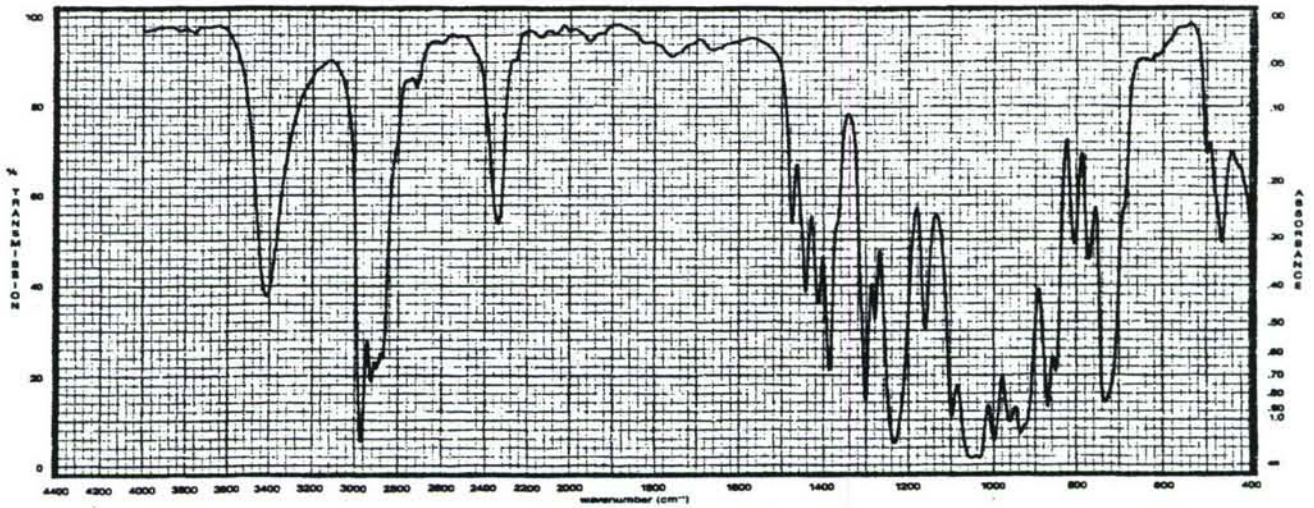


Figure 85B DIETHYL METHYLPHOSPHONITE (TR), LIQUID, CF/KBr, AFTER 1 HOUR OF EXPOSURE TO ATMOSPHERIC MOISTURE

cm^{-1} ms (P^{+3}-CH_3 rock), 734 cm^{-1} ms (POC, ν P-C). After 1 hour of exposure to atmospheric moisture (***Figure 85B***) the bands indicative of the hydrolysis product **YL** (P^{+5} moiety) have increased in intensity, while those pertaining to **TR** (P^{+3} moiety) are decreasing in intensity. For example, the 1302 cm^{-1} (δ_{sy} P^{+5}-CH_3) band is now more intense than the 1281 cm^{-1} (δ_{sy} P^{-3}-CH_3) band. The band at 998 cm^{-1} (P-H deformation) has also increased in intensity. The band at 961 cm^{-1} (ν C-C of P^{+5}-OEt) has become stronger than that for the P^{+3} compound at 935 cm^{-1}. Also, the band at 870 cm^{-1} (P^{-3}-CH_3 rock) has decreased in intensity and a new band has appeared at

849 cm^{-1} (P^{+5}-CH_3). This conversion of the compound by hydrolysis from the P^{+3} state to the P^{+5} state continues through the 2nd and 21st hour periods (***Figures 85C*** and ***85 D*** respectively). The bands indicative of **YL**, ethyl hydrogenmethylphosphinate, become more predominant as time progresses.

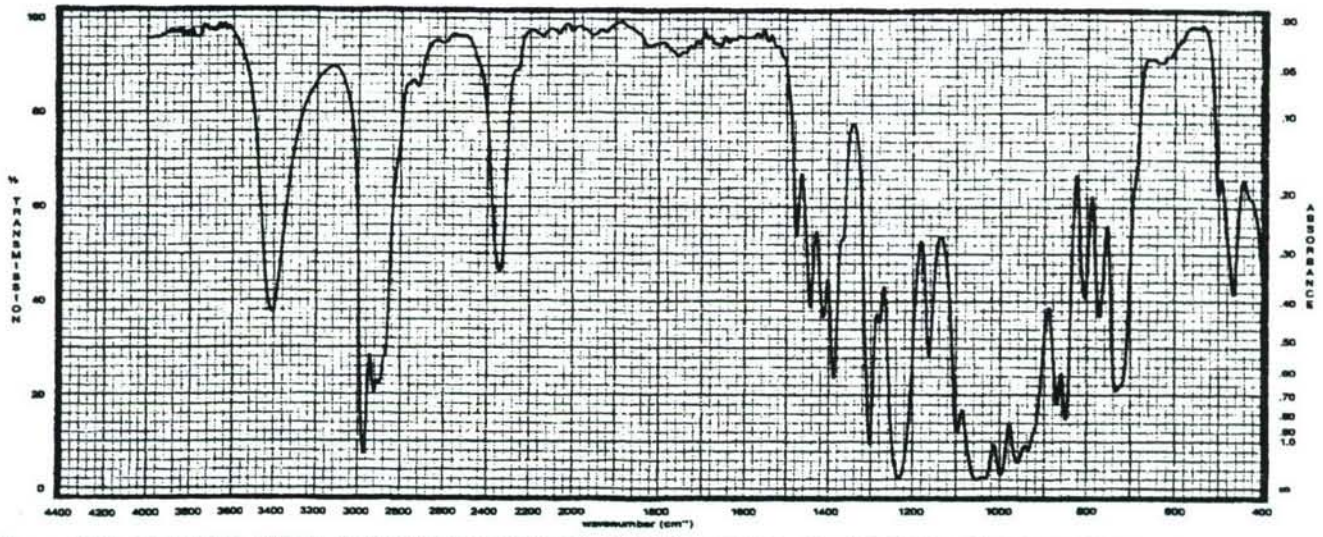


Figure 85C DIETHYL METHYLPHOSPHONITE (TR), LIQUID, CF/KBr, AFTER 2 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

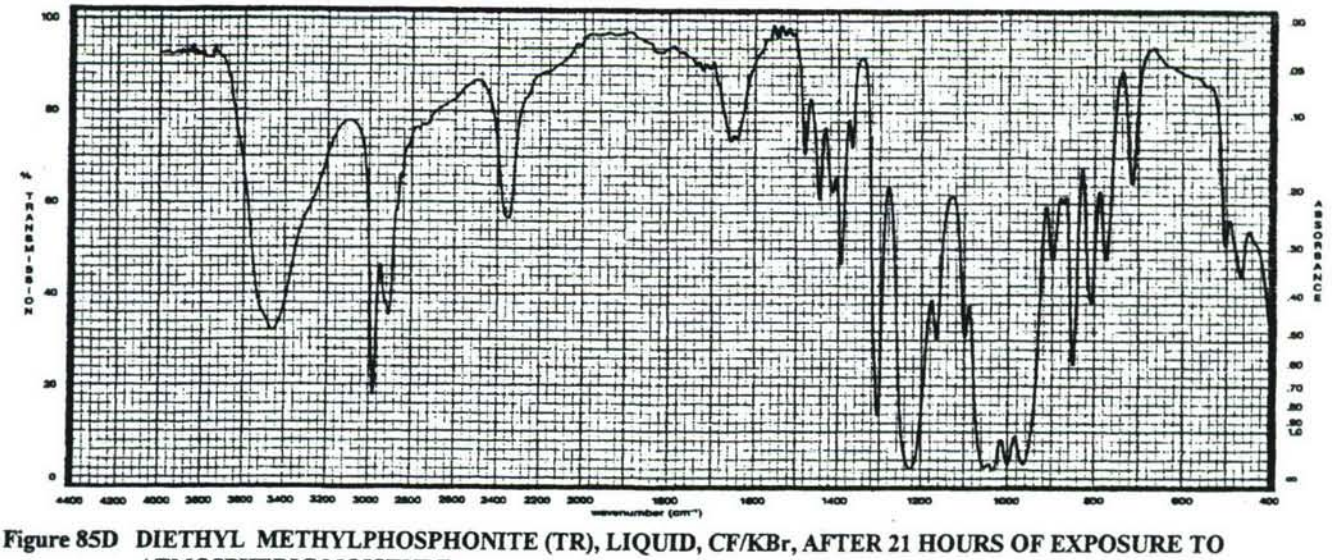


Figure 85D DIETHYL METHYLPHOSPHONITE (TR), LIQUID, CF/KBr, AFTER 21 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

However, after 7 days of exposure to atmospheric moisture a dramatic change is evident in the spectrum (***Figure 85E***). The compound formed from the hydrolysis of **TR**, namely **YL**, has been further hydrolyzed to the acid, methylphosphinic acid, CH_3 P=O(H)(OH). Bands due to the POH moiety are now visible in the spectrum near

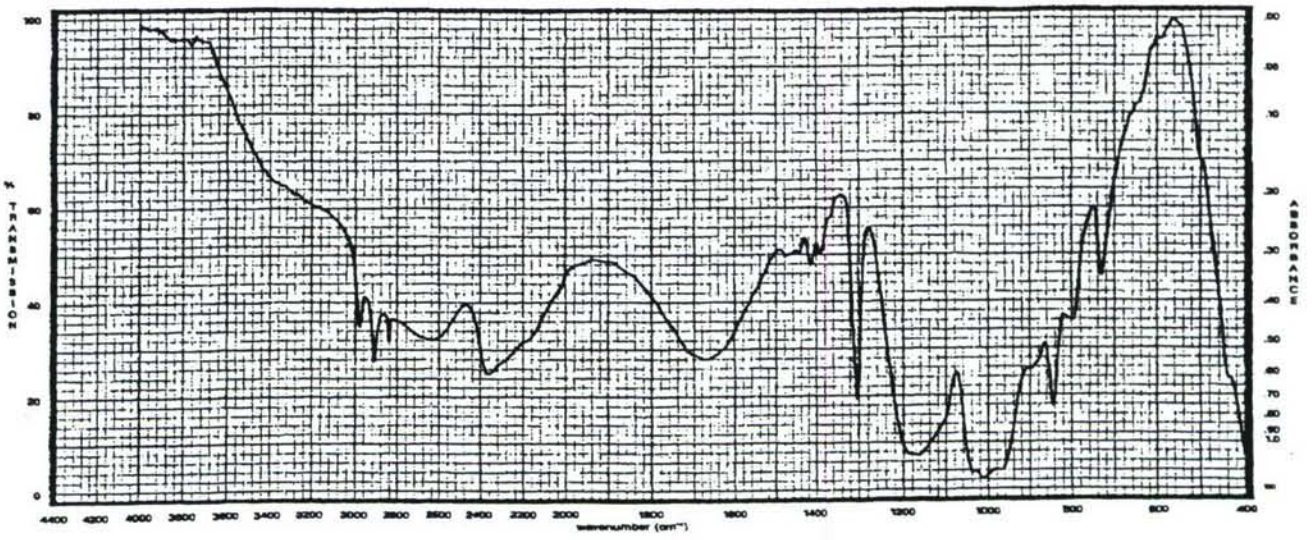


Figure 85E DIETHYL METHYLPHOSPHONITE (TR), LIQUID, CF/KBr, AFTER 7 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

2640, 2200, 1670 and 969 cm^{-1}. Other bands may be assigned as follows: 2375 cm^{-1} w (ν P-H), 1417 cm^{-1} vw (δ_{as} P-CH_3), 1395 cm^{-1} vw (ω OCH_2 , from residual **YL**), 1305 cm^{-1} m (δ_{sy} P-CH_3), 1182 cm^{-1} (ν P=O), 1010 cm^{-1} s (P-H deformation), 969 cm^{-1} s (ν P-OH), 844 cm^{-1} m (P-CH_3 rock, 733 cm^{-1} w (ν P-C). Thus, the hydrolysis of **TR** may be depicted as follows:

$$CH_3P(OCH_2CH_3)_2 \xrightarrow{-HOH} CH_3P{=}O(H)(OCH_2CH_3) \xrightarrow{-HOH} CH_3P{=}O(H)(OH) + CH_3CH_2OH$$

(TR) **(YL)** **(methylphosphinic acid)**

3.3.4 Diethyl ethylphosphonite CH_3CH_2-P(O-CH_2-CH_3)$_2$

The infrared spectrum spectrum of a liquid film of diethyl ethylphosphonite between KBr discs (windows) is given in ***Figure 86***. The band assignments are as follows: 3426 and 1650 cm^{-1} vw (H_2O), 2975 cm^{-1} s, 2933 cm^{-1} ms, 2907 cm^{-1} vw and 2878 cm^{-1} ms (ν CH_3 and ν CH_2), 1476 cm^{-1} w (δ OCH_2), 1457 and 1443 cm^{-1} m (δ_{as} CH_3), 1411 cm^{-1} vvw (δ P-CH_2), 1386 cm^{-1} ms (ω OCH_2), 1362 cm^{-1} vw (δ_{sy} CH_3), 1290 cm^{-1} w and 1251 cm^{-1} vw (ω, τ CH_2 of P-Et), 1223 cm^{-1} vw [ν P=O of possibly Et-P=O(H)(OEt), which would have a calculated value of 1224 cm^{-1}], 1162 cm^{-1} m and 1100 cm^{-1} ms (CH_3 rock of POEt, characteristic), 1048 and 1033 cm^{-1} s (ν P-O-C, some contribution from ν C-C of P-Et), 916 cm^{-1} s (ν C-C of POEt), 769, 742

and 714 cm^{-1} ms (POC and CH_2 rock of P-Et), 684 cm^{-1} m (ν P-C ?).

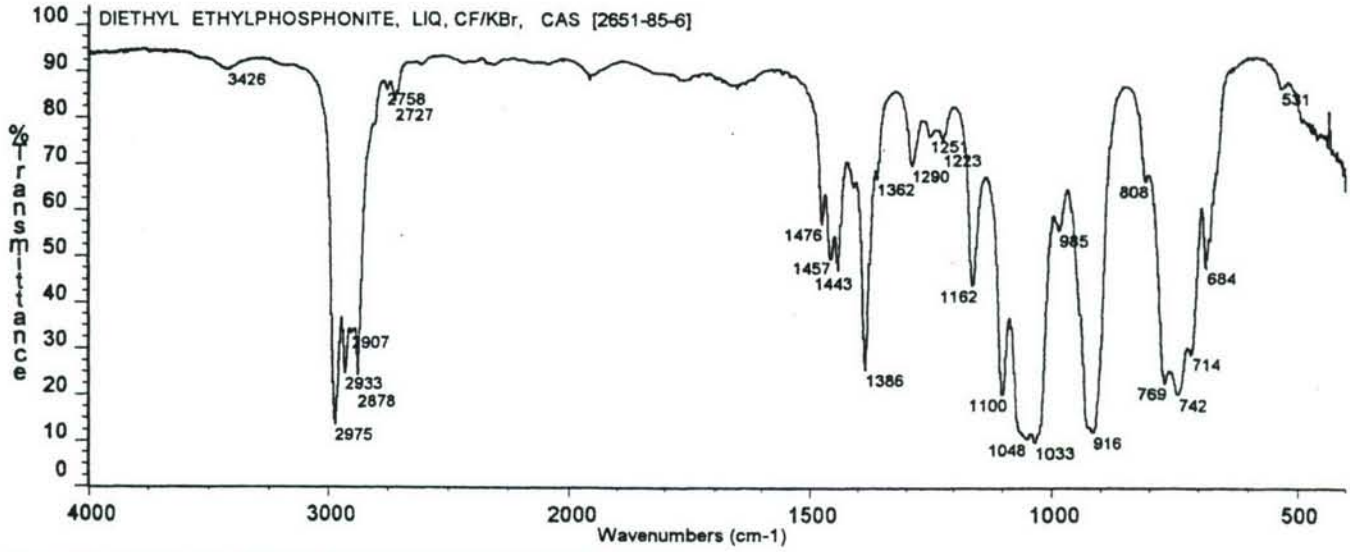


Figure 86 DIETHYL ETHYLPHOSPHONITE, LIQUID, CF/KBr

The infrared spectra illustrating the effect of atmospheric moisture on a liquid film of diethyl ethylphosphonite are reproduced as ***Figures 87A*** and ***87B***. After 2.5 hours of exposure to atmospheric moisture, the infrared spectrum (***Figure 87A***) shows a weak band near 2345 cm^{-1} assignable to a P-H stretching vibration. A strong band also appears near 1219 cm^{-1} and is assigned to a P=O strech. As stated previously, these bands (2345 and 1219 cm^{-1}) are believed to be due to the formation of ethyl hydrogenethylphosphinate, $CH_3CH_2P{=}O(H)(OEt)$ [calculated ν P=O of 1224 cm^{-1}]. The amount of water in the spectra is increasing greatly as evidenced by the bands near 3440 and 1650 cm^{-1}. Gradually broad bands begin to appear near 2740 and near 2200 cm^{-1} due to POH (***Figure 87B***). The phosphoryl stretching vibration begins to decrease in value eventually occurring near 1180 cm^{-1} (27 days, ***Figure 87B***). The bands due to the POEt moiety are almost completely gone from the spectrum. The P-Ethyl group still shows bands near 1275, 1236, 751 and 702 cm^{-1} (77 days, ***Figure 87B***). The P-acid, $CH_3CH_2P{=}O(H)(OH)$, ethylphosphinic acid (hydrogen ethylhydrogenphosphinate) is believed to be eventually formed. The hydrolysis of diethyl ethylphosphonite may thus be summarized as follows:

$CH_3CH_2P(OEt)_2$ -HOH→ $CH_3CH_2P{=}O(H)(OEt)$ -HOH→ $CH_3CH_2P{=}O(H)(OH)$ + EtOH .

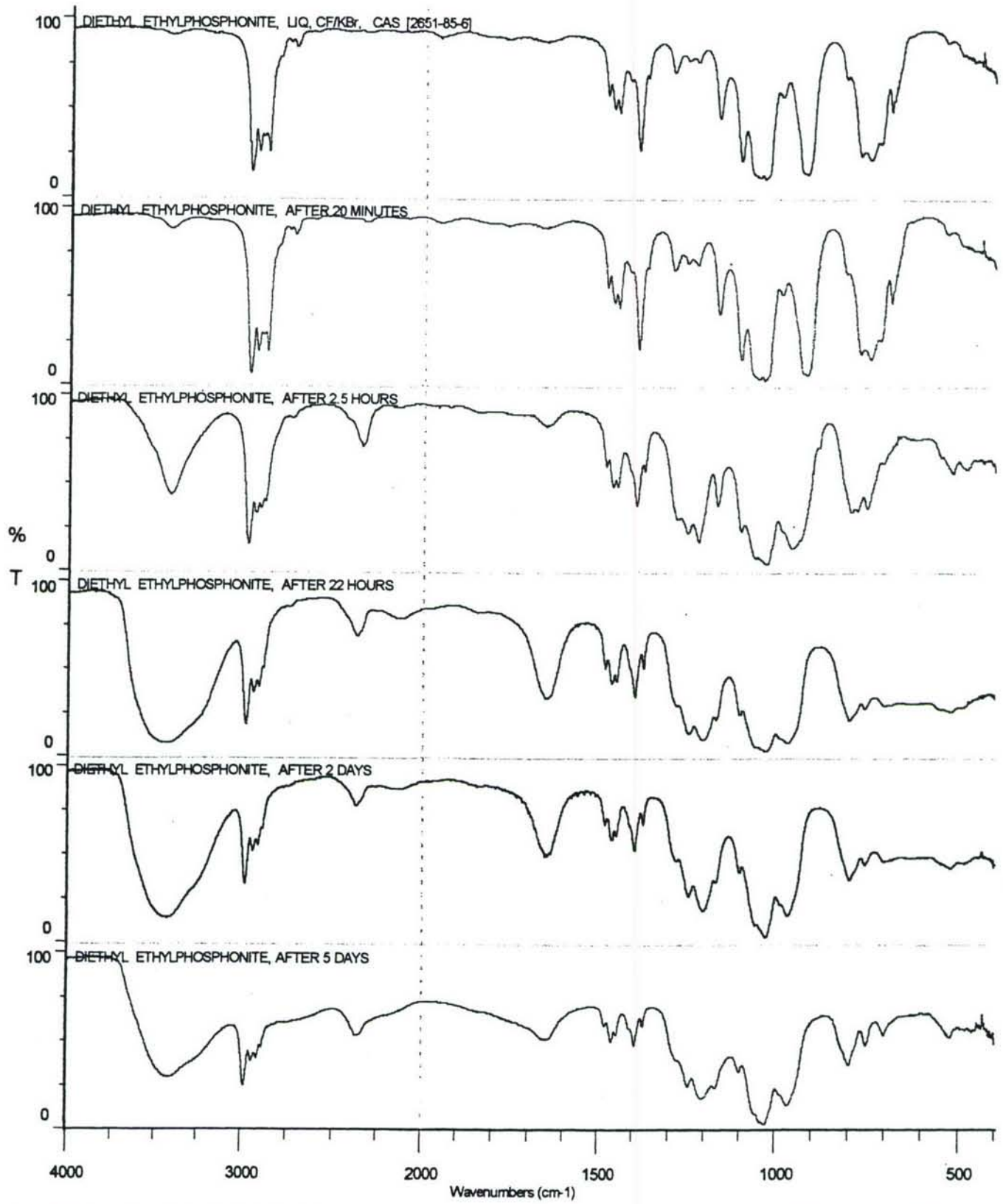


Figure 87A DIETHYL ETHYLPHOSPHONITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

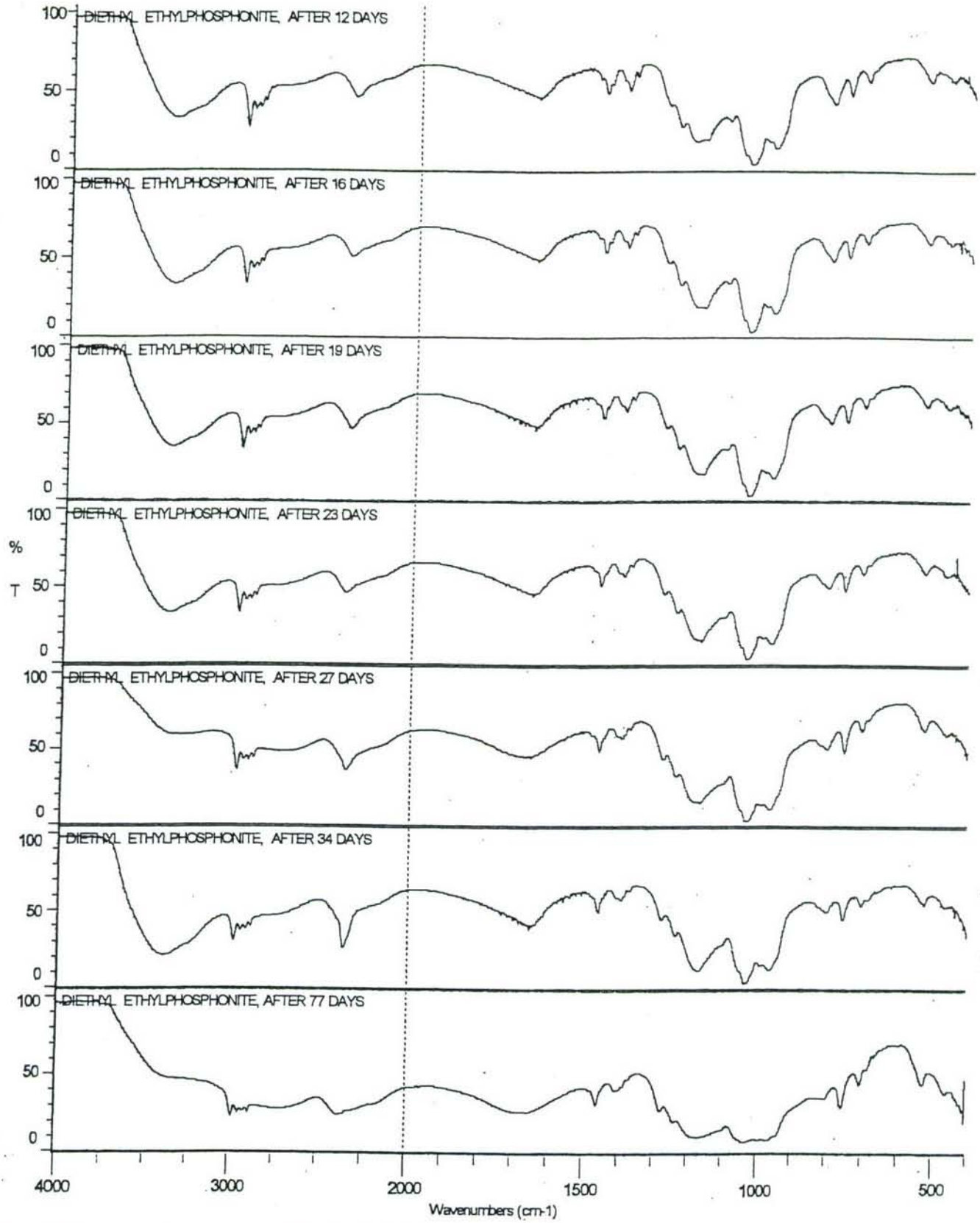


Figure 87B DIETHYL ETHYLPHOSPHONITE, LIQUID CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.3.5 Dibutyl butylphosphonite $H_9C_4P(O\text{-}C_4H_9)_2$

The infrared spectrum of dibutyl butylphosphonite as a liquid film between KBr windows is given in ***Figure 88***. The band assignments are as follows: 3433 cm^{-1} vvw (H_2O), 3179 cm^{-1} vvw (ν OH alcohol ?), 2958 cm^{-1} s (ν_{as} CH_3), 2934 cm^{-1} ms ($\nu_{as}CH_2$), 2873 cm^{-1} ms (ν_{sy} CH_3 amd CH_2), 1466 cm^{-1} m (δ CH_2) 1433 cm^{-1} vw (δ_{as} CH_3), 1405 cm^{-1} vvw (δ P-CH_2), 1379 cm^{-1} m (ω O-CH_2 and δ_{sy} CH_3), 1299 cm^{-1} vw and 1251 cm^{-1} w (ω, τ CH_2), 1232 cm^{-1} w [possible ν P=O from either H_9C_4 P=O$(OC_4H_9)_2$ or H_9C_4 P=O(H)(OC_4H_9), calculated as 1238 and 1224 cm^{-1} respectively; however, the actual observed value of the ν P=O for the phosphonate compound is 1249 cm^{-1} and thus the observed 1251 cm^{-1} band may be actually due to the P=O stretch of the phosphonate compound][r], 1164 cm^{-1} vvw, 1148 cm^{-1} w and 1118 cm^{-1} w (CH_3 rock of PO-*n*-butyl, characteristic ?), 1066 cm^{-1} m and 1023ms (ν P-O-C), 966 cm^{-1} ms (ν C-C of P-O-*n*-Butyl), 876 cm^{-1} m)POC, 773 cm^{-1} m (CH_2 rock ?), 722 cm^{-1} m (ν P-C ?).

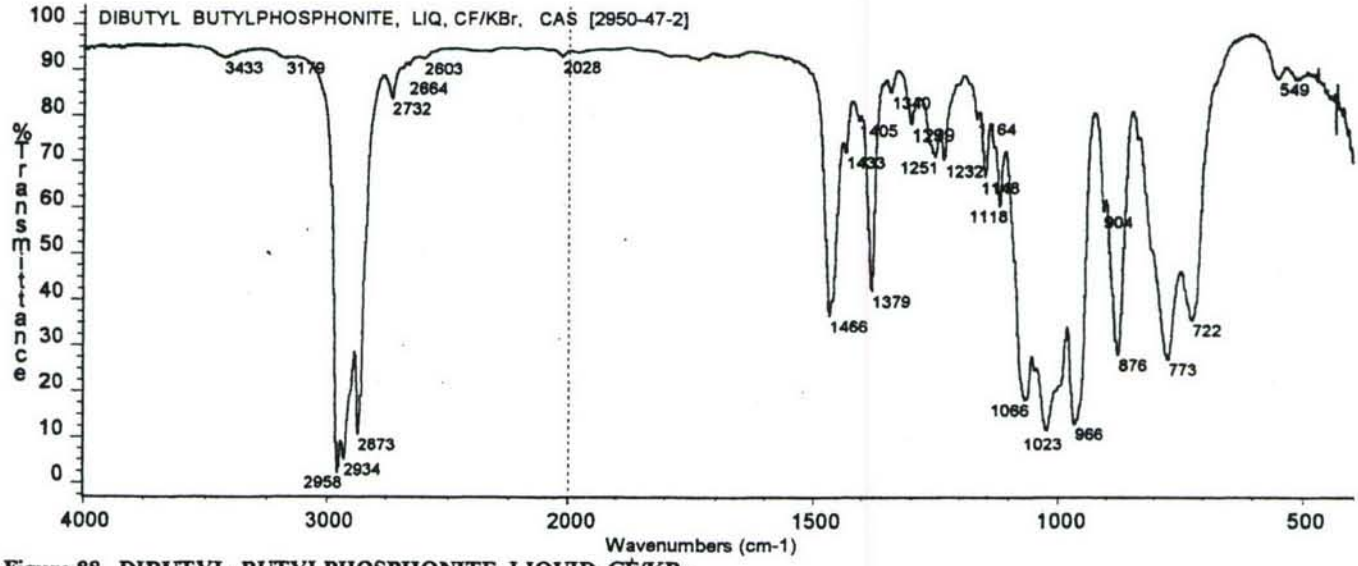


Figure 88 DIBUTYL BUTYLPHOSPHONITE, LIQUID, CF/KBr

The infrared spectra showing the effect of atmospheric moisture on the liquid film of dibutyl butylphosphonite are reproduced as ***Figures 89A*** and ***89B***. After an exposure period of 2 hours the band near 1249 cm^{-1} shows an increase in intensity. A new band appears near 2330 cm^{-1}. These bands may be assigned to

[r] The infrared spectrum of dibutyl butylphosphonate can be found in the section labeled **Phosphonates** (3.5.8).

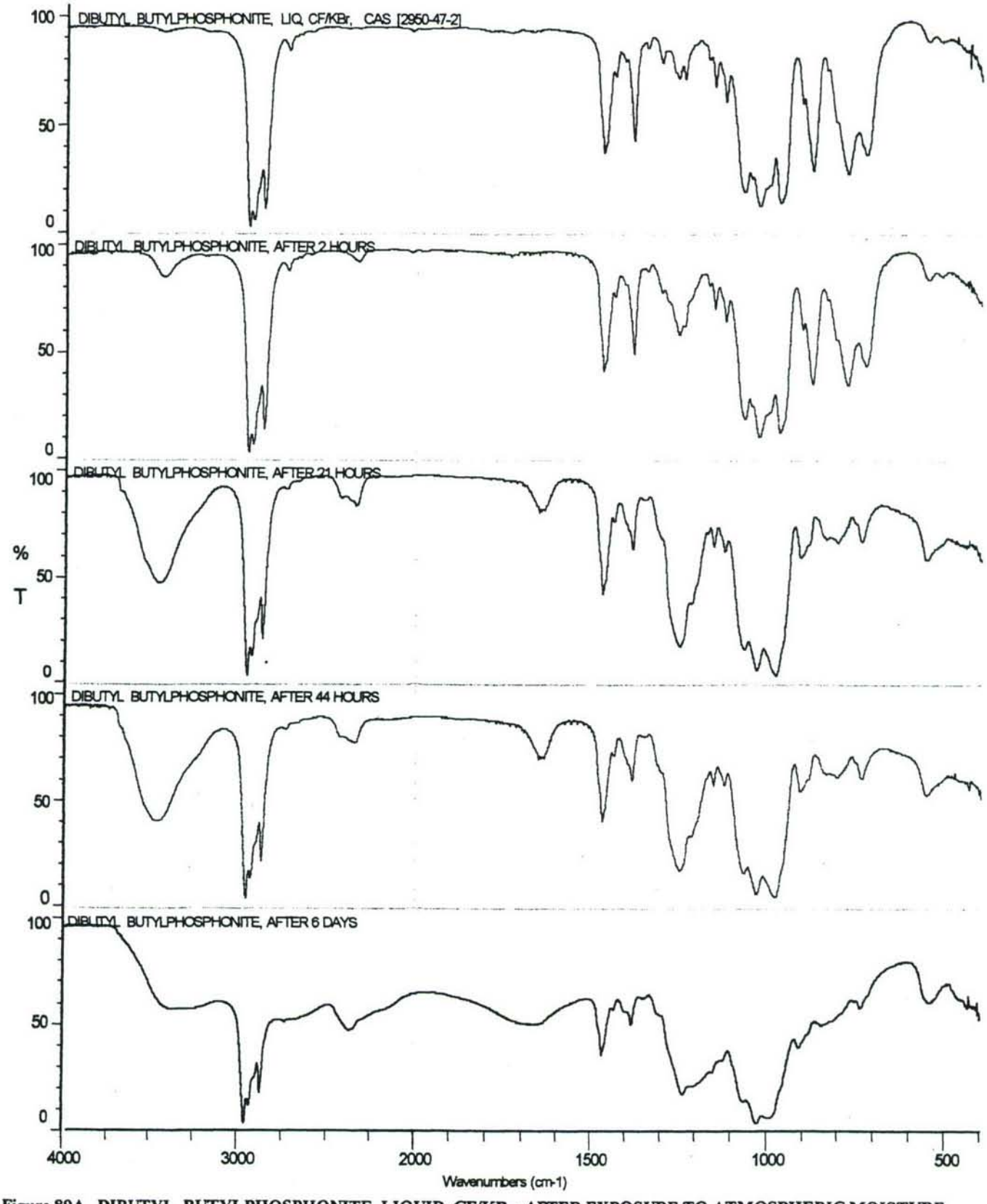


Figure 89A DIBUTYL BUTYLPHOSPHONITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

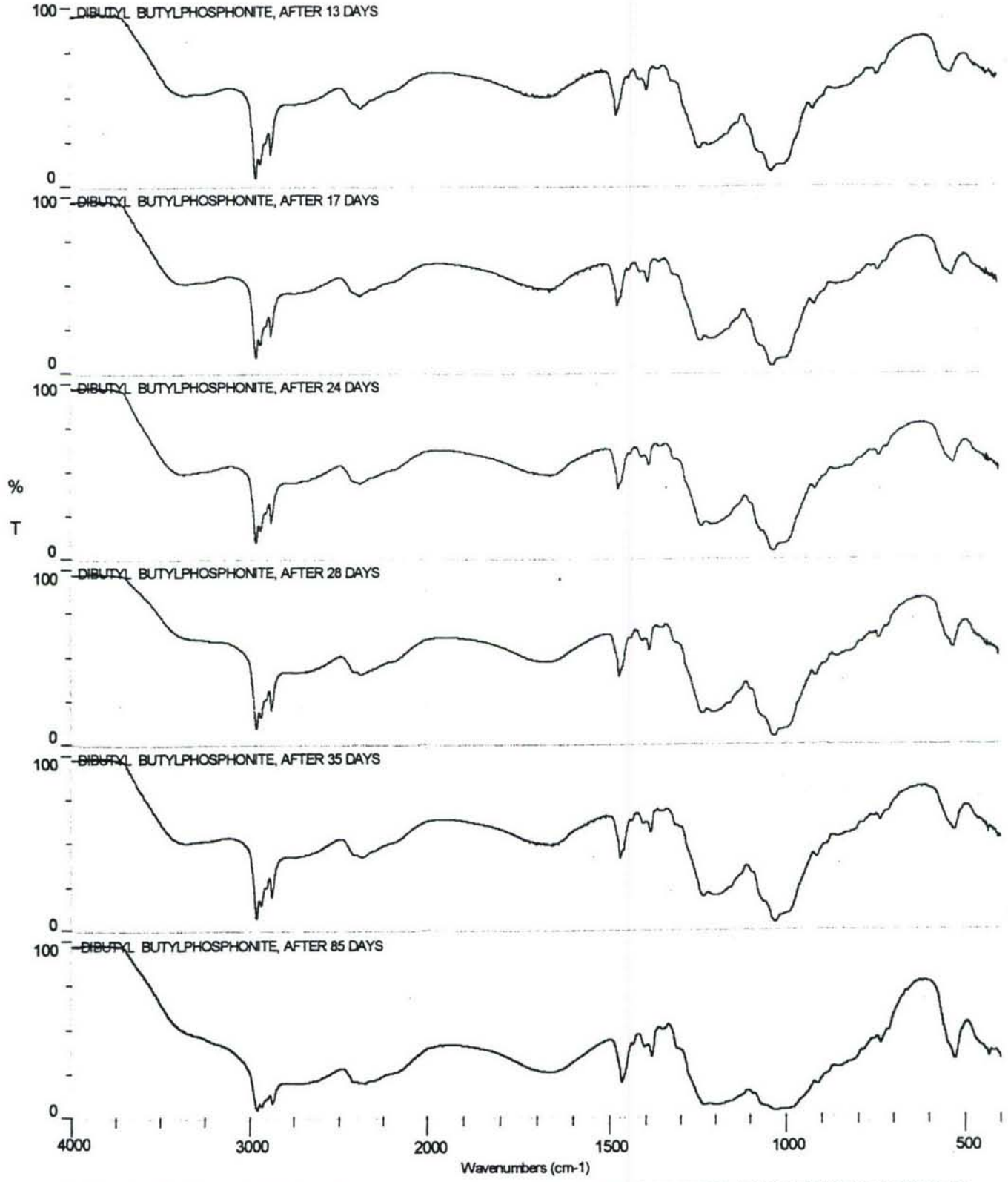


Figure 89B DIBUTYL BUTYLPHOSPHONITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

P=O and P-H stretching vibrations respectively. The P=O stretch (1249 cm^{-1})is probably due to the formation of $H_9C_4P{=}O(OC_4H_9)_2$, dibutyl butylphosphonate, from the oxidation of the original phosphonite. This phosphonate P=O band shows an increase in intensity through the 44 hours exposure period (***Figure 89A***). The band at 2330 cm^{-1} is assigned to the P-H stretch from $H_9C_4P{=}O(H)(OC_4H_9)$, and is due to the hydrolysis of the original phosphonite. By the 6th day of exposure, the spectrum shows additional broad bands near 2735, 2200 and 1650 cm^{-1} assignable to the POH group. These acid bands are present up to the last spectrum determined, namely, after 85 days of exposure. The PH moiety still appears to be present given the band near 2370 cm^{-1}, even though this band is in the broad POH band near 2300 cm^{-1}. The P-acid(s) formed may be coming not only from the hydrolyis reaction but also from the oxidation followed by hydrolysis as follows:

$H_9C_4P\ (OC_4H_9)_2$ -HOH→ $H_9C_4P{=}O(H)\ (OC_4H_9)$ -HOH→ $H_9C_4P{=}O(H)(OH)$

$H_9C_4P\ (OC_4H_9)_2$ -[O]→ $H_9C_4P{=}O(OC_4H_9)_2$ -HOH→ $H_9C_4P{=}O(OH)\ (OC_4H_9)$ -perhaps-HOH→ $H_9C_4P{=}O(OH)_2$?

3.3.6 Di-*n*-butyl phenylphosphonite $H_5C_6P(O\text{-}n\text{-}C_4H_9)_2$

The infrared spectrum of di-*n*-butyl phenylphosphonite as a liquid film between KBr windows is given in ***Figure 90***. The band assignments are as follows: 3438 cm^{-1} vw (H_2O), 3072 and 3056 cm^{-1} w, 3005 cm^{-1} vw (ν C-H aromatic), 2959 cm^{-1} s (ν_{as} CH_3), 2935 cm^{-1} ms (ν_{as} CH_2), ca 2905 cm^{-1} sh (ν_{sy} CH_3), 2873 cm^{-1} ms (ν_{sy} CH_2), 2337 cm^{-1} vw (ν P-H impurity), 1592 cm^{-1} vw, 1481 cm^{-1} sh and 1435 cm^{-1} m (aromatic ring), 1465

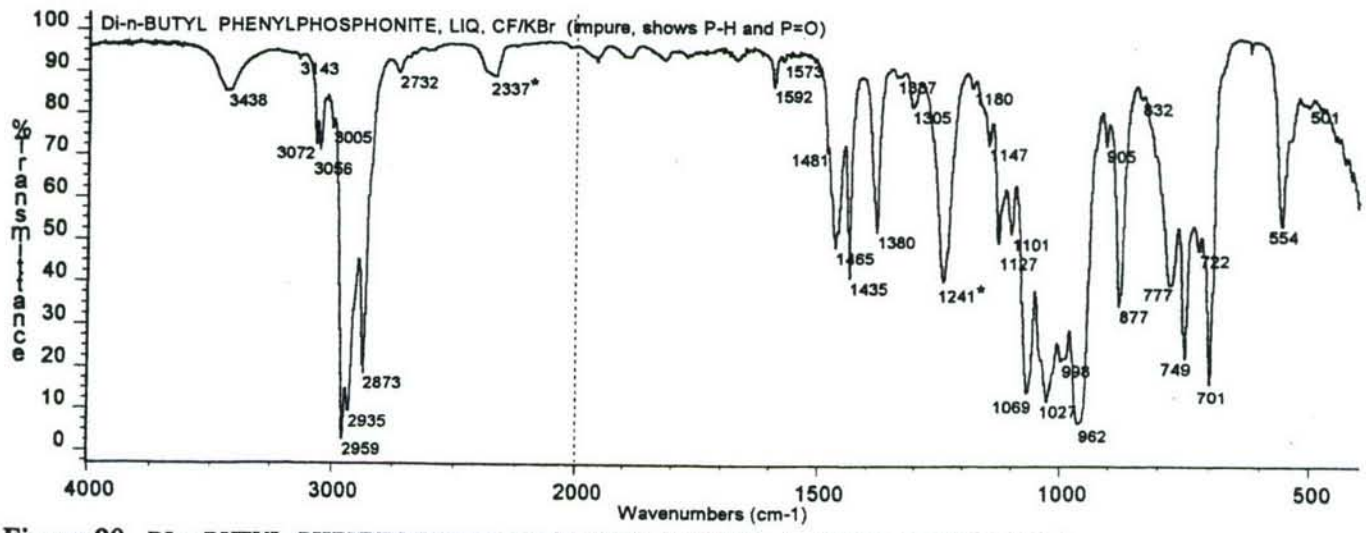


Figure 90 **DI-*n*-BUTYL PHENYLPHOSPHONITE, LIQUID, CF/KBr** (*IMPURE, SHOWS P-H, P=O)

cm^{-1} m (δ_{as} CH_3), 1380 cm^{-1} m (δ_{sy} CH_3, some ω OCH_2 ?), 1241 cm^{-1} m [ν P=O from impurity, perhaps $H_5C_6P{=}O(OC_4H_9)_2$, which would have a calculated ν P=O of 1242 cm^{-1}; a shoulder occurs near 1230 cm^{-1} which could be due to the P=O stretch of $H_5C_6P{=}O(H)(OC_4H_9)$, which would have a calculated value of 1228 cm^{-1}], 1180, 1147 and 1127 cm^{-1} vw-m (β C-H mono-substituted aromatic ring, plus some contribution from the ω and τ of the CH_2 moiety), 1101 cm^{-1} m (phenyl-P), 1069 cm^{-1} ms, 1027 cm^{-1} ms, 998 cm^{-1} m (ν P-O-C), 962 cm^{-1} s (ν C-C), 877 cm^{-1} m (POC), 777, 749 cm^{-1} m-ms (γ C-H mono-substituted aromatic ring), 701 cm^{-1} ms (aromatic ring deformation).

3.3.7 Ethyl 2-diisopropylaminoethyl methylphosphonite (**QL**) $CH_3P(OCH_2CH_3)[OCH_2CH_2N(i\text{-}C_3H_7)_2]$

The infrared spectrum of ethyl 2-diisopropylaminoethyl methylphosphonite (**QL**) as a liquid film between CsI windows is reproduced as ***Figure 91A***. The band assignments are as follows: 2969 cm^{-1} s, 2932 cm^{-1} ms, 2875 cm^{-1} m (ν CH_3 and CH_2), 2713 cm^{-1} vw and 2606 cm^{-1} vw (these two bands seem to appear when the $-N(i\text{-}C_3H_7)_2$ moiety is present), 2116 cm^{-1} m (ν N=C=N of the carbodiimide for ***Figure 91B***), 1465 cm^{-1} w and 1443 cm^{-1} sh (δ CH_3 and CH_2), 1412 cm^{-1} vw (δ_{as} P-CH_3), 1385 cm^{-1} m (partly ω O-CH_2 and δ_{sy} CH_3), 1362 cm^{-1} m (δ_{sy} CH_3), 1310 cm^{-1} vw (δ_{sy} P^{+5}-CH_3 of perhaps **QLO**, ethyl 2-diisopropylaminoethyl methylphosphonate ?), 1278 cm^{-1} w (δ_{sy} P^{+3}-CH_3), 1148 cm^{-1} w and 1120 cm^{-1} w (isopropyl moiety), 1160 cm^{-1} sh (CH_3 rock of POEt), 1099 cm^{-1} m (ν C-N ?, CH_3 rock of POEt), 1053 cm^{-1} s, 1032 cm^{-1} s, 1020 cm^{-1} sh and 1004 cm^{-1} sh (ν P-O-C), 925 cm^{-1} m (ν C-C of POEt), 869 cm^{-1} ms (P-CH_3 rock and CH_3 rock of isopropyl), 800 cm^{-1} vw (POC), 727 cm^{-1} ms (POC and ν P-C ?).

QL can undergo both hydrolysis and oxidation. With traces of water, **QL** can undergo moisture catalyzed disproportionation to produce **TR** [diethyl methylphosphonite, $CH_3P(OEt)_2$] and **LT** [bis(2-diisopropylamino-ethyl) methylphosphonite, $CH_3P[OCH_2CH_2N(i\text{-}C_3H_7)_2]]$. Also, in the presence of moisture **YL** [ethyl hydrogen-methylphosphinate, CH_3 P=O(H)(OEt)] and/or **QA** [2-diisopropylaminoethyl hydrogenmethylphosphinate, $CH_3P{=}O(H)[OCH_2\ CH_2N(i\text{-}C_3H_7)_2]]$ might also be formed. The hydrolysis of **QL** with a weight excess of water results in the formation of **KB** (2-diisopropylaminoethanol), ethanol and methylphosphonous acid [$CH_3P\ (OH)_2$,

i.e. $CH_3P{=}O(H)(OH)$]. In the presence of sulfur a very toxic compound, **CV** [ethyl 2-diisopropylaminoethyl methylphosphonothionate, $CH_3P{=}S(OEt)[O\text{-}CH_2CH_2\text{-}N(i\text{-}C_3H_7)_2]$], may be formed[a].

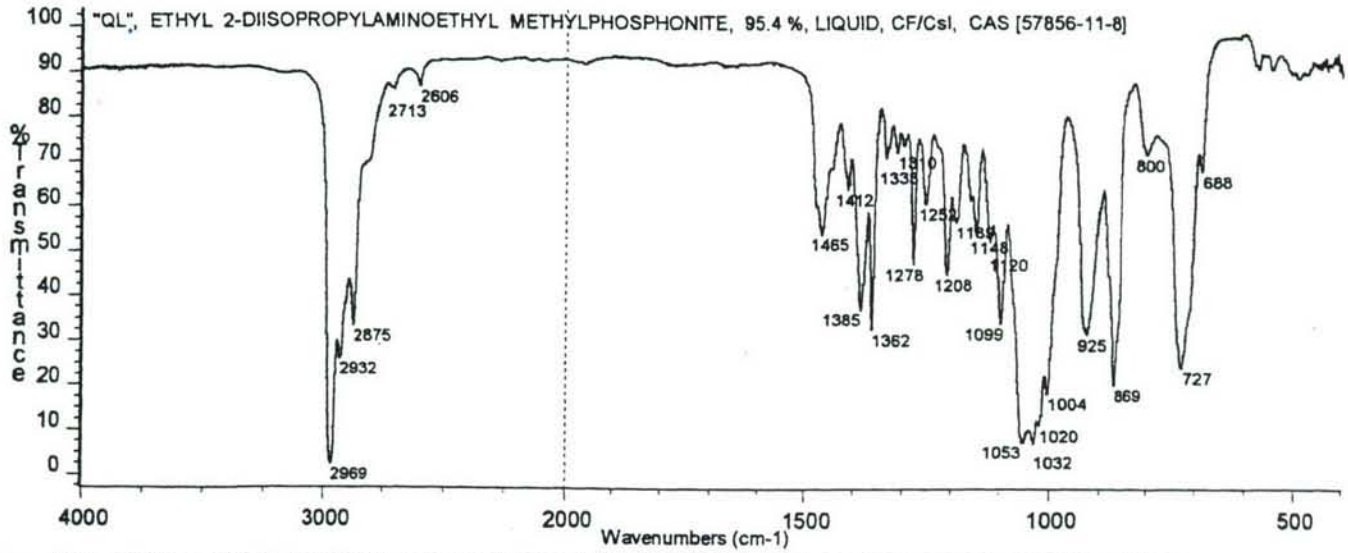


Figure 91A **ETHYL 2-DIISOPROPYLAMINOETHYL METHYLPHOSPHONITE (QL), 95.4%, LIQUID, CF/CsI**

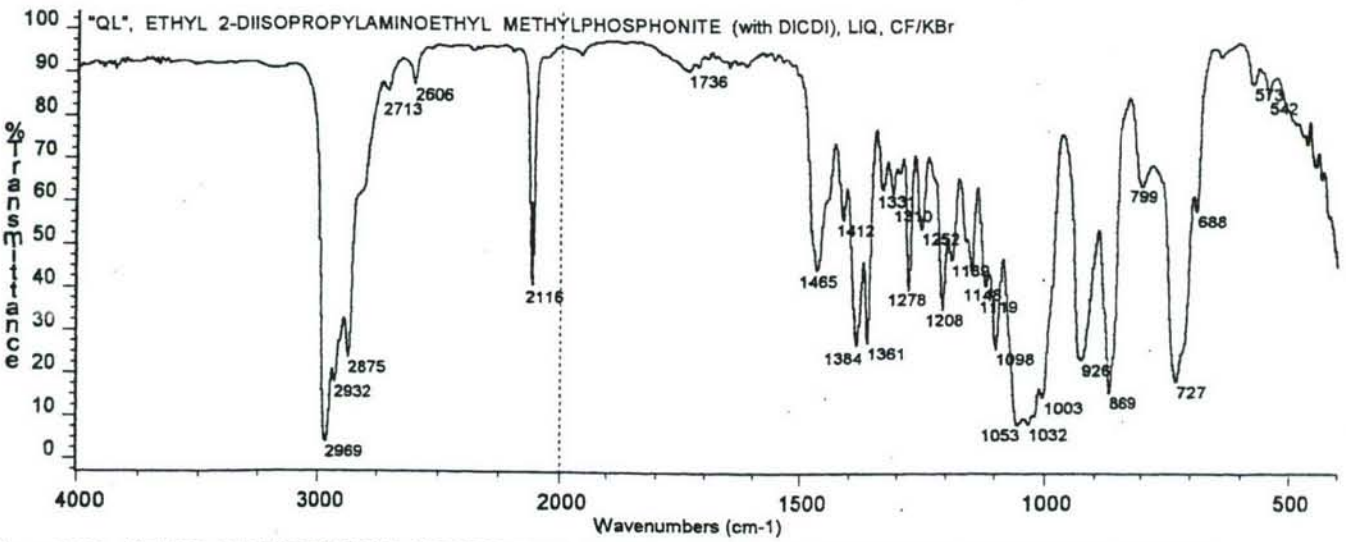


Figure 91B **ETHYL 2-DIISOPROPYLAMINOETHYL METHYLPHOSPHONITE (QL) WITH 1,3-DIISOPROPYL CARBODIIMIDE (DICDI), LIQUID, CF/KBr**

The effect of atmospheric moisture on **QL** is illustrated by the the infrared spectra reproduced in *Figures 92A* and *92B*. After one day of exposure to atmospheric moisture, the infrared spectrum for the liquid

[a] See the Chemical Research and Development Center (now Edgewood Research, Development and Engineering Center, U.S. Army Chemical and Biological Defense Command, i.e., CBDCOM, Aberdeen Proving Ground, MD 21010) MSDS on **QL**, dated 27 December 1985.

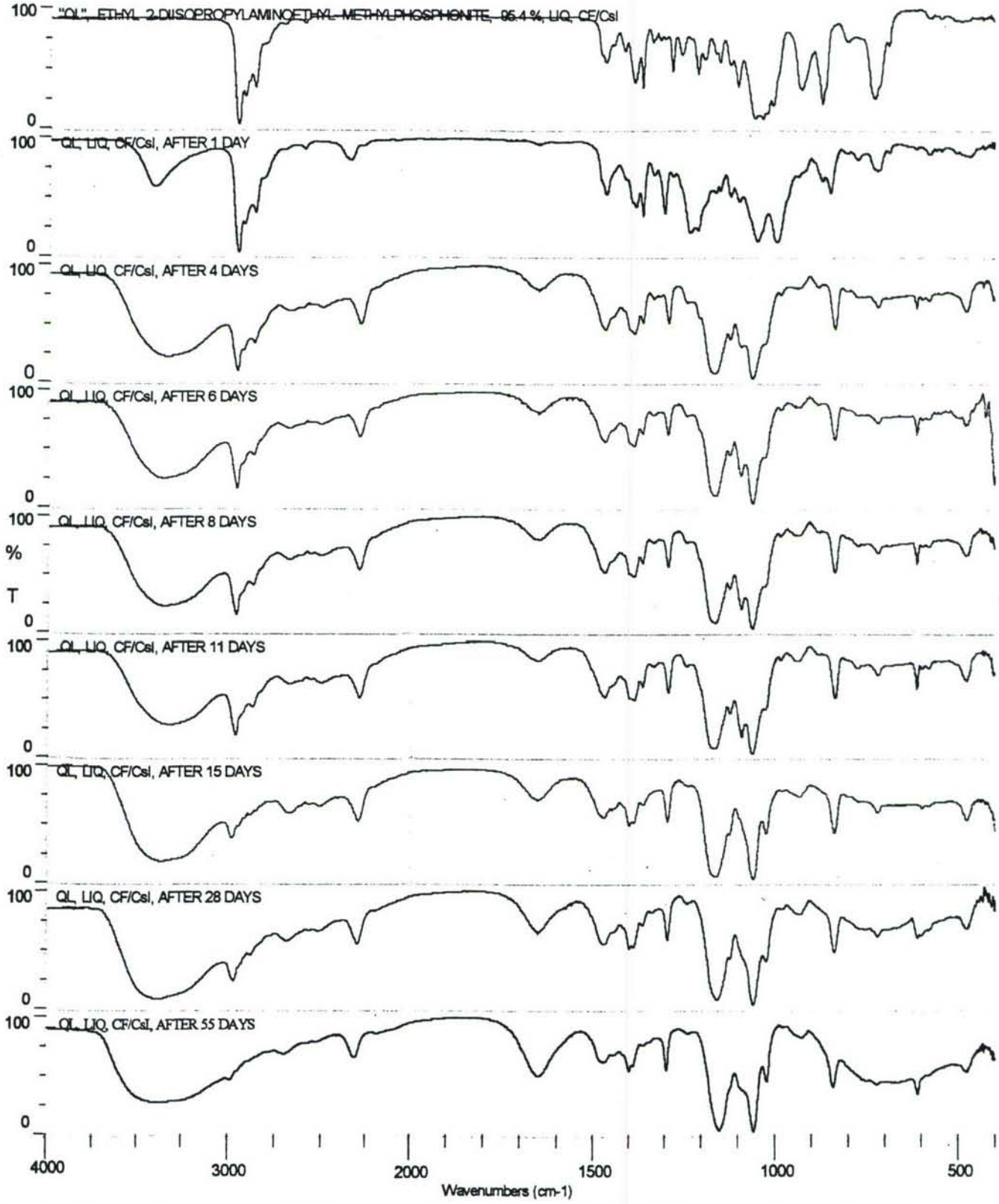


Figure 92 A ETHYL 2-DIISOPROPYLAMINOETHYL METHYLPHOSPHONITE (QL), LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

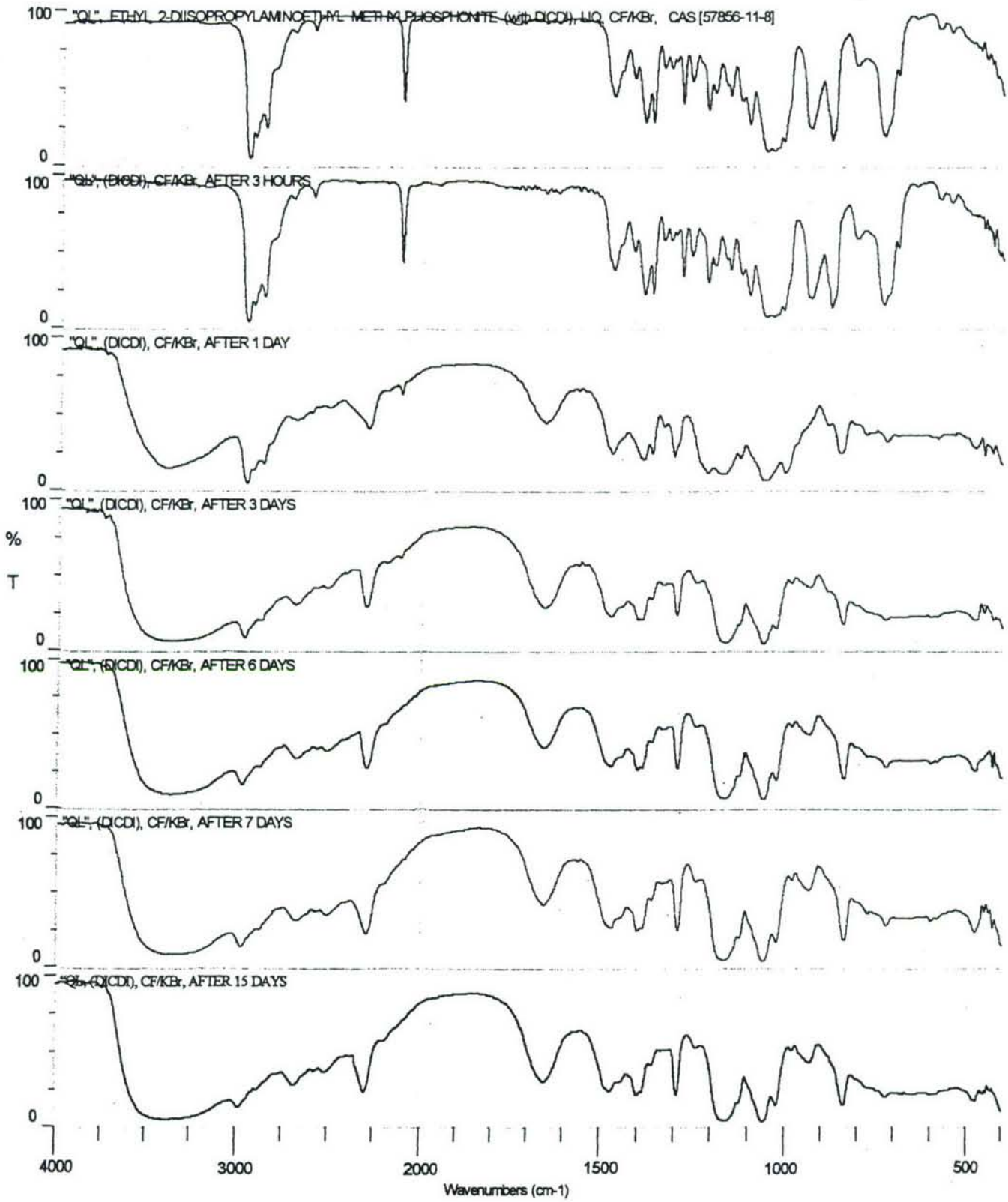


Figure 92B ETHYL 2-DIISOPROPYLAMINOETHYL METHYLPHOSPHONITE (QL), STABILIZED WITH DICI (1,3-DI-ISOPROPYLCARBODIIMIDE), LIQUID, CF/LKBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

film of **QL** shows a weak band at 2347 cm^{-1} which is assigned to a P-H stretching vibration. A new band also appears at 1230 cm^{-1} and is assigned to a P=O stretching vibration. The compounds **YL**, $CH_3P{=}O(H)(OEt)$, and **KB** $[HOCH_2CH_2N(iPr)_2]$ have been formed by hydrolysis of **QL** $[CH_3P(OEt)[OCH_2CH_2N(i\text{-}C_3H_7)_2]$ -HOH-> **YL** + **KB**]. However, after 4 days the infrared spectrum has dramatically changed. The P=O stretching band that was at 1230 cm^{-1} and the δ_{sy} P-CH_3 band at 1301 cm^{-1} (due to **YL**) are now gone from the spectrum. The ν P-H band has decreased in value to 2291 cm^{-1}, and new weak bands are present at 2681and 2509 cm^{-1}. Two strong bands are also present at 1163 and 1060 cm^{-1} and are believed to be attributable to the asymmetric and symmetric stretching vibrations of the PO_2^- anion. The two weak bands at 2681 and 2509 cm^{-1} are believed to be due to the NH^+ group. A band at 1289 cm^{-1} is assigned to the δ_{sy} P-CH_3. Weak bands occurring at 1090 and 612 cm^{-1} and are assigned to Cs_2SO_4 from the CsI windows. It is thought that the **YL** hydrolyzed to form the acid, $CH_3P{=}O(OH)(H)$, and together with the **KB** (from the hydrolysis) exists as the species $[CH_3P(O_2^-)H]$ $HO\text{-}CH_2\text{-}CH_2\text{-}NH^{\oplus}(i\text{-}C_3H_7)_2$. The hydrolysis may thus be summarized as follows:

$$\underset{\textbf{(QL)}}{CH_3P(OEt)(OCH_2CH_2N(i\text{-}C_3H_7)_2} \text{ -HOH-> } \underset{\textbf{(YL)}}{CH_3P{=}O(OEt)(H)} + \underset{\textbf{(KB)}}{HO\text{-}CH_2CH_2N(i\text{-}C_3H_7)_2}$$

$$\underset{\textbf{(YL)}}{CH_3P{=}O(OEt)(H)} \text{ -HOH-> } CH_3P{=}O(OH)(H) + \underset{\textbf{(KB)}}{HO\text{-}CH_2CH_2N(i\text{-}C_3H_7)_2} \rightarrow [CH_3P(O_2)H]^- \; HO\text{-}CH_2\text{-}CH_2\text{-}\underset{H}{N^{\oplus}}(i\text{-}C_3H_7)_2$$

As a demonstration of the above conclusion, a drop of methylphosphinic acid $[CH_3P{=}O(OH)(H)]$ was mixed with a drop of **KB,** placed between KBr windows, and infrared spectra determined. These spectra are reproduced in ***Figure 93***. The spectrum of the prepared mix shows bands at ca 3300 cm^{-1} (ν OH), 2680 and 2505 cm^{-1} (NH^+), 2290 cm^{-1} (ν P-H), 1290 cm^{-1} (δ_{sy} P-CH_3), 1162 and 1060 cm^{-1} (ν_{as} and ν_{sy} PO_2^- anion). The bands for the hydrolyzed **QL** and the prepared mix are comparable in value, the only differences being the bands in the **QL** spectrum due to Cs_2SO_4 (from the CsI windows) at 1090 and 612 cm^{-1}.

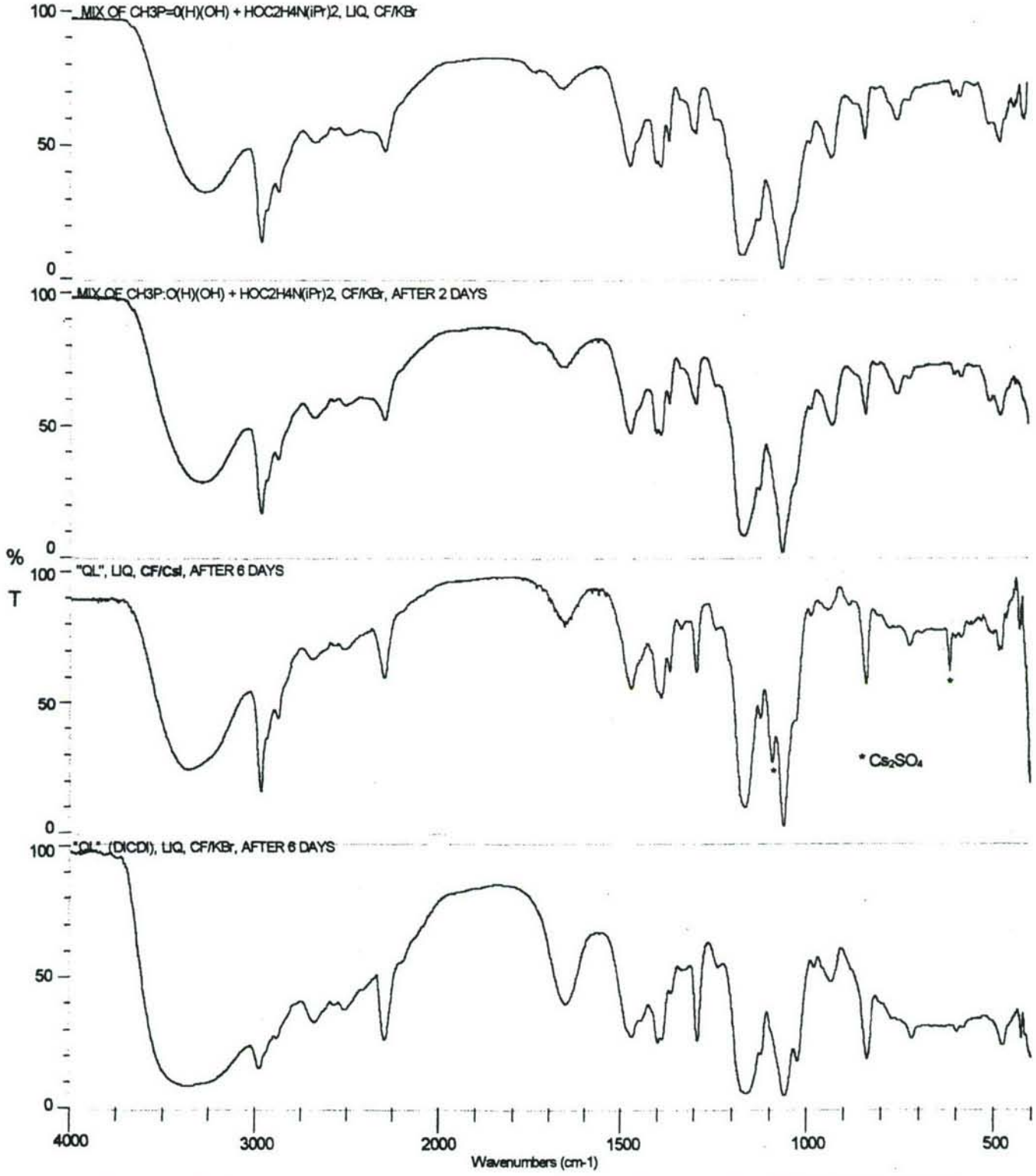


Figure 93 INFRARED SPECTRA FOR A MIX OF METHYLPHOSPHINIC ACID AND KB (2-DIISOPROPYLAMINO - ETHANOL), LIQUID, CF/KBr (FROM THE INITIAL MIXING TO AFTER 2 DAYS). THE BOTTOM 2 SPECTRA ARE FOR QL (AS FILMS BETWEEN CsI AND KBr WINDOWS) AFTER 6 DAYS, AND ARE PRESENTED FOR COMPARISON PURPOSES.

3.3.8 Bis(2-diisopropylaminoethyl) methylphosphonite (**LT**) $CH_3P[OCH_2CH_2N(i\text{-}C_3H_7)_2]_2$

The infrared spectrum for a liquid film of bis(2-diisopropylaminoethyl) methylphosphonite (**LT**) between KBr windows is given in ***Figure 94***. **LT** was mentioned in the previous section under **QL**, ethyl 2-diisopropylaminoethyl methylphosphonite, as one of the possible products formed (the other being **TR**, diethyl methylphosphonite) from the moisture catalyzed disproportionation of **QL** in the presence of traces of water.. The band assignments are as follows: 3174 cm^{-1} vvw (ν OH alcohol ?), 2966 cm^{-1} s (ν_{as} CH_3), 2933 cm^{-1} sh (ν_{as} CH_2), 2873 cm^{-1} ms (ν_{sy} CH_3), 2832 cm^{-1} w (ν_{sy} CH_2), 2712 cm^{-1} vw and 2605 cm^{-1} vw (these two bands seem to occur in this area when the -N(iPr)$_2$ group is present), 1465 cm^{-1} (δ_{as} CH_3 and δ CH_2), 1411 cm^{-1} vw (δ_{as} P-CH_3), 1380 cm^{-1} m and 1362 cm^{-1} ms (δ_{sy} CH_3 isopropyl, note: the 1380 cm^{-1} band may be due in part to ω OCH_2 ?), 1309 cm^{-1} vw (possible δ_{sy} P^{+5}-CH_3), 1277 cm^{-1} w (δ_{sy} P^{+3}-CH_3), ca 1225 cm^{-1} sh (possible ν P=O of **QA**, $CH_3P{=}O(H)[OCH_2CH_2N(iPr)_2]$, which has a calculated ν P=O of 1228 cm^{-1})[t] , 1208 cm^{-1} m (ν C-N ?), 1148 cm^{-1} w and 1120 cm^{-1} w (isopropyl skeletal ?), 1032 cm^{-1} and 1001 cm^{-1} ms (ν P-O-C), 895 cm^{-1} w and 869 cm^{-1} m (CH_3 rock of isopropyl and P-CH_3 moieties), 799 cm^{-1} w (POC), 725 cm^{-1} m (POC, ν P-C of P-CH_3 ?).

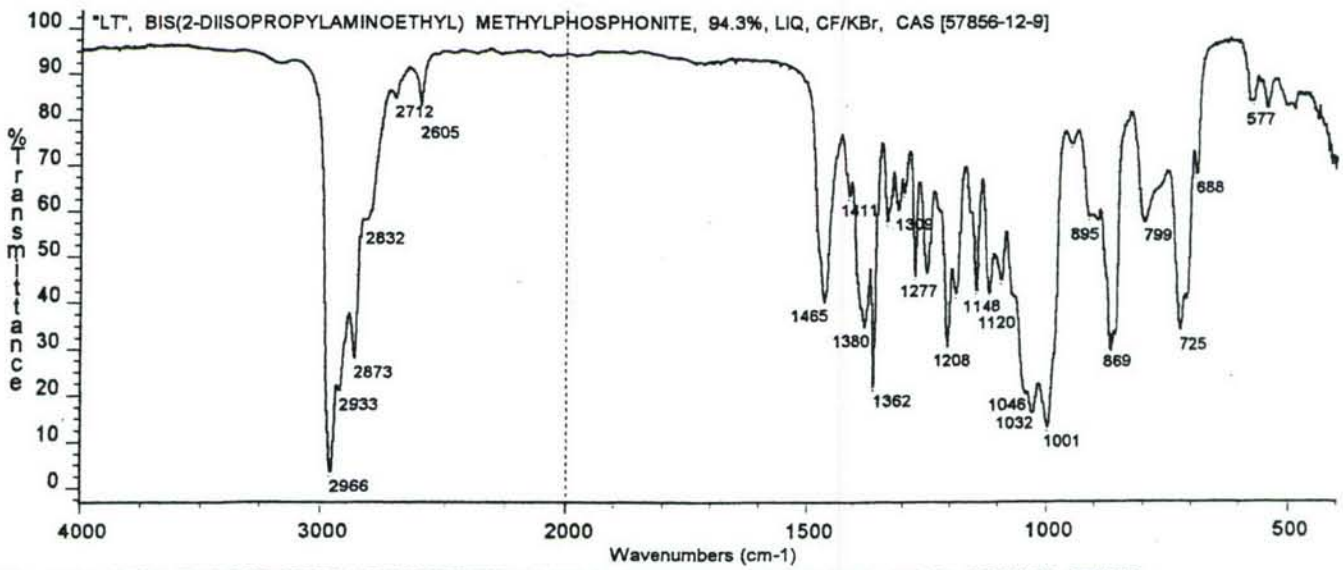


Figure 94 BIS(2-DIISOPROPYLAMINOETHYL) METHYLPHOSPHONITE (LT), 94.3%, LIQUID, CF/KBr

[t] For the calculation of the P=O stretching frequency see Thomas L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", Chapter 2, Heyden & Son Ltd., London, 1974.

The infrared spectra showing the effect of atmospheric moisture on a liquid film of bis(2-diisopropy-aminoethyl) methylphosphonite (**LT**) over a period of forty days is given in ***Figures 95A*** and ***95B***. By the 4th day of exposure to atmospheric moisture the infrared spectrum shows a weak band at 2356 cm^{-1} assignable to a P-H stretch, and a strong band at 1231 cm^{-1} assignable to a P=O stretching vibration. Bands also appear at 1300 cm^{-1} (δ_{sy} P-CH_3), 1045 cm^{-1} (ν P-O-C) and 988 cm^{-1} (P-H deformation). These *new* bands are due to the formation of **QA**, $CH_3P{=}O(H)[OCH_2CH_2N(i\text{-}C_3H_7)_2]$, 2-diisopropylaminoethyl methylphosphinate (see section on phosphinates), as a result of the hydrolysis of **LT**. A new band was also indicated near 2276 cm^{-1}. This band became increasingly stronger while the band at 2356 cm^{-1} became less intense as time passed. The phosphoryl stretching band near 1231 cm^{-1} began to decrease in intensity and was gradually replaced by two strong bands near 1170 and 1060 cm^{-1}. Other bands near 2665 and 2500 cm^{-1} were also formed and can be assigned to NH^+. The P-CH_3 moiety is still present as indicated by the band near 1290 cm^{-1}. The product of hydrolysis of **LT** after 40 days looks quite similar to that formed from the hydrolysis of **QA,** which will be discussed later. Thus the hydrolysis of **LT** may be represented as follows:

$CH_3P[OCH_2CH_2N(i\text{-}C_3H_7)_2]_2$ $\xrightarrow{-H_2O}$ $CH_3P{=}O(H)[OCH_2CH_2N(i\text{-}C_3H_7)_2]$ + **KB**

(**LT**) (**QA**)

$\xrightarrow{-H_2O}$ $CH_3P{=}O(H)(OH)$ + HO-CH2CH2N(i-C_3H_7)$_2$ $\rightarrow$ $[CH_3P(O_2^-)H]$ $HO\text{-}CH_2CH_2NH^+(i\text{-}C_3H_7)_2$.

(methylphosphinic acid) (**KB**)

3.3.9 Methyl pinacolyl methylphosphonite $CH_3\text{-}P(OCH_3)[O\text{-}HC(CH_3)\text{-}C(CH_3)_3]$

The infrared spectrum of methyl pinacolyl methylphosphonite (methyl 1,2,2-trimethylpropyl methyl-phosphonite) as a liquid film between KBr windows is given in ***Figure 96***. The band assignments are as follows: 2974 cm^{-1} s, 2960 cm^{-1} sh, 2909 and 2871 cm^{-1} m, 2829 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 2341 cm^{-1} vvw (ν P-H, impur-ity, hydrolysis product), 1480 and 1457 cm^{-1} w (δ_{as} CH_3), 1413 cm^{-1} vw (δ_{as} P-CH_3), 1394 cm^{-1} w, 1375 cm^{-1} m [δ_{sy} CH_3 from $C(CH_3)_3$], 1364 cm^{-1} m (δ_{sy} CH_3C), 1346 cm^{-1} vw (δ -C-H), 1300 cm^{-1} vw (possible δ_{sy} P^{+5}-CH_3 hydrolysis product), 1279 cm^{-1} w (δ_{sy} P^{+3}-CH_3), 1240 cm^{-1} vw [possible ν P=O of $CH_3P{=}O(OMe)(OPinacolyl)$, which would have a calculated value of 1240 cm^{-1}], 1226 cm^{-1} vvw [possible ν P=O of $CH_3P{=}O(H)(OPinacolyl)$,

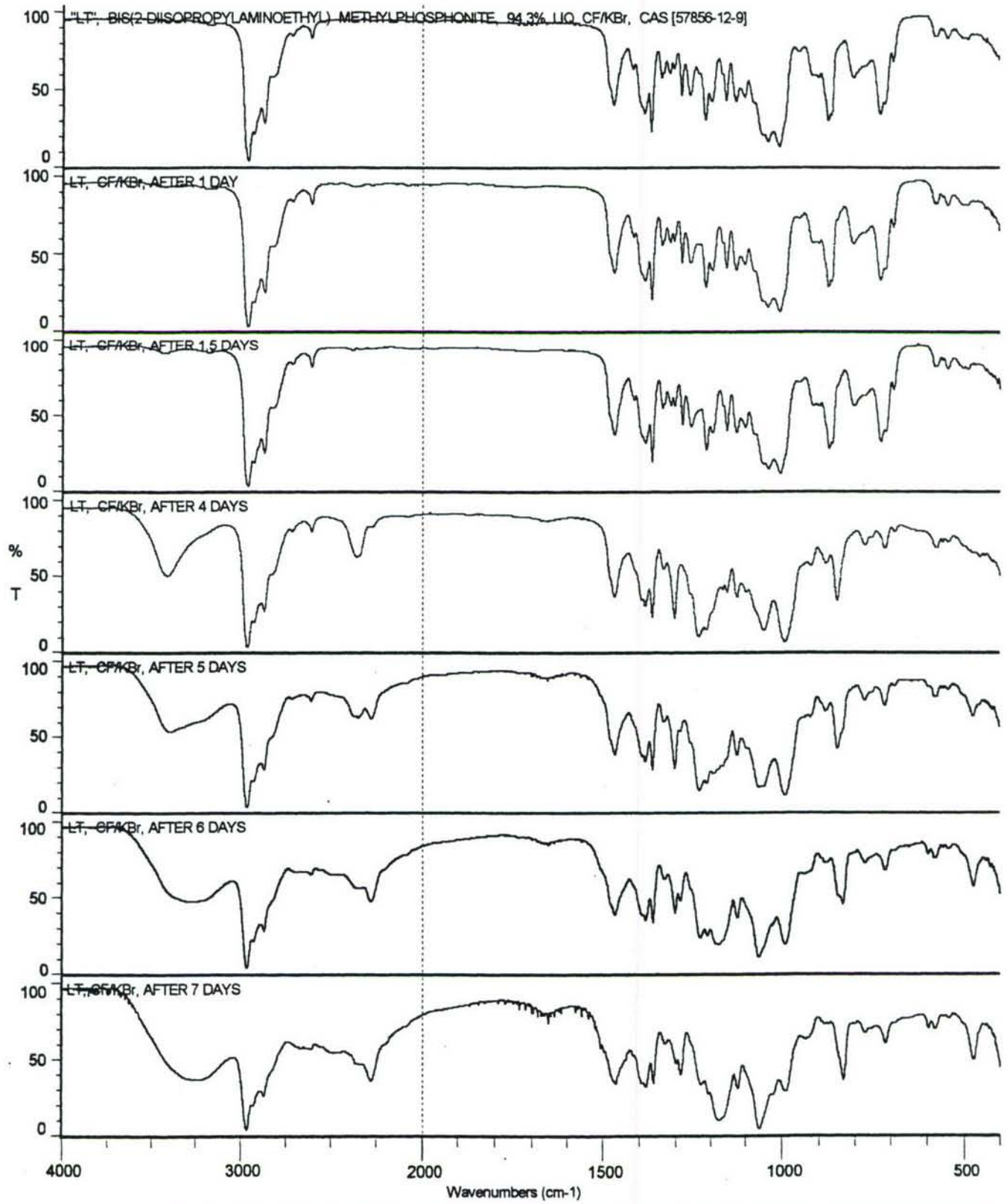


Figure 95A BIS(2-DIISOPROPYLAMINOETHYL) METHYLPHOSPHONITE (LT), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

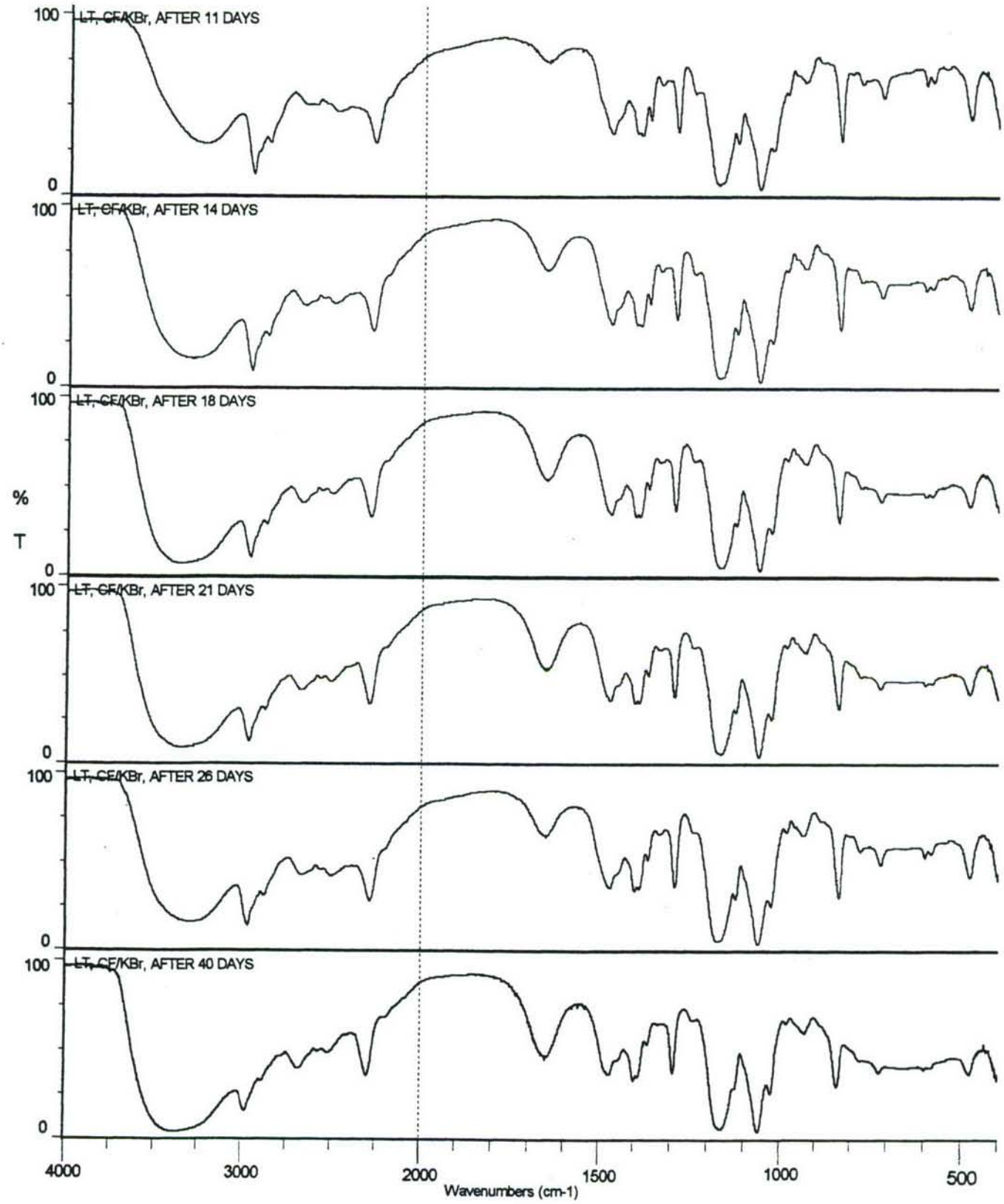


Figure 95B BIS(2-DIISOPROPYLAMINOETHYL) METHYLPHOSPHONITE (LT), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

which would have a calculated value of 1224 cm^{-1}], 1209 cm^{-1} vw [possible skeletal vibration of $C(CH_3)_3$?], 1180 cm^{-1} vw (CH_3 rock of $POCH_3$, characteristic), 1113 cm^{-1} w and 1081 cm^{-1} s (pinacolyl moiety), 1057 cm^{-1} sh, 1047 cm^{-1} ms, 1027 cm^{-1} ms and 1008 cm^{-1} s (ν P-O-C), 944 cm^{-1} s and 930 cm^{-1} ms (pinacolyl moiety), 870 cm^{-1} ms (P-CH_3 rock), 769 cm^{-1} m (POC), 720 cm^{-1} m and 707 cm^{-1} sh (pinacolyl moiety), 684 cm^{-1} w (ν P-C).

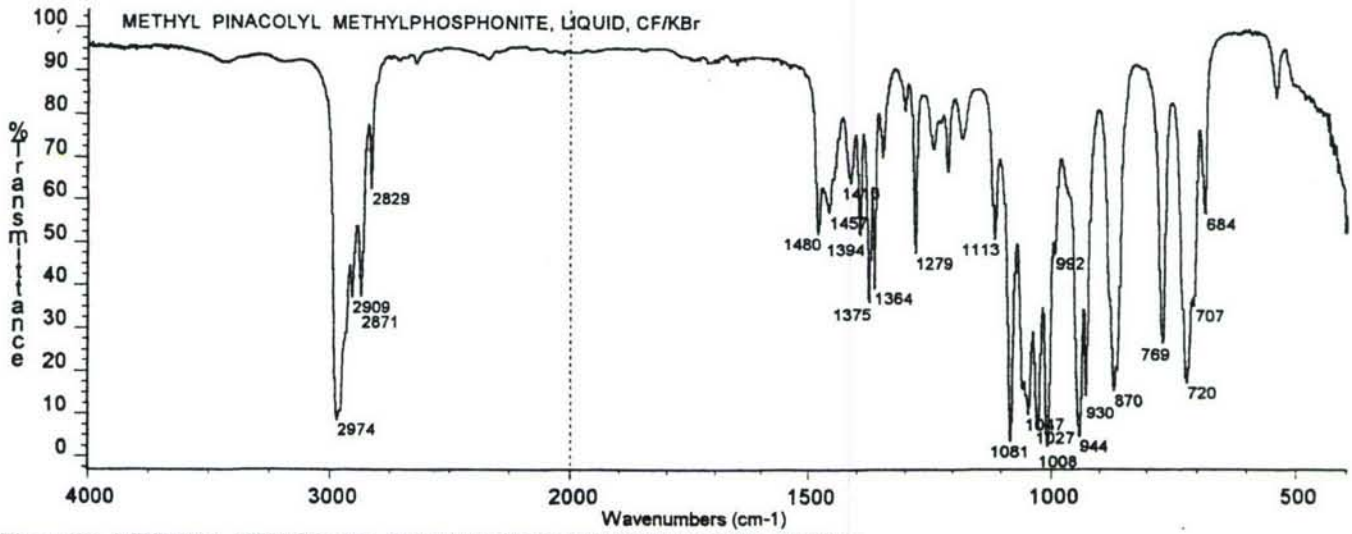


Figure 96 METHYL PINACOLYL METHYLPHOSPHONITE, LIQUID, CF/KBr

The effect of atmospheric moisture on the thin film of methyl pinacolyl methylphosphonite is illustrated by the infrared spectra reproduced in ***Figure 97***. After 2 days of exposure to atmospheric moisture the infrared spectrum shows a weak band at 2350 cm^{-1} assignable to a P-H stretching vibration. A strong band at 1232 cm^{-1} is due to a phosphoryl stretch, while the band at 1302 is assigned to the δ_{sy} of a P^{+5}-CH_3 group. The $POCH_3$ group is gone as indicated by the lack of bands at 2829 and 1180 cm^{-1}. The original compound apparently has hydrolyzed to pinacolyl hydrogenmethylposphinate, $CH_3P{=}O(H)[O\text{-}HC(CH_3)\text{-}C(CH_3)_3]$, which would have a calculated P=O stretch of 1224 cm^{-1}. The spectrum after 3 days is essentially the same as that for 2 days except for the presence of more water near 3475 and 1650 cm^{-1}.

3.4 Phosphinites

3.4.1 Methyl di-*n*-butylphosphinite $(n\text{-}C_4H_9)_2$ P-OCH_3

The infrared spectrum for a liquid film of methyl di-*n*-butylphosphinite between KBr windows is

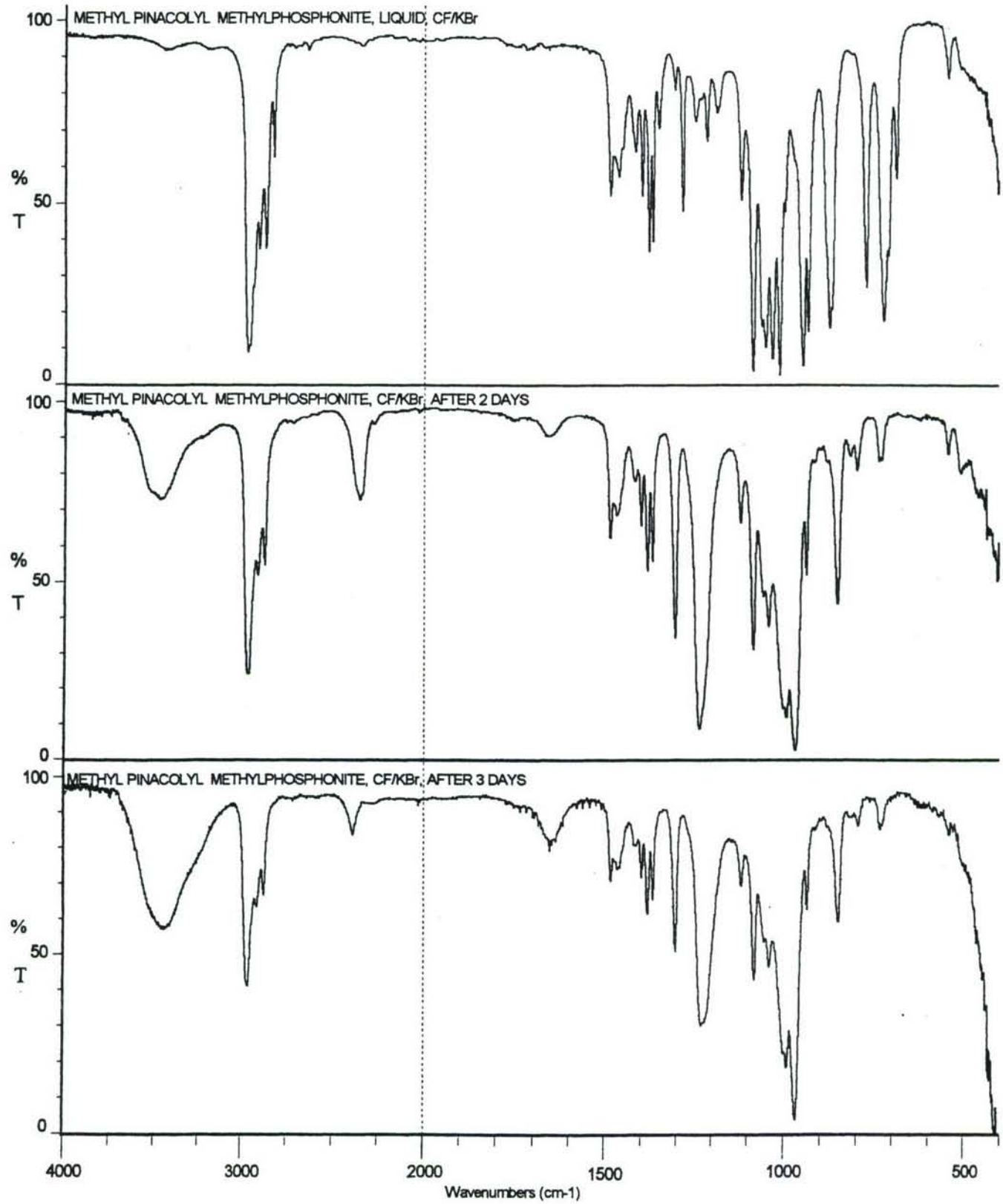


Figure 97 METHYL PINACOLYL METHYLPHOSPHONITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

given in ***Figure 98***. The band assignments are as follows: 2958 cm^{-1} s (ν_{as} CH_3), 2928 cm^{-1} s (ν_{as} CH_2), 2873 cm^{-1} ms (ν_{sy} CH_3), 2860 cm^{-1} sh (ν_{sy} CH_2), 2824 cm^{-1} m (ν OCH_3), 1465 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1405 cm^{-1} vw (δ P-CH_2), 1378 cm^{-1} w (δ_{sy} CH_3), 1297 and 1235 cm^{-1} vw (ω, τ CH_2 ?), 1179 cm^{-1} w (CH_3 rock of $POCH_3$, characteristic), 1059 and 1034 cm^{-1} ms (ν P-O-C), 785 cm^{-1} w (POC), 726 cm^{-1} m (CH_2 rock, ν P-C ?), 682 cm^{-1} w (ν P-C).

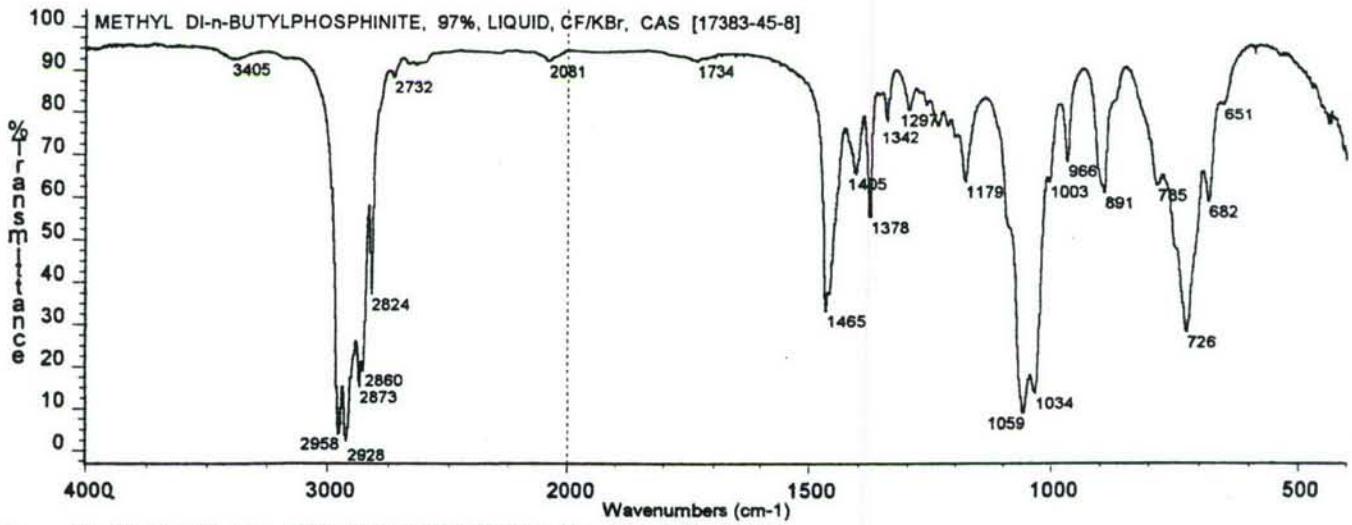


Figure 98 METHYL DI-*n*-BUTYLPHOSPHINITE, 97%, LIQUID, CF/KBr

The effect of atmospheric moisture on a liquid film of methyl di-*n*-butylphosphinite is illustrated by the infrared spectra reproduced in ***Figures 99A*** and ***99B***. After 4 hours of exposure the infrared spectrum shows a new band near 2305 cm^{-1} assignable to a P-H stretching vibration. A new band also occurs near 1201 cm^{-1} that may be due to a P=O stretch. The compound dibutylphosphine oxide, $(H_9C_4)_2P{=}O(H)$, should be forming from the hydrolysis of the original phosphinite. Dibutylphosphine oxide would have a calculated P=O stretch of 1190 cm^{-1}. As time progresses a band near 1231 cm^{-1} becomes quite prominent in the spectrum. This band at 1231 cm^{-1} is not close to the calculated value of the P=O stretch (1206 cm^{-1}) of compound $(H_9C_4)_2P{=}O(OCH_3)$, which would have formed if the original compound had been oxidized. If a pyro compound had formed, such as $(H_9C_4)_2PO\text{-}O\text{-}PO(C_4H_9)_2$, it would have a calculated P=O stretch of 1222 cm^{-1}. As time progresses a somewhat broad band appears near 1170 cm^{-1}, which could be due to the P=O stretch from the P-acid, $(H_9C_4)_2P{=}O(OH)$, and would result from the hydrolysis of $(H_9C_4)_2P{=}O(OCH_3)$ if the original phosphinite had first been oxidized.

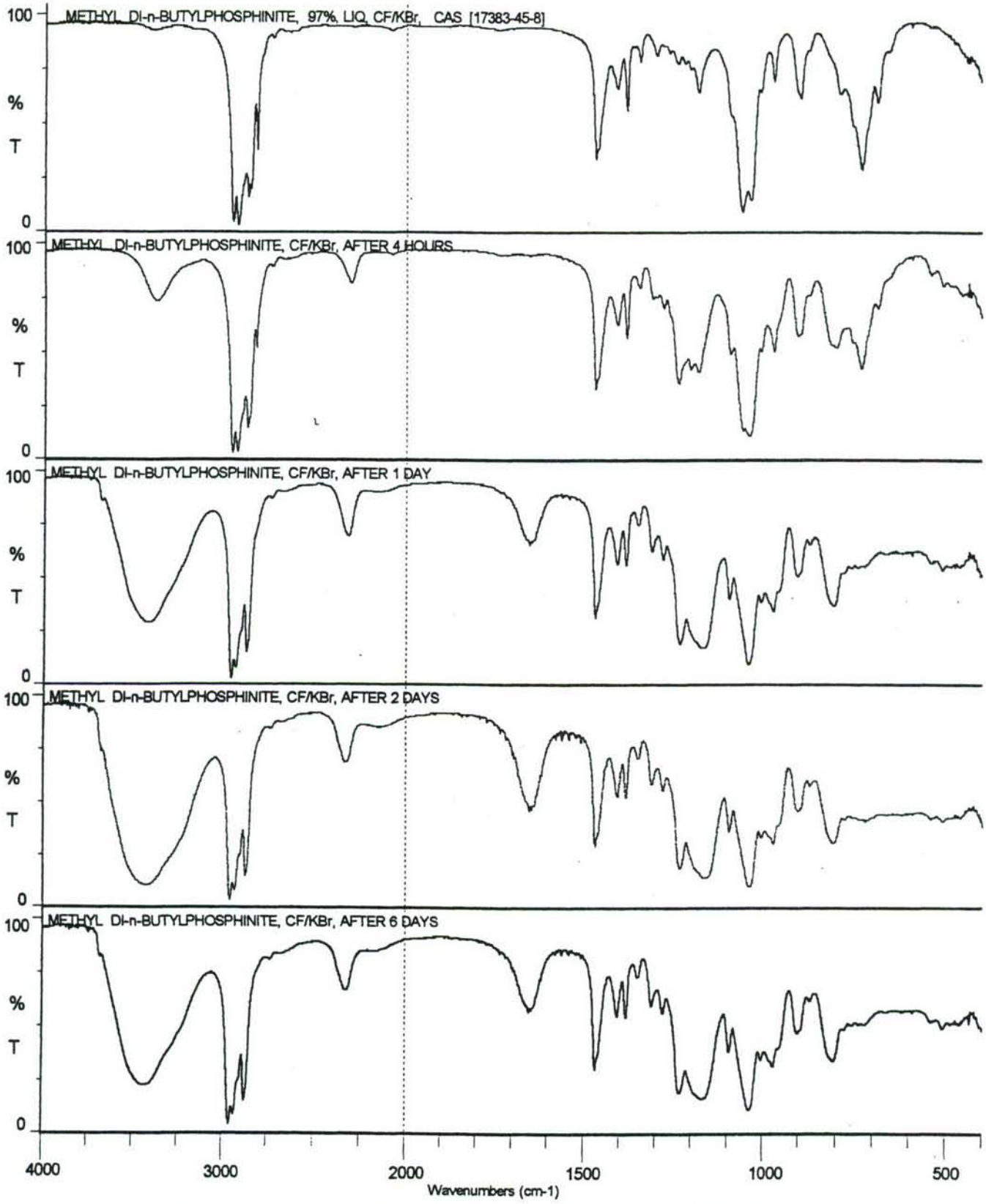


Figure 99A METHYL DI-*n*-BUTYLPHOSPHINITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

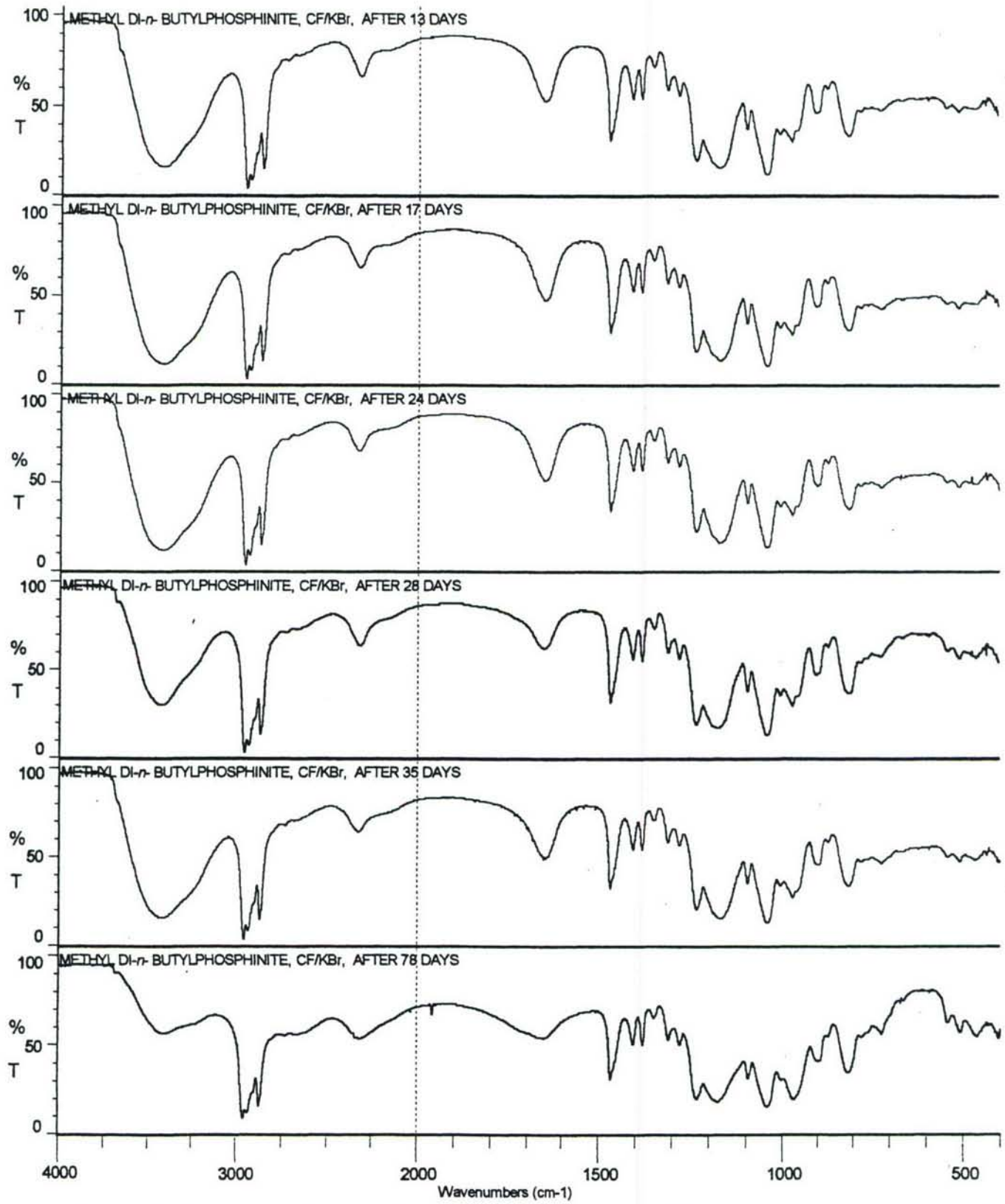


Figure 99B METHYL DI-*n*-BUTYLPHOSPHINITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

Broad bands do occur near 2670 and 2300 cm^{-1} and are quite evident in the 78th day spectrum (***Figure 99B***). These bands may be assigned to the POH moiety. It appears the resultant spectra are a mixture of products from the hydrolysis and oxidation of the original phosphinite as follows:

$(H_9C_4)_2P\text{-}OCH_3$ $\text{-HOH}\rightarrow$ $(H_9C_4)_2P{=}O(H)$ + CH_3OH

$(H_9C_4)_2P\text{-}OCH_3$ $\text{-[O]}\rightarrow$ $(H_9C_4)_2P{=}O(OCH_3)$ $\text{-HOH}\rightarrow$ $(H_9C_4)_2P{=}O(OH)$ + CH_3OH .

3.4.2 Methyl di-*tert*-butylphosphinite $[(CH_3)_3C]_2P\text{-}OCH_3$

The infrared spectrum of methyl di-*tert*-butylphosphinite as a liquid film between KBr windows is given in ***Figure 100***. The band assignments are as follows: 3412 cm^{-1} vw (H_2O), 3199 cm^{-1} vvw (ν OH alcohol ?), 2966 cm^{-1} sh and 2942 cm^{-1} ms (ν_{as} CH_3), 2898 and 2863 cm^{-1} m (ν_{sy} CH_3), 2826 cm^{-1} m (ν OCH_3), 1472 cm^{-1} m (δ_{as} CH_3), 1385 cm^{-1} w and 1363 cm^{-1} m (δ_{sy} CH_3), 1232 cm^{-1} w and 1197 cm^{-1} m (*t*-butyl skeletal), 1176 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1053 cm^{-1} s (ν P-O-C), 1010 cm^{-1} m (*t*-butyl), 936 cm^{-1} m (CH_3 rock of *t*-butyl), 807 cm^{-1} m (POC), 722 cm^{-1} ms and 672 cm^{-1} w (ν P-C).

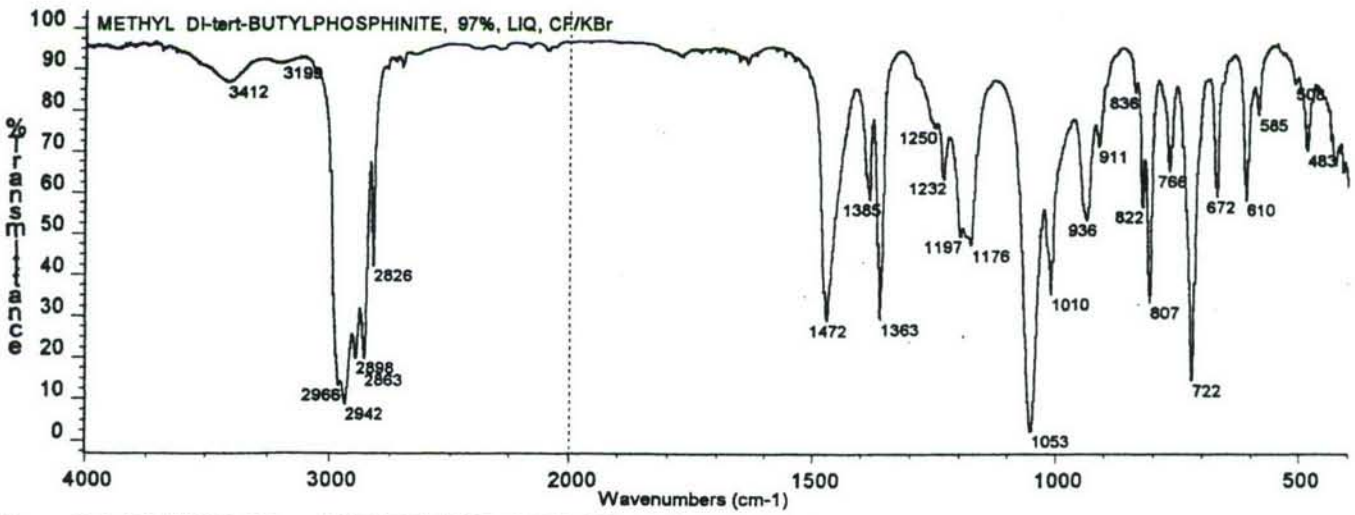


Figure 100 METHYL DI-*tert*-BUTYLPHOSPHINITE, 97%, LIQUID, CF/KBr

The effect of atmospheric moisture on the liquid film of methyl di-*tert*-butylphosphinite is illustrated by the infrared spectra given in ***Figures 101A*** and ***101B***. After 18 hours of exposure, the infrared spectrum shows a very weak band near 2287 cm^{-1} assignable to a P-H stretching vibration. A shoulder near 1195 cm^{-1} can

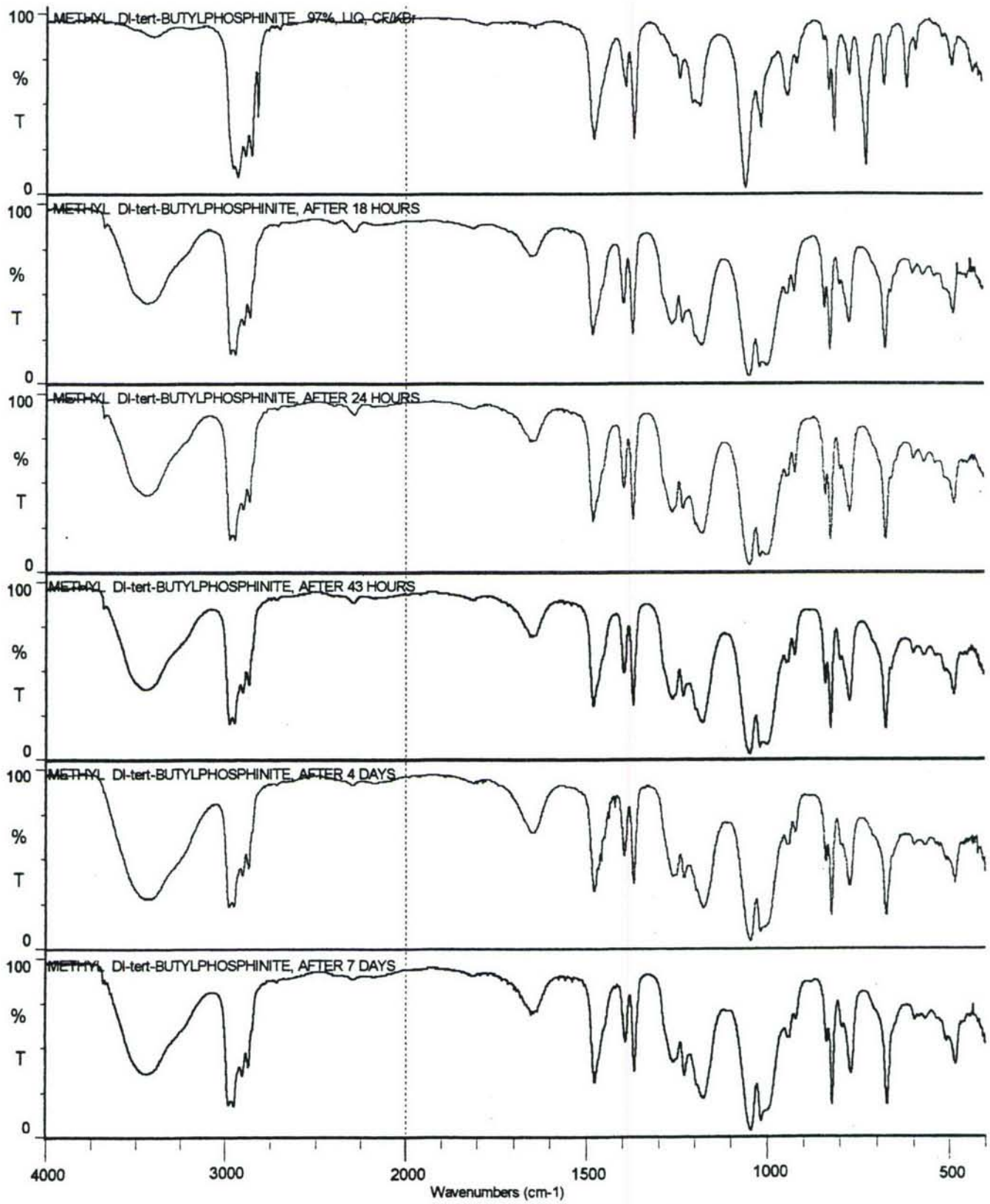


Figure 101A METHYL DI-*tert*-BUTYLPHOSPHINITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

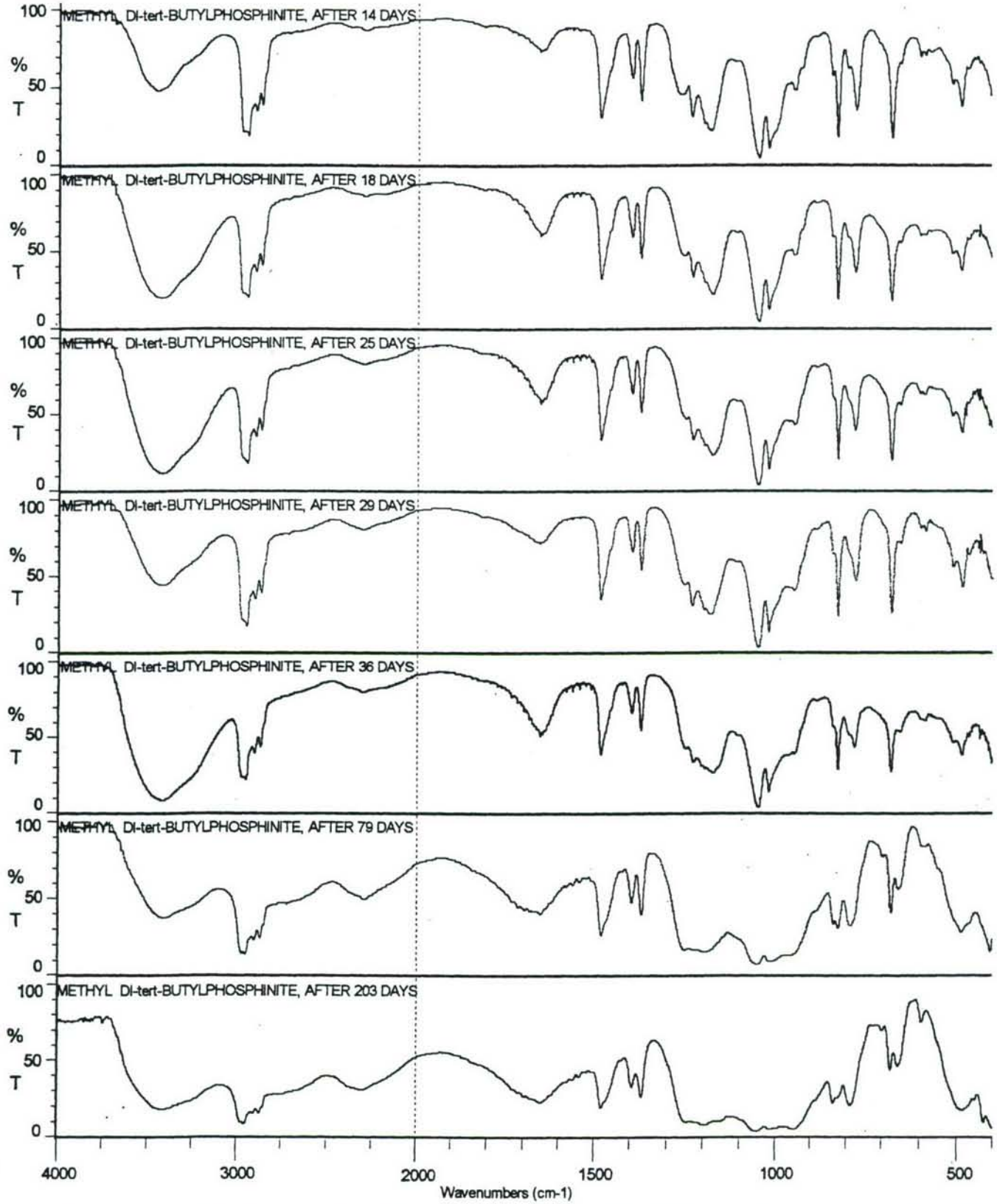


Figure 101B METHYL DI-*tert*-BUTYLPHOSPHINITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

be assigned to P=O stretching. The compound, di-*tert*-butylphosphine oxide, $[(CH_3)_3C]_2P{=}O(H)$, may be forming. This compound would have a calculated P=O stretch of 1198 cm^{-1}. Bands near 1259 and 1228 cm^{-1} may be due to the *t*-butyl moiety. An ill-defined shoulder, that may be due to the formation of methyl di-*tert*-butylphosphinate, $[(CH_3)_3C]_2P{=}O(OCH_3)$, appears near 1217 cm^{-1}. This compound would have a calculated P=O stretch near 1214 cm^{-1}. As time progresses, the P-H band near 2287 cm^{-1} decreases in intensity, and the band becomes more diffuse and broad. This band together with bands forming near 2700 cm^{-1} (see 79th day, ***Figure 101B***) and 1650 cm^{-1} can be assigned to POH bands. A compound such as di-*tert*-butylphosphinic acid, $[(CH_3)_3C]_2P{=}O(OH)$, may be forming. Thus, two effects seem to be occurring; hydrolysis and oxidation followed by hydrolysis.

$[(CH_3)_3C]_2P\text{-}OCH_3$ $\text{-HOH}\rightarrow$ $[(CH_3)_3C]_2P{=}O(H)$

$[(CH_3)_3C]_2P\text{-}OCH_3$ $\text{-[O]}\rightarrow$ $[(CH_3)_3C]_2P{=}O(OCH_3)$ $\text{-HOH}\rightarrow$ $[(CH_3)_3C]_2P{=}O(OH)$

3.4.3 Butyl diphenylphosphinite $(C_6H_5)_2P\text{-}C_4H_9$

The infrared spectrum for a liquid film of butyl diphenylphosphinite between KBr windows is given in ***Figure 102***. The band assignments are as follows: 3417 cm^{-1} vw (H_2O, 3070 and 3054 cm^{-1} w and 3002 cm^{-1} vw (ν C-H aromatic), 2957 cm^{-1} ms (ν_{as} CH_3), 2932 cm^{-1} ms (ν_{as} CH_2), ca 2905 cm^{-1} sh vvw (ν_{sy} CH_3), 2871 cm^{-1} m

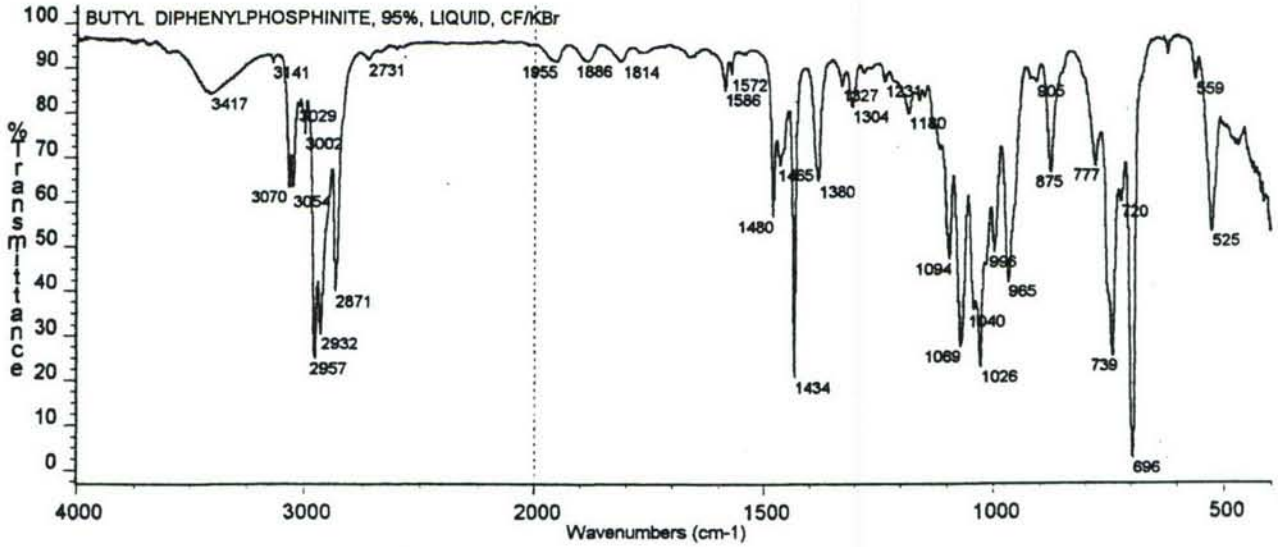


Figure 102 BUTYL DIPHENYLPHOSPHINITE, 95%, LIQUID, CF/KBr

(ν_{sy} CH_2), 1568 cm^{-1} vw, 1572 cm^{-1} vvw, 1480 cm^{-1} w, 1434 cm^{-1} ms (aromatic ring), 1465 cm^{-1} vw (δ CH_2, δ_{as} CH_3), 1380 cm^{-1} w (ω OCH_2, δ_{sy} CH_3), 1094 cm^{-1} m (phenyl-P), 1069 and 1026 cm^{-1} ms (ν P-O-C), 965 cm^{-1} m (ν C-C of POC_4H_9), 739 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 696 cm^{-1} s (mono-substituted aromatic ring deformation).

3.5 Phosphoryl (P=O) Containing Compounds

3.5.1 Phosphoryl Stretching Frequency

The phosphoryl stretching frequency varies as a result of the chemical nature of the various substituents on the phosphorus atom. These variations have been attributed to the effects of the electronegativities of the substituents.[u] Thus, the inductive effect of the substituents on the phosphorus atom is considered to be the predominant effect in determining the phosphoryl frequency. A straight-line relationship has been derived by Bell et al.[v] for a plot of phosphoryl stretching frequency versus the summed electronegativities of the substituents on the phosphorus atom. Thomas and Chittenden[w] also derived an expression, ν**P=O = 930 + 40**$\Sigma\pi$, relating the phosphoryl stretching frequency to what they named phosphorus inductive (**PI**) constants (denoted by the symbol π). These π constants were a measure of the inductive effect of the groups attached to the phosphorus atom, and are empirical values that were chosen to give the best possible fit for the most compounds. Thus, the equation may be used to obtain an appoximation or prediction of the P=O stretching frequency for a given compound. For the majority of organophosphorus compounds examined, the calculated phosphoryl frequencies were found to be within ± 12 cm^{-1} of the observed values. Table 1 lists the phosphorus inductive constants for various substituent groups as given by Thomas[1].

---

[u] Daasch, L.W. and Smith, D.C., *Anal. Chem.* **23**, 853 (1951).
Gore, R.C., *Discussions Faraday Soc.* **9**, 138 (1950).
Christol, C. and Christol, H.J., *J. Chem. Phys.* **62**, 246 (1965)

[v] Bell, J.V., Heisler, J., Tannenbaum, H. and Goldenson, J., *J. Amer. Chem. Soc.* **76**, 5185 (1954).

[w] Thomas, L.C. and Chittenden, R.A., *Spectrochim. Acta.* **20**, 467 (1964).

TABLE 1

PHOSPHORUS INDUCTIVE CONSTANTS FOR SUBSTITUENT GROUPS

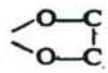
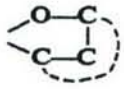
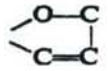
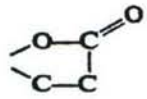
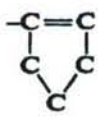
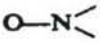
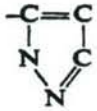
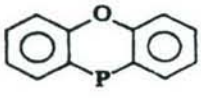
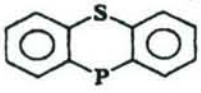
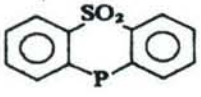
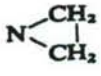
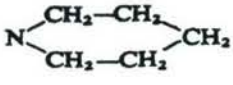
Group	π	*Group*	π
CH_3	2·1	OCH_3	2·9
CH_2	2·0	OCH_2	2·85
CH	1·8	OCH	2·75
C	2·1	$OCH_2C_6H_5$	2·7
–C═C (α or β)	2·4	OCH_2CH_2Cl	3·0
–C═O (α or β)	2·5	OC═C	3·1
–C═O γ or greater	2·35	OC_6H_5	3·0
$C(O)NR_2$ (β)	2·2	OC_6H_4X	3·1
CR_2Cl	2·7	OC(O)–	3·4
$CRCl_2$	2·9	$-O-P^{V}$	3·3
CCl_3	3·0	$-O-P^{III}$	2·9
CR_2Br	2·55		6·0
CF_3	3·6		
CF_2R	3·0		6·2
$CH(OR)_2$	2·1		
$C_6H_{5-n}X_n$	2·4		5·5
C_6F_5	2·5		
	2·5		4·9
	2·2		5·9
$C-P^{V}$	2·4		
	2·9		4·4
			3·2
	2·0	$O-SiR_3$	3·0
		NH_2	1·85
		NHR	2·0
C═NOH	2·6	$NHSiR_3$	2·0

TABLE 1 (continued)

Group	π	*Group*	π
C≡CR	2·7	$NHCOCCl_3$	2·8
C≡N	3·5	NHCHO	2·7
	5·2	NHP^{V}	2·1
		NHCOOR	2·4
	4·5	NHCON	1·9
		NR_2	2·4
		$NRSO_2R$	2·8
	4·0	$N(NR_2)(SiR_3)$	3·0
		NCl_2	3·3
	2·6	N=C=S	3·3
		N=C=O	3·6
N=CHOR	2·3	$SCCl_3$	2·8
N=CRNR	2·7		4·5
$N=P^{V}$	2·6		
	2·2	ScR	2·4
		SiR_3	2·4
	1·7	Br_3	8·2
		Br_2	5·5
		Br	3·1
	3·1	Cl_3	9·0
		Cl_2	6·3
N_3	3·0	Cl	3·4
$-P^{V}$	1·5	F_3	12·0
$-P^{\oplus}$	3·5	F_2	8·0
S-Alkyl	2·4	F	3·9
S-Aryl	2·5	H	2·5
SP^{V}	2·9		

3.5.2 P-OH Frequencies

No PI constants (π) are given for OH groups by Thomas[1] due to the unpredictable magnitude of the effect of hydrogen bonding on the phosphoryl stretching band. However, Thomas[1] has derived a similar expression that relates the variation of the P-O(H) stretching vibration to the sum of the phosphorus inductive constants of the *other* substituents attached to the phosphorus atom. Thus, the P-O(H) frequency may be given by ν**P-O(H) = 650 + 40**$\sum\pi$. Here the values for the atom doubly bonded to the phosphorus atom, **O** and **S**, are the Pauling electronegativity values, 3.5 and 2.5 respectively. According to Thomas[1] the P-O(H) bond absorbs in the 1040-909 cm^{-1} region. The agreement between the observed and calculated frequencies for the P-O(H) group is not as good as that obtained for the phosphoryl group, varying in the order of 15-25 cm^{-1}. This relationship does not apply to compounds having two OH groups on the phosphorus atom. These acids have two bands in the regions of 1030-972 cm^{-1} and 950-917 cm^{-1}, which may be assigned to the asymmetric and symmetric vibrations of the P-O(H) group[1]. The phosphorus acids, containing one and two OH groups, have very broad infrared bands near 2725-2525, 2350-2080, and 1740-1600 cm^{-1}. In acids with two OH groups per phosphorus, the 1740-1600 cm^{-1} band when present, is weaker than the bands in the of 2725-2525 and 2350-2080 cm^{-1} regions[1]. In the case of one OH group per phosphorus, the 1740-1600 cm^{-1} region band is the strongest of the three.[1]

3.5.3 **Phosphoric Acids** $HO\text{-}P{=}O(OR)_2$

3.5.3.1 Phosphoric Acid $O{=}P(OH)_3$

The infrared spectrum of phosphoric acid (H_3PO_4) as a liquid film between Itrans 6 windows is given in ***Figure 103***. The band assignments are as follows: 2883, 2342 and 1654 cm^{-1} broad (POH), 1144 cm^{-1} (ν P=O), 1013 cm^{-1} s and 889 cm^{-1} w (ν P-OH), 490 cm^{-1} P=O deformation.

3.5.3.2 Di-(2-ethylhexyl) Phosphoric Acid $HO\text{-}P{=}O[O\text{-}CH2\text{-}CH(CH_2CH_3)\text{-}(CH_2)_3\text{-}CH_3]_2$

The infrared spectrum of di-(2-ethylhexyl) phosphoric acid as a liquid film between KBr windows is given in ***Figure 104***. The band assignments are as follows: 2960 cm^{-1} ms (ν_{as} CH_3), 2932 cm^{-1} ms (ν_{as} CH_2),

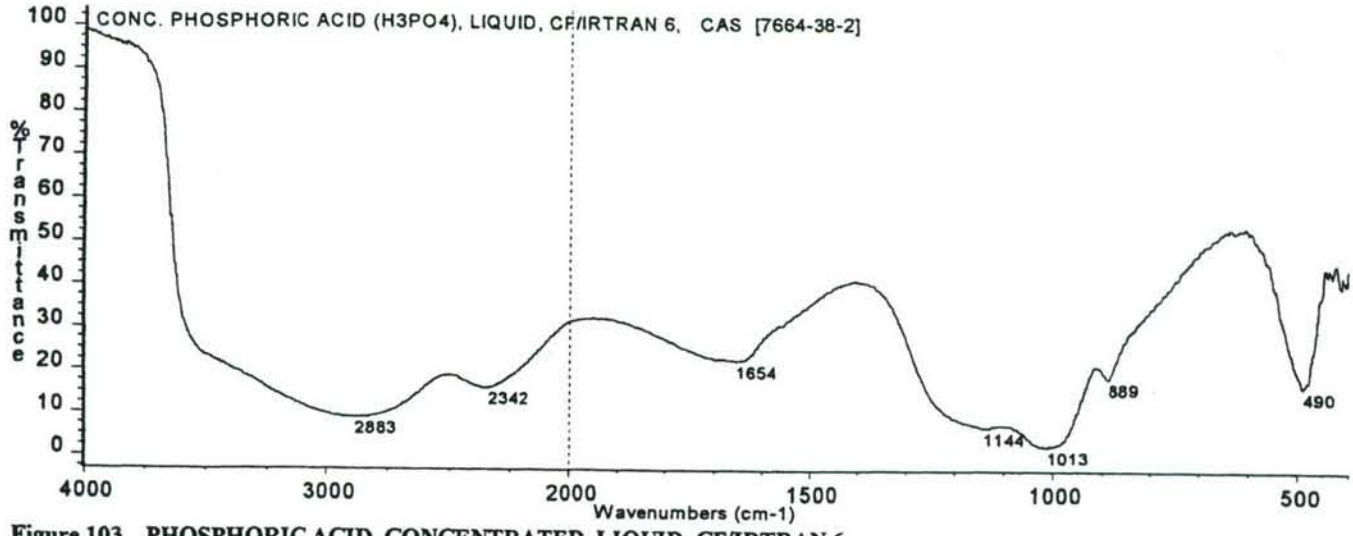


Figure 103 PHOSPHORIC ACID, CONCENTRATED, LIQUID, CF/IRTRAN 6

2874 cm^{-1} m (ν_{sy} CH_3), 2861 cm^{-1} m (ν_{sy} CH_2), 2614 cm^{-1} w, 2333 cm^{-1} w and ca 1660 w all broad (POH), 1464 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1380 cm^{-1} w (δ_{sy} CH_3), 1230 cm^{-1} m (ν P=O), 1157 and 1114 cm^{-1} vw (ω,τ CH_2, ?), 1033 cm^{-1} s [ν P-O-C, and ν P-O(H)], 799 and 782 cm^{-1} vw (POC), 728 cm^{-1} vw (CH_2 rock ?).

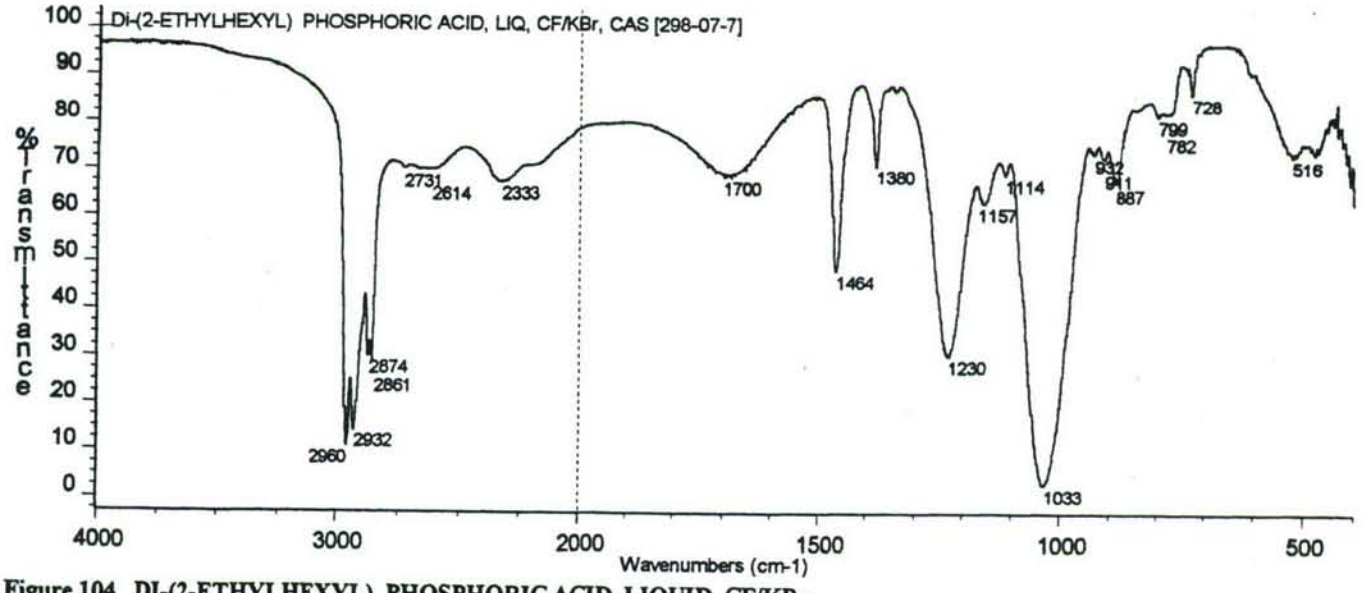


Figure 104 DI-(2-ETHYLHEXYL) PHOSPHORIC ACID, LIQUID, CF/KBr

3.5.4 Phosphonic Acids $R\text{-}P{=}O(OH)_2$

3.5.4.1 Phosphorous Acid $P(OH)_3 \rightarrow H\text{-}P{=}O(OH)_2$

The infrared spectrum of phosphorous acid as a solid between CsI discs (windows) is given as ***Figure***

105. The band assignments are as follows: ca 2900 cm^{-1} m broad, ca 2300 cm^{-1} w and ca 2150 sh, and ca 1540 cm^{-1} w broad (P-OH), ca 1220 sh (P-OH in plane bending ?), ca 1135 cm^{-1} s (ν P=O), ca 1020 with sh near 1000 cm^{-1} s (ν_{as} P-OH and P-H deformation), ca 950 cm^{-1} s (ν_{sy} P-OH), ca 795 cm^{-1} m (P-OH out of plane bending ?), ca 540 cm^{-1} s (P=O deformation).

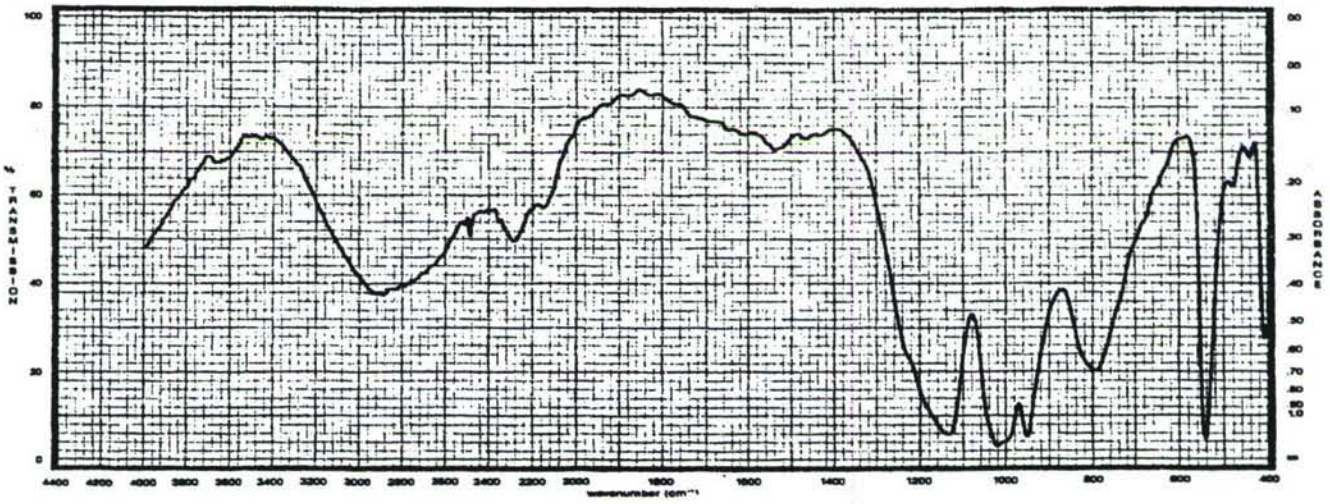


Figure 105 PHOSPHOROUS ACID, SOLID BETWEEN CsI DISCS (WINDOWS)

3.5.4.2 Methylphosphonic Acid $CH_3P{=}O(OH)_2$

The infrared spectrum of methylphosphonic acid as a KBr pellet is given in Figure 106. The band assignments are as follows: 3013 cm^{-1} vvw (ν_{as} CH_3), 2934 cm^{-1} vvw (ν_{sy} CH_3), 2744 cm^{-1} m broad, 2337 cm^{-1} m broad, and ca 1610 cm^{-1} vw (POH), 1534 cm^{-1} vvw (2 x 767 = 1534 cm^{-1}), 1423 and 1415 cm^{-1} vw (δ_{as} P-CH_3), 1323 cm^{-1} m (δ_{sy} P-CH_3), 1260 cm^{-1} m broad (P-OH in plane bending ?), 1185, 1155 and 1115 cm^{-1} (ν P=O), 1011 cm^{-1} and 954 cm^{-1} s (ν_{as} and ν_{sy} P-OH), 891 cm^{-1} vw (P-CH_3 rock ?), 767 cm^{-1} ms (ν P-C), 495 and 458 cm^{-1} ms-s (δ P=O).

3.5.4.3 Hydroxymethylphosphonic Acid $HOCH_2P{=}O(OH)_2$

The infrared spectrum of solid hydroxymethylphosphonic acid as both a KBr pellet and as a solid between KBr discs (windows) is reproduced as ***Figure 107***. The band assignments are as follows: 3220 (3212) cm^{-1} (ν O-H), 2923 (2921) cm^{-1} vw (ν CH_2), 2811 (2801) cm^{-1} m, 2649 (2650) cm^{-1} w, 2287 (2286) cm^{-1} m and

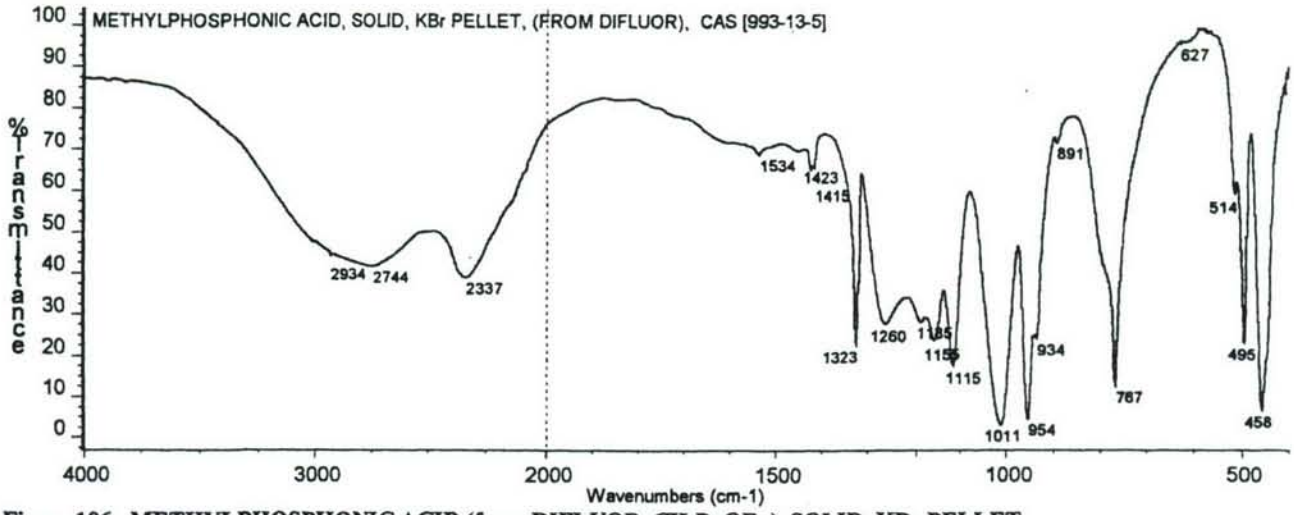


Figure 106 METHYLPHOSPHONIC ACID (from DIFLUOR, $CH_3P{=}OF_2$), SOLID, KBr PELLET

1559 (1559) cm^{-1} w (POH), 1636 cm^{-1} w (H_2O), 1437 (1437) cm^{-1} w and 1418 (1417) cm^{-1} vw (δ CH_2), 1325 (1324) cm^{-1} w (β OH alcohol ?), 1238 and 1218 (1238 and 1217) cm^{-1} m (β PO-H ?), 1131 (1127) cm^{-1} ms (ν P=O), 1057 (1057 cm^{-1} w (ν C-O alcohol), 1005 and 958 (1002 and 951) cm^{-1} s (ν_{as} and ν_{sy} P-OH), 751 (750) cm^{-1} m (ν P-C), 540 and 514 (539 and 513) cm^{-1} m (P=O deformation).

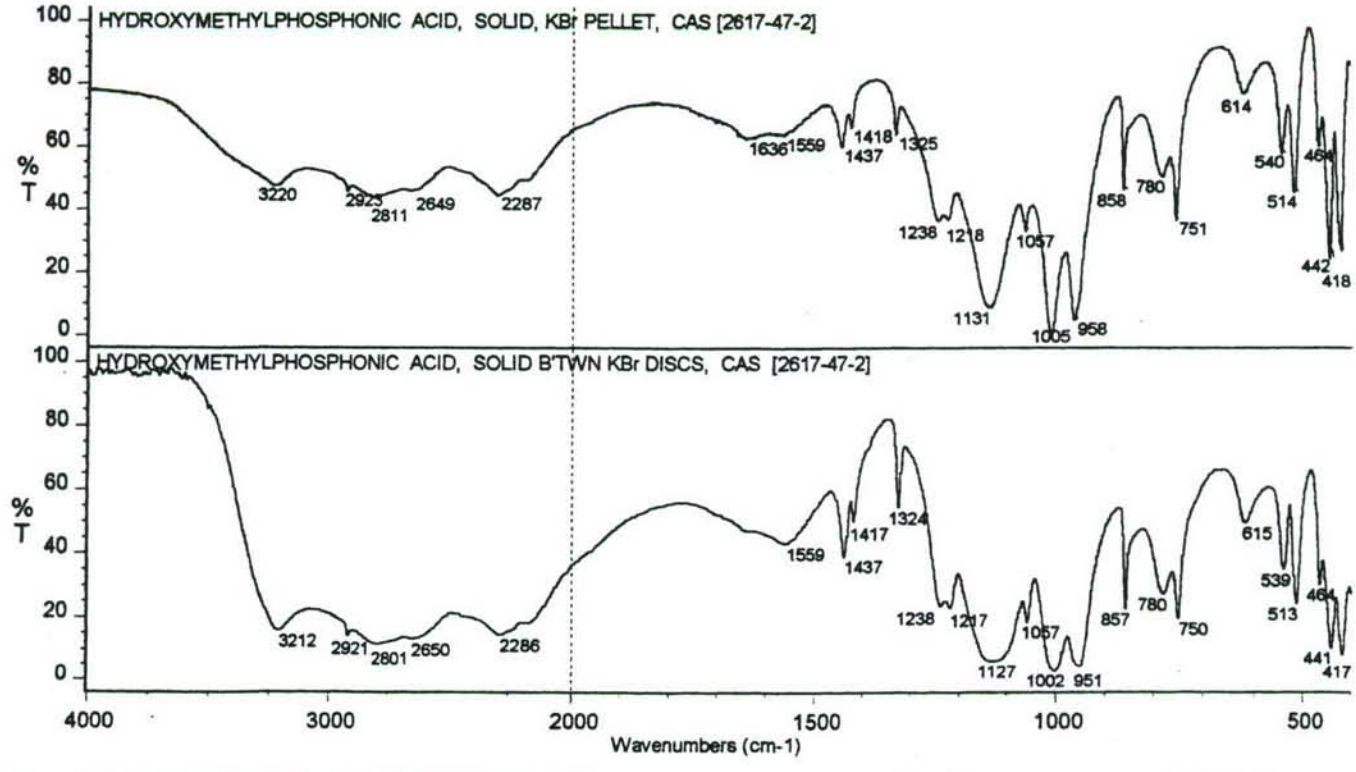


Figure 107 HYDROXYMETHYLPHOSPHONIC ACID, *UPPER PLOT* -- AS A KBr PELLET, *LOWER PLOT*--AS A SOLID BETWEEN KBr DISCS (WINDOWS)

3.5.4.4 Chloromethylphosphonic Acid $Cl\text{-}CH_2\text{-}P{=}O(OH)_2$

The infrared spectrum for chloromethylphosphonic acid as a solid between KBr discs (windows) is give in ***Figure 108***. The band assignments are as follows: 3014 cm^{-1} vvw (ν_{as} CH_2), 2958 cm^{-1} vvw (ν_{sy} CH_2), ca 2820 ms broad, 2253 w broad and 1735 cm^{-1} m broad (POH), 1401 cm^{-1} m (δ CH_2), 1245 cm^{-1} m (ω CH_2),

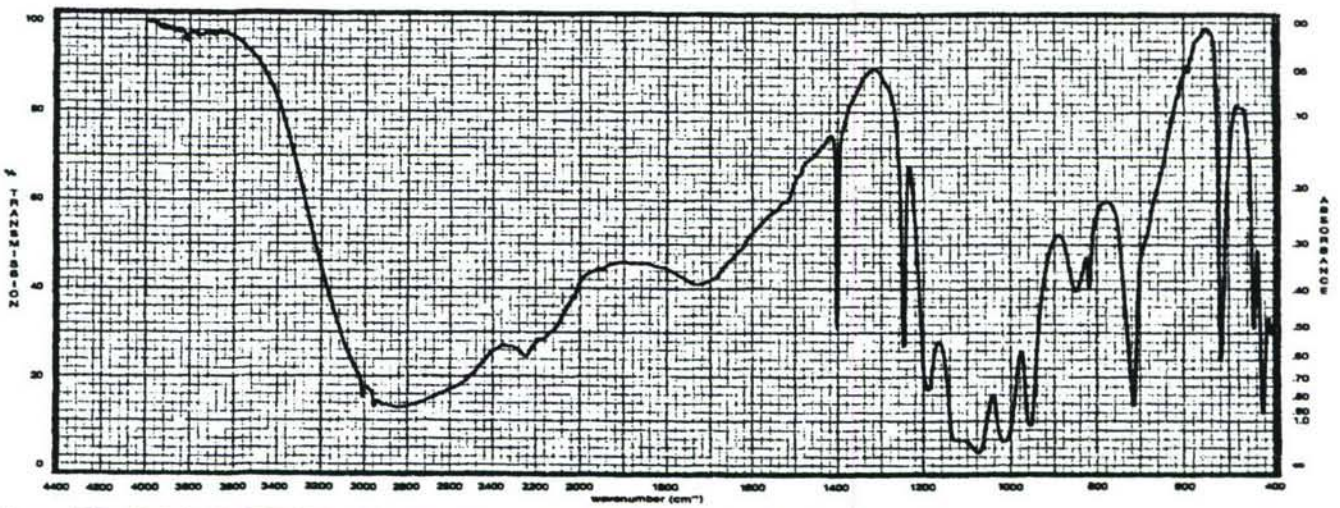


Figure 108 CHLOROMETHYLPHOSPHONIC ACID, SOLID BETWEEN KBr DISCS (WINDOWS)

1187 cm^{-1} m (POH in plane bending ? or ν P=O ?), 1126 cm^{-1} sh, 1073 cm^{-1} s (ν P=O ?), 1013 cm^{-1} s (ν_{as} P-OH), 951 cm^{-1} ms (ν_{sy} P-OH), 711 cm^{-1} m (ν C-Cl), 514 cm^{-1} m (P=O deformation).

3.5.4.5 Dichloromethylphosphonic Acid $Cl_2CH\text{-}P{=}O(OH)_2$

The infrared spectrum of dichloromethylphosphonic acid as a solid between KBr discs (windows) is given as ***Figure 109***. The band assignments are as follows: 2993 cm^{-1} vvw (ν C-H), ca 2640 w broad, ca 2230 and 2150 cm^{-1} (POH), 1204 and 1189 cm^{-1} ms (ν P=O), 1031 cm^{-1} s and 954 cm^{-1} ms (ν_{as} and ν_{sy} P-OH), 763 cm^{-1} ms (ν_{as} CCl_2), 678 cm^{-1} w (ν_{sy} CCl_2 ?), 482 cm^{-1} s (P=O deformation).

3.5.4.6 Trichloromethylphosphonic Acid $Cl_3C\text{-}P{=}O(OH)_2$

The infrared spectrum of trichloromethylphosphonic acid as a solid between KBr discs (windows) is given in ***Figure 110***. The band assignments are as follows: 3402 cm^{-1} m (H_2O), 2775 (2700) cm^{-1} w, 2234 (2171) cm^{-1} w broad and ca 1690 (1661) cm^{-1} w broad, ca 1635 cm^{-1} w (H_2O), 1306 (ca 1310) cm^{-1} vw, 1188

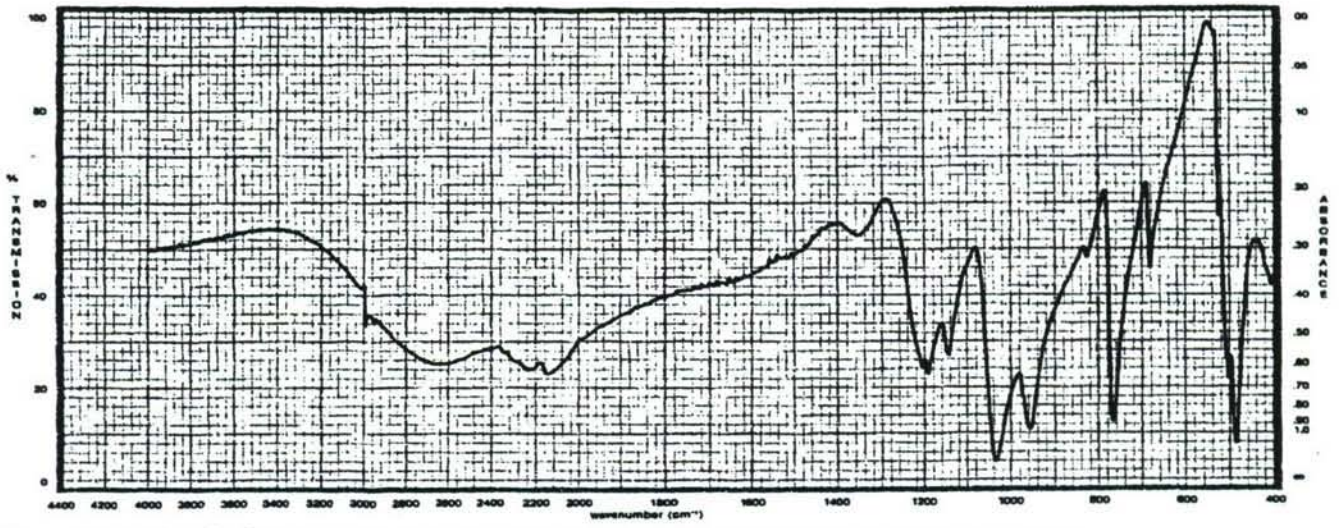


Figure 109 DICHLOROMETHYLPHOSPHONIC ACID, SOLID BETWEEN KBr DISCS (WINDOWS)

(1189) cm^{-1} w (ν P=O ?), 1057 (1056) cm^{-1} s and 982 (971) cm^{-1} w (ν_{as} and ν_{sy} P-OH), 762 (761) cm^{-1} ms (ν CCl_3), 556 (532) cm^{-1} m (P=O deformation or is it ν_{sy} CCl_3 ?).

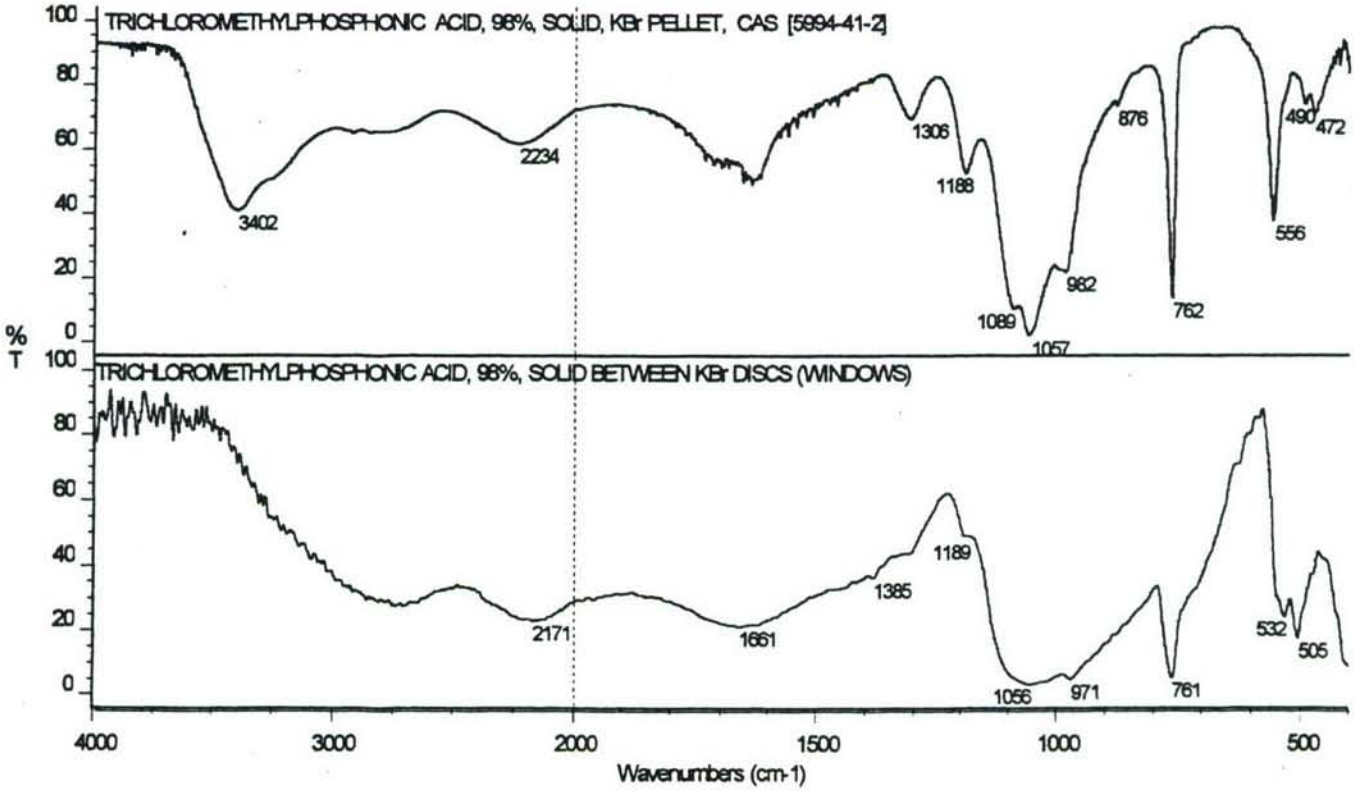


Figure 110 TRICHLOROMETHYLPHOSPHONIC ACID, 98%, *UPPER PLOT*--AS A KBr PELLET, *LOWER PLOT*--AS A SOLID BETWEEN KBr DISCS (WINDOWS)

3.5.4.7 Mono Sodium Salt of Methylphosphonic Acid CH_3-P=O(OH)(ONa)

The infrared spectrum of the mono sodium salt of methylphosphonic acid as a KBr pellet and as a pellet after drying is given in ***Figure 111***. The band assignments for the dried pellet are as follows: 3378 and

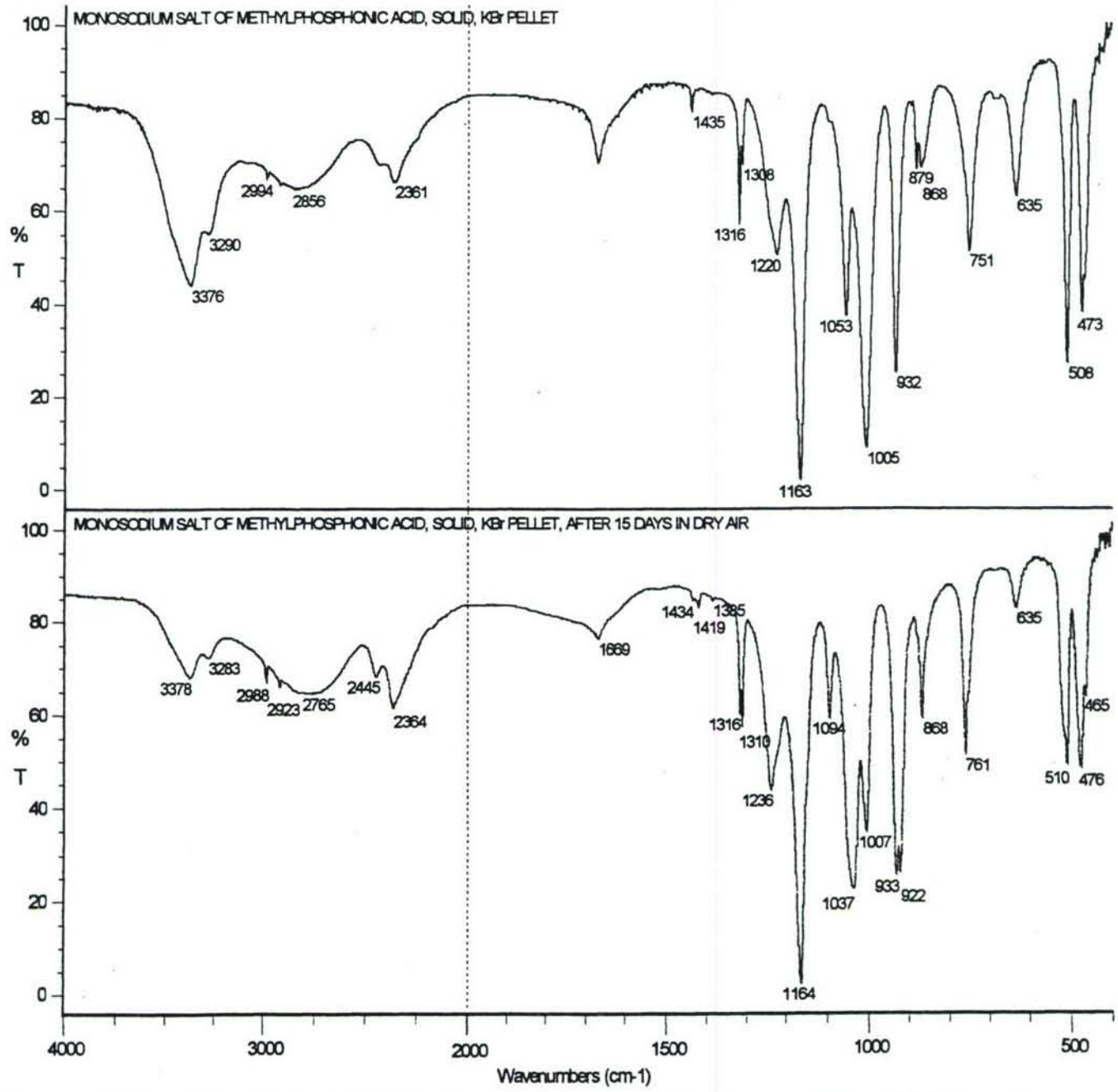


Figure 111 METHYLPHOSPHONIC ACID, MONO-SODIUM SALT, *UPPER PLOT*-- SOLID, KBr PELLET; *LOWER PLOT* -- KBr PELLET AFTER DRYING FOR 15 DAYS IN DRY AIR PURGE

3283 cm^{-1} w-vw (H_2O), 2988 and 2923 cm^{-1} both vw (ν_{as} amd ν_{sy} CH_3), 2765 cm^{-1} w broad, 2445 cm^{-1} vw and 2364 cm^{-1} w and near 1700 cm^{-1} w broad (POH), 1419 cm^{-1} vvw (δ_{as} PCH_3), 1385 cm^{-1} vvw (KNO_3 from the KBr), 1316 and 1310 cm^{-1} w (δ_{sy} P-CH_3), 1236 cm^{-1} w-m (β OH ?), 1164 cm^{-1} s (ν_{as} PO_2^-), 1037 cm^{-1} m (ν_{sy} PO_2^-), 1007 cm^{-1} m (ν P-OH), 933 and 922 cm^{-1} m (P-CH_3), 761 cm^{-1} w (ν P-C), 510 and 476 cm^{-1} m (PO_2^- deformation). Notice the difference in band intensities and positions between the dried and wet samples. The only difference between these two samples was that the original KBr pellet (the upper spectrum in ***Figure 113***) was allowed to remain in the dry air purge of the instrument for 15 days. The pellet was then re-scanned and thus became the lower spectrum in ***Figure 111***.

3.5.4.8 Disodium Salt of Methylphosphonic Acid CH_3-P=O$(ONa)_2$

The infrared spectrum for the disodium salt of methylphosphonic acid (disodium methylphosphonate, **NA_2 MP**) as a KBr pellet, at various levels of dryness, is given in ***Figure 112***. Both the mono- and di- sodium salts of methylphosphonic acid have been discussed previously.[x] The band assignments are as follows: 3285 cm^{-1} ms, 3147 cm^{-1} ms, 2333 cm^{-1} w and 1701 cm^{-1} vw (H_2O), 2998 cm^{-1} vvw (ν CH_3), 1426 cm^{-1} vvw (δ_{as} P-CH_3), 1313 cm^{-1} w (δ_{sy} P-CH_3), 1058 cm^{-1} s (ν_{as} $PO_3^=$), 976 and 967 cm^{-1} m (ν_{sy} $PO_3^=$), 837 cm^{-1} w (P-CH_3 rock ?), 762 cm^{-1} m (ν P-C), 526 and 489 cm^{-1} w ($PO_3^=$ deformation).

3.5.4.9 Ethylphosphonic Acid CH_3-CH_2-P=O$(OH)_2$

The infrared spectrum of ethylphosphonic acid, as both a KBr pellet and as a solid between KBr discs windows), is given in ***Figure 113***. The band assignments are as follows: 3390 cm^{-1} w (H_2O), 2984 (2988) cm^{-1} vw (ν_{as} CH_3), 2947 (2948) cm^{-1} vw (ν_{as} CH_2), 2924 (2921) cm^{-1} vvw (ν_{sy} CH_3), 2889 (2881) cm^{-1} vw (ν_{sy} CH_2), ca 2830 (2692) cm^{-1} m broad, 2310 (2288) cm^{-1} w broad (POH), 1636 (ca 1650) cm^{-1} w broad (POH and H_2O), 1462 (1452) cm^{-1} w (δ_{as} CH_3), 1412 (1410) cm^{-1} vw (δ P-CH_2), 1387 (1386) vvw (δ_{sy} CH_3), 1286 and 1243 cm^{-1}

[x] Piffath, R.J. and Sass, S., Edgewood Arsenal Technical Report EC-TR-76060, "Application of Infrared and Raman Spectroscopy to the Analysis of Phosphonic Acids and Their Salts (GB-Related Compounds)", June 1976. Approved for Public Release.
Piffath, R.J., "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part I. G-Agents and Related Compounds", 1999. Approved for Public Release.

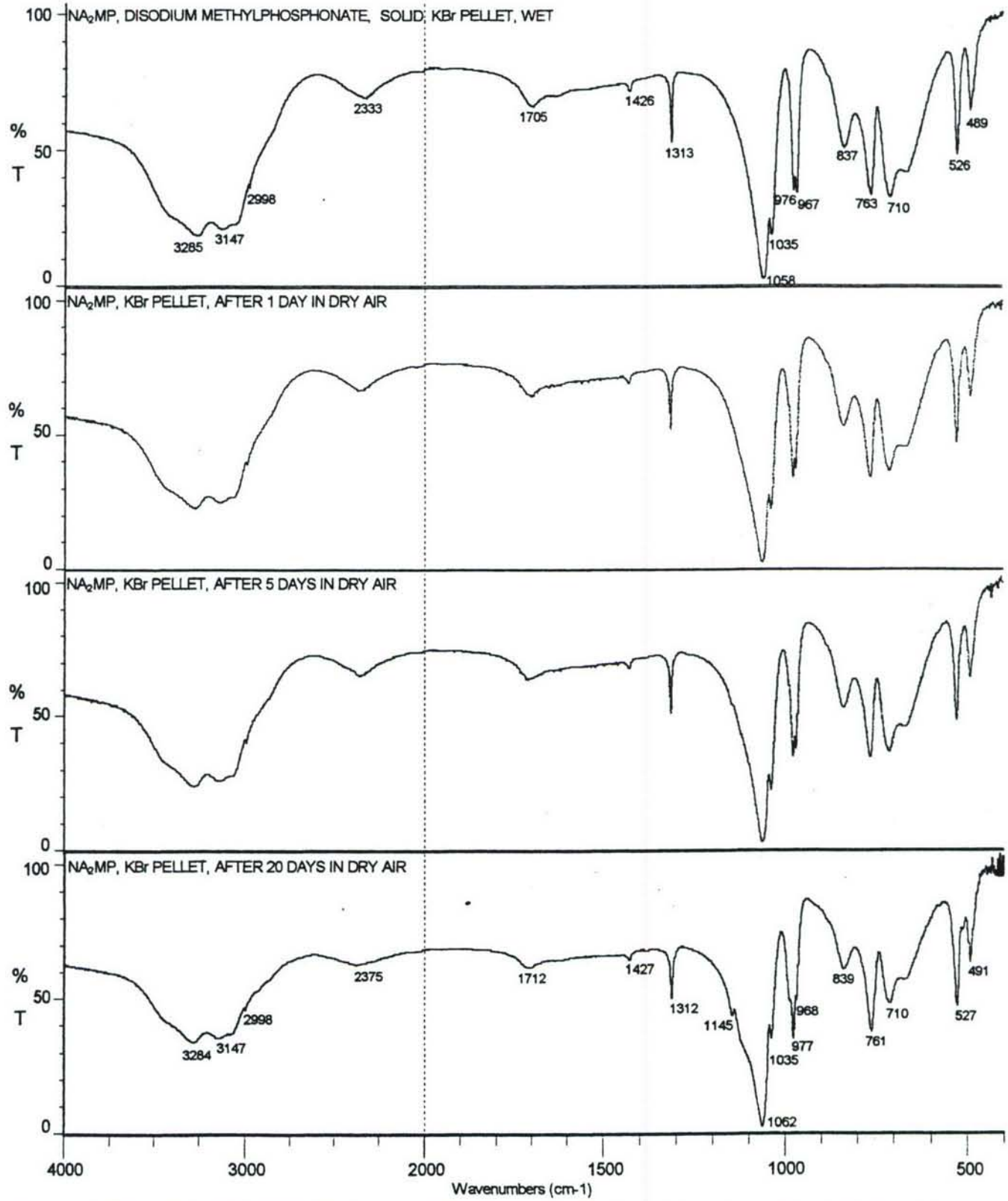


Figure 112 DISODIUM SALT OF METHYLPHOSPHONIC ACID (DISODIUM METHYLPHOSPHONATE , NA_2MP), SOLID, KBr PELLET AT VARYING DEGREES OF DRYNESS

w (P-Ethyl, ω and τ CH_2), 1135 (1144 vw, 1106 ms) cm^{-1} ms (ν P=O), 1021 (1027), 994 (985) and 942 (937) cm^{-1} s-ms (ν C-C of P-Ethyl , and ν P-OH), 746 (740) cm^{-1} vw and 723 (724) cm^{-1} w (P-Ethyl, CH_2 rock and ν P-C), 504, 450 (506 sh , 451) cm^{-1} w (P=O deformation).

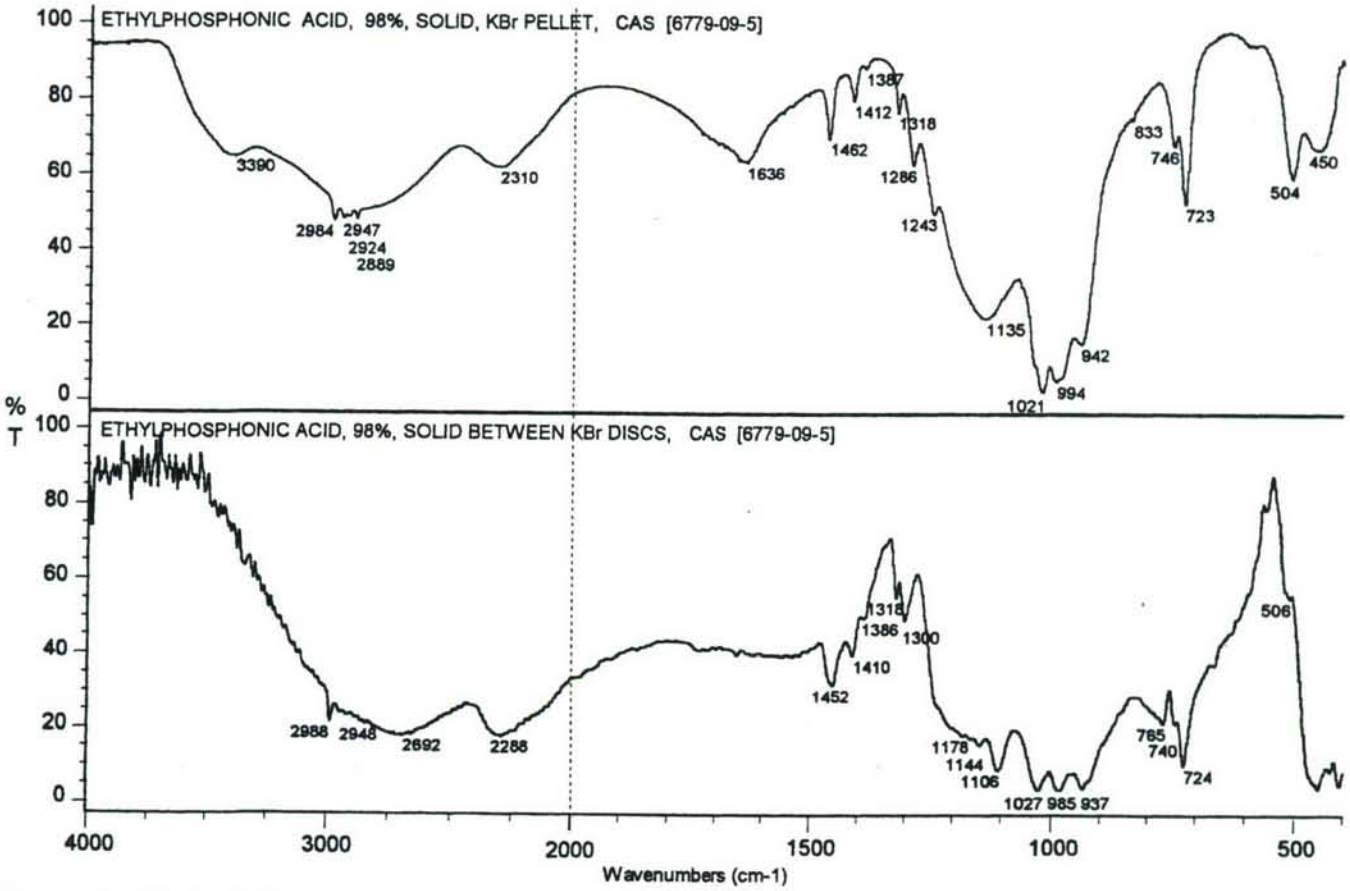


Figure 113 ETHYLPHOSPHONIC ACID SOLID, *UPPER PLOT*--AS A KBr PELLET, *LOWER PLOT*--AS A SOLID BETWEEN KBr DISCS (WINDOWS)

3.5.4.10 2-Chloroethylphosphonic Acid $Cl\text{-}CH_2\text{-}CH_2\text{-}P{=}O(OH)_2$

The infrared spectrum of 2-chloroethylphosphonic acid is given in ***Figure 114***. The band assignments, for the sample as a **solid between CsI discs**, are as follows: 2980, 2916 and 2848 cm^{-1} vvw (ν_{as} and ν_{sy} CH_2), 2719 cm^{-1} ms broad, 2293 cm^{-1} m broad and 1591 cm^{-1} w broad (POH), 1437 cm^{-1} m (δ CH_2), 1410 cm^{-1} w (δ P-CH_2), 1236 cm^{-1} ms (ω CH_2-Cl), 1196 or 1134 cm^{-1} ms (ν P=O), 1021 cm^{-1} and 949, 930 cm^{-1} s (ν_{as} and ν_{sy} P-OH), 783, 750 and 729 cm^{-1} m-ms (ν C-Cl, CH_2 rock and ν P-C), 537 and 520 cm^{-1} m and 472, 446 cm^{-1} ms (P=O deformation).

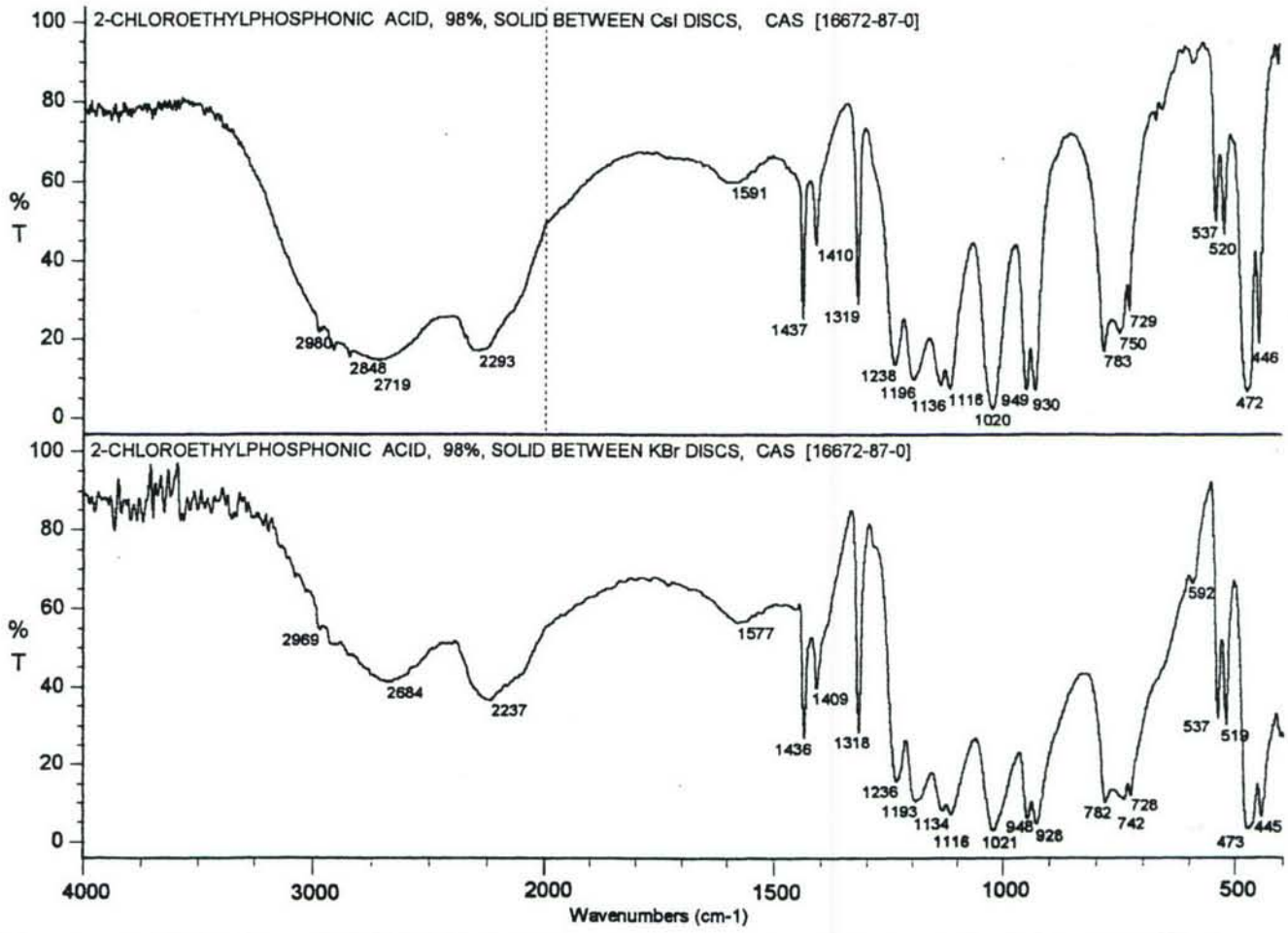


Figure 114 2-CHLOROETHYLPHOSPHONIC ACID, 98%, *UPPER PLOT*–SOLID BETWEEN CsI DISCS (WINDOWS), *LOWER PLOT*–SOLID BETWEEN KBr DISCS (WINDOWS)

3.5.4.11 1-Aminoethylphosphonic Acid $CH_3\text{-}CH(NH_2)\text{-}P{=}O(OH)_2$

The infrared spectrum of 1-aminoethylphosphonic acid is given in ***Figure 115***. The band assignments are as follows: 2962 cm^{-1} ms broad band due to the ν_{as} and ν_{sy} NH_3^+, composed of numerous sub-bands (2841, 2710,2603 and 2518 cm^{-1} due to combination bands of NH_3^+ bending vibrations), 2120 cm^{-1} w (due to the combination band of the NH_3^+ torsional oscillation near 480 cm^{-1} and the δ_{as} NH_3^+ near 1600 cm^{-1}), 1616 cm^{-1} m (δ_{as} NH_3^+), 1533 cm^{-1} ms (δ_{sy} NH_3^+), 1460 cm^{-1} w (δ_{as} CH_3), 1386 cm^{-1} w (δ_{sy} CH_3), 1306 cm^{-1} vvw (δ -CH), 1148 cm^{-1} s (ν_{as} PO_2^-), 1041 cm^{-1} s (ν PO_2^-), 932 cm^{-1} s (ν P-OH), 699 cm^{-1} ms (ν P-C ?), 482 cm^{-1} ms (PO_2^- deformation and NH_3^+ torsion). Thus, the compound exists as the zwitterion, $CH_3\text{-}HC(NH_3^+)\text{-}P(O_2^-)OH$.

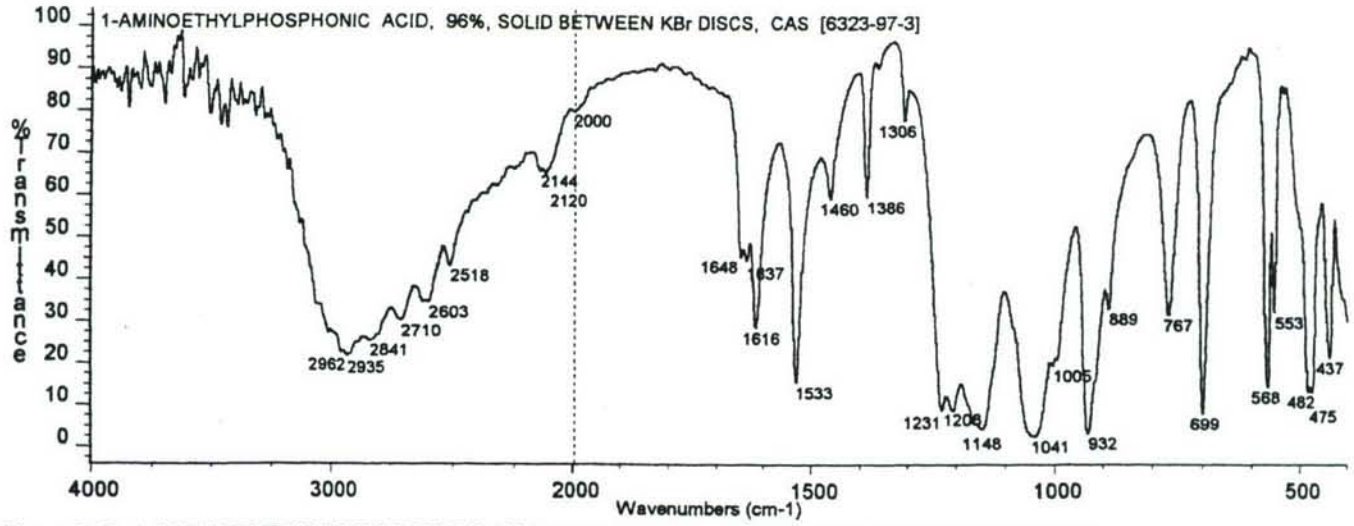


Figure 115 1-AMINOETHYLPHOSPHONIC ACID, 96%, SOLID BETWEEN KBr DISCS (WINDOWS)

3.5.4.12 2-Aminoethylphosphonic Acid $H_2N\text{-}CH_2\text{-}CH_2\text{-}P{=}O(OH)_2$

The infrared spectrum for 2-aminoethylphosphonic acid as a solid between CsI discs (windows) is given in ***Figure 116***. The band assignments are as follows: ca 3000-2500 cm^{-1} vw broad band with sub-bands due to NH_3^+ (and some POH), 2176 cm^{-1} vw (NH_3^+, 1645 + 484 = 2129 cm^{-1} ?), 1645 cm^{-1} vw (δ_{as} NH_3^+), 1481

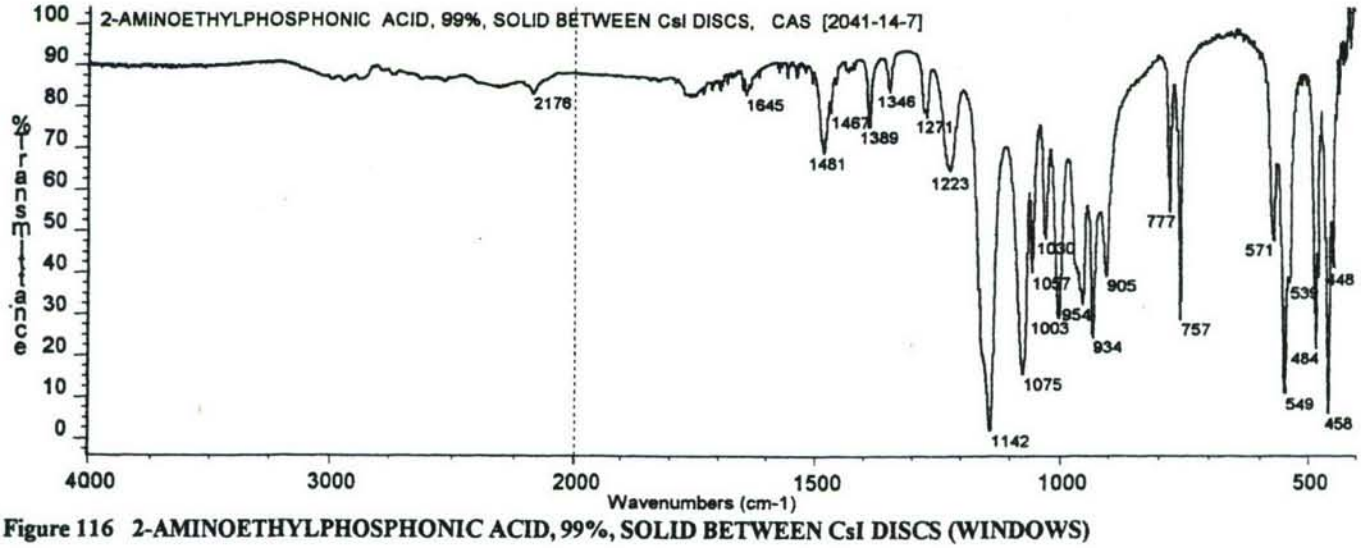


Figure 116 2-AMINOETHYLPHOSPHONIC ACID, 99%, SOLID BETWEEN CsI DISCS (WINDOWS)

cm^{-1} w (δ CH_2), 1271 cm^{-1} vw and 1223 cm^{-1} w (ω, τ CH_2 ?), 1142 cm^{-1} s (ν_{as} PO_2^-), 1075 cm^{-1} ms (ν PO_2^-), 934 cm^{-1} m (ν P-OH), 777 and 757 cm^{-1} w-m (CH_2 rock and ν P-C), 549 cm^{-1} ms (δ PO_2^- ?), 484 cm^{-1} m (NH_3^+ ?). 2-Aminoethylphosphonic acid also appears to exist as a zwitterion, namely, $(H_3N^+)CH_2\text{-}CH_2\text{-}P(O_2^-)OH$.

3.5.4.13 3-Aminopropylphosphonic Acid $H_2N\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}P{=}O(OH)_2$

The infrared spectrum of 3-aminopropylphosphonic acid as a solid between CsI discs (windows) is given in ***Figure 117***. The band asssignments are as follows: ca 3000-2200 cm^{-1} a series of weak sub-bands (2906, 2821, 2751, 2673, 2591 and 2499 cm^{-1}) indicative of the ν_{as} and ν_{sy} NH_3^+, and combination bands of NH_3^+ bending vibrations; 2151 cm^{-1} vw (due to the combination band of the NH_3^+ torsional oscillation, which occurs near 480 cm^{-1}, and the δ_{as} NH_3^+, which occus near 1600 cm^{-1}); the bands due to the POH occur under these

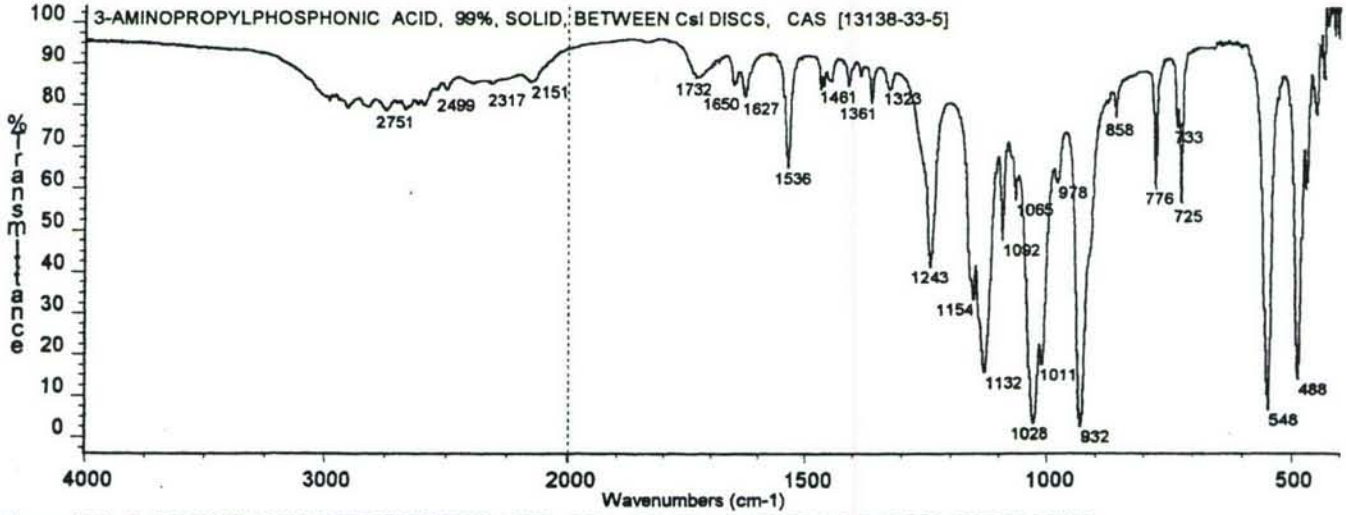


Figure 117 3-AMINOPROPYLPHOSPHONIC ACID, 99%, SOLID BETWEEN CsI DISCS (WINDOWS)

NH_3^+ bands near 2700, 2300 cm^{-1} and 1730 cm^{-1} , 1650 and 1627 cm^{-1} vw (δ_{as} NH_3^+), 1536 cm^{-1} w (δ_{sy} NH_3^+), 1467 cm^{-1} vw (δ CH_2), 1409 cm^{-1} vw (δ P-CH_2), 1132 cm^{-1} ms (ν_{as} PO_2^-), 1028 cm^{-1} s (ν_{sy} PO_2^-), 932 cm^{-1} s (ν P-OH), 776 and 725 cm^{-1} w (CH_2 rock and ν P-C ?), 548 cm^{-1} s (δ PO_2^-), 488 cm^{-1} ms (NH_3^+ torsion ?).

3.5.4.14 2-Carboxyethylphosphonic Acid (3-phosphonopropionic acid) $HO\text{-}C(=O)\text{-}CH_2\text{-}CH_2\text{-}P{=}O(OH)_2$

The infrared spectrum of 2-carboxyethylphosphonic acid (3-phosphonopriopionic acid) as a KBr pellet is given in ***Figure 118***. The band assignments are as follows: near 3000 cm^{-1} m, broad (partly ν O-H carboxylic acid and partly POH), 2280 cm^{-1} w, broad (POH), 1819 cm^{-1} vvw (1020 + 800 = 1820 cm^{-1}), 1719 cm^{-1} ms (ν C=O), 1438 cm^{-1} w (possible in-plane bending of carboxylic acid C-O-H), 1425 cm^{-1} m (δ CH_2), 1403 cm^{-1} w (δ P-CH_2), 1270 cm^{-1} s (ν C-O carboxylic acid), 1211 cm^{-1} ms (ν P=O), 1065 and 1053 cm^{-1} m (ν C-C), 1020 cm^{-1} s

(ν_{as} P-OH), 941 cm^{-1} s (ν_{sy} P-OH, plus some contribution from the carboxylic acid dimer OH out of plane wag), 800 cm^{-1} m (CH_2 rock ?), 751 cm^{-1} m (ν P-C ?), 508 cm^{-1} s (deformation of P=O, C=O ?).

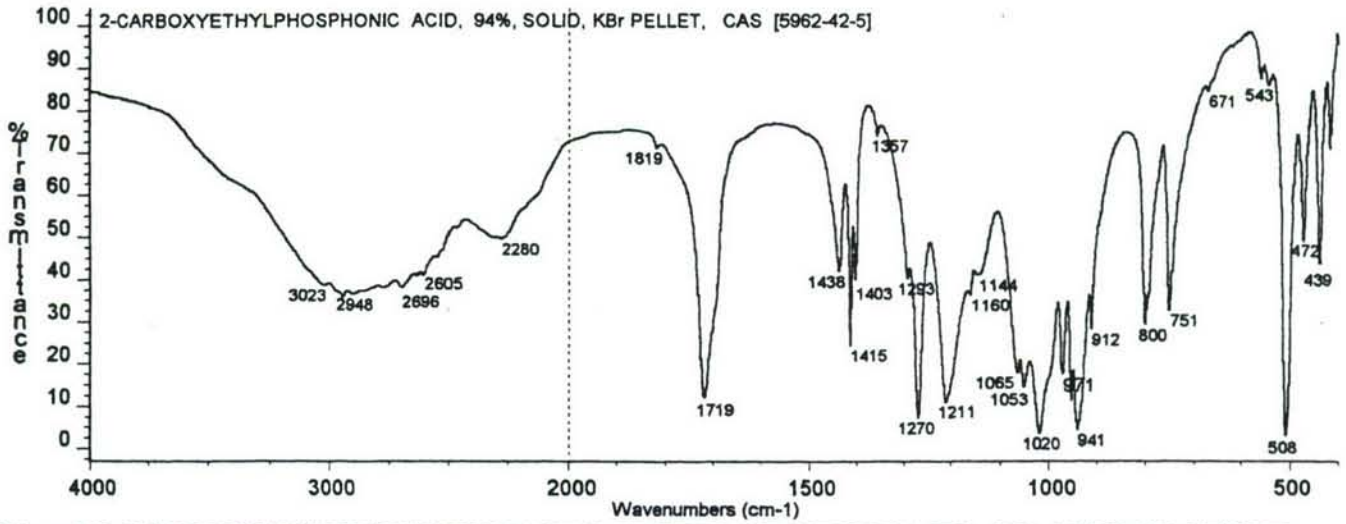


Figure 118 2-CARBOXYETHYLPHOSPHONIC ACID (3-PHOSPHONOPROPIONIC ACID), 94%, SOLID, KBr PELLET

3.5.4.15 Phosphonoacetic Acid (carboxymethylphosphonic acid) HO-C(=O)-CH_2P=O$(OH)_2$

The infrared spectrum of phosphonoacetic acid (carboxymethylphosphonic acid) as a KBr pellet is given in ***Figure 119***. The band assignments are as follows: 2885 cm^{-1} vw (ν_{as} CH_2), 2932 cm^{-1} vw (ν_{sy} CH_2), ca 3000 cm^{-1} w broad (partly due to ν OH carboxylic acid and partly POH), 2661 and 2539 cm^{-1} w (due to overtones and combinations of the carboxylic acid ν C-O and in plane OH bend near the 1300 and 1420 cm^{-1} regions), ca

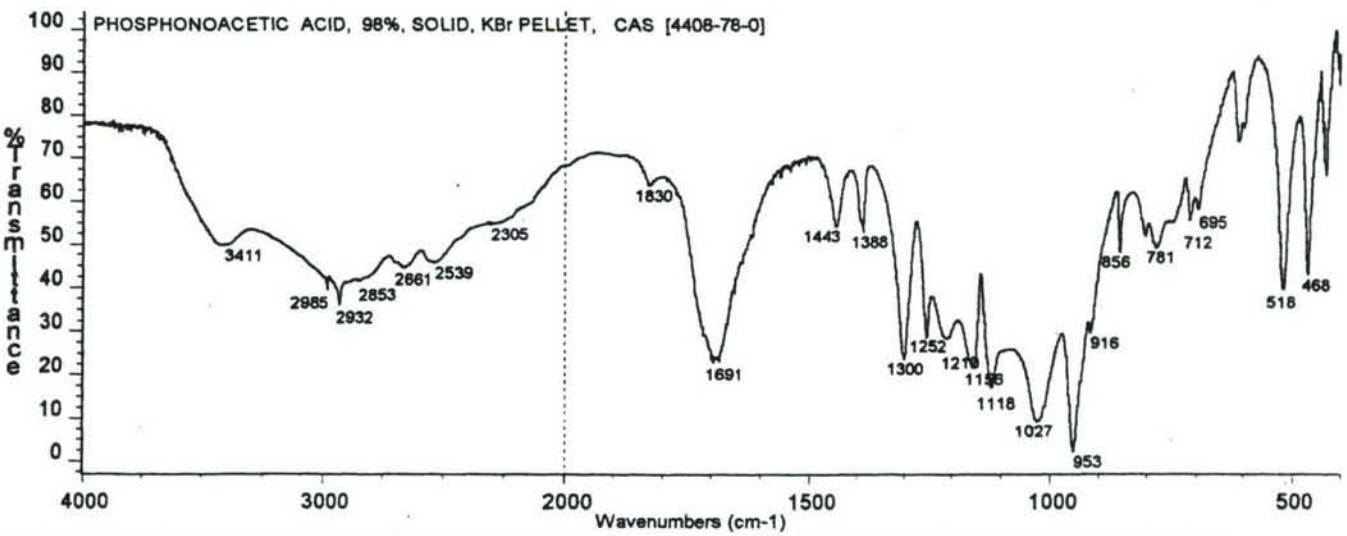


Figure 119 PHOSPHONOACETIC ACID (CARBOXYMETHYLPHOSPHONIC ACID), 98%, SOLID, KBr PELLET

2300 cm^{-1} w (POH), 1830 cm^{-1} vw (1027 + 802 = 1829), ca 1690 cm^{-1} m (ν C=O), 1443 cm^{-1} w (possible in plane bending of carboxylic acid C-O-H), 1388 cm^{-1} w (δ CH_2), 1300, 1252 cm^{-1} m (caboxylic acid ν C-O), 1210 and 1156 cm^{-1} m (ν P=O), 1027 cm^{-1} ms (ν_{as} P-OH), 953 cm^{-1} cm^{-1} s (ν_{sy} P-OH and carboxylic acid out of plane OH wag), 782 cm^{-1} w (CH_2 rock ?), 712 cm^{-1} w (ν P-C ?), 518, 468 cm^{-1} m (P=O, C=O deformantions ?).

3.5.4.16 Propylphosphonic Acid CH_3-CH_2-CH_2-P=O$(OH)_2$

The infrared spectrum of propylphosphonic acid is from the hydrolysis of propylphosphonic dichloride and the hydrolysis of 1-propanephosphonic acid cyclic anhydride as given in ***Figure 120***. The band assignments are as follows: 2967 cm^{-1} w (ν_{as} CH_3), 2937 cm^{-1} vw (ν_{as} CH_2), 2910 cm^{-1} vvw (ν_{sy} CH_3), 2879 cm^{-1} vw (ν_{sy} CH_2), 2740, 2278 and ca 1660 cm^{-1} w, broad (POH), 1467 cm^{-1} w (δ CH_2 and δ_{as} CH_3), 1407 cm^{-1} vw (δ P-CH_2), 1384 cm^{-1} vw (δ_{sy} CH_3), 1253 and 1222 cm^{-1} m (CH_2 ω, τ), 1195 cm^{-1} ms (ν P=O), 1082 cm^{-1} vw and 1042 cm^{-1} w (ν C-C ?), 1003 and 956 cm^{-1} s (ν_{as} and ν_{sy} P-OH), 777 and 721 cm^{-1} m (CH_2 rock and ν P-C), 518 cm^{-1} m (P=O deformation).

3.5.4.17 Isopropylphosphonic Acid $(CH_3)_2$CH-P=O$(OH)_2$

The infrared spectrum of isopropylphosphonic acid as a solid between KBr discs (windows) and as a KBr pellet is given in ***Figure 121***. The band assignments are as follows: 3420 and 1629 cm^{-1} w (H_2O, KBr pellet only), 2981 and 2880 cm^{-1} vw (ν_{as} and ν_{sy} CH_3), 2941 cm^{-1} vvw (ν -C-H), ca 2700, 2250 and 1590 cm^{-1} m-w, broad (POH), 1470, 1451 cm^{-1} w (δ_{as} CH_3), 1393 and 1372 cm^{-1} vw (δ_{sy} CH_3), ca 1290-1280 cm^{-1} w (P-iPr ?), ca 1190, 1132 cm^{-1} m (isopropyl moiety ?), 1074 ms (ν P=O ? or perhaps at 1132 cm^{-1} ?), 1008 and 931 cm^{-1} s-ms (ν_{as} and ν_{sy} P-OH), 692 cm^{-1} w (ν P-C), 522 and 503 cm^{-1} ms (P=O deformation).

3.5.4.18 *n*-Butylphosphonic Acid CH_3-CH_2-CH_2-CH_2-P=O$(OH)_2$

The infrared spectrum of *n*-butylphosphonic acid as a solid between KBr discs (windows) and as a KBr pellet is give in ***Figure 122***. The band assignments are as follows: 2959 cm^{-1} vw (ν_{as} CH_3), 2935 cm^{-1} vw (ν_{as} CH_2), 2874 cm^{-1} vw (ν_{sy} CH_3), ca 2865 cm^{-1} sh (ν_{sy} CH_2), ca 2700 cm^{-1} m broad, 2316 cm^{-1} m broad (POH), ca

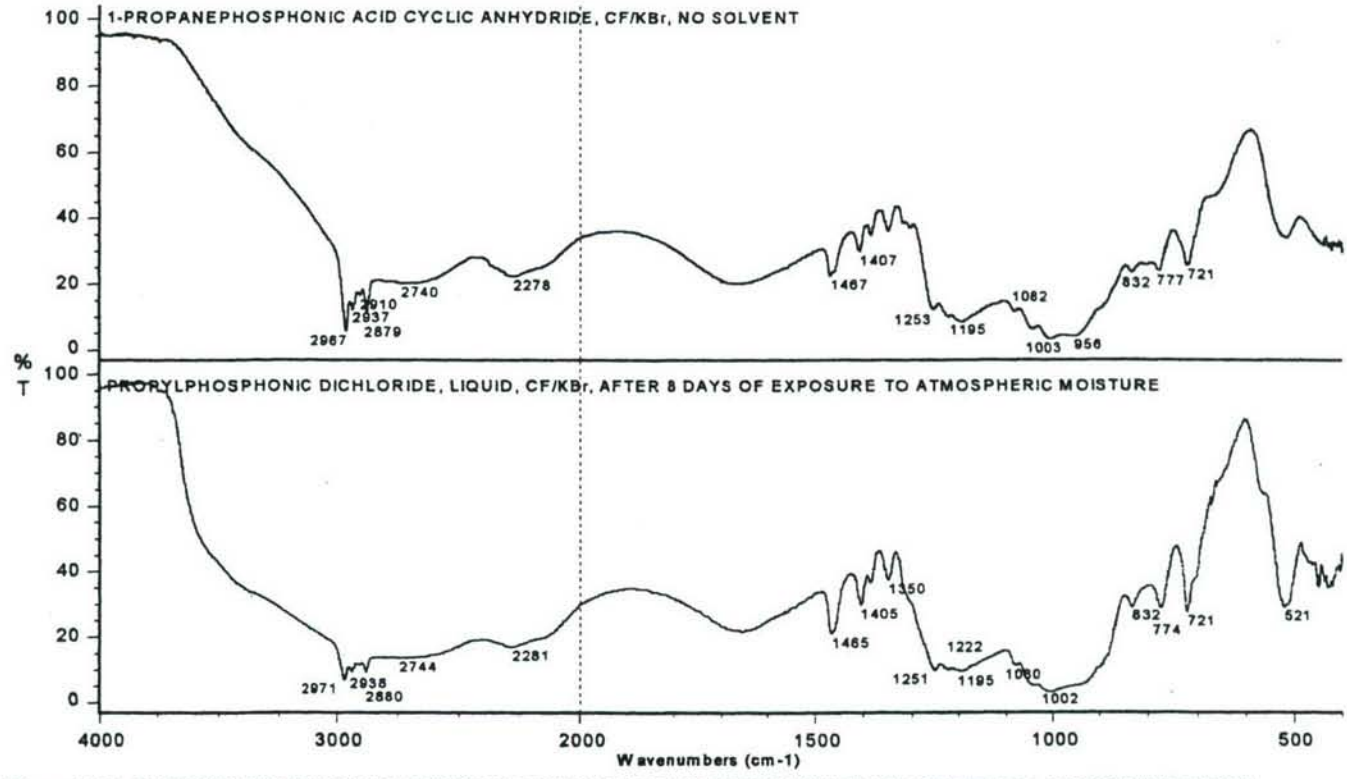


Figure 120 PROPYLPHOSPHONIC ACID FROM THE HYDROLYSIS OF (A) *UPPER SPECTRUM*– 1-PROPANEPHOS - PHONIC ACID CYCLIC ANHYDRIDE, CF/KBr, AND (B) *LOWER SPECTRUM*-- PROPYLPHOSPHONIC DICHLORIDE, CF/KBr, AFTER 8 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

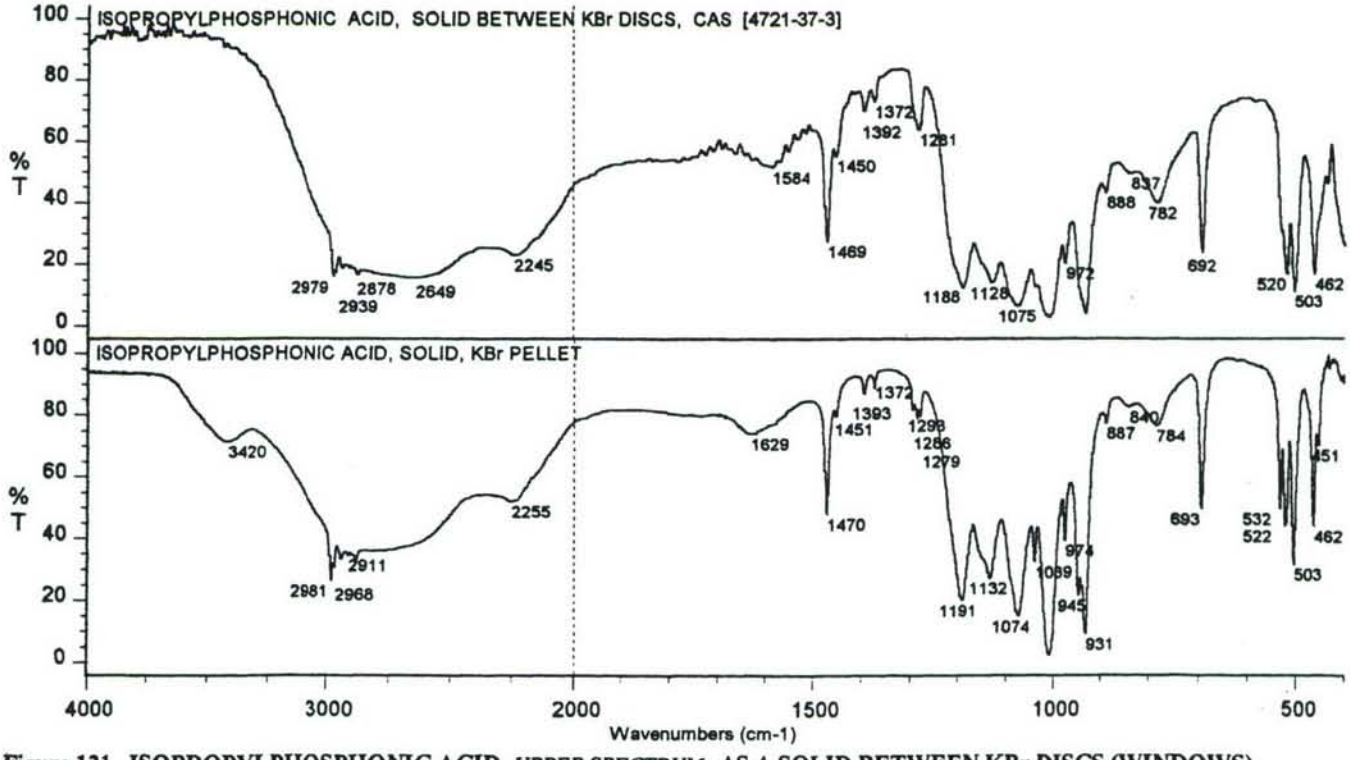


Figure 121 ISOPROPYLPHOSPHONIC ACID, *UPPER SPECTRUM*--AS A SOLID BETWEEN KBr DISCS (WINDOWS), *LOWER SPECTRUM* --SOLID AS A KBr PELLET

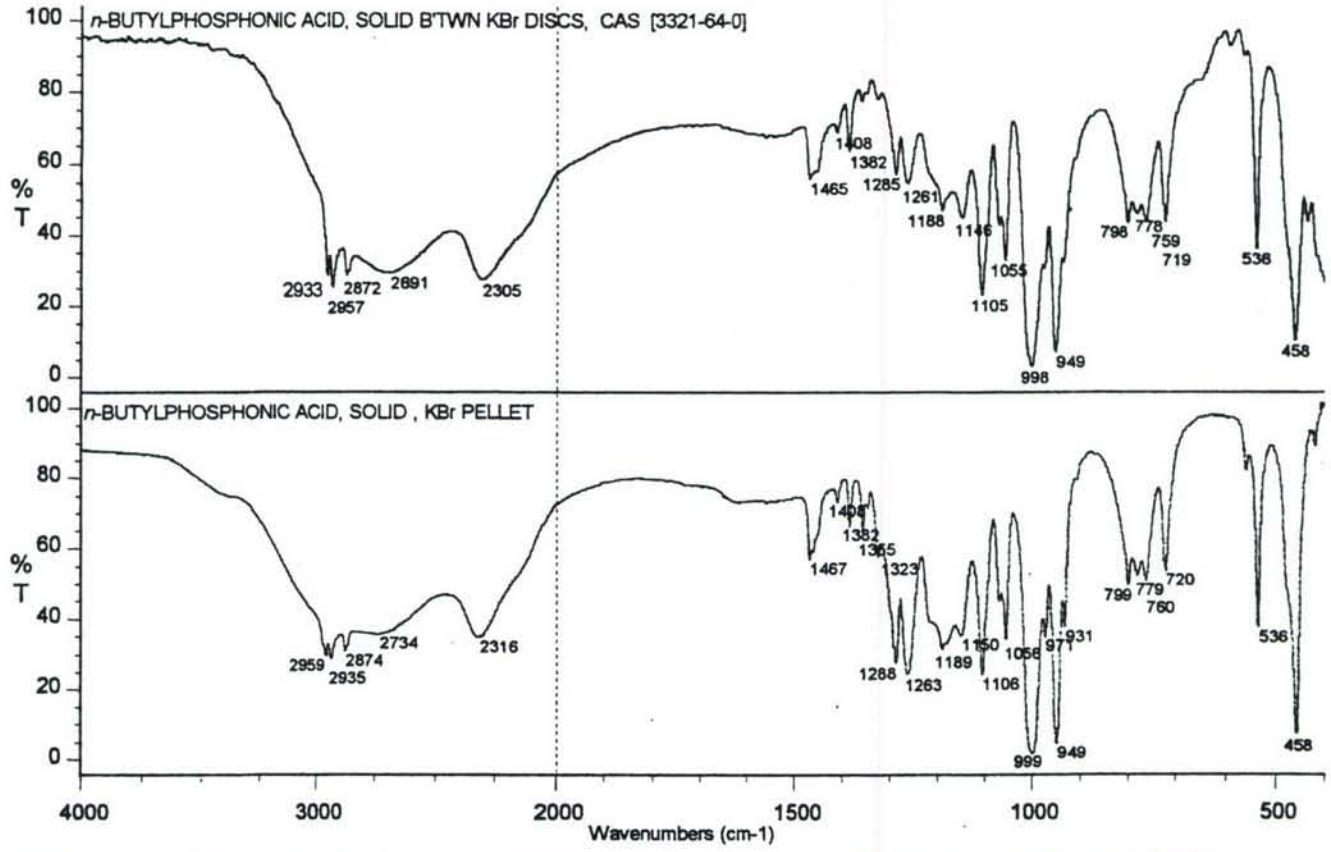


Figure 122 ***n*-BUTYLPHOSPHONIC ACID, *UPPER SPECTRUM*--AS A SOLID BETWEEN KBr DISCS (WINDOWS), *LOWER SPECTRUM*--AS A KBr PELLET**

1630 cm^{-1} vw broad (POH, also some H_2O in the KBr pellet spectrum), 1467 cm^{-1} w (δ CH_2, and δ_{as} CH_3), 1408 cm^{-1} vw (δ P-CH_2), 1382 cm^{-1} w (δ_{sy} CH_3), 1288 and 1263 cm^{-1} m (ω CH_2), 1189, 1150 cm^{-1} m (part of a broad band, ν P=O), 1106 and 1056 cm^{-1} m (ν C-C), 999 and 949 cm^{-1} s (ν_{as} P-OH, and ν_{sy} P-OH), 799, 779 and 760 cm^{-1} w-m (CH_2 rock), 720 cm^{-1} w-m (ν P-C), 536 cm^{-1} m and/or 458 cm^{-1} s (P=O deformation).

3.5.4.19 <u>*tert*-Butylphosphonic Acid</u> $(CH_3)_3C\text{-}P{=}O(OH)_2$

The infrared spectrum of *tert*-butylphosphonic acid as a solid between KBr discs (windows) is given in ***Figure 123***. The band assignments are as follows: 2978 cm^{-1} w (ν_{as} CH_3), 2875 cm^{-1} vw (ν_{sy} CH_3), ca 2780 cm^{-1} m broad and 2311 cm^{-1} m broad (POH), 1481 cm^{-1} m (δ_{as} CH_3), 1397 cm^{-1} vw and 1370 cm^{-1} w (δ_{sy} CH_3), 1243 and 1217 cm^{-1} m (*t*-butyl skeletal), 1192 cm^{-1} ms and 1147 cm^{-1} m (ν P=O), 1005 cm^{-1} s (ν_{as} P-OH), 921 cm^{-1} s (ν_{sy} P-OH), 651 cm^{-1} ms (ν P-C ?), 502 and 486 cm^{-1} ms (P=O deformation).

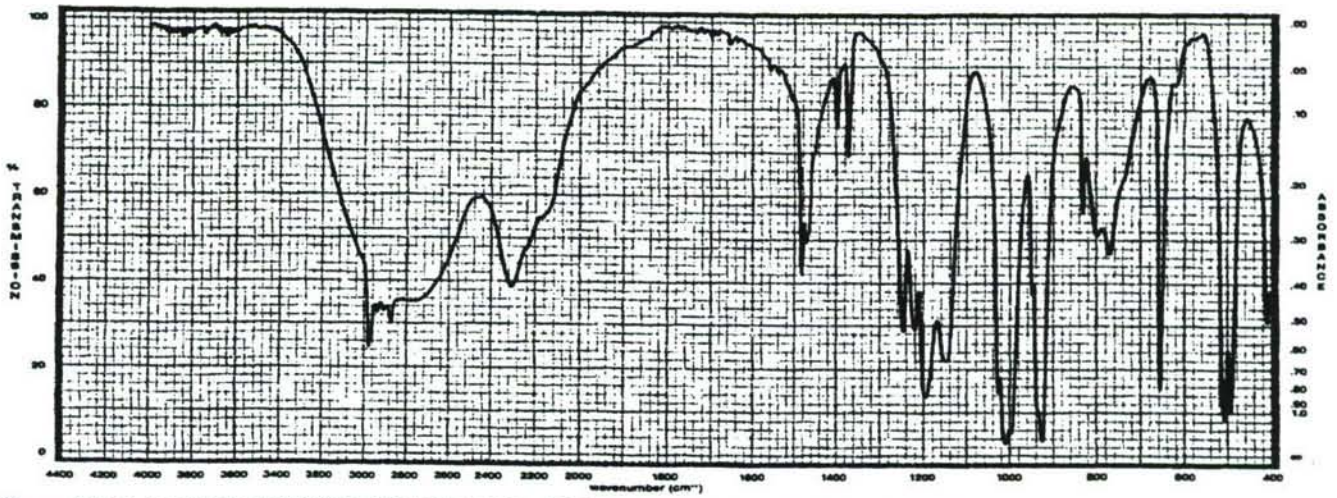


Figure 123 *tert*-**BUTYLPHOSPHONIC ACID, 98%, SOLID BETWEEN KBr DISCS (WINDOWS)**

3.5.4.20 Pentyl- Through Octadecyl- Phosphonic Acids

The infrared spectra for the rest of the series of phosphonic acids (i.e., pentyl- through octadecyl-) shall be presented as spectra only, with no commentary. n-Pentylphosphonic acid is given in ***Figure 124***.

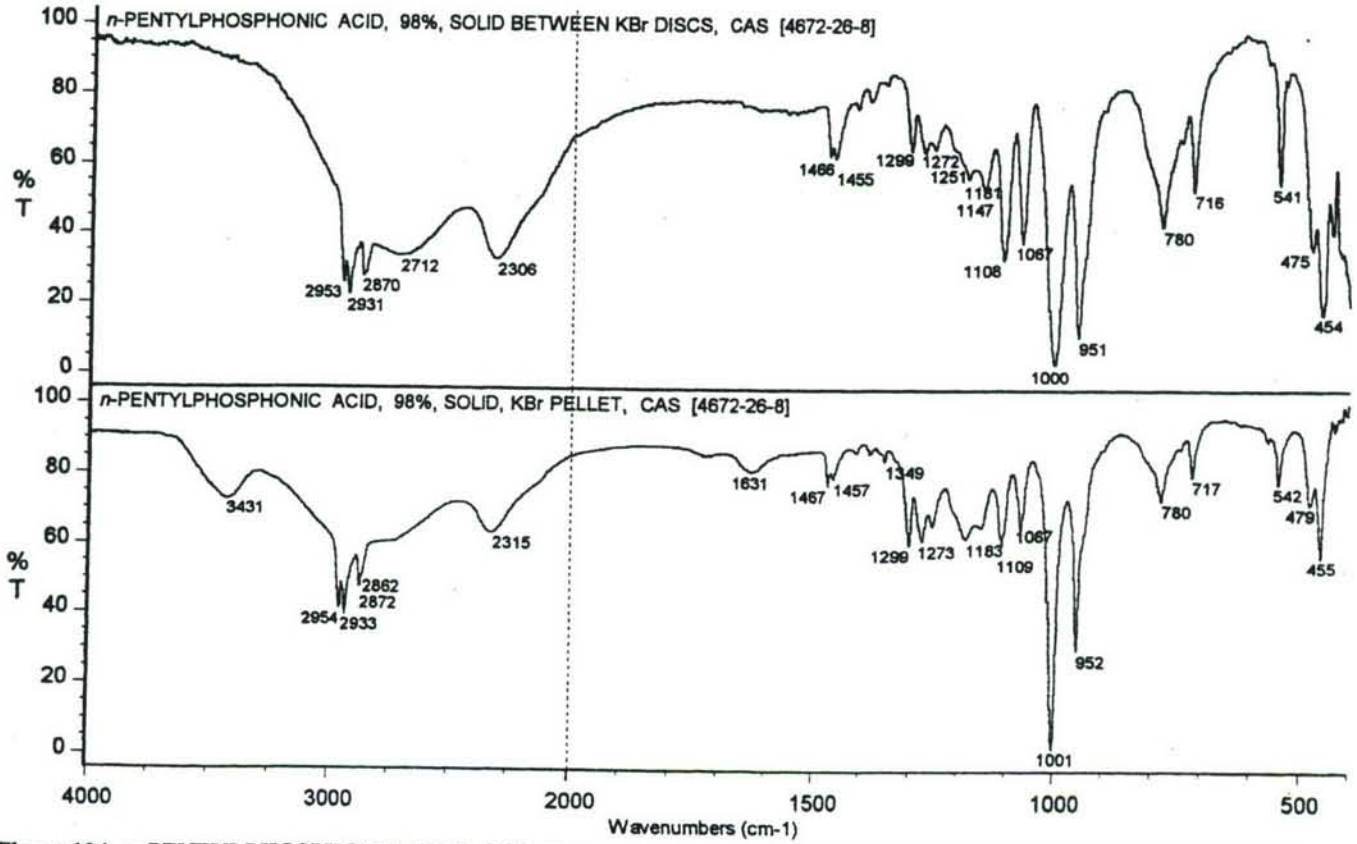


Figure 124 *n*-**PENTYLPHOSPHONIC ACID, 98%,** ***UPPER SPECTRUM*****--AS A SOLID BETWEEN KBr DISCS (WINDOWS),** ***LOWER SPECTRUM*****--SOLID, KBr PELLET**

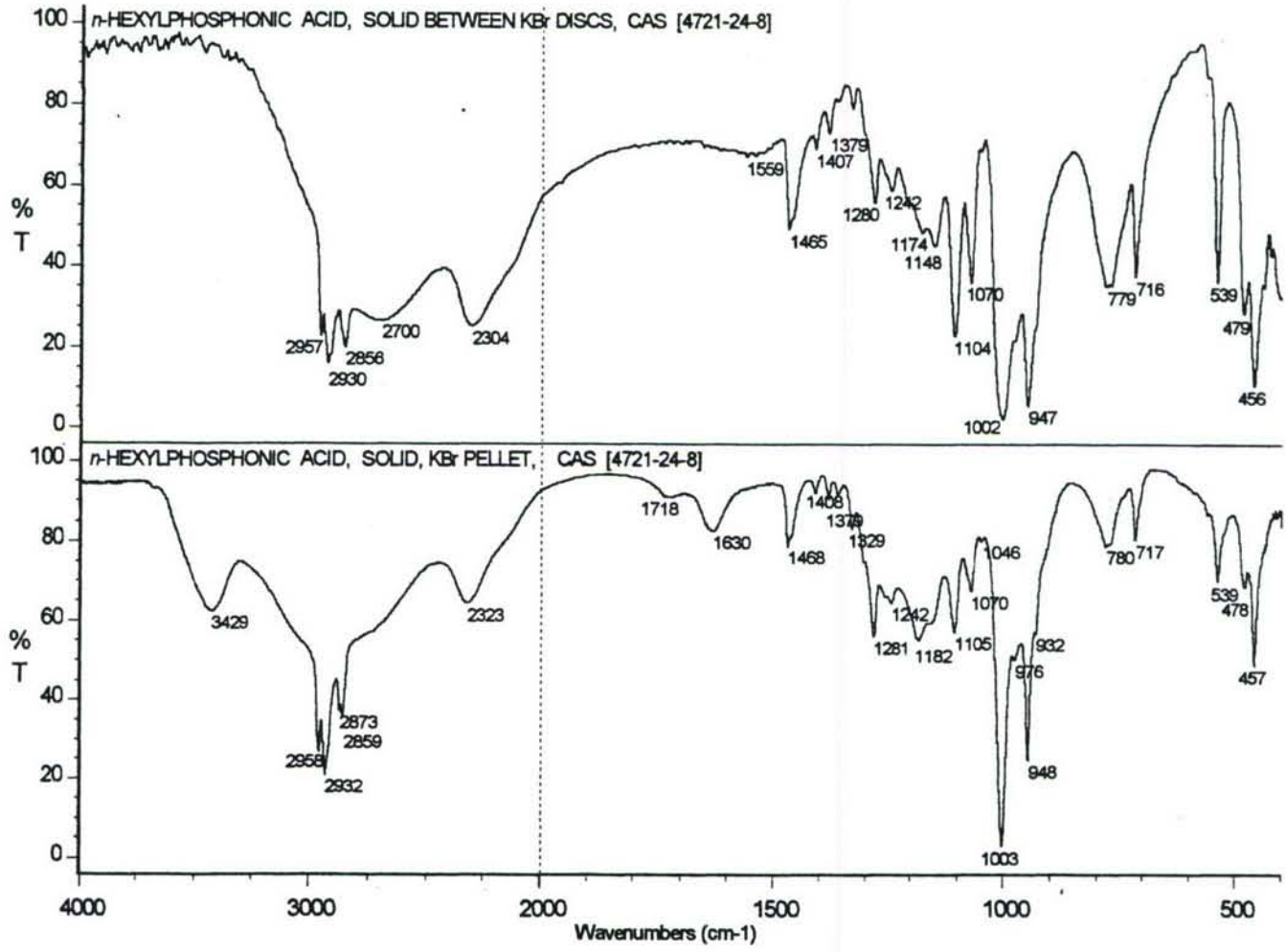


Figure 125 ***n*-HEXYLPHOSPHONIC ACID, 98%,** ***UPPER SPECTRUM*--SOLID BETWEEN KBr DISCS (WINDOWS),** ***LOWER SPECTRUM*--SOLID , KBr PELLET**

The infrared spectrum of *n*-hexylphosphonic acid is given in ***Figure 125***, while that for *n*-heptylphosphonic acid is give in ***Figure 126***. The infrared spectrum of solid *n*-octylphosphonic acid is given in ***Figure 127***, while the infrared spectrum of *n*-nonylphosphonic acid is reproduced as ***Figure 128***. The infrared spectrum for *n*-decylphosphonic acid is given as ***Figure 129***; *n*-undecylphosphonic acid as ***Figure 130***; *n*-tetradecylphosphonic acid $[CH_3(CH_2)_{13}P{=}O(OH)_2]$ as ***Figure 131***; *n*-heptadecylphosphonic acid $[CH_3(CH_2)_{16}P{=}O(OH)_2]$ as ***Figure 132*** and *n*-octadecylphosphonic acid $[CH_3(CH_2)_{17}P{=}O(OH)_2]$ as ***Figure 133***.

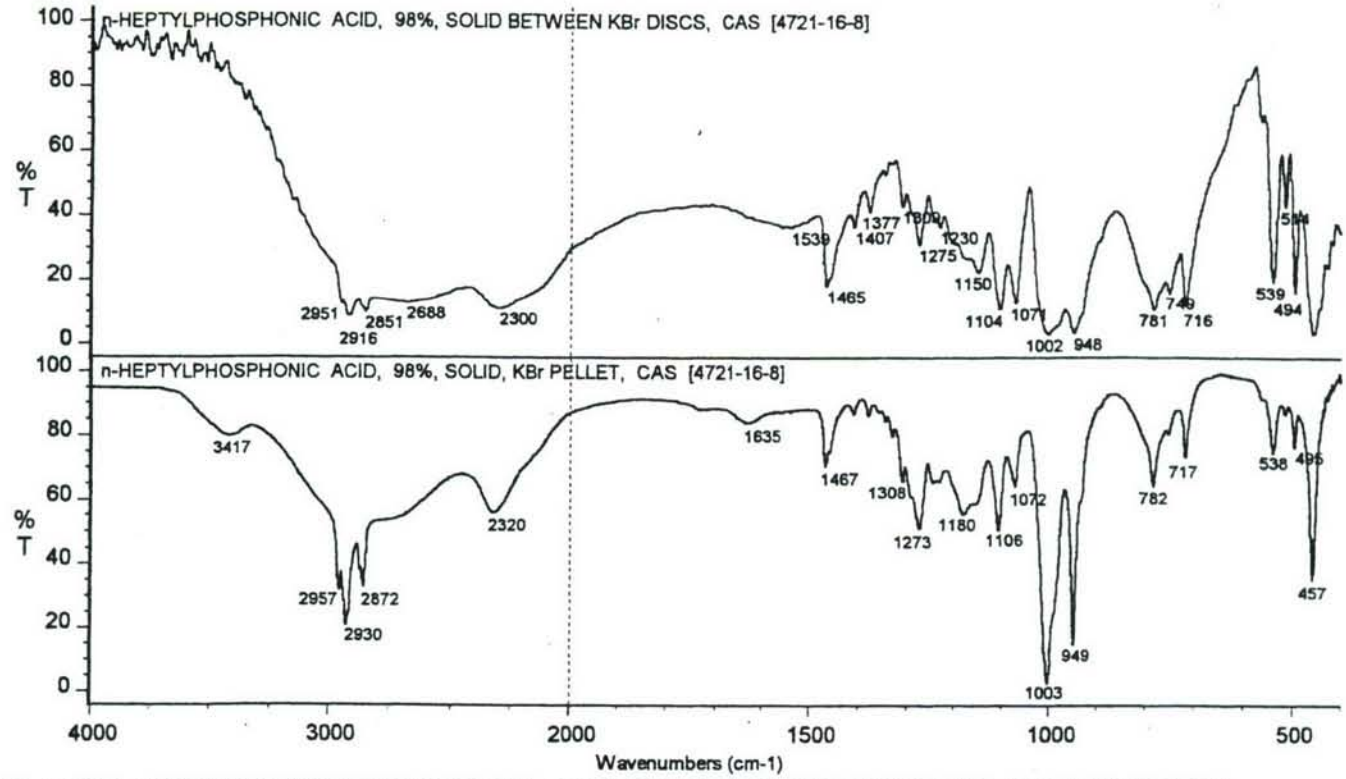


Figure 126 *n*-**HEPTYLPHOSPHONIC ACID, 98%,** *UPPER SPECTRUM*--**SOLID BETWEEN KBr DISCS (WINDOWS),** *LOWER SPECTRUM*--**SOLID, KBr PELLET**

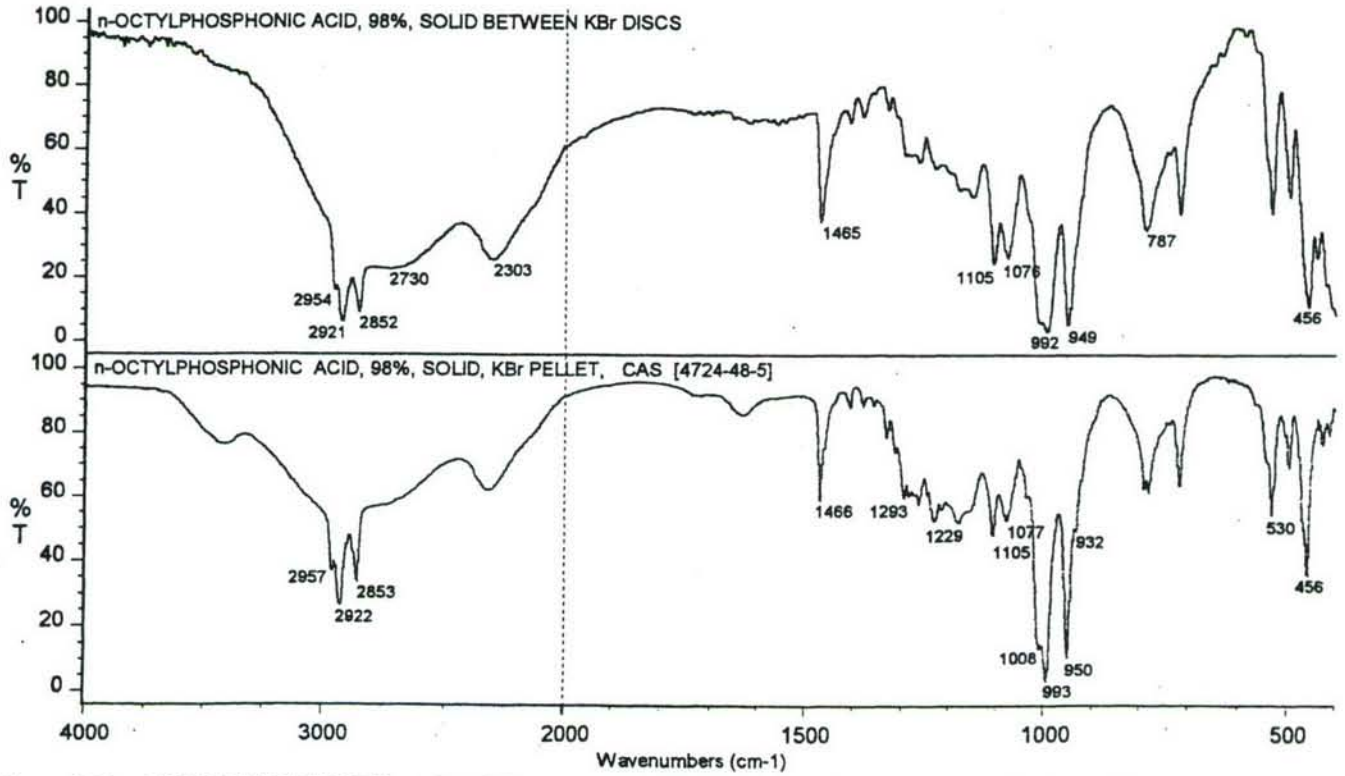


Figure 127 *n*-**OCTYLPHOSPHONIC ACID, 98%,** *UPPER SPECTRUM*--**SOLID, BETWEEN KBr DISCS (WINDOWS),** *LOWER SPECTRUM*--**SOLID, KBr PELLET**

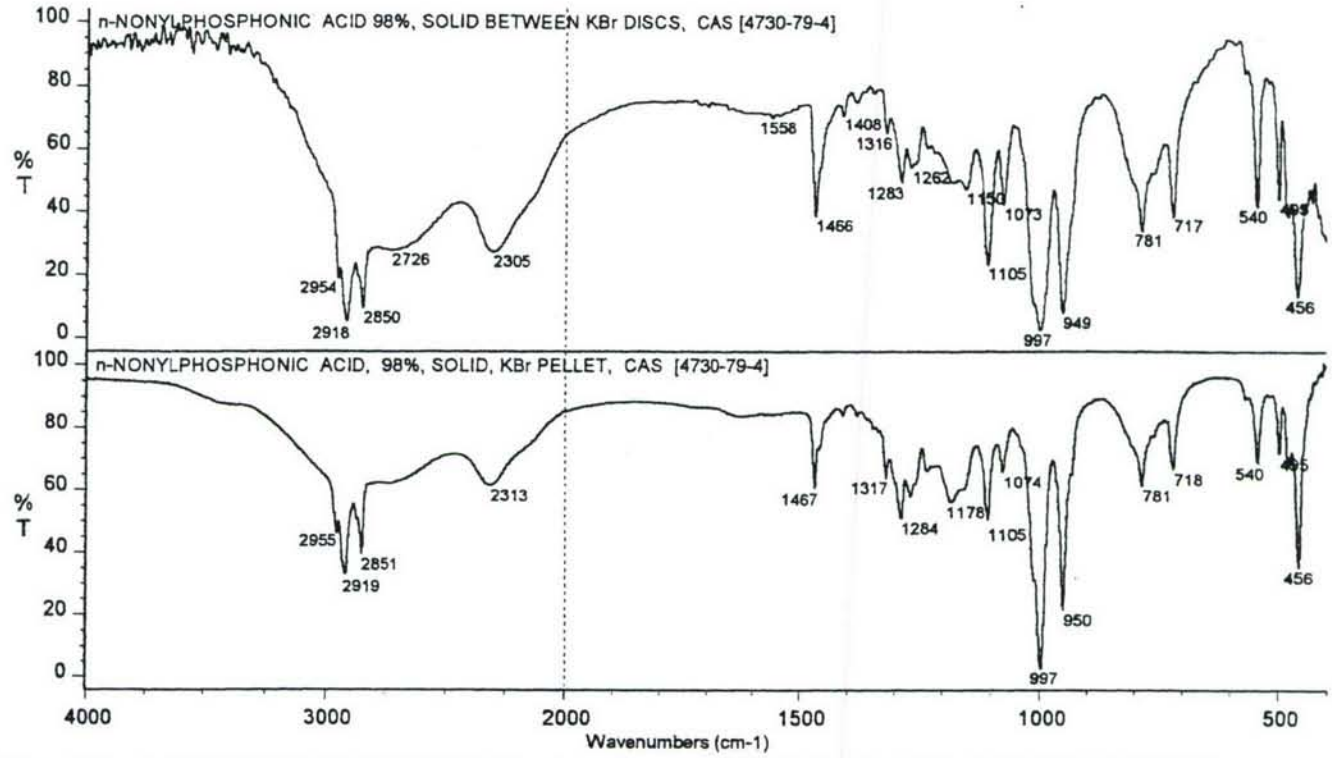


Figure 128 *n*-NONYLPHOSPHONIC ACID, 98%, *UPPER SPECTRUM* –SOLID BETWEEN KBr DISCS (WINDOWS), *LOWER SPECTRUM*–SOLID, KBr PELLET

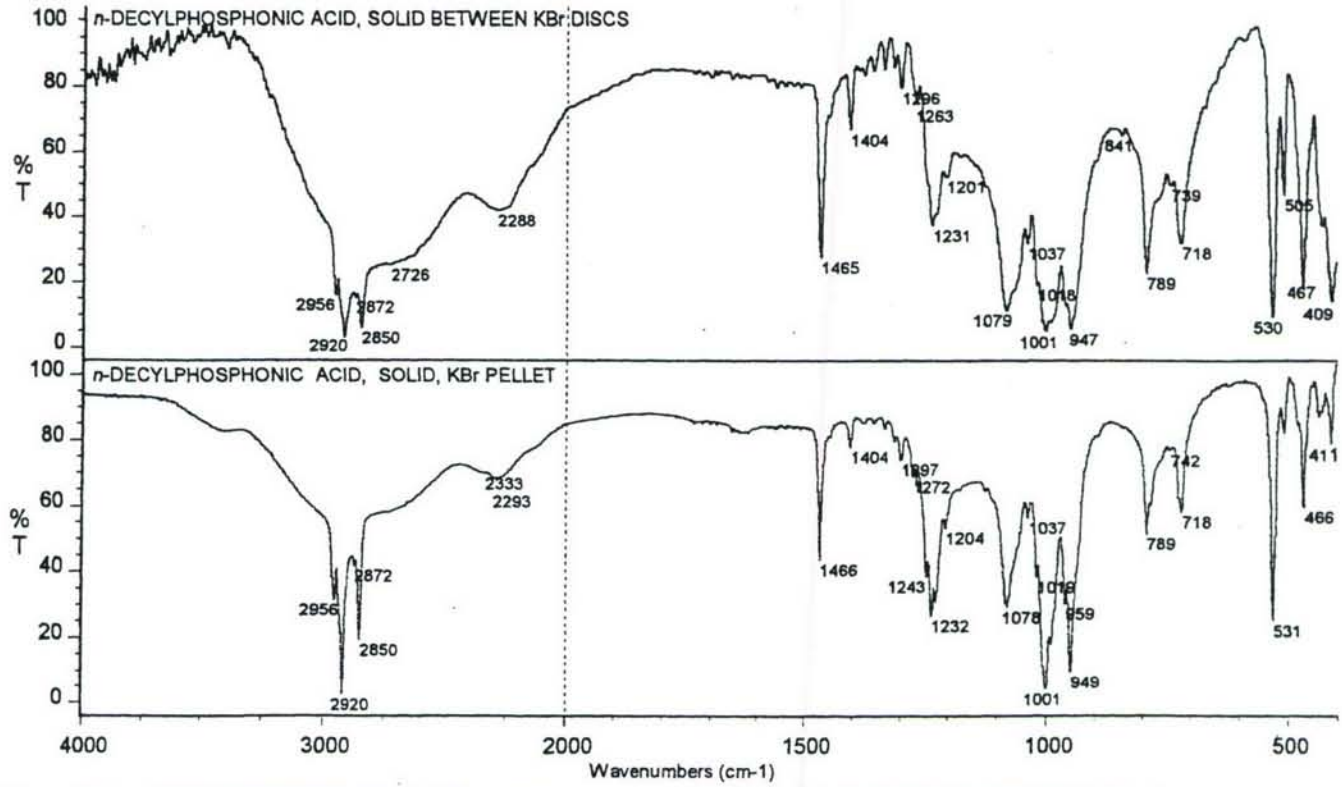


Figure 129 *n*-DECYLPHOSPHONIC ACID, *UPPER SPECTRUM*–SOLID BETWEEN KBr DISCS (WINDOWS), *LOWER SPECTRUM*–SOLID, KBr PELLET

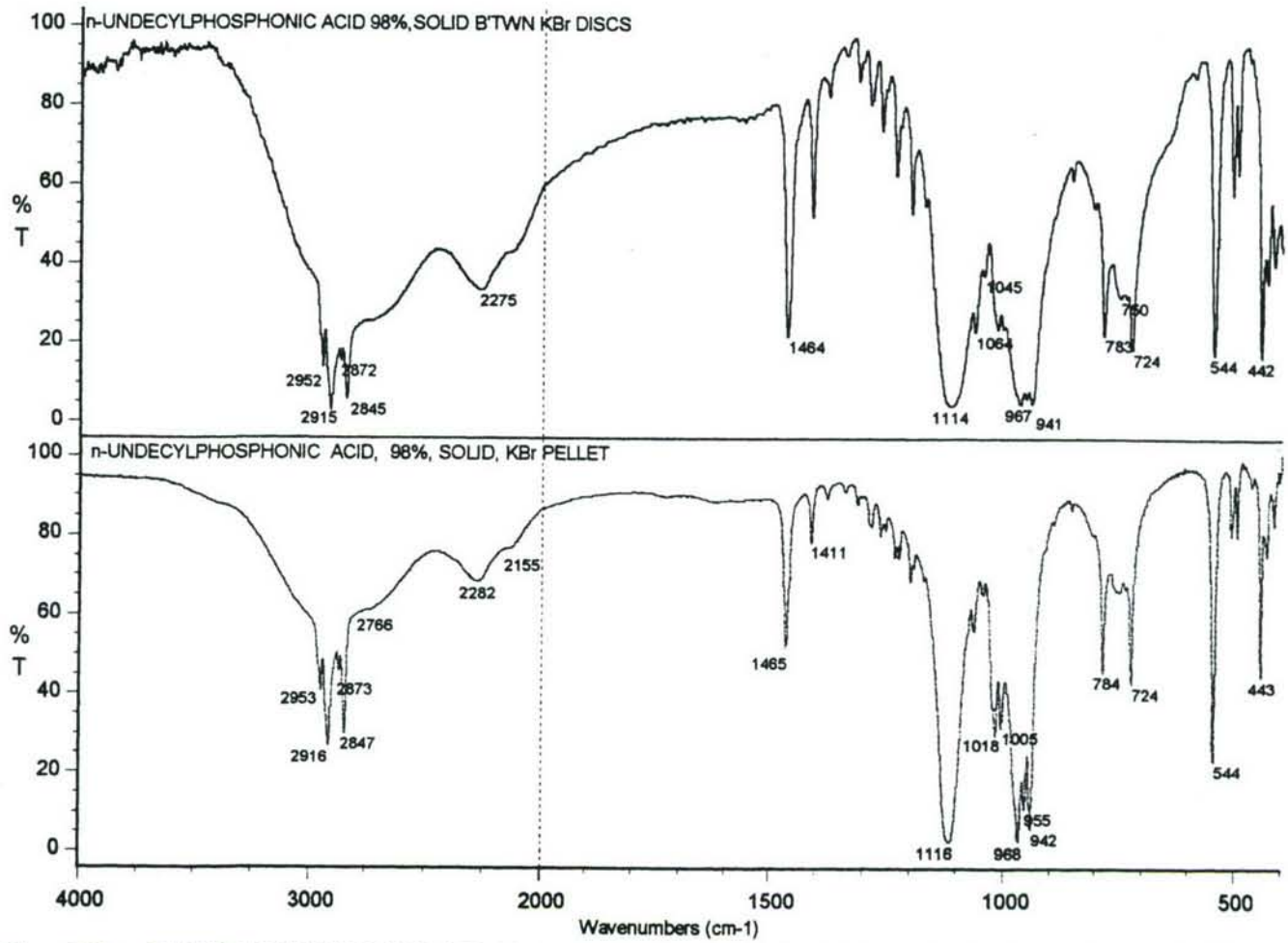


Figure 130 ***n*-UNDECYLPHOSPHONIC ACID, 98%,** ***UPPER SPECTRUM*--SOLID BETWEEN KBr DISCS (WINDOWS),** ***LOWER SPECTRUM*--SOLID, KBr PELLET**

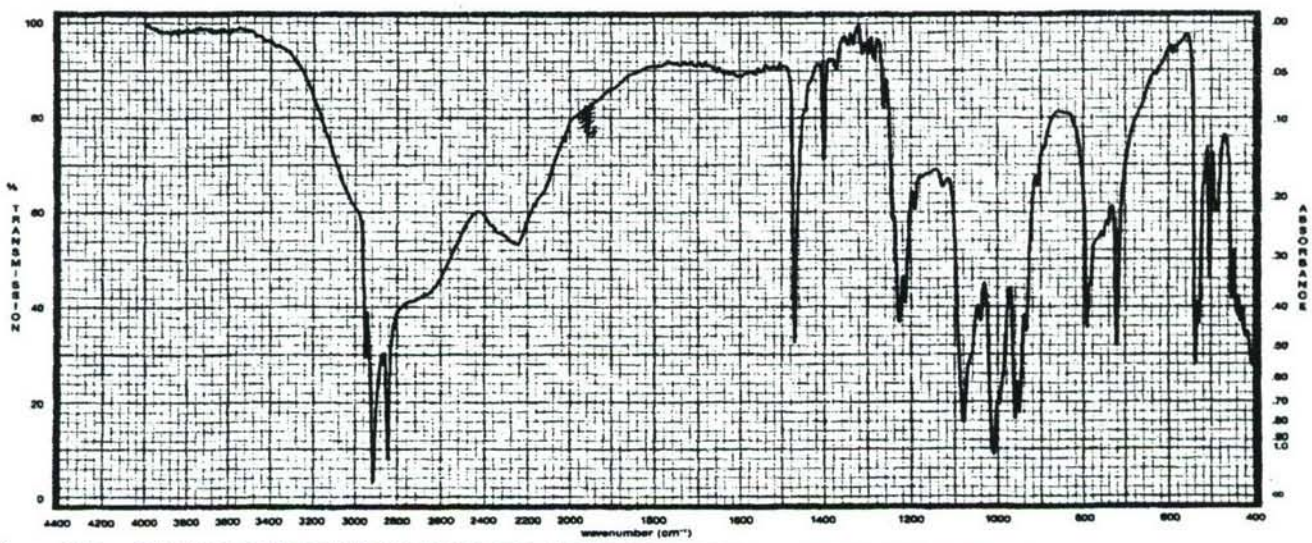


Figure 131 ***n*-TETRADECYLPHOSPHONIC ACID, SOLID BETWEEN KBr DISCS (WINDOWS)**

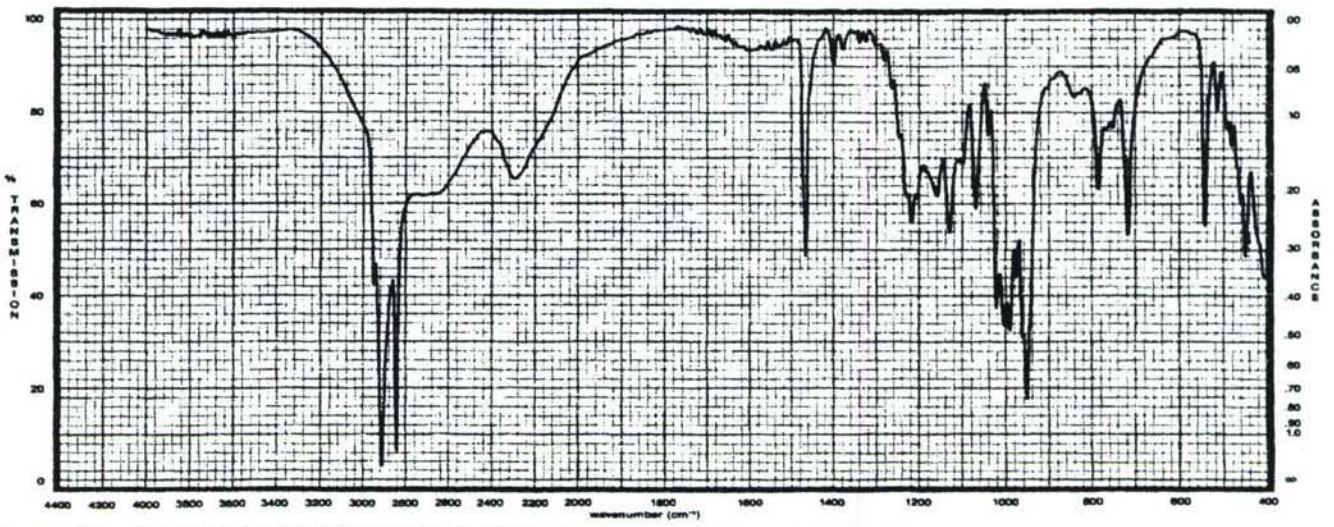


Figure 132 ***n*-HEPTADECYLPHOSPHONIC ACID, SOLID BETWEEN KBr DISCS (WINDOWS)**

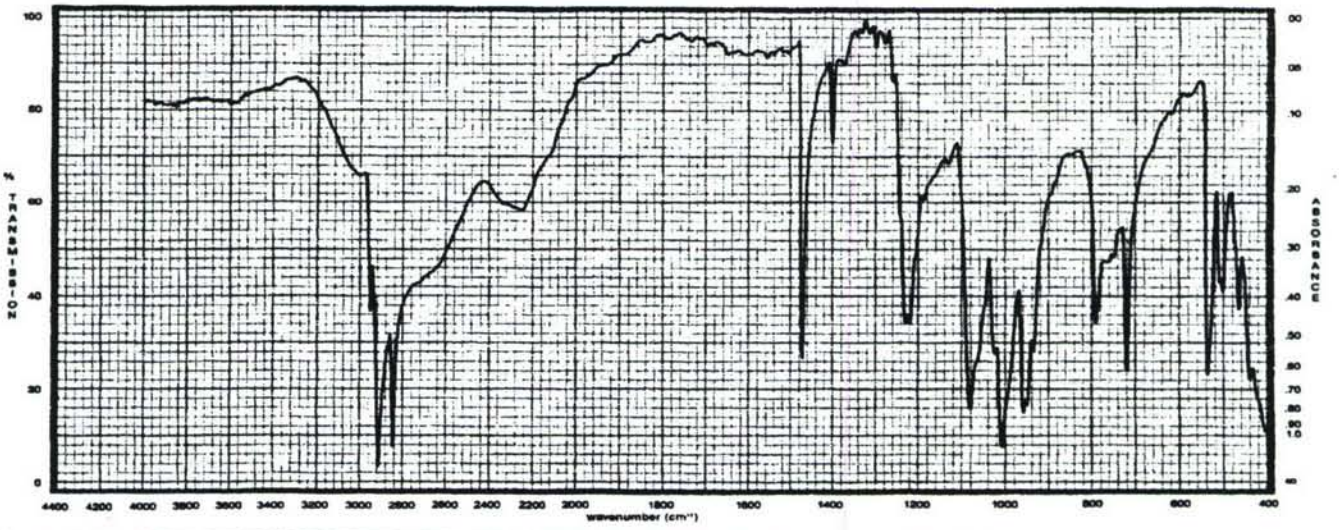


Figure 133 ***n*-OCTADECYLPHOSPHONIC ACID, SOLID BETWEEN KBr DISCS (WINDOWS)**

3.5.4.21 Cyclohexylphosphonic Acid $C_6H_{11}P{=}O(OH)_2$

The infrared spectrum of cyclohexylphosphonic acid is given in ***Figure 134***. The band assignments are as follows: 3429 cm^{-1} w and 1635 cm^{-1} vw (H_2O), 2936 cm^{-1} m 2861 cm^{-1} w (ν_{as} and ν_{sy} CH_2), 2794 and 2324 cm^{-1} broad (POH), 1453 cm^{-1} m (δ CH_2), 1231 cm^{-1} m (CH_2 ω, τ or is it ν P=O ?), 1144, 1118 cm^{-1} m (ν P=O or ω, τ CH_2 ?), 1006 cm^{-1} s (ν_{as} P-OH), 946 cm^{-1} s (ν_{sy} P-OH), 886 cm^{-1} w (cyclohexyl ring ?), 553 cm^{-1} m, 494 cm^{-1} ms (P=O deformation ?).

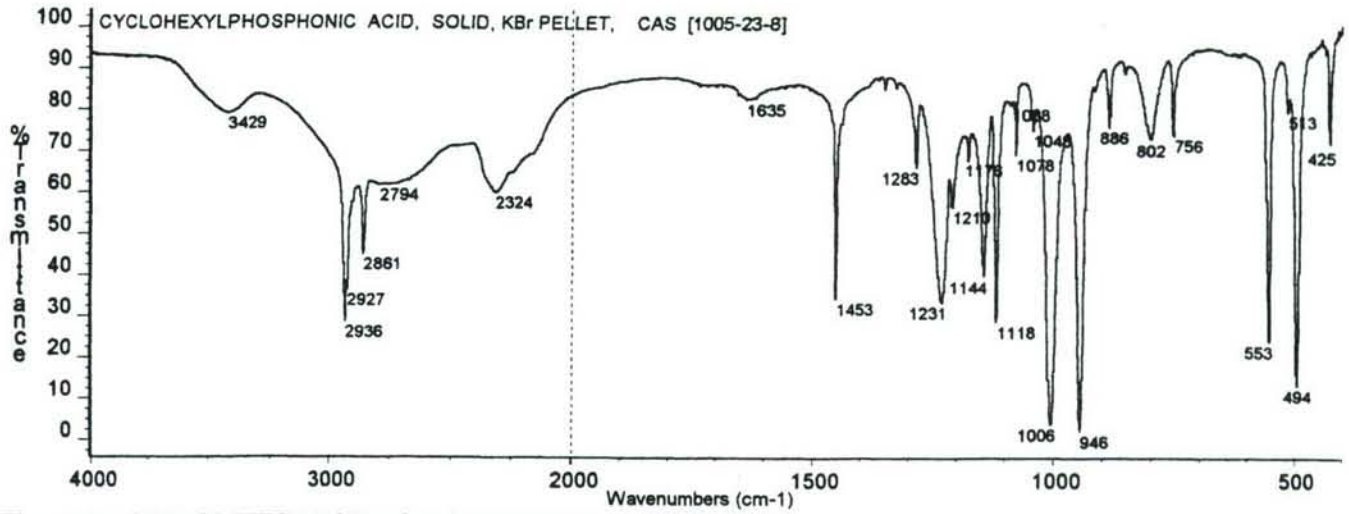


Figure 134 CYCLOHEXYLPHOSPHONIC ACID, SOLID, KBr PELLET

3.5.4.22 Phenylphosphonic Acid C_6H_5-P=O(OH)$_2$

The infrared spectrum of phenylphosphonic acid as a solid between KBr discs and as a KBr pellet is given in ***Figure 135***. The band assignments (for the KBr pellet) are as follows: 3416 cm^{-1} w and ca 1620 cm^{-1} vvw (H_2O), 3082 cm^{-1} vvw (ν C-H aromatic ring), 2730 cm^{-1} m and 2278 cm^{-1} w, both broad (POH), 1592 cm^{-1} w, 1488 cm^{-1} vw and 1439 cm^{-1} m (aromatic ring), 1221 cm^{-1} m (β OH ?), 1145 cm^{-1} s (β C-H mono-substituted aromatic ring, ν P=O ?), 1082 cm^{-1} m phenyl-P, ν P=O ?), 1020 cm^{-1} s (ν_{as} P-OH), 999 cm^{-1} vw (β C-H mono-substituted aromatic ring ?), 940 cm^{-1} ms (ν_{sy} P-OH), 756 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 696 cm^{-1} ms (mono-substituted aromatic ring deformation), 491 cm^{-1} m (P=O deformation ?).

3.5.4.23 4-Methoxyphenylphosphonic acid 4-CH_3O-C_6H_4-P=O(OH)$_2$

The infrared spectrum of 4-methoxyphenylphosphonic acid as a solid between KBr discs and as a KBr pellet is given as ***Figure 136***. The band assignments for the sample as a KBr pellet are as follows: 3422 cm^{-1} w (H_2O), 3017 cm^{-1} vvw (ν C-H aromatic ring), 2977 cm^{-1} vvw (ν CH_3), 2842 cm^{-1} vw (OCH_3), ca 2900 cm^{-1} m broad and 2249 vw broad (POH), 1599 cm^{-1} m, 1573 cm^{-1} w, 1511 cm^{-1} ms and 1461 cm^{-1} w (aromatic ring), 1440 cm^{-1} w (δ OCH_3), 1302 cm^{-1} m (aryl ether ν C-O), 1174 cm^{-1} s (ν P=O), 1080 cm^{-1} ms (phenyl-P), 1020 cm^{-1} m (ν_{as} P-OH), 1001 cm^{-1} ms (alkyl ether C-O), 921 cm^{-1} m (ν_{sy} P-OH), 840 cm^{-1} m (γ C-H para-substituted

aromatic ring), 535 cm^{-1} s (para-substituted aromatic ring).

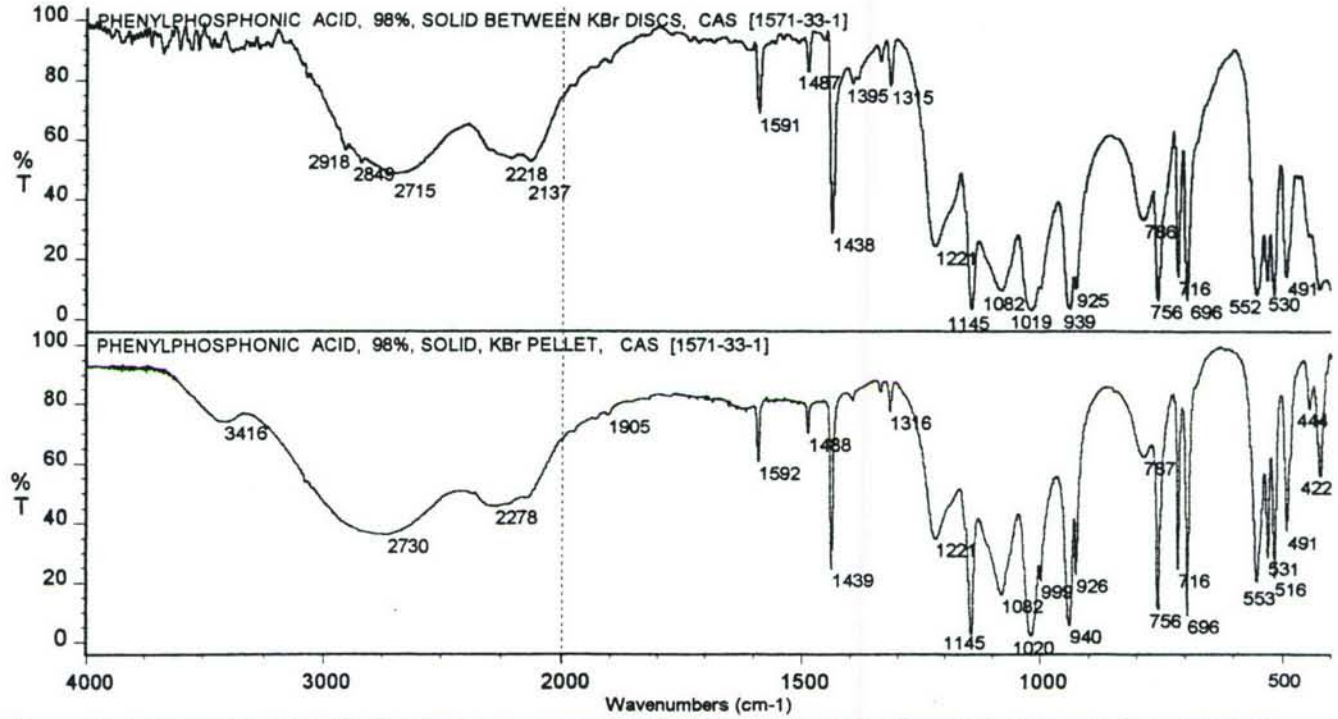


Figure 135 PHENYLPHOSPHONIC ACID, 98%, UPPER SPECTRUM--AS A SOLID BETWEEN KBr DISCS (WINDOWS), LOWER SPECTRUM--SOLID, KBr PELLET

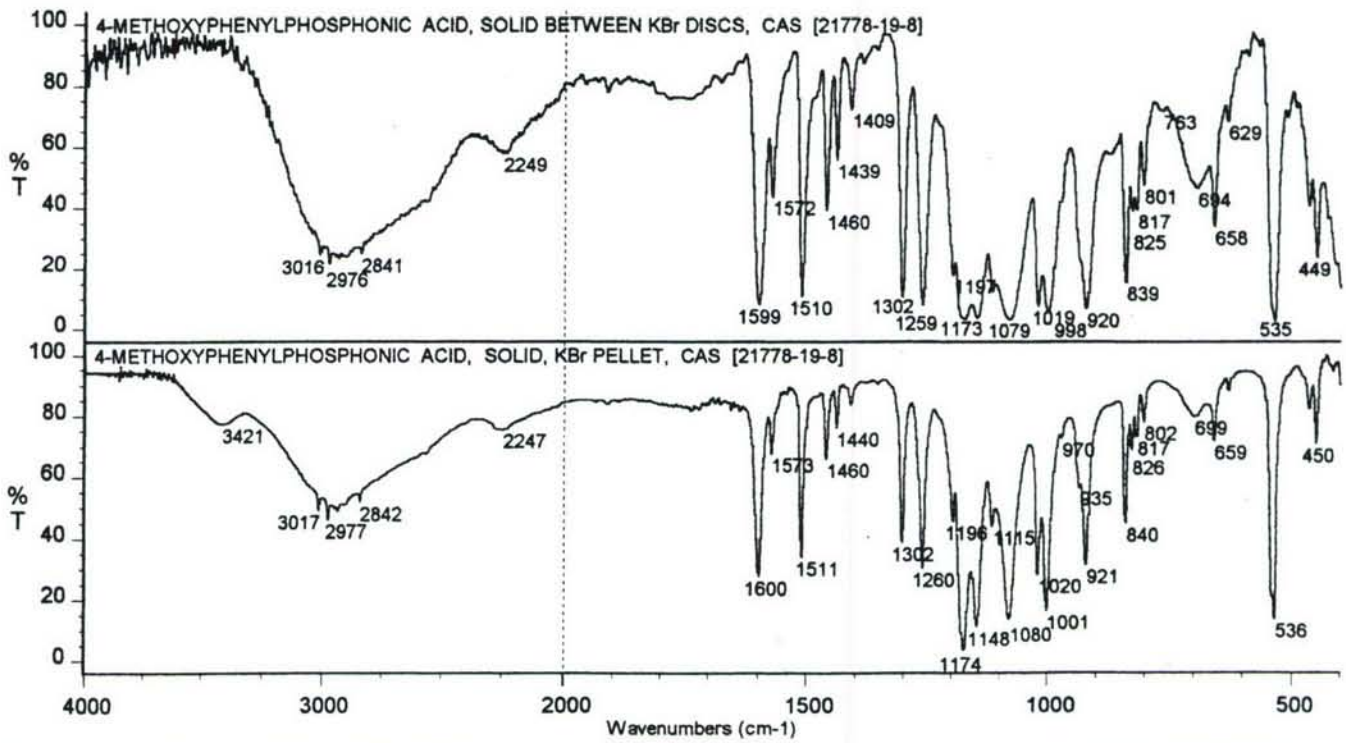


Figure 136 4-METHOXYPHENYLPHOSPHONIC ACID, *UPPER SPECTRUM*--SOLID BETWEEN KBr DISCS (WINDOWS) *LOWER SPECTRUM*--SOLID, KBr PELLET

3.5.4.24 1-Naphthylmethylphosphonic Acid $C_{10}H_7\text{-}CH_2\text{-}P{=}O(OH)_2$

The infrared spectrum of 1-naphthylmethylphosphonic acid is presented as a KBr pellet in ***Figure 137***. The band assignments are as follows: 3048 and 3003 cm^{-1} vw (ν C-H aromatic), 2917 cm^{-1} vw (ν CH_2), 2711 and 2255 cm^{-1} w-m, broad (POH), 1597 cm^{-1} w, 1577 cm^{-1} vvw, 1512 cm^{-1} w, 1413 and 1396 cm^{-1} w (aromatic ring), 1156 cm^{-1} m (ν P=O), 1017 and 1006 cm^{-1} s (ν_{as} P-OH), 957 and 951 cm^{-1} ms (ν_{sy} P-OH), 800 cm^{-1} m (3 adjacent H, 1-naphthalene), 774 cm^{-1} s (4 adjacent H, 1-naphthalene), 491 cm^{-1} m, 446 cm^{-1} ms (P=O deformation).

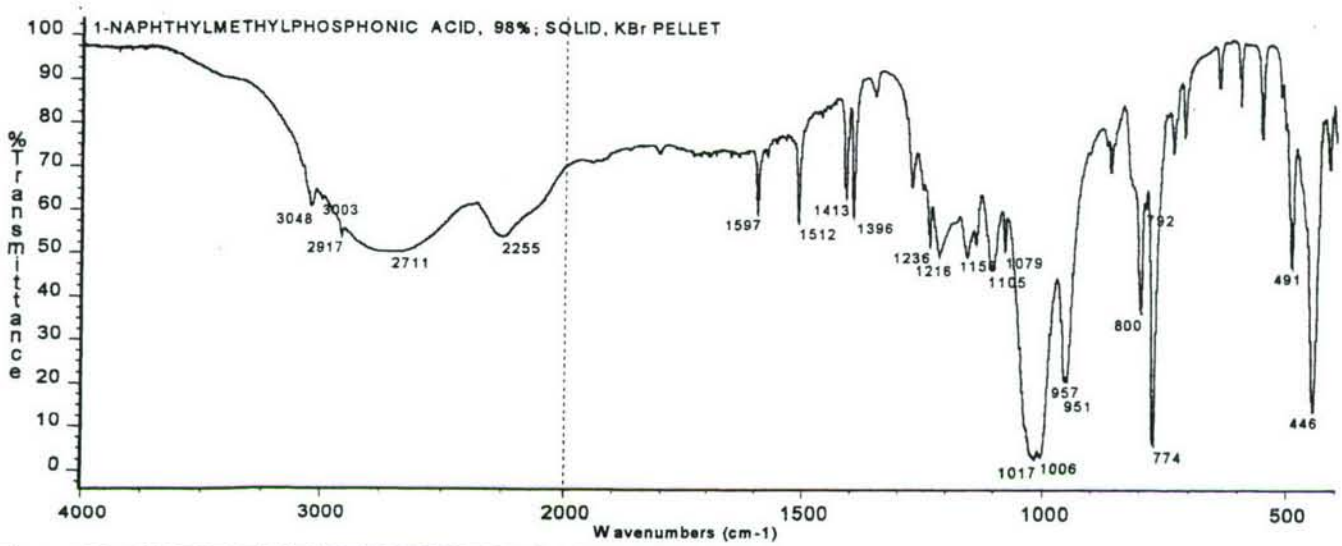


Figure 137 1-NAPHTHYLMETHYLPHOSPHONIC ACID, 98%, SOLID, KBr PELLET

3.5.4.25 Methylenediphosphonic Acid $(HO)_2P{=}O\text{-}CH_2\text{-}P{=}O(OH)_2$

The infrared spectrum for methylenediphosphonic acid as a solid between KBr discs, and as a KBr pellet is given as ***Figure 138***. The band assignments, based on the KBr pellet, are as follows: 2975 cm^{-1} vw (ν_{as} CH_2), 2930 cm^{-1} vw (ν_{sy} CH_2), 2809 cm^{-1} m, broad and 2301 cm^{-1} m, broad (POH), 1631 cm^{-1} vw broad (H_2O and some POH), 1373 cm^{-1} vw (δ CH_2), 1156 cm^{-1} ms (ν P=O), 1025 cm^{-1} s (ν_{as} P-OH), 967 cm^{-1} ms (ν_{sy} P-OH), 817 and 770 cm^{-1} m-w (P-CH_2-P ?), 510 cm^{-1} ms (P=O deformation).

3.5.4.26 1,1-Ethylidenediphosphonic Acid $(HO)_2P(=O)\text{-}CH(CH_3)\text{-}P{=}O(OH)_2$

The infrared spectrum of 1,1-ethylidenediphosphonic acid as a KBr pellet is given as the upper spectrum in ***Figure 139***.

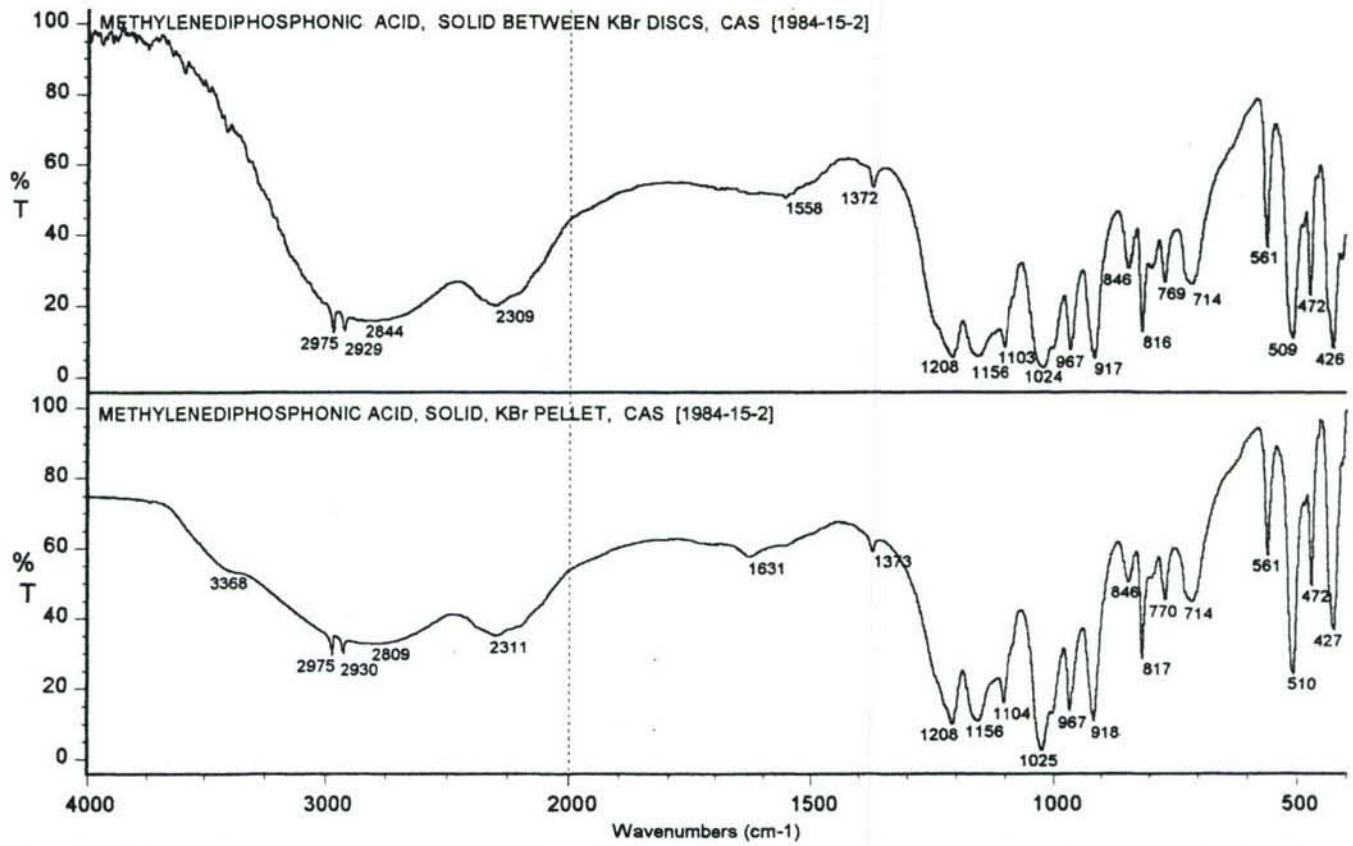


Figure 138 METHYLENEDIPHOSPHONIC ACID, *UPPER SPECTRUM*--AS A SOLID BETWEEN KBr DISCS (WINDOWS), *LOWER SPECTRUM*--SOLID, KBr PELLET

The band assignments for the KBr pellet of 1,1-ethylidenediphosphonic acid are as follows: 2916 cm^{-1} vw (ν CH_3), 2848 cm^{-1} m, broad band and 2269 cm^{-1} m, broad (POH), 1636 cm^{-1} w, broad (H_2O and POH), 1462 cm^{-1} w (δ CH_3), 1148 cm^{-1} ms (ν P=O), 1023 cm^{-1} s (ν_{as} P-OH), 925 cm^{-1} ms (ν_{sy} P-OH), 693 cm^{-1} w (ν P-C ?), 504 cm^{-1} ms (P=O deformation).

3.5.4.27 <u>1,2-Ethylenediphosphonic Acid</u> $(HO)_2P(=O)\text{-}CH_2\text{-}CH_2\text{-}P=O(OH)_2$

The infrared spectrum of 1,2-ethylenediphosphonic acid as a KBr pellet is reproduced as the *lower* spectrum in ***Figure 139***. The band assignments are as follows: 2943 cm^{-1} vvw (ν_{as} CH_2), 2854 cm^{-1} vvw (ν_{sy} CH_2), ca 2800 cm^{-1} m, broad (POH), 2266 cm^{-1} w, broad (POH), ca 1640 cm^{-1} vvw (POH, H_2O), 1409 cm^{-1} m (δ P-CH_2), 1218 cm^{-1} w (ω,τ CH_2), 1185 cm^{-1} ms (ν P=O), 1062 cm^{-1} ms and 1023 cm^{-1} s (ν_{as} P-OH), 962 and 931 cm^{-1} ms (ν_{sy} P-OH), 768 cm^{-1} m and 756 cm^{-1} ms (CH_2 rock), 709 cm^{-1} m (ν P-C), 493 and 485 cm^{-1} s (δ P=O).

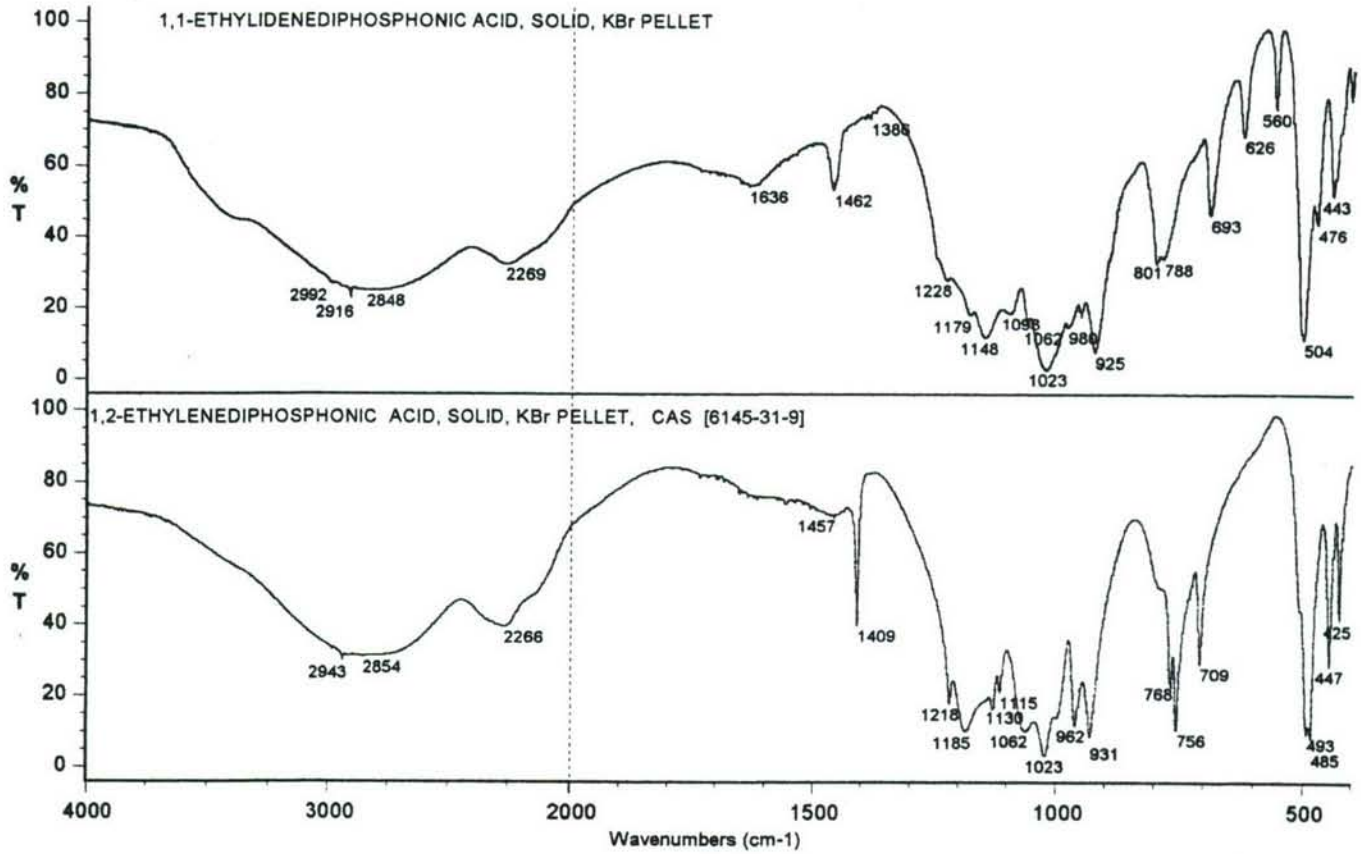


Figure 139 ***UPPER SPECTERUM*--1,1-ETHYLIDENEDIPHOSPHONIC ACID, SOLID, KBr PELLET**
***LOWER SPECTRUM*--1,2-ETHYLENEDIPHOSPHONIC ACID, SOLID, KBr PELLET**

3.5.4.28 Dimethylmethylenediphosphonic Acid $(HO)_2P(=O)\text{-}C(CH_3)_2\text{-}P=O(OH)_2$

The infrared spectrum of dimethylmethylenediphosphonic acid as a solid between CsI discs (windows) is given in ***Figure 140***. The band assignments are as follows: ca 2840 cm^{-1} m broad, ca 2230 w broad and ca 1600 vw broad (POH), l461 cm^{-1} w (δ_{as} CH_3), 1397 and 1377 cm^{-1} vvw (δ_{sy} CH_3), 1148 cm^{-1} ms (ν P=O), 1034 cm^{-1} s (ν_{as} P-OH), 932 cm^{-1} ms (ν_{sy} P-OH), 505 cm^{-1} ms (P=O deformation).

3.5.4.29 Propylenediphosphonic Acid $(HO)_2P(=O)\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}P=O(OH)_2$

The infrared spectrum of propylenediphosphonic acid as a KBr pellet is given in ***Figure 141***. The band assignments are as follows: 3403 cm^{-1} w and 1620 cm^{-1} vw (H_2O), 2919 cm^{-1} vvw (ν_{as} CH_2), 2852 cm^{-1} vvw (ν_{sy} CH_2), ca 2800 m broad, 2285 w broad and ca 1717 cm^{-1} vw (POH), 1461 cm^{-1} vw (δ CH_2), 1415 cm^{-1} vw (δ P-CH_2), 1257 and 1209 cm^{-1} w (ω, τ CH_2), 1182 cm^{-1} m, 1133 cm^{-1} w (ν P=O ?), 1083 cm^{-1} s, 1039 cm^{-1} w (ν

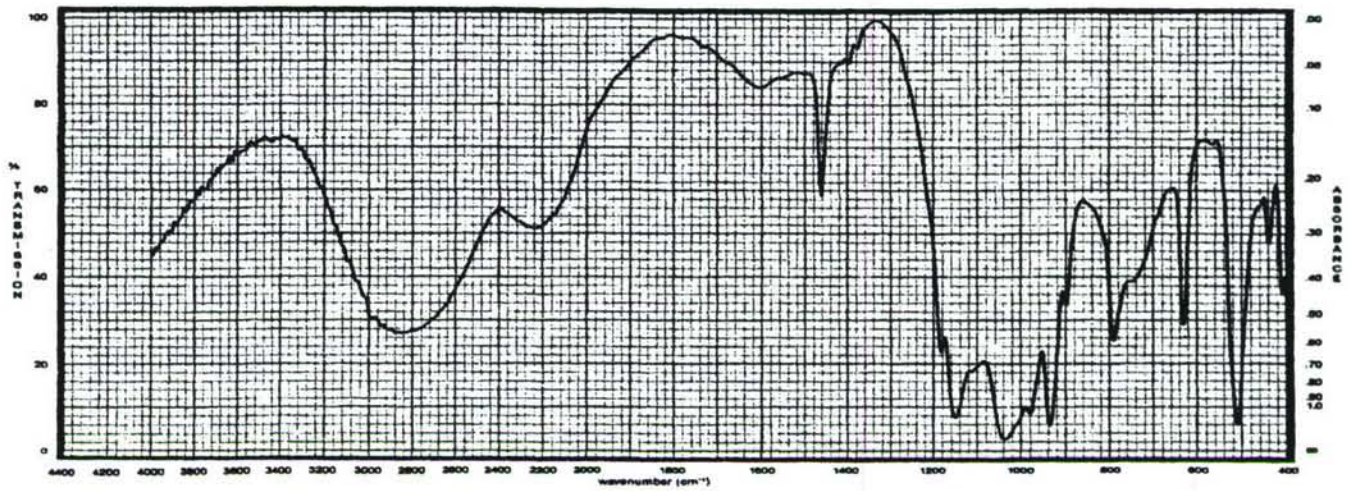


Figure 140 DIMETHYLMETHYLENEDIPHOSPHONIC ACID, SOLID BETWEEN CsI DISCS (WINDOWS)

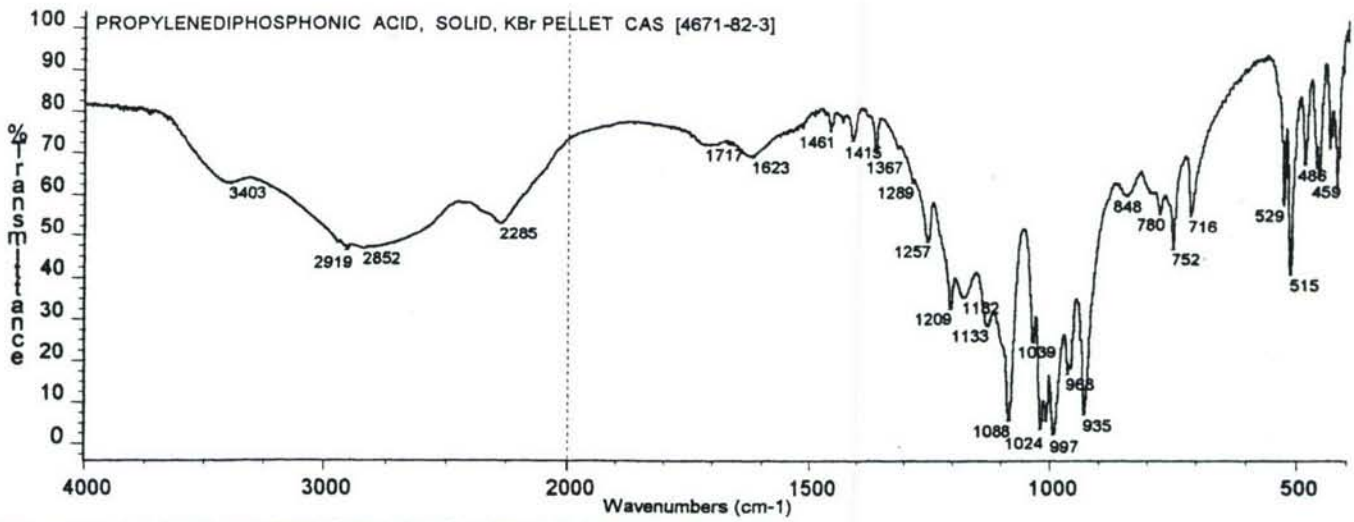


Figure 141 PROPYLENEDIPHOSPHONIC ACID, SOLID, KBr PELLET

C-C ?), 1024, 1013 and 997 cm^{-1} s (ν_{as} P-OH), 935 cm^{-1} ms (ν_{sy} P-OH), 752 cm^{-1} w (CH_2 rock), 716 cm^{-1} w (ν P-C ?), 515 cm^{-1} m (P=O deformation).

3.5.4.30 Methylphosphonofluoridic Acid **(Fluoro Acid)** CH_3-P=O(F)(OH)

The infrared spectrum of methylphosphonofluoridic acid (**Fluoro Acid**) as a liquid film is reproduced as ***Figure 142***. The band asssignments are as follows: 3012 cm^{-1} vw (ν_{as} CH_3), 2936 cm^{-1} vw (ν_{sy} CH_3), 2590 cm^{-1} and 2282, 2179 and 1666 cm^{-1} m and broad (POH), 1418 cm^{-1} vw (δ_{as} P-CH_3), 1384 cm^{-1} vvw (KNO_3 from

the KBr windows used to contain the liquid film), 1323 cm^{-1} ms (δ_{sy} P-CH_3), 1244 cm^{-1} ms, broad (ν P=O), 1031 cm^{-1} s (ν P-OH), 917 cm^{-1} ms (P-CH_3 rock), 851 cm^{-1} ms (ν P-F), 759 cm^{-1} m (ν P-C), 477 cm^{-1} m (δ P-F ?).

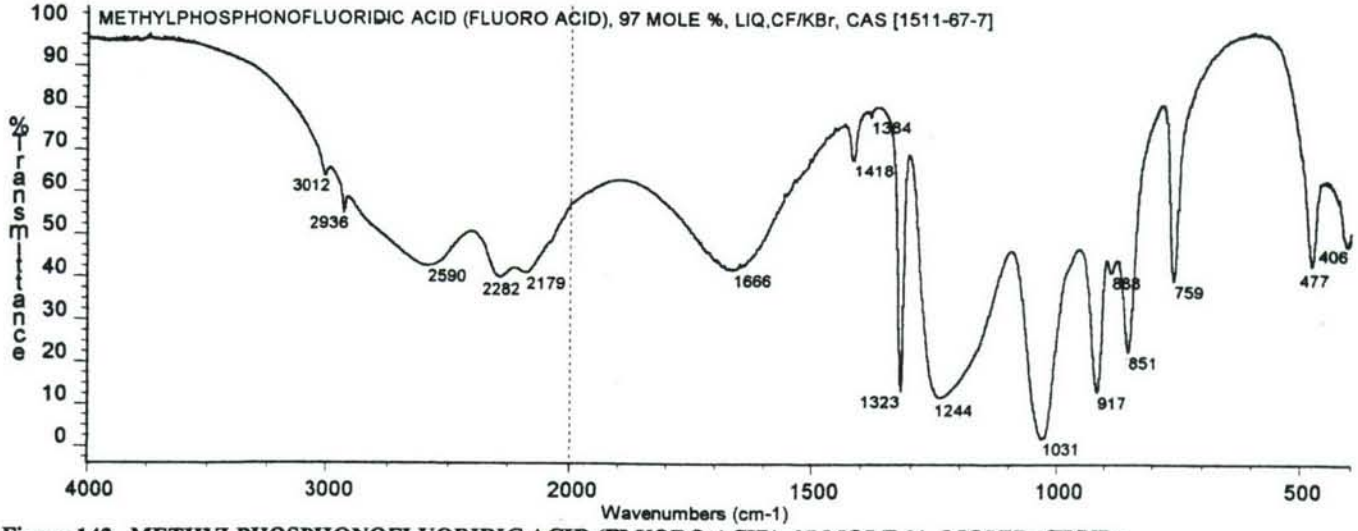


Figure 142 METHYLPHOSPHONOFLUORIDIC ACID (FLUORO ACID), 97 MOLE %, LIQUID, CF/KBr

3.5.4.31 Ethyl Methylphosphonic Acid (**EMPA, VX Acid**) CH_3-P=O(OH)(O-CH_2CH_3)

The compound, ethyl methylphosphonic acid (**EMPA**), is produced on the hydrolysis of **VX** [Ethyl S-(2-diisopropylamino)ethyl methylphosphonothiolate]. The infrared spectrum of **EMPA** is given as ***Figure 143***.

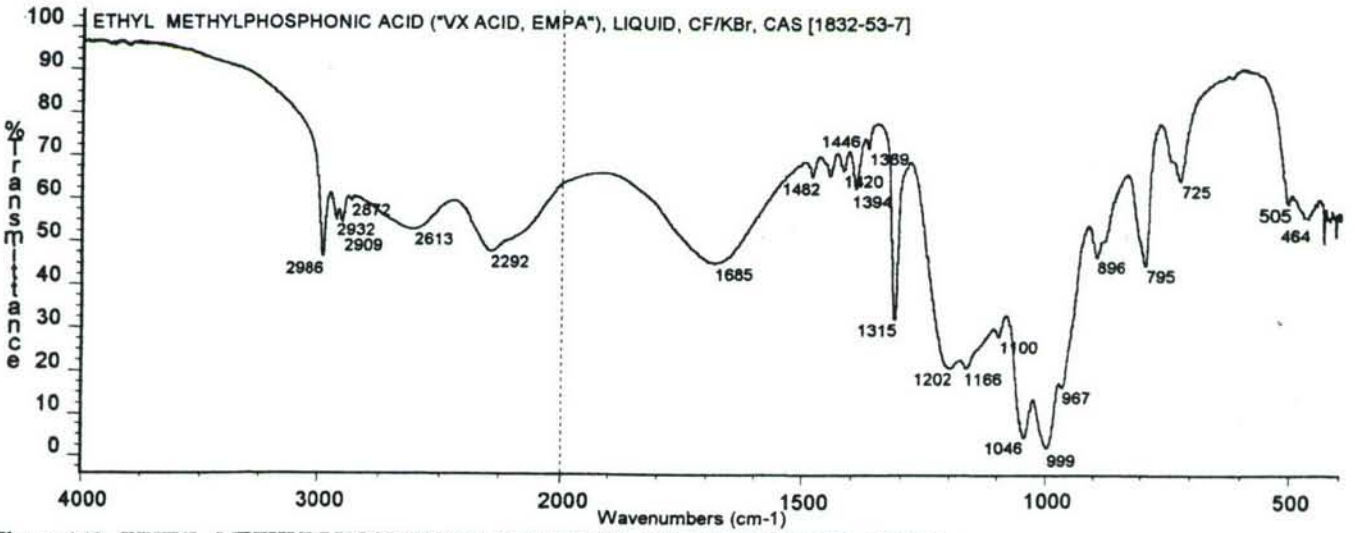


Figure 143 ETHYL METHYLPHOSPHONIC ACID (EMPA, VX ACID), LIQUID, CF/KBr

The band assignments are as follows: 2986 cm^{-1} w (ν_{as} CH_3), 2932 cm^{-1} vw (ν_{as} CH_2), 2909 cm^{-1} (ν_{sy} CH_3), 2872 cm^{-1} vvw (ν_{sy} CH_2), 2613, 2292 and 1685 cm^{-1} all w broad (POH), 1482 cm^{-1} vw (δ OCH_2), 1446 cm^{-1} vw (δ_{as}

CH_3), 1420 cm^{-1} vw (δ_{as} P-CH_3), 1394 cm^{-1} vw (ω OCH_2), 1369 cm^{-1} vvw (δ_{sy} CH_3), 1315 cm^{-1} m (δ_{sy} P-CH_3), 1202 cm^{-1} ms (ν P=O), 1166 and 1100 cm^{-1} vw (CH_3 rock of POEt), 1046 cm^{-1} s (ν P-O-C), 999 cm^{-1} s (ν P-OH), 967 cm^{-1} sh (ν C-C of POEt), 896 cm^{-1} w (P-CH_3 rock), 795 cm^{-1} w (POC), 725 cm^{-1} w (ν P-C), 505, 464 cm^{-1} w (δ P=O).

3.5.4.32 Isopropyl Methylphosphonic Acid (**IMPA, GB Acid**) CH_3-P=O(OH)[O-$CH(CH_3)_2$]

The infrared spectrum of isopropyl methylphosphonic acid (**IMPA, GB Acid**) is reproduced as ***Figure 144***. The compound, **IMPA**, is a product from the hydrolysis of **GB** (**Sarin**, isopropyl methylphosphonofluoridate). The band assignments for **IMPA** are as follows: 2981 cm^{-1} m (ν_{as} CH_3), 2934 cm^{-1} w (ν_{sy} CH_3), 2878 cm^{-1} vw (ν C-H), 2639, 2292 and 1685 cm^{-1} w and broad (POH), 1469 cm^{-1} vw, 1457 cm^{-1} vvw (δ_{as} CH_3), 1420 cm^{-1} vw (δ_{as} P-CH_3), 1387 and 1376 cm^{-1} w (δ_{sy} CH_3 isopropyl doublet), 1314 cm^{-1} m (δ_{sy} P-CH_3), 1203 cm^{-1} ms (ν P=O), 1179, 1143 and 1108 cm^{-1} w (characteristic of P-O-Isopopyl), 1004 cm^{-1} s (ν P-O-C), 906 cm^{-1} w (P-CH_3 rock), 877 cm^{-1} vw (CH_3 rock, isopropyl ?), 783 cm^{-1} w (POC), 730 cm^{-1} vw (ν P-C), 510 cm^{-1} w (δ P=O).

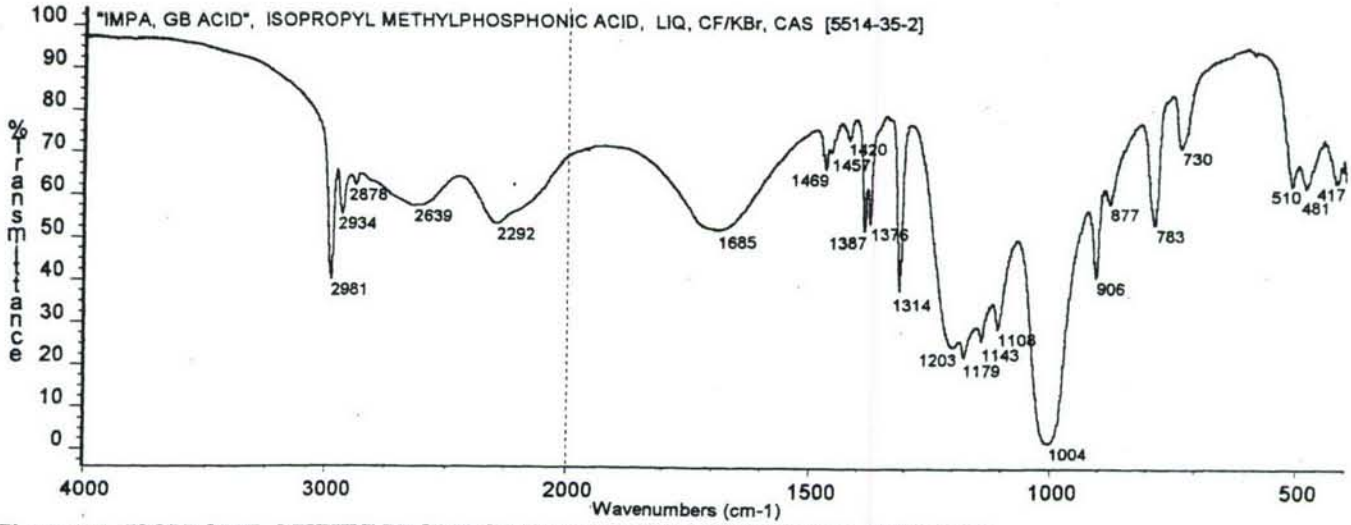


Figure 144 ISOPROPYL METHYLPHOSPHONIC ACID (IMPA, GB ACID), LIQUID, CF/KBr

3.5.4.33 Ethyl Isopropylphosphonic Acid (**EIPA**) $(CH_3)_2$CH-P=O(OH)(O-CH_2-CH_3)

The infrared spectrum of a liquid film of ethyl isopropylphosphonic acid (**EIPA**) between KBr windows is given in ***Figure 145***. The band assignments are as follows: 2980 cm^{-1} m (ν_{as} CH_3), 2938 cm^{-1} w

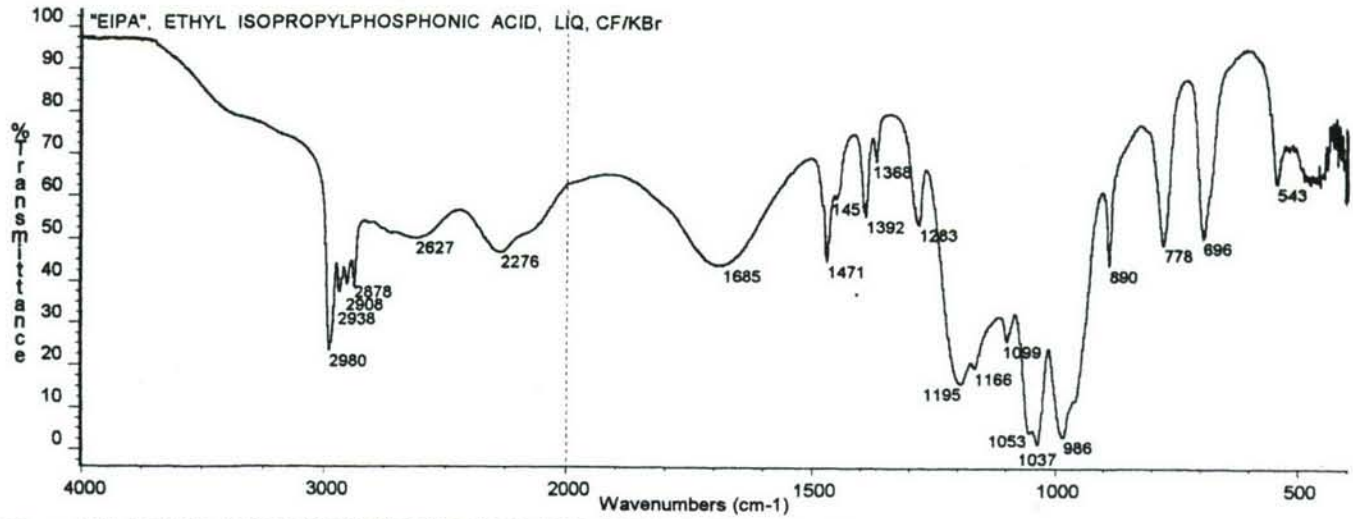


Figure 145 ETHYL ISOPROPYLPHOSPHONIC ACID (EIPA), LIQUID, CF/KBr

(ν_{as} CH_2), 2908 cm^{-1} vw (ν_{sy} CH_3), 2878 cm^{-1} w (ν_{sy} CH_2), 2627 cm^{-1}, 2276 cm^{-1} and 1685 cm^{-1} w and broad (POH), 1471 cm^{-1} w (δ OCH_2), 1451 cm^{-1} vw (δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2 and δ_{sy} CH_3 isopropyl), 1368 cm^{-1} vw (δ_{sy} CH_3), 1283 cm^{-1} w (P-isopropyl ?), 1195 cm^{-1} ms (ν P=O), 1166 and 1099 cm^{-1} vw (CH_3 rock of POEt, characteristic), 1053 cm^{-1} sh and 1037 cm^{-1} s (ν P-O-C), 986 cm^{-1} s (ν C-C of POEt and ν P-OH which may absorb near the shoulder on the band near 960 cm^{-1}), 890 cm^{-1} w (isopropyl moiety, CH_3 rock ?), 778 cm^{-1} w (POC), 696 cm^{-1} w (ν P-C), 543 cm^{-1} w (P=O deformation ?). See also ***Figure 121*** (isopropylphosphonic acid) which shows a band near 1285 cm^{-1}. This band, together with the 1283 cm^{-1} band for **EIPA** may be indicative of a *possible* characteristic band for the P-isopropyl group. More data is needed to confirm this assertion.

3.5.4.34 Pinacolyl Methylphosphonic Acid **(GD Acid, PMPA)** CH_3-P=O(OH)[O-CH(CH_3-C(CH_3)$_3$

The infrared spectrum of pinacolyl methylphosphonic acid (**GD Acid, PMPA**) as a liquid film between CsI windows is reproduced as ***Figure 146***. The compound is a hydrolysis product of **GD (Soman)**, pinacolyl methylphosphonofluoridate. The band assignments are as follows: 2964 cm^{-1} m, 2912 cm^{-1} vw and 2874 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 2651, 2296 and 1680 cm^{-1} all weak and broad (POH), 1482 cm^{-1} w and 1464 cm^{-1} vw (δ_{as} CH_3), 1418 cm^{-1} vvw (δ_{as} P-CH_3), 1397 cm^{-1} vw and 1380 cm^{-1} w [δ_{sy} CH_3 from $C(CH_3)_3$], 1366 cm^{-1} w (δ_{suy} CH_3 from C-CH_3), 1312 cm^{-1} m (δ_{sy} P-CH_3), 1209 cm^{-1} ms (ν P=O), 1115 cm^{-1} vw, 1079 cm^{-1} w and 1051

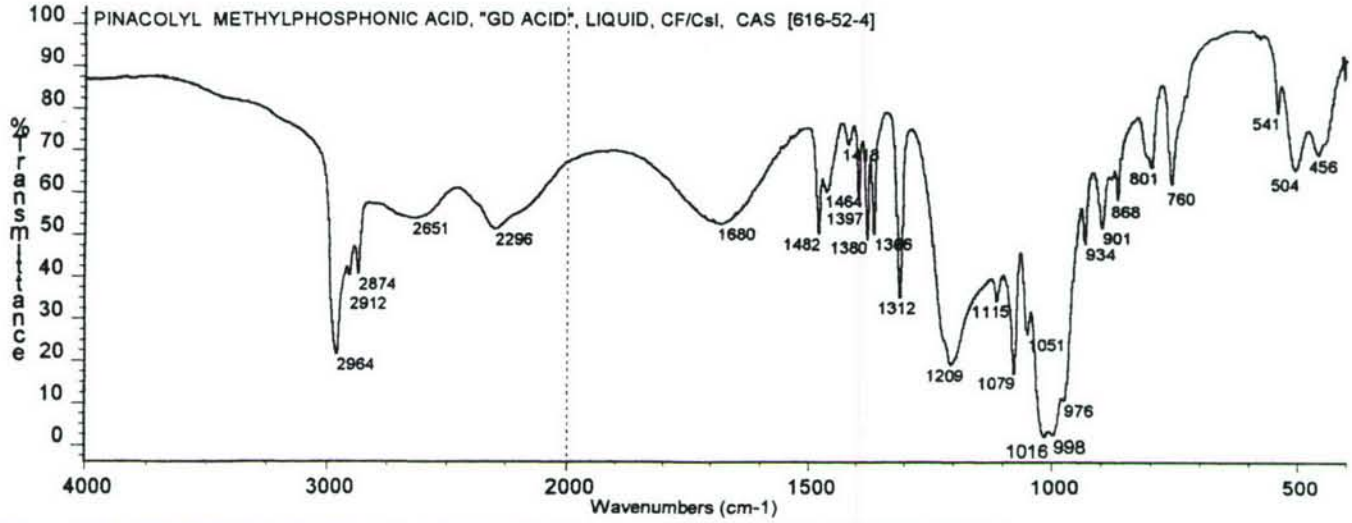


Figure 146 PINACOLYL METHYLPHOSPHONIC ACID (GD ACID, PMPA), LIQUID, CF/CsI

cm^{-1} w (pinacolyl moiety), 1016 and 998 cm^{-1} s (ν P-O-C), 976 cm^{-1} sh (ν C-C, ν P-OH), 934, 868 and 760 cm^{-1} all weak (pinacolyl moiety), 901 cm^{-1} w (P-CH_3 rock), 801 cm^{-1} w POC), 504 cm^{-1} w P=O deformation).

3.5.4.35 Cyclohexyl Methyphosphonic Acid **(GF Acid)** CH_3-P=O(OH)(O-C_6H_{11})

The infrared spectrum of a liquid film of cyclohexyl methylphosphonic acid (**GF Acid**), or cyclohexyl hydrogen methylphosphonate, between KBr windows is presented as ***Figure 147***. The band assignments are as follows: 2937 cm^{-1} ms (ν_{as} CH_2), 2860 cm^{-1} m (ν_{sy} CH_2), 2261, 2292 and 1670 cm^{-1} all weak and broad (POH), 1452 cm^{-1} w (ring δ CH_2), 1419 cm^{-1} vw (δ_{as} P-CH_3), 1313 cm^{-1} w (δ_{sy} P-CH_3), 1202 cm^{-1} ms (ν P=O), 1042 cm^{-1}

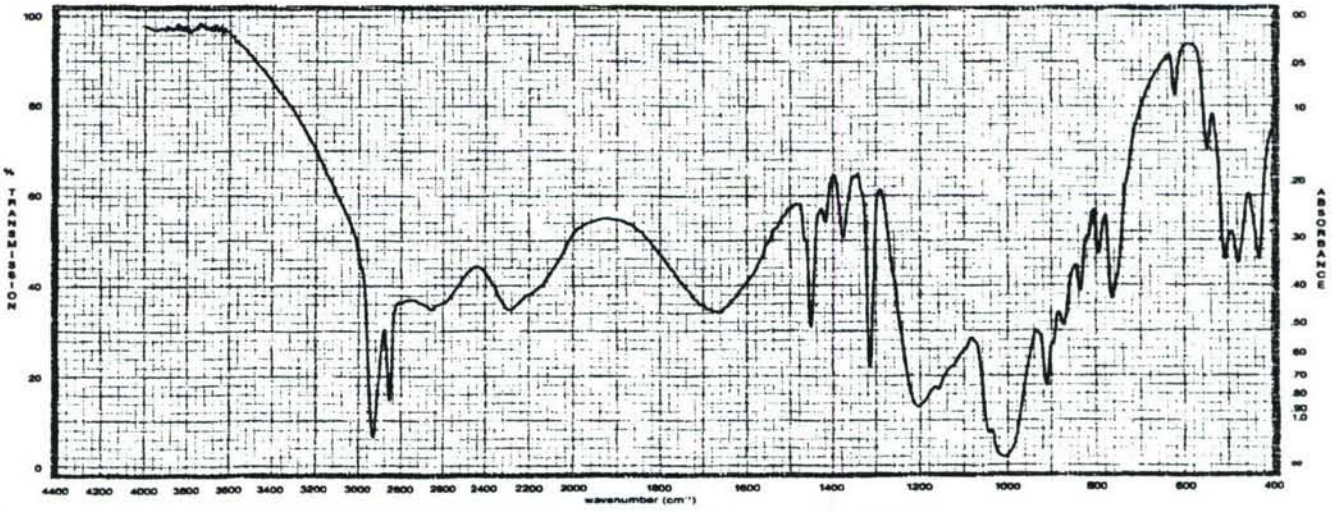
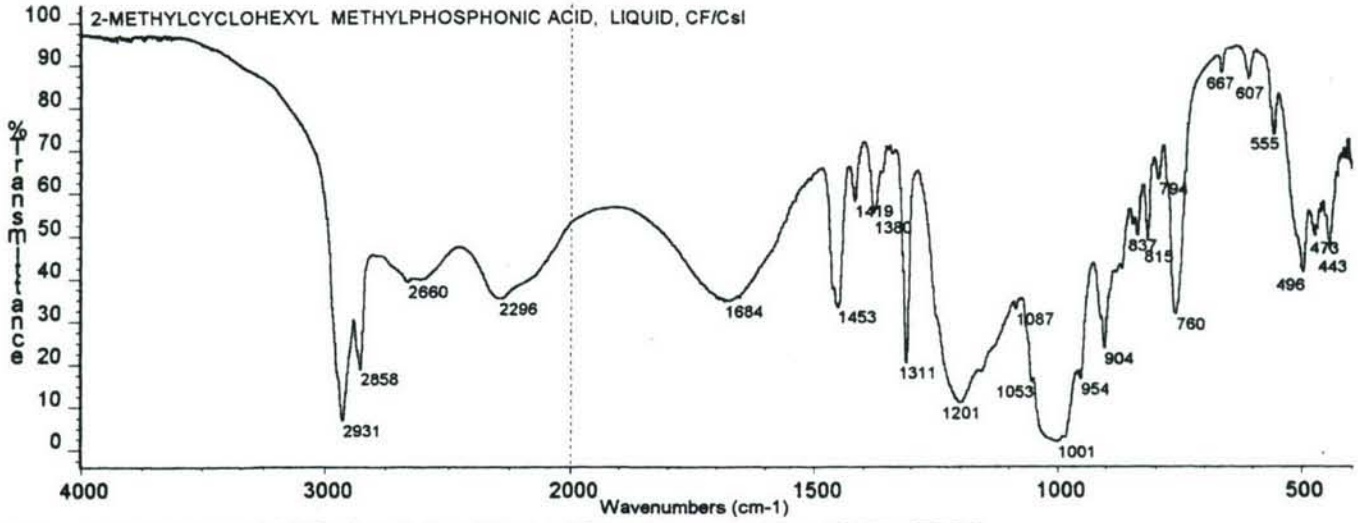


Figure 147 CYCLOHEXYL METHYLPHOSPHONIC ACID (GF ACID), LIQUID, CF/KBr

sh and 1007 cm^{-1} s (ν P-O-C, also ν P-OH below 1000 cm^{-1}), 909 cm^{-1} w ($P-CH_3$ rock), 762 cm^{-1} w m (POC).

3.5.4.36 2-Methylcyclohexyl Methylphosphonic Acid $CH_3-P{=}O(OH)[O-C_6H_{10}-(2-CH_3)]$

The infrared spectrum of a liquid film of 2-methylcyclohexyl methylphosphonic acid (or 2-methylcyclohexyl hydrogen methylphosphonate) is given in ***Figure 148***. The compound is a hydrolysis product of 2-methylcyclohexyl methylphosphonofluoridate. The band assignments for the acid are as follows: 2931 cm^{-1} s



Fighure 148 2-METHYLCYCLOHEXYL METHYLPHOSPHONIC ACID, LIQUID, CF/CsI

2858 cm^{-1} ms (ν_{as} and ν_{sy} CH_3 and CH_2), 2660 cm^{-1} , 2296 cm^{-1} and ca 1680 cm^{-1} all weak and broad (POH), 1453 cm^{-1} w (δ_{as} CH_3 and δ CH_2), 1419 cm^{-1} vw (δ_{as} $P-CH_3$), 1380 cm^{-1} vw (δ_{sy} CH_3), 1311 cm^{-1} m (δ_{sy} $P-CH_3$), 1053 cm^{-1} sh and 954 cm^{-1} sh (cyclohexyl ring ?), 1001 cm^{-1} s (ν P-O-C and also ν P-OH, possible shoulder at 987 cm^{-1} ?), 904 cm^{-1} m ($P-CH_3$ rock), 760 cm^{-1} m (POC), 496 cm^{-1} w (P=O deformation).

3.5.5 **Phosphinic Acids** $HO-P{=}O(R)_2$

3.5.5.1 Hypophosphorous Acid $H-P(OH)_2 \rightarrow H-P{=}O(OH)(H)$

The infrared spectrum for a liquid film of hypophosphorous acid (50 wt % solution in water) is given in ***Figure 149***. The band assignments are as follows: ca 3400 cm^{-1} s (H_2O), ca 2800 cm^{-1} sh and ca 2200 cm^{-1} sh (POH), 2403 cm^{-1} w (ν P-H), 1650 cm^{-1} m (H_2O, some POH), 1184 cm^{-1} ms (ν P=O), 1066 cm^{-1} m (ν P-OH ?), 977 cm^{-1} m and 806 cm^{-1} w (P-H deformations), ca 720 w broad (H_2O).

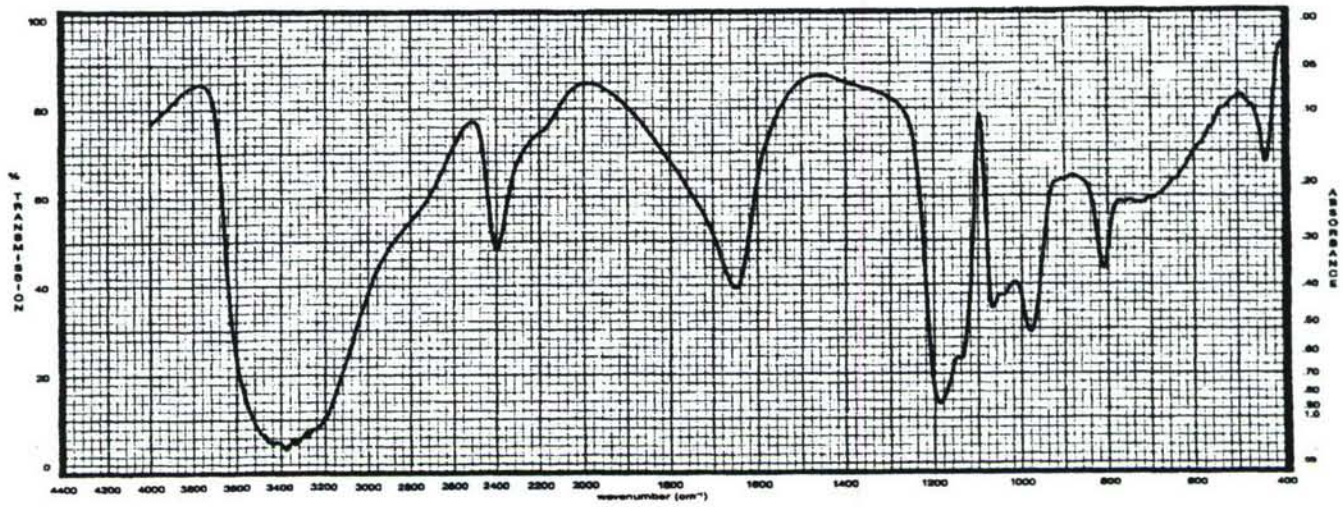


Figure 149 HYPOPHOSPHOROUS ACID, 50 Wt % IN H_2O, LIQUID, CF/CdTe

3.5.5.2 Dimethylphosphinic Acid $(CH_3)_2P{=}O(OH)$

Infrared spectra for dimethylphosphinic acid, as a solid between KBr and CsI windows and as a wet and dried KBr pellet, are represented as ***Figure 150***. The spectra (A) and (B) show the effect of grinding the sample between the different window materials (KBr and CsI). Notice that there is some difference in the relative intensities of the individual bands between the two salt windows, which may be due to differences in grinding times. The grinding differences may be related to the hardness (or conversely the softness) of the two different window materials. As stated previously (see **Sample Handling** section) a small amount of the solid sample was actually ground while between the salt windows. Spectra (C) and (D) show the effect of drying on the KBr pellet prepared for dimethylphosphinic acid. The *same* pellet was use in both cases, the only difference being spectrum (D) was for a drier pellet than that represented by spectrum (C). The relative band intensities show changes as the pellet becomes drier (compare the intensities of the 1156 and 980 cm^{-1} bands as well as the POH bands for the two pellet spectra).

The band assignments for dimethylphosphinic acid as a solid between CsI discs (windows) are: 2982 cm^{-1} vvw (ν_{as} CH_3), 2917 cm^{-1} vvw (ν_{sy} CH_3), 2607 cm^{-1} vw broad, 2280 and 2193 cm^{-1} vw broad and ca 1700 cm^{-1} w broad (POH, notice that for phosphinic acids, with one OH group per phosphorus, the band near 1700 cm^{-1}

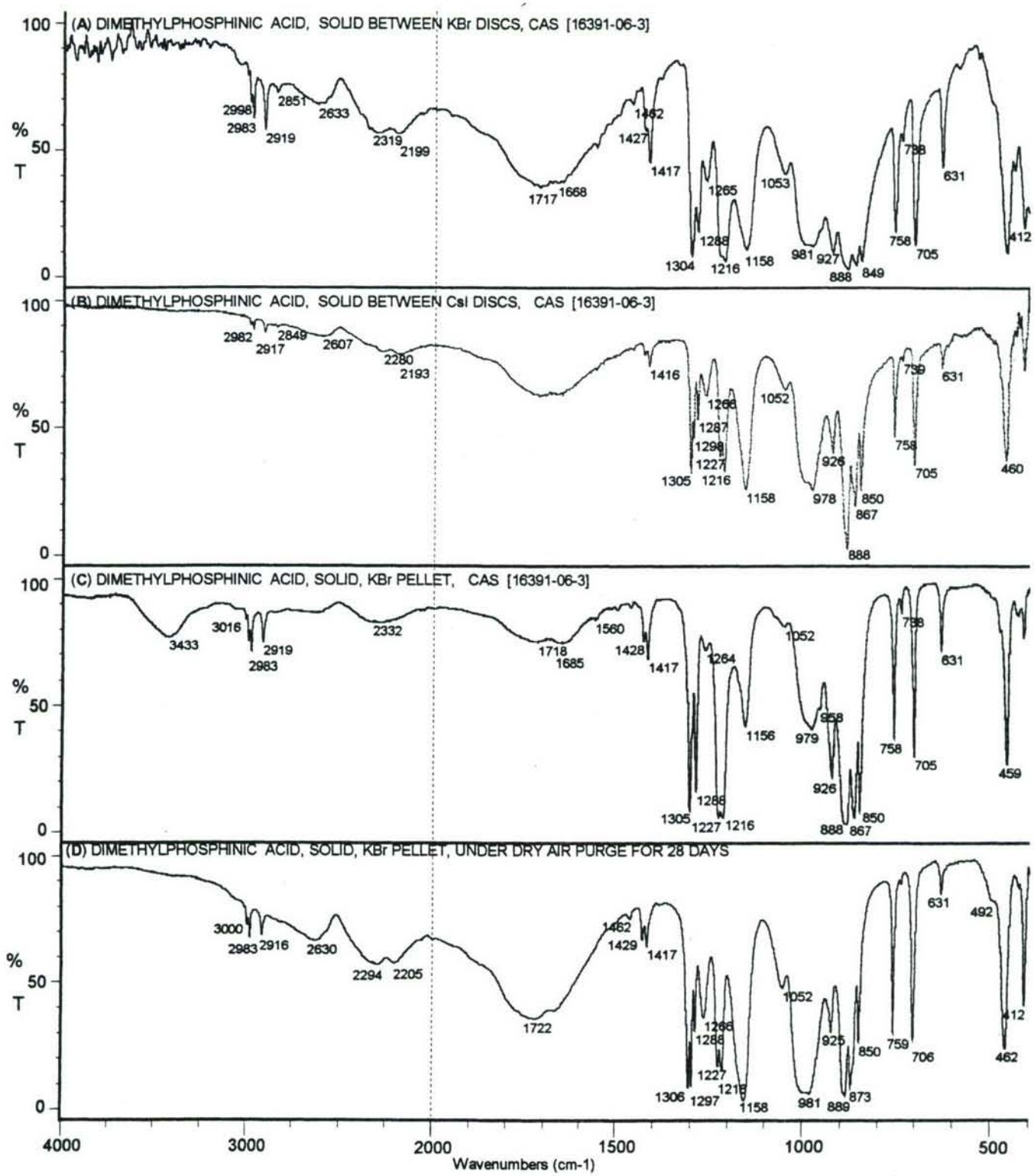


Figure 150 (A) DIMETHYLPHOSPHINIC ACID, SOLID BETWEEN KBr DISCS (WINDOWS)
(B) DIMETHYLPHOSPHINIC ACID, SOLID BETWEEN CsI DISCS (WINDOWS)
(C) DIMETHYLPHOSPHINIC ACID, SOLID, KBr PELLET
(D) DIMETHYLPHOSPHINIC ACID, SOLID, KBr PELLET KEPT UNDER A DRY AIR PURGE FOR 28 DAYS

is the strongest), 1420 cm^{-1} sh and 1416 cm^{-1} vw (δ_{as} P-CH_3), 1305, 1298 and 1287 cm^{-1} m-w (δ_{sy} P-CH_3, multiple bands), 1227 and 1216 cm^{-1} m (OH deformation), 1158 cm^{-1} m (ν P=O), 978 cm^{-1} m (ν P-OH), (926), 888, 867 and 850 cm^{-1} s-m (P-CH_3 rock)[y], 758 cm^{-1} w and 705 cm^{-1} m (ν P-C), 460 cm^{-1} m (P=O deformation).

3.5.5.3 Bis(hydroxymethyl)phosphinic Acid $(HO\text{-}CH_2)_2P{=}O\ (OH)$

The infrared spectrum for bis(hydroxymethyl)phosphinic acid as a liquid film between KBr windows is given in ***Figure 151***. The band assignments are as follows: 3330 cm^{-1} s (ν O-H), 2902 cm^{-1} vw (ν_{as} CH_2), 2825 cm^{-1} vw (ν_{sy} CH_2), ca 2650, 2282 and 1647 cm^{-1} all w and broad (POH), 1424 cm^{-1} w (δ CH_2), ca 1390 cm^{-1} sh (β OH), 1314 cm^{-1} vvw (ω CH_2), 1163 cm^{-1} ms (ν P=O), 1047 cm^{-1} ms (ν C-O), 968 cm^{-1} ms (ν P-OH), 851 cm^{-1} m (C-O ?), 765 cm^{-1} vw (CH_2 rock, ν P-C ?), 685 vw (γ OH ?).

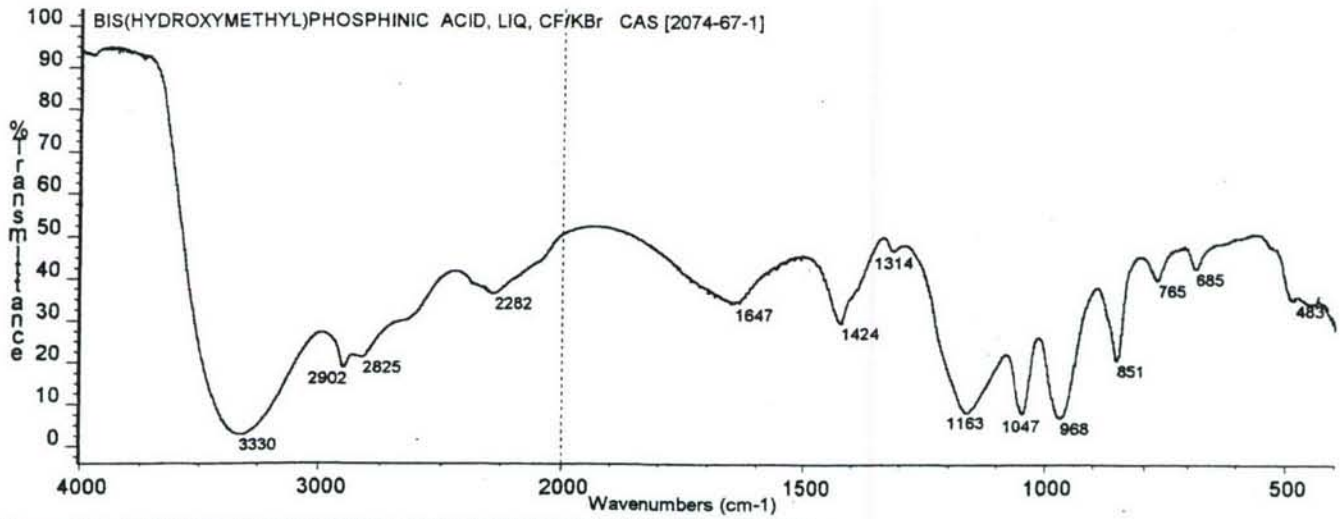


Figure 151 BIS(HYDROXYMETHYL)PHOSPHINIC ACID, LIQUID, CF/KBr

3.5.5.4 Diethylphosphinic Acid $(CH_3CH_2)_2P{=}O(OH)$

The infrared spectra of diethylphosphinic acid is discussed under the hydolysis of diethylphosphinic chloride, $(CH_3CH_2)_2P{=}O(Cl)$, in the section (3.5.9) entitled *Phosphinic Halides*.

[y] When two methyl groups are attached to the same P^{+5} atom at least two, and often three or more, bands occur between 958-835 cm^{-1}. For P^{+3} compounds containing two P-CH_3 groups the absorption is compex and falls within the range of similar P^{+5} compounds. See Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 95,97, Heyden & Son Ltd., London, 1974.

3.5.5.5 Di-*n*-butylphosphinic Acid $(CH_3CH_2CH_2CH_2)_2P{=}O(OH)$

The infrared spectrum of di-*n*-butylphosphonic acid is given in ***Figure 152***. The band assignments are as follows: 3436 cm^{-1} w (H_2O), 2957 cm^{-1} m (ν_{as} CH_3), 2930 cm^{-1} w (ν_{as} CH_2), 2873 cm^{-1} w (ν_{sy} CH_3, CH_2), 2620 cm^{-1} wv broad, 2264 and 2138 cm^{-1} vw and 1632 cm^{-1} w all broad (POH, some H_2O contribution at 1632 cm^{-1}), 1467 cm^{-1} w (δ CH_2 and δ_{as} CH_3), 1409 cm^{-1} vvw (δ P-CH_2), 1378 cm^{-1} vw (δ_{sy} CH_3), 1256 and 1225 cm^{-1} vw (CH_2 ω, τ), 1153 cm^{-1} s (ν P=O), 1090 and 1054 cm^{-1} vw-w (ν C-C), 973 cm^{-1} s (ν P-OH), 764 and 724 cm^{-1} w (CH_2 rock, ν P-C), 548 cm^{-1} w (P=O deformation ?).

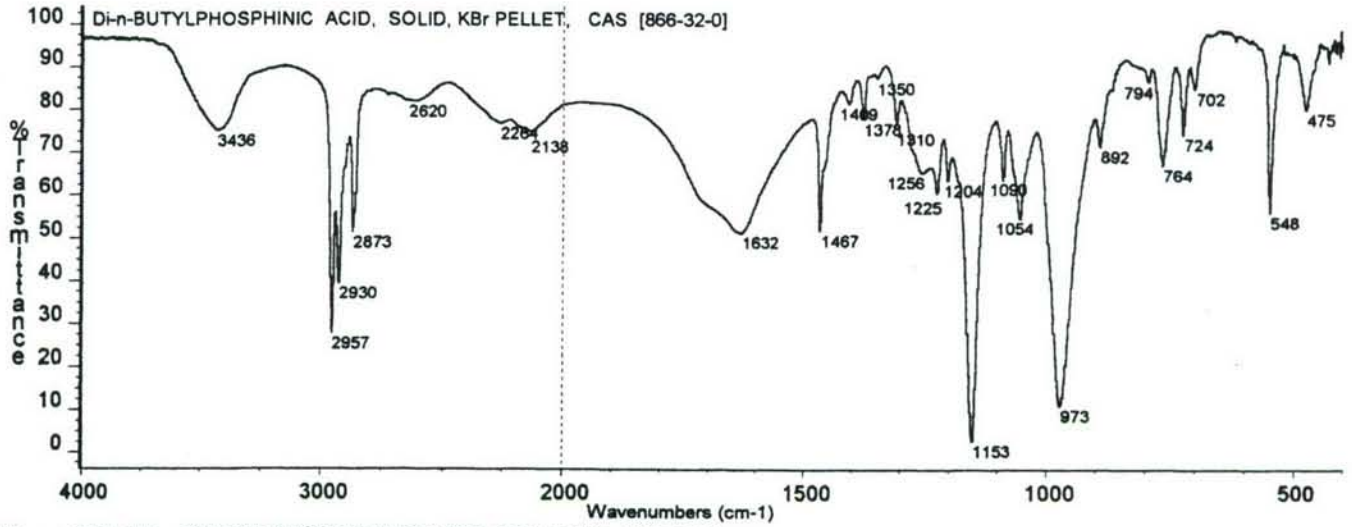


Figure 152 DI-*n*-BUTYLPHOSPHINIC ACID, SOLID KBr PELLET

3.5.5.6 Phenylphosphinic Acid C_6H_5-P=O(OH)(H)

The infrared spectrum of phenylphosphinic acid as a solid between KBr windows and as a KBr pellet is reproduced as ***Figure 153***. The band assignments for the KBr pellet spectrum (which contains somewhat less sample than the spectrum of the solid between KBr windows) is as follows: 3440 cm^{-1} w (H_2O), 3082, 3064 and 3027 cm^{-1} vvw (aromatic ring ν C-H), 2603, 2272 and 2165 and 1670 w and broad (POH), 2408 cm^{-1} vw (ν P-H), 1590 cm^{-1} w, 1571 cm^{-1} vw, 1484 cm^{-1} vw and 1440 cm^{-1} m (aromatic ring), 1199 and 1153 cm^{-1} ms (ν P=O), 1103 cm^{-1} m (phenyl-P), 1072, 1027 and 1004 cm^{-1} vw (β C-H mono-substituted aromatic ring), 988 and 980 cm^{-1} s (ν P-OH and P-H deformation), 752 cm^{-1} ms (γ C-H mono-substituted ring), 693 cm^{-1} ms (δ mono-substituted

aromatic ring), 534 cm^{-1} ms (aromatic ring ?), 464 cm^{-1} w (P=O deformation ?).

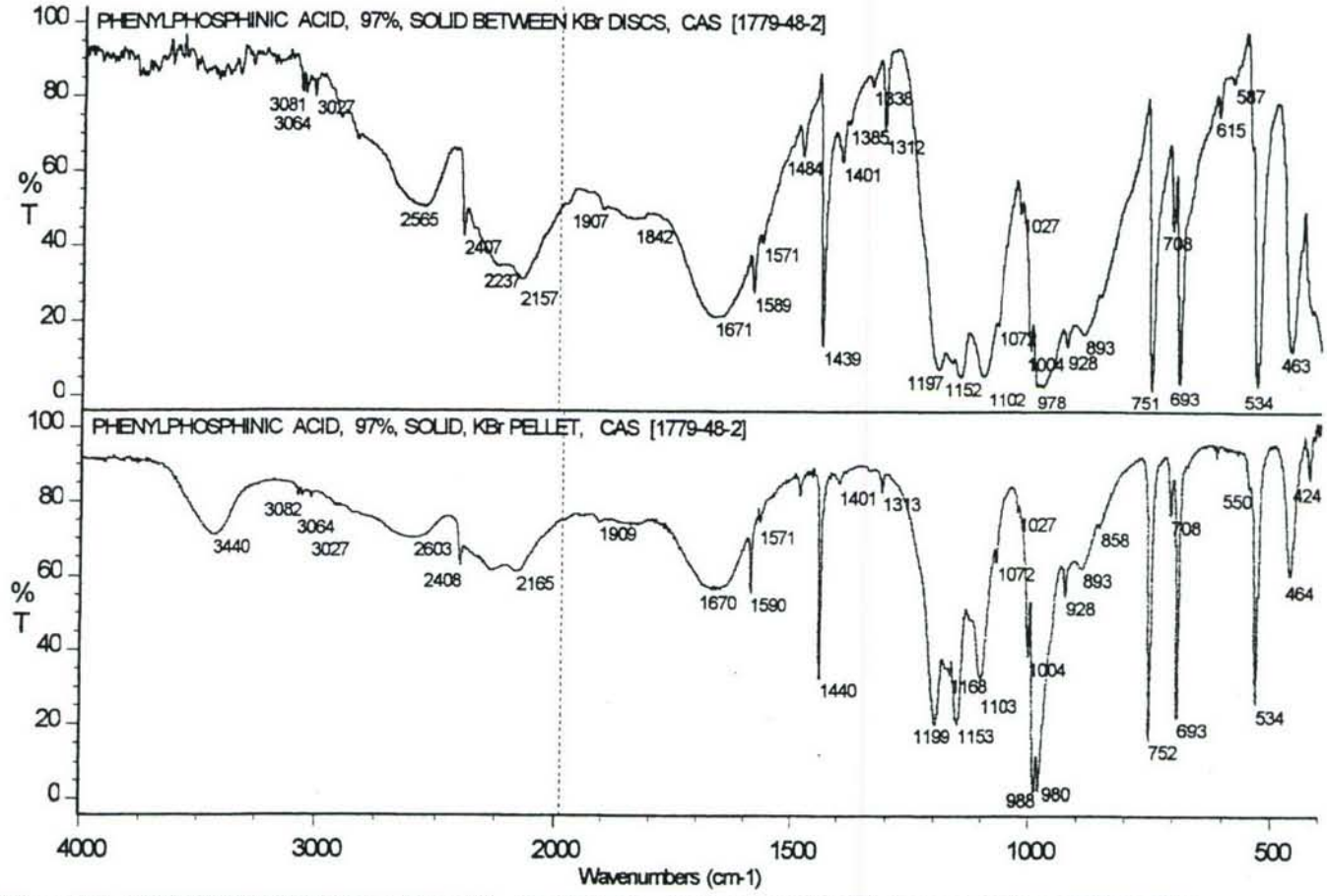


Figure 153 PHENYLPHOSPHINIC ACID, 97%, *UPPER SPECTRUM* –SOLID BETWEEN KBr DISCS (WINDOWS), *LOWER SPECTRUM*–SOLID AS A KBr PELLET

3.5.5.7 Diphenylphosphinic Acid $(C_6H_5)_2P{=}O(OH)$

The infrared spectrum of diphenylphosphinic acid as a solid between KBr windows and a a KBr pellet is given in ***Figure 154***. Band assignments for the KBr pellet spectrum are as follows: 3432 cm^{-1} w (H_2O), 3077 and 3056 cm^{-1} vvw (ν C-H aromatic ring), 2615 cm^{-1} vw broad, 2153 cm^{-1} vw broad and 1685, 1647 cm^{-1} w broad (POH), 1589 cm^{-1} vw 1485 cm^{-1} vw and 1439 cm^{-1} m (aromatic ring), 1180 cm^{-1} m (ν P=O), 1131 cm^{-1} m (phenyl-P), 1070, 1028 and 1003 cm^{-1} vw (β C-H mono-substituted aromatic ring), 961 cm^{-1} s (ν P-OH), 758 cm^{-1} w and 729 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 703 cm^{-1} sh and 693 cm^{-1} m (δ mono-substituted aromatic ring), 554 cm^{-1} m (aromatic ring ?).

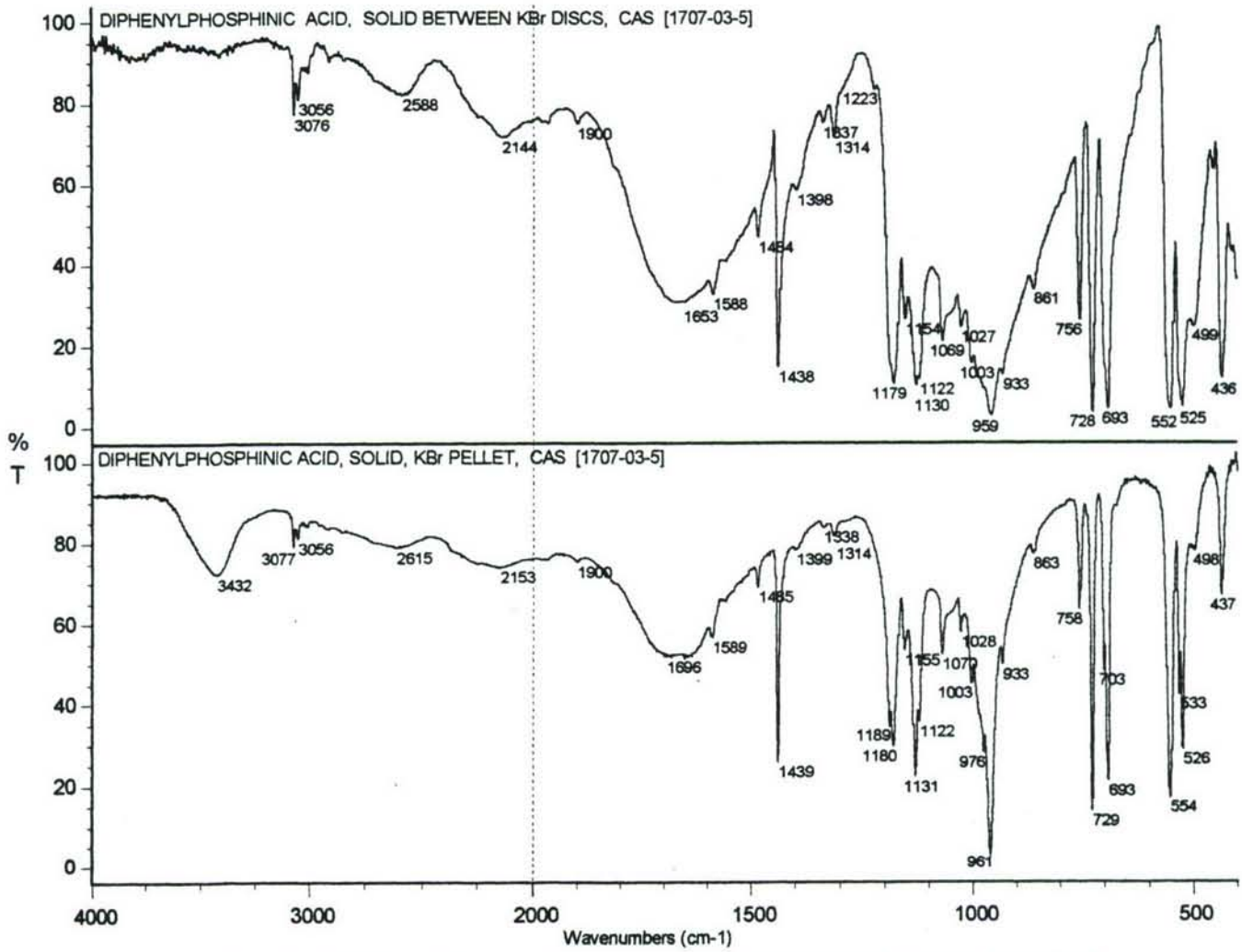


FIGURE 154 DIPHENYLPHOSPHINIC ACID, *UPPER SPECTRUM*--SOLID BETWEEN KBr DISCS (WINDOWS), *LOWER SPECTRUM*--SOLID AS A KBr PELLET

3.5.5.8 Bis(4-methoxypenyl)phosphinic Acid $(4\text{-}CH_3O\text{-}C_6H_4)_2P{=}O(OH)$

The infrared spectrum of bis(4-methoxyphenyl)phosphinic acid as a solid between CsI windows is given in ***Figure 155***. The band assignments are as follows: 3007 cm^{-1} vvw (ν C-H aromatic ring), 2838 cm^{-1} vvw (OCH_3), ca 2300 vw abroad and ca 1670 cm^{-1} vw broad (POH), 1598 cm^{-1} m, 1570 cm^{-1} vw, 1504 cm^{-1} w 1441 cm^{-1} vw (aromatic ring), 1296, 1253 cm^{-1} w-m (νC_{aryl}-O), 1203 and 1177 cm^{-1} m (ν P=O), 1129 cm^{-1} s (phenyl-P), 1027 cm^{-1} ms (νC_{alkyl}-O), 953 cm^{-1} m (ν P-OH), 834, 805 cm^{-1} m (para-substituted aromatic ring), 544 cm^{-1} s (aromatic ring).

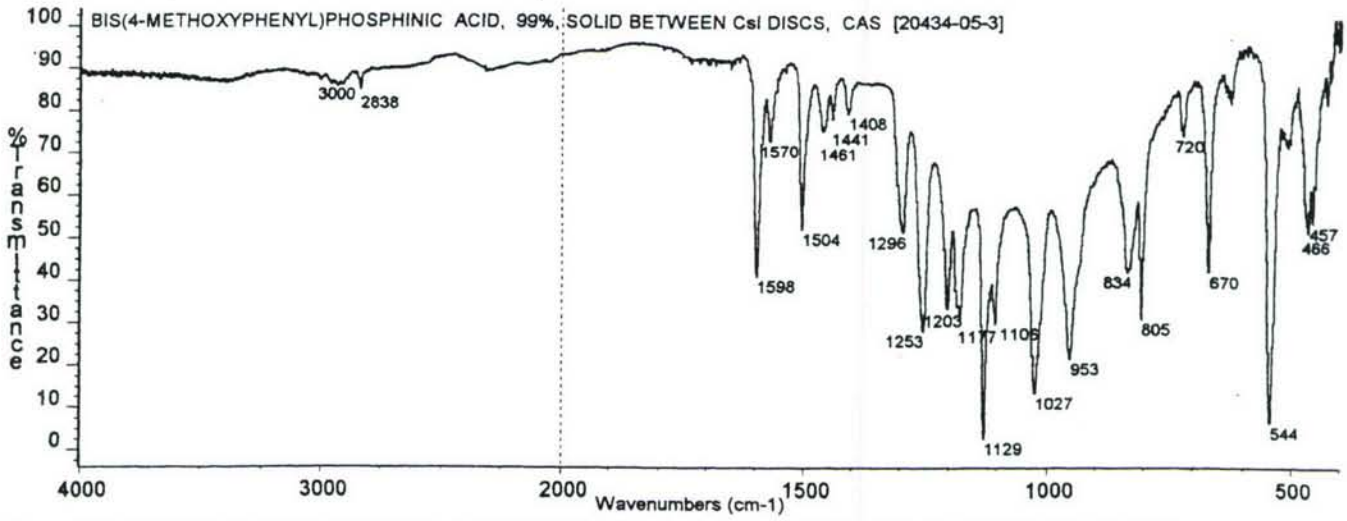


Figure 155 BIS(4-METHOXYPHENYL)PHOSPHINIC ACID, 99%, SOLID BETWEEN CsI DISCS (WINDOWS)

3.5.6 **Phosphine Oxides** $(R)_3P=O$

3.5.6.1 Trimethylphosphine Oxide $(CH_3)_3P=O$

The infrared spectrum of trimethylphosphine oxide as a wet and dried solid between CsI discs (windows) is reproduced as ***Figure 156***. The **upper spectrum** of the original solid between CsI discs shows the presence of water at 3301 and 1708 cm^{-1}. Other bands may be assigned as follows: 2961 cm^{-1} ms (ν_{as} CH_3), 2912 and 2896 cm^{-1} w (ν_{sy} CH_3), 1432 and 1416 cm^{-1} w and 1405 cm^{-1} sh (δ_{as} CH_3-P), 1332 cm^{-1} vw, 1305 cm^{-1} sh and 1296 cm^{-1} ms and 1284 cm^{-1} ms (δ_{sy} CH_3-P), 1141 cm^{-1} ms (ν P=O), 960 and 947 cm^{-1} s (P-CH_3 $rock_{as}$), 869 cm^{-1} sh and 866 cm^{-1} ms (P-CH_3 $rock_{sy}$), 752 cm^{-1} and 737 cm^{-1} sh (ν P-C). The **lower spectrum** of the *dried* solid between CsI discs shows the following bands: 2982 cm^{-1} ms (ν_{as} CH_3), 2912 cm^{-1} m (ν_{sy} CH_3), 1433 and 1416 cm^{-1} ms and 1407 cm^{-1} sh (δ_{as} CH_3-P), 1332 cm^{-1} m, 1300 and 1283 cm^{-1} s (δ_{sy} CH_3-P), 1166 cm^{-1} s (ν P=O), 955 cm^{-1} sh and 945 cm^{-1} s (P-CH_3 $rock_{as}$), 870 cm^{-1} sh and 862 cm^{-1} s (P-CH_3 $rock_{sy}$), 740 cm^{-1} s (ν P-C). Notice that the P=O stretching frequency of the dried sample (1166 cm^{-1}) is 25 cm^{-1} higher than the P=O stretching frequency of the wet sample (1141 cm^{-1}).

3.5.6.2 Tris(hydroxymethyl)phosphine Oxide (Phosphinylidynetrimethanol) $(HO\text{-}CH_2)_3P=O$

The infrared spectrum of tris(hydroxymethyl)phosphine oxide as a solid between KBr discs is given in

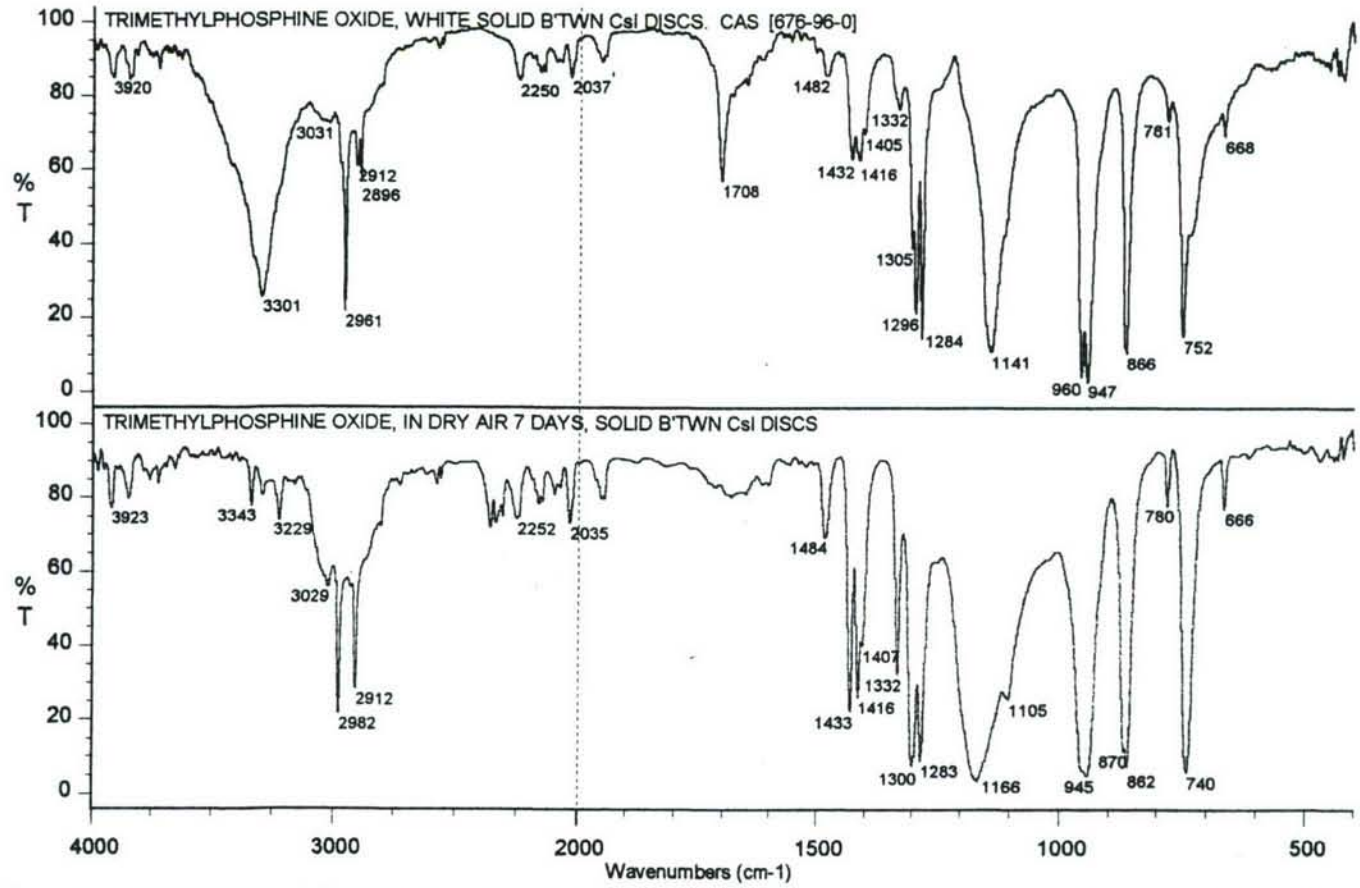


Figure 156 TRIMETHYLPHOSPHINE OXIDE, SOLID BETWEEN CsI DISCS (WINDOWS), *UPPER SPECTRUM*--SOLID AS RECEIVED BETWEEN CsI DISCS
***LOWER SPECTRUM*--SOLID BETWEEN CsI DISCS AFTER 7 DAYS IN DRY AIR PURGE**

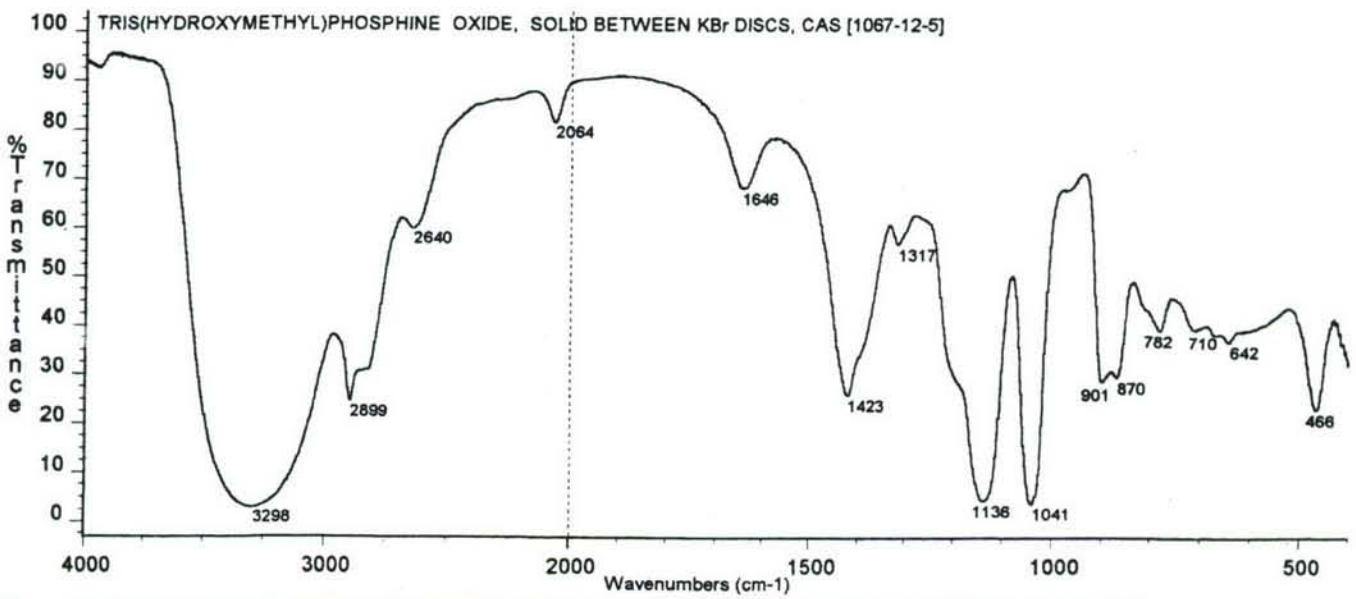


Figure 157 TRIS(HYDROXYMETHYL)PHOSPHINE OXIDE, SOLID BETWEEN KBr DISCS (WINDOWS)

Figure 157. The band assignments for solid tris(hydroxymethyl)phosphine oxide are as follows: 3298 cm^{-1} s (ν OH), 2899 cm^{-1} m (ν_{as} CH_2), ca 2940 cm^{-1} sh (ν_{sy} CH_2), 1646 cm^{-1} w (H_2O), 1423 cm^{-1} m (δ CH_2 and β OH), 1317 cm^{-1} vw (ω, τ CH_2), 1136 cm^{-1} s (ν P=O), 1041 cm^{-1} s (ν C-O), 901 and 870 cm^{-1} m (CH_2 rock ?), 710 cm^{-1} vw (ν P-C ?), 642 cm^{-1} vw (γ OH), ca 600 cm^{-1} vw broad (H_2O), 466 cm^{-1} w (P=O deformation ?).

3.5.6.3 Di-*n*-butylphosphine Oxide $(n\text{-}C_4H_9)_2P{=}O(H)$

The infrared spectrum of di-*n*-butylphosphine oxide as a KBr pellet is presented as ***Figure 158***. The band assignments are as follows: ca 3430 cm^{-1} vw and ca 1630 cm^{-1} (H_2O), 2956 cm^{-1} m (ν_{as} CH_3), 2927 cm^{-1} m ($\nu_{as}CH_2$), 2872 and 2860 cm^{-1} w (ν_{sy} CH_3 and ν_{sy} CH_2), 2332 cm^{-1} vw (ν P-H), 1467 cm^{-1} w (δ CH_2), 1457 cm^{-1} sh (δ_{as} CH_3), 1407 cm^{-1} vvw (δ P-CH_2), 1377 cm^{-1} vw (δ_{sy} CH_3), 1305 cm^{-1} vw, 1280 cm^{-1} vvw, 1225 cm^{-1} w and 1204 cm^{-1} vw (ω, τ CH_2), 1166 cm^{-1} s (ν P=O), 1096 cm^{-1} w (CH_3 rock ?), 1051 and 999 cm^{-1} vw (ν C-C), 954 and 895 cm^{-1} w (P-H deformations ?), 773 cm^{-1} w (CH_2 rock ?), 726 cm^{-1} vw (ν P-C).

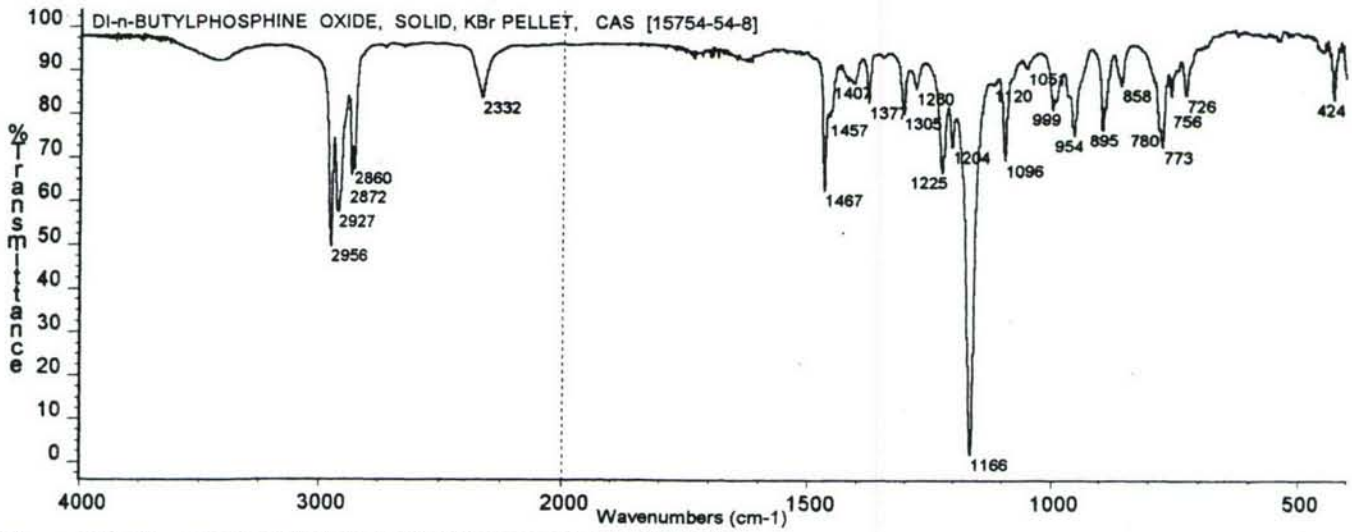


Figure 158 DI-*n*-BUTYLPHOSPHINE OXIDE, SOLID, KBr PELLET

3.5.6.4 Tributylphosphine Oxide $(C_4H_9)_3P{=}O$

The infrared spectrum of tributylphosphine oxide as a solid between CsI windows is given in ***Figure 159***. The band assignments are as follows: 3420 and ca 1650 cm^{-1} w ((H_2O), 2957 cm^{-1} s (ν_{as} CH_3), 2931 cm^{-1} s (ν_{as} CH_2), 2871 cm^{-1} ms (ν_{sy} CH_3 and CH_2), 1466 cm^{-1} ms (δ CH_2 and δ_{as} CH_3), 1410 cm^{-1} w (δ P-CH_2), 1378

cm^{-1} m (δ_{sy} CH_3), 1346 cm^{-1} vw, 1306 cm^{-1} w, 1277 cm^{-1} w and 1221 cm^{-1} ms (ω, τ CH_2), 1155 cm^{-1} s (ν P=O), 1094 cm^{-1} m (CH_3 rock ?), 1045, 1006 and 968 cm^{-1} w (ν C-C), 801 cm^{-1} m (CH_2 rock ?), 748 and 727 cm^{-1} w (ν P-C), 486 cm^{-1} w (P=O deformation ?).

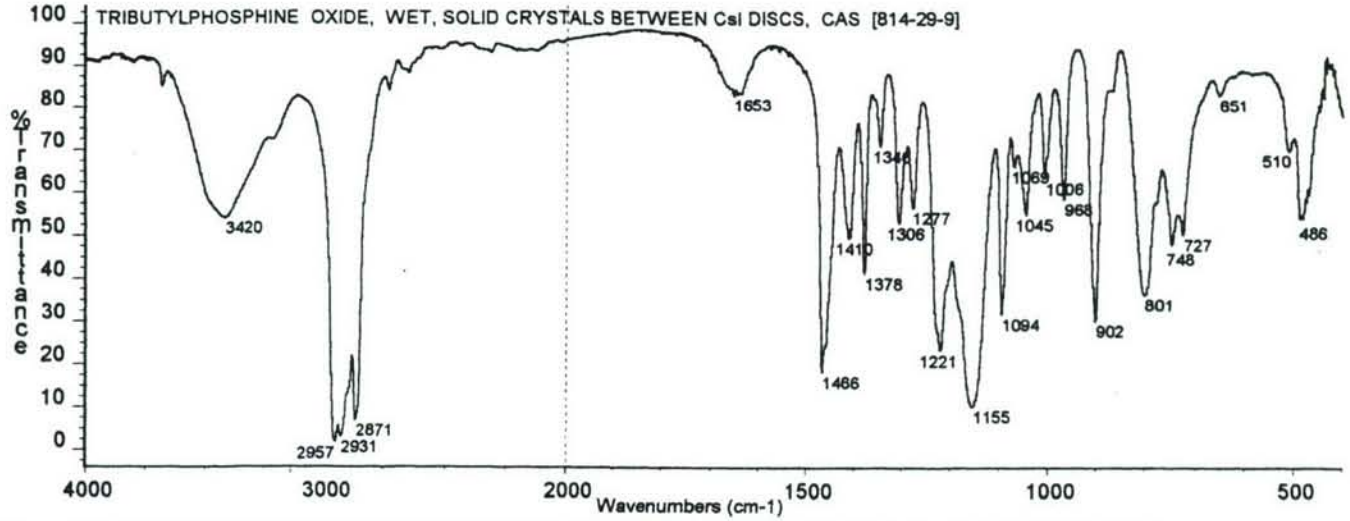


Figure 159 TRIBUTYLPHOSPHINE OXIDE, SOLID CRYSTALS (WET) BETWEEN CsI DISCS (WINDOWS)

3.5.6.5 Tri-*n*-octylphosphine Oxide $(C_8H_{17})_3P=O$

The infrared spectrum of tri-*n*-octylphosphine oxide as a KBr pellet is presented in ***Figure 160***. The band assignments are as follows: 3425 and ca 1630 cm^{-1} vw (H_2O), 2952 cm^{-1} m (ν_{as} CH_3), 2921 cm^{-1} s (ν_{as} CH_2), 2869 cm^{-1} sh (ν_{sy} CH_3), 2852 cm^{-1} ms (ν_{sy} CH_2), 1466 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1412 cm^{-1} vw (δ P-CH_2), 1323, 1284, 1261 cm^{-1} vw and 1244 and 1205 cm^{-1} w (ω, τ CH_2), 1151 cm^{-1} s and 1146 cm^{-1} sh (ν P=O), 1119 cm^{-1} vw (CH_3 rock ?), 850 cm^{-1} vw, 821 cm^{-1} w , 777 cm^{-1} vw, 757 cm^{-1} w (CH_2 rock ?), 722 w cm^{-1} (ν P-C ?), 505 cm^{-1} vw (P=O deformation ?).

3.5.6.6 Tricyclohexylphosphine Oxide $(C_6H_{11})_3P=O$

The infrared spectrum of tricyclohexylphosphine oxide as a KBr pellet is given in ***Figure 161***. The band assignments are as follows: 3432 cm^{-1} vw and ca 1630 cm^{-1} vvw (H_2O), 2927 cm^{-1} ms (ν_{as} CH_2), 2853 cm^{-1} m (ν_{sy} CH_2), 1445 cm^{-1} w (δ CH_2), 1157 cm^{-1} s (ν P=O), 895 cm^{-1} w (cyclohexyl ring), 546, 533 cm^{-1} m (P=O deformation).

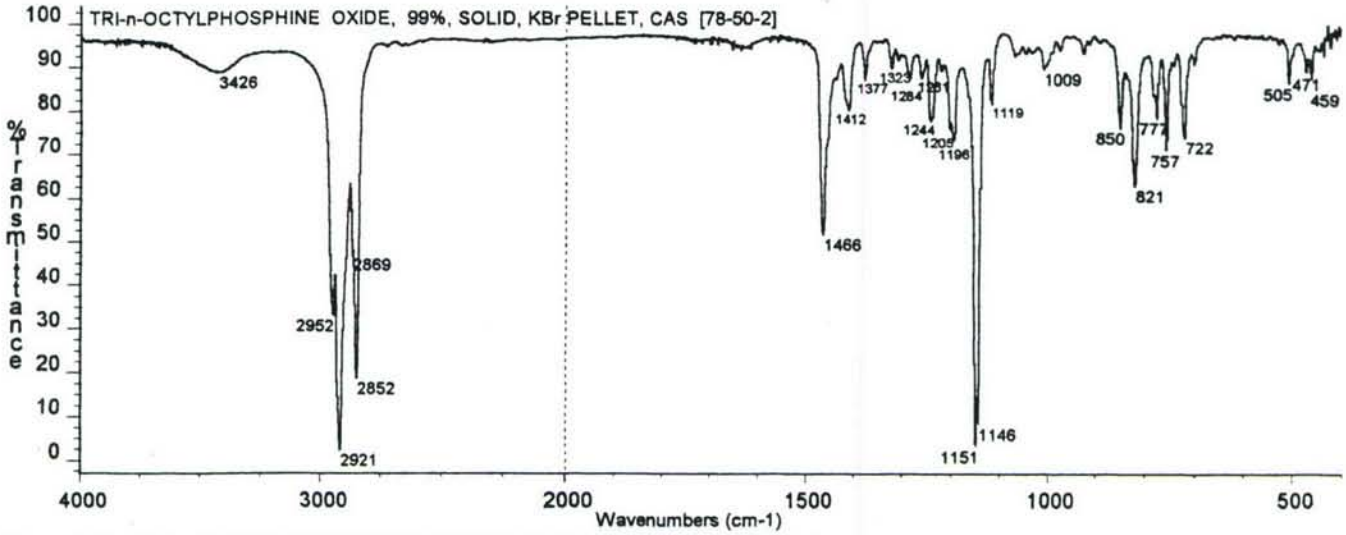


Figure 160 TRI-*n*-OCTYLPHOSPHINE OXIDE, 99%, SOLID, KBr PELLET

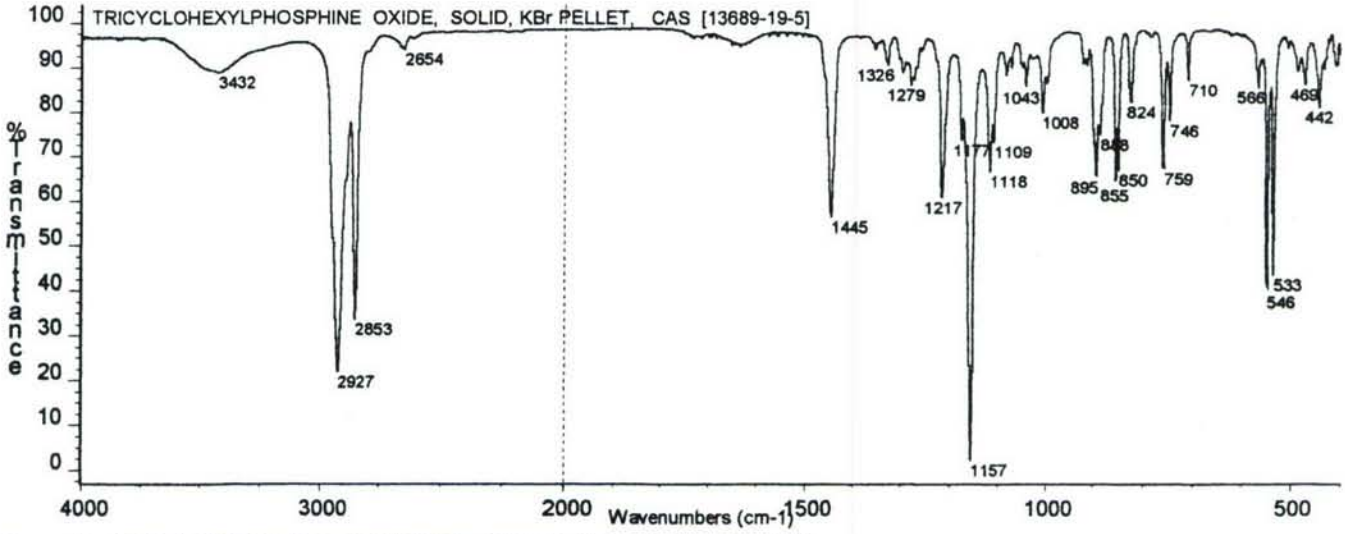


Figure 161 TRICYCLOHEXYLPHOSPHINE OXIDE, SOLID, KBr PELLET

3.5.6.7 Isopropyldiphenylphosphine Oxide $(C_6H_5)_2P{=}O[CH(CH_3)_2]$

The infrared spectrum for isopropyldiphenylphosphine oxide as a KBr pellet is given in ***Figure 162***. The band assignments are as follows: 3434 and ca 1650 cm^{-1} w (H_2O), 3053 cm^{-1} vw and 3022 cm^{-1} vvw (ν C-H aromatic), 2961 cm^{-1} vw, 2925 cm^{-1} vw and 2868 cm^{-1} vvw (ν CH_3 and ν -CH), 1591 cm^{-1} vvw, 1490 cm^{-1} vvw, 1438 cm^{-1} m (aromatic ring), 1466 cm^{-1} vw (δ_{as} CH_3), 1385 and 1364 cm^{-1} vvw (δ_{sy} CH_3), 1184 cm^{-1} s (ν P=O), 1159 cm^{-1} vw (isopropyl skeletal/β C-H mono-substituted aromatic ring), 1120 cm^{-1} w (phenyl-P), 1072, 1032 and

997 cm^{-1} vw (β C-H mono-substituted aromatic ring), 935 cm^{-1} vvw (CH_3 rock, isopropyl), 753 cm^{-1} vw (γ C-H mono-substituted aromatic ring), 722, 711 and 699 cm^{-1} ms-m (δ mono-substituted aromatic ring), 661 cm^{-1} vw (ν P-C ?), 547 and 540 cm^{-1} s (aromatic ring).

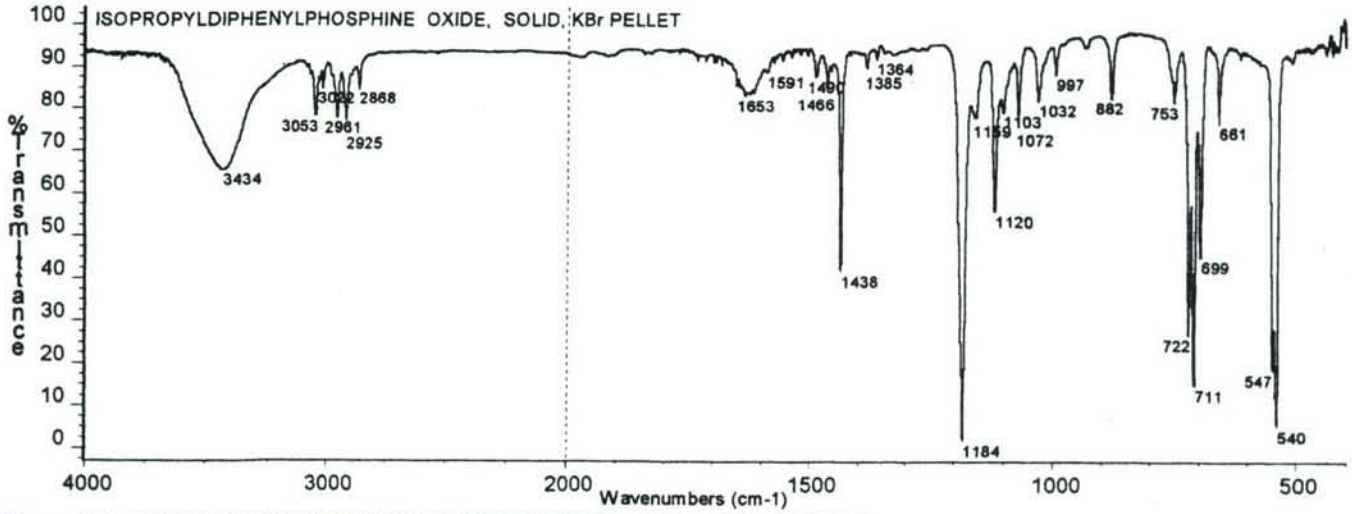


Figure 162 ISOPROPYLDIPHENYLPHOSPHINE OXIDE, SOLID, KBr PELLET

3.5.6.8 Diphenylphosphine Oxide $(C_6H_5)_2P{=}O(H)$

The infrared spectrum for a KBr pellet of diphenylphosphine oxide is given in ***Figure 163***. The band assignments are as follows: 3060 cm^{-1} vw, 3049 cm^{-1} w and 3017 cm^{-1} vw (ν C-H aromatic ring), 2369 cm^{-1} w (ν P-H), 1590 cm^{-1} w, 1487 cm^{-1} w, 1438 cm^{-1} ms (aromatic ring), 1190 and 1187 cm^{-1} s (ν P=O), 1122 cm^{-1} ms (phenyl-P), 1162 cm^{-1} m, 1072 cm^{-1} w, 1028 cm^{-1} vw and 998 cm^{-1} vw (β C-H, mono-substituted aromatic

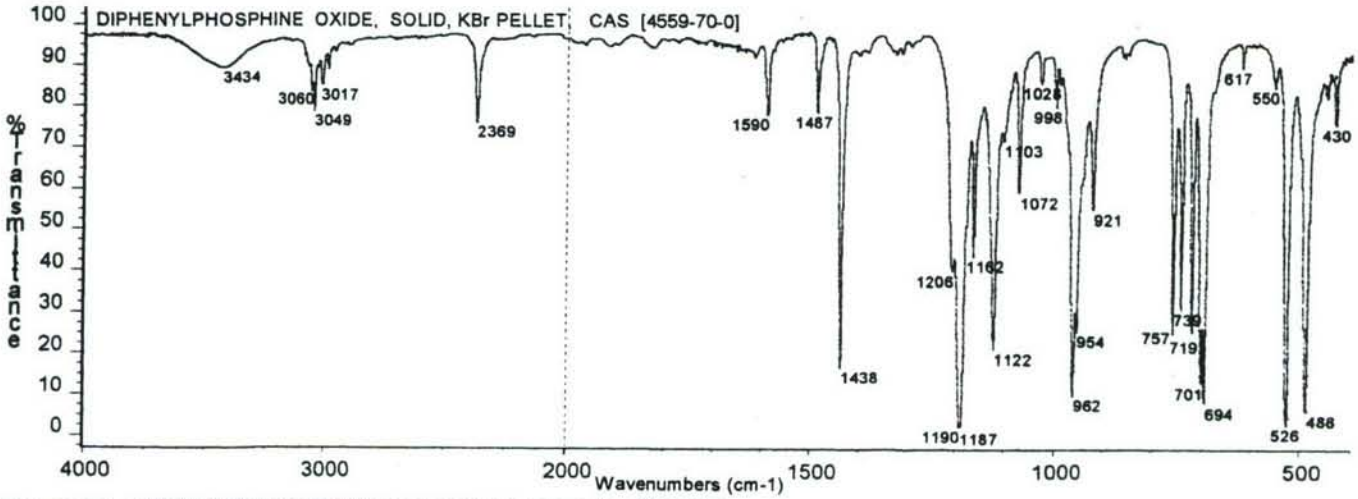


Figure 163 DIPHENYLPHOSPHINE OXIDE, SOLID, KBr PELLET

ring), 962 and 954 cm^{-1} ms (P-H deformation), 757 and 739 cm^{-1} m (γ C-H, mono-substituted aromatic ring), 701 and 694 cm^{-1} ms (δ mono-substituted aromatic ring), 526 and 488 cm^{-1} s (aromatic ring/P=O deformation ?).

3.5.6.9 Triphenylphosphine Oxide $(C_6H_5)_3P=O$

The infrared spectrum of triphenylphosphine oxide as a KBr pellet is reproduced in ***Figure 164***. The band assignments are as follows: 3436 cm^{-1} w (H_2O), 3075, 3056, 3037, and 3021 vvw-vw (ν C-H aromatic), 1591 cm^{-1} vw, 1484 cm^{-1} vw, 1439 cm^{-1} m (aromatic ring), 1190 cm^{-1} ms (ν P=O), 1121 cm^{-1} ms (phenyl-P), 1164, 1072, 1026 and 996 cm^{-1} vw (β C-H mono-substituted aromatic ring), 755, 748 cm^{-1} w (γ C-H mono-substituted aromatic ring), 722, 698 cm^{-1} ms (δ mono-substituted aromatic ring), 541 cm^{-1} s (aromatic ring), 506 cm^{-1} vw (P=O deformation ?).

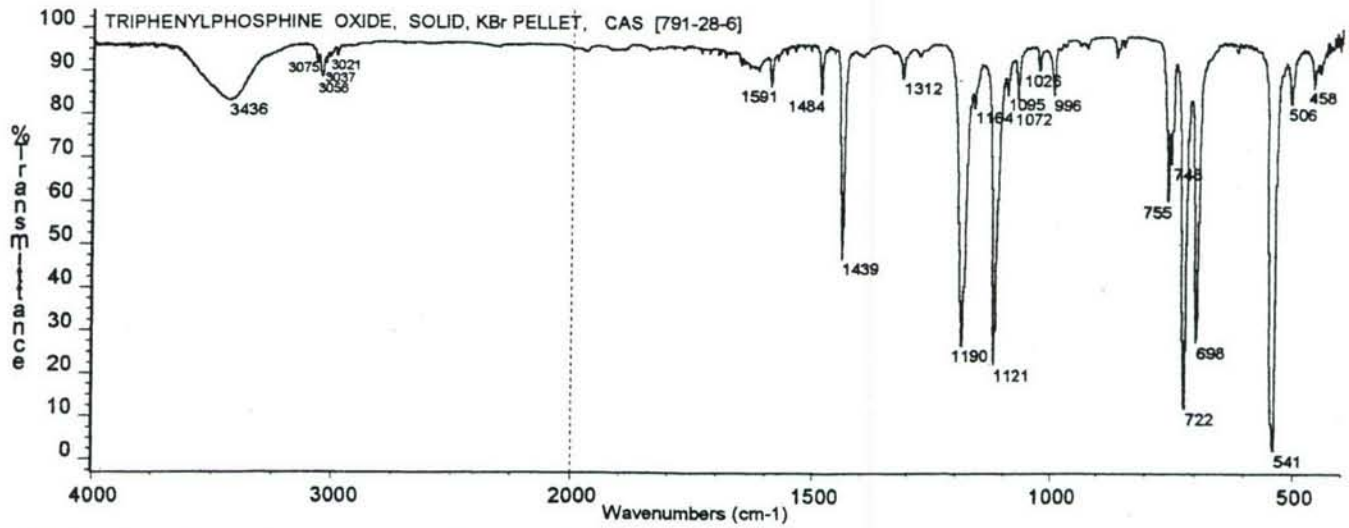


Figure 164 TRIPHENYLPHOSPHINE OXIDE, SOLID, KBr PELLET

3.5.6.10 Diphenyl(methoxymethyl)phosphine Oxide $(C_6H_5)_2P=O(CH_2\text{-}O\text{-}CH_3)$

The infrared spectrum of diphenyl(methoxymethyl)phosphine oxide as a solid between KBr discs (windows) is given in ***Figure 165***. The band assignments are as follows: 3056 and 3025 cm^{-1} w-vw (ν C-H aromatic), 2937 and 2916 cm^{-1} w (ν_{as} CH_3 and CH_2), 2859 cm^{-1} vw (ν_{sy} CH_2), 2821 cm^{-1} w (OCH_3), 1591 cm^{-1} vw, 1482 cm^{-1} vw and 1438 cm^{-1} ms (aromatic ring), 1464 cm^{-1} vw (δ_{as} and δ_{sy} CH_3), 1390 cm^{-1} vvw (δ P-CH_2), 1190 cm^{-1} s (ν P=O), 1120 cm^{-1} m (phenyl-P), 1100 cm^{-1} s (ν_{as} C-O-C), 1156, 1072, 1028 and 997 cm^{-1} vw (β

C-H mono substituted aromatic ring), 870 cm^{-1} m (COC ?), 747 cm^{-1} s (γ C-H mono-substituted aromatic ring), 719, 700 cm^{-1} s (δ mono-substituted aromatic ring), 549, 512 cm^{-1} s (aromatic ring, δ P=O ?).

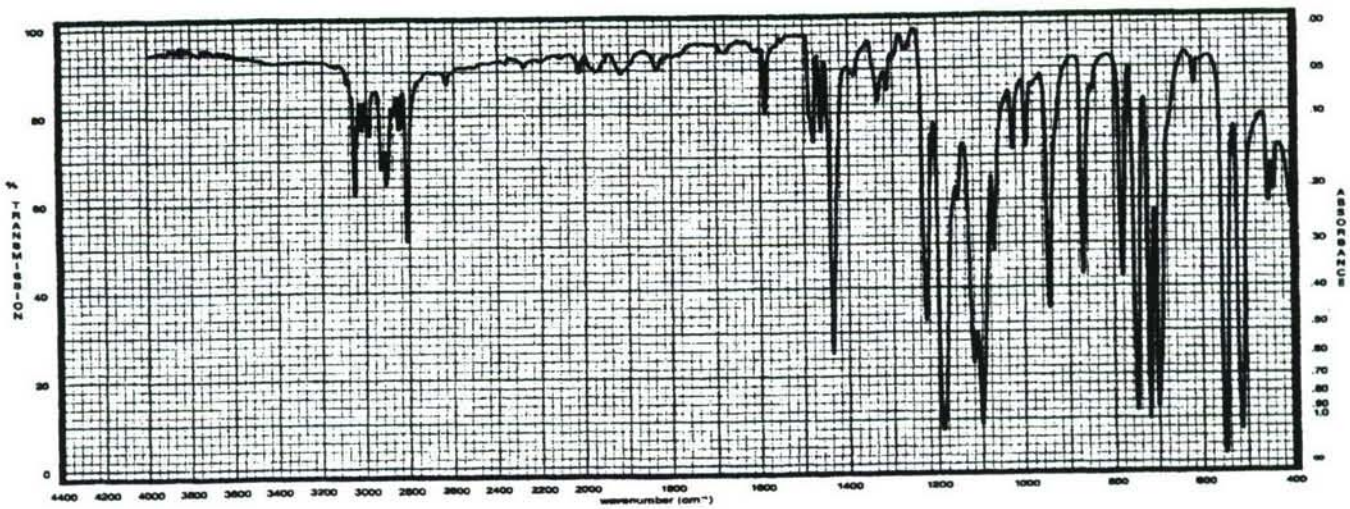


Figure 165 DIPHENYL(METHOXYMETHYL)PHOSPHINE OXIDE, SOLID BETWEEN KBr DISCS (WINDOWS)

3.5.6.11 Methyl(*n*-butyl)benzylphosphine Oxide $CH_3\text{-}P{=}O(n\text{-}C_4H_9)(CH_2\text{-}C_6H_5)$

The infrared spectrum of methyl(*n*-butyl)benzylphosphine oxide as a KBr pellet is given in ***Figure 166***. The band assignments are as follows: 3431 cm^{-1} vw (H_2O), 3085; 3062 and 3029 cm^{-1} vw (ν C-H aromatic ring), 2958 cm^{-1} m (ν_{as} CH_3), 2932 cm^{-1} m (ν_{as} CH_2), 2905 cm^{-1} sh (ν_{sy} CH_3), 2872 w (ν_{sy} CH_2), 1602 cm^{-1} w, 1496 cm^{-1} m and 1454 cm^{-1} m (aromatic ring), 1466 cm^{-1} vw (δ CH_2, δ_{as} CH_3), 1417 cm^{-1} vw (δ P-CH_2, δ_{as} P-CH_3), 1379 cm^{-1} vvw (δ_{sy} CH_3), 1293 cm^{-1} m (δ_{sy} P-CH_3), 1236 cm^{-1} w and 1200 cm^{-1} m (ω, τ CH_2), 1174 cm^{-1}

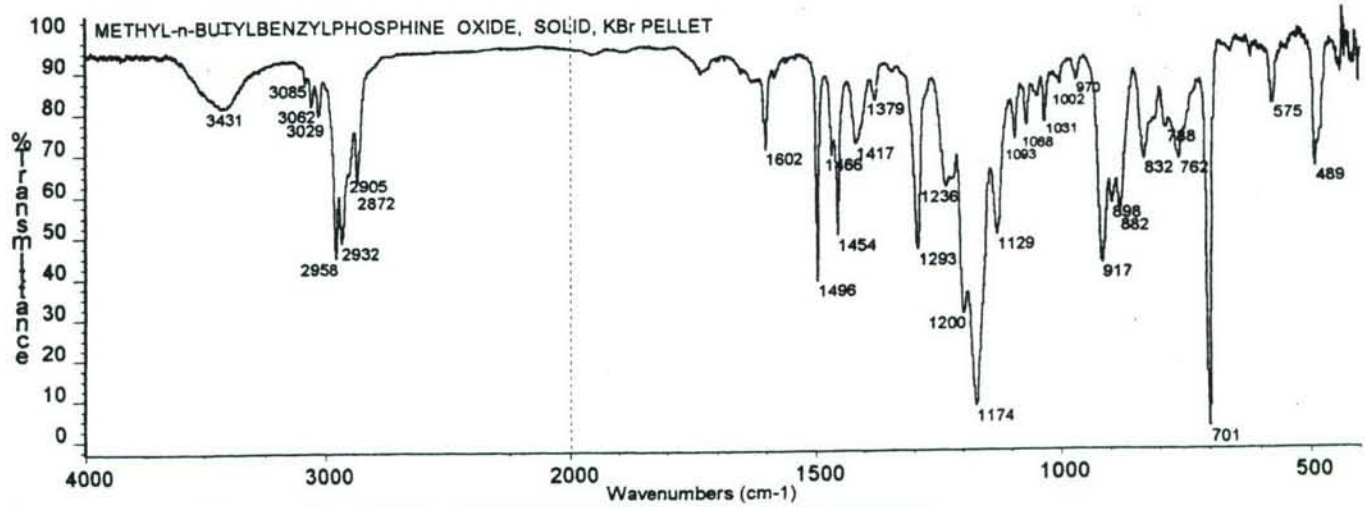


Figure 166 METHYL(*n*-BUTYL)BENZYLPHOSPHINE OXIDE, SOLID, KBr PELLET

ms (ν P=O), 1129 cm^{-1} w (phenyl-CH_2 ?), 1068, 1031 and 1002 cm^{-1} vvw (β C-H mono-substituted aromatic ring), 917 cm^{-1} m (P-CH_3 rock), 762 cm^{-1} w (γ C-H mono-substituted aromatic ring), 701 cm^{-1} s (δ mono-substituted aromatic ring), 489 cm^{-1} w (P=O deformation ?).

3.5.7 **Phosphonic Halides**[z] $R\text{-}P{=}O(X)_2$

3.5.7.1 Methylphosphonic Chlorofluoride $CH_3P{=}O(Cl)(F)$

The infrared spectrum for methylphosphonic chlorofluoride as a liquid film and as a vapor is given in ***Figure 167***. The compound is a precursor for the preparation of G-Agents. The band assignments for the liquid phase are as follows: 3009 cm^{-1} w (ν_{as} CH_3), 2927 cm^{-1} w (ν_{sy} CH_3), 2821 cm^{-1} vvw and 2567 cm^{-1} vw (POH impurity, hydrolysis product), 1409 cm^{-1} w (δ_{as} P-CH_3), 1384 cm^{-1} vvw (KNO3 from the KBr windows), 1319 cm^{-1} s (δ_{sy} P-CH_3), 1292 cm^{-1} s (ν P=O), 1006 cm^{-1} w (ν P-OH, hydrolysis product), ca 950 cm^{-1} sh (possible ν P-O-P pyro ?), 922 cm^{-1} s and 901 cm^{-1} ms (P-CH_3 antisymmetrical and symmetrical rocking respectively), 858 cm^{-1} ms (ν P-F), 762 cm^{-1} s (ν P-C), ca 652 vvw (pyro ?), 541 cm^{-1} s (ν P-Cl), 470 cm^{-1} w (P=O deformation ?), 423 cm^{-1} ms (P-F bending).

The infrared spectra depicting the effect of atmospheric moisture on methylphosphonic chlorofluoride as a liquid film between KBr windows has been discussed previously.[z] The spectra showed the formation of **Fluoro Acid,** methylphosphonofluoridic acid, $CH_3P{=}O(F)(OH)$, followed by the eventual formation of **MPA**, methylphosphonic acid, $CH_3P{=}O(OH)_2$.

The effect of atmospheric moisture on the vapor phase spectra of methylphosphonic chlorofluoride has also been discussed.[z] The formation of HCl, SiF_4, **Difluor** ($CH_3P{=}OF_2$), and K_2SiF_6 was also discussed[z]. In short the HCl comes from the hydrolysis of the compound. The silicon tetrafluoride, SiF_4,(1035 and 1030 cm^{-1})

---

[z] A number of the phosphonic halides are discussed in "Infrared Spectroscopic Observations On The Fate Of Organophosphorus Compounds Exposed To Atmospheric Moisture. Part I. G-Agents And Related Compounds", Piffath, R.J., U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423. Approved For Public Release. (1999)
See also, Some Comments On The Infrared Spectra Of CH_3POF_2, CH_3PSF_2, CH_3PSCl_2, CH3$POCl_2$, CH3POClF, $CH_3PO(C{\equiv}N)(F)$, And $CH_3PO(C{\equiv}N)(OEt)$, Piffath, R.J., U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423. (In Preparation, 1999).

comes from the reaction of HF with the glass walls of the gas cell. The potassium hexafluorosilicate, K_2SiF_6, results from the action of SiF_4 and HF with the KBr windows of the gas cell.

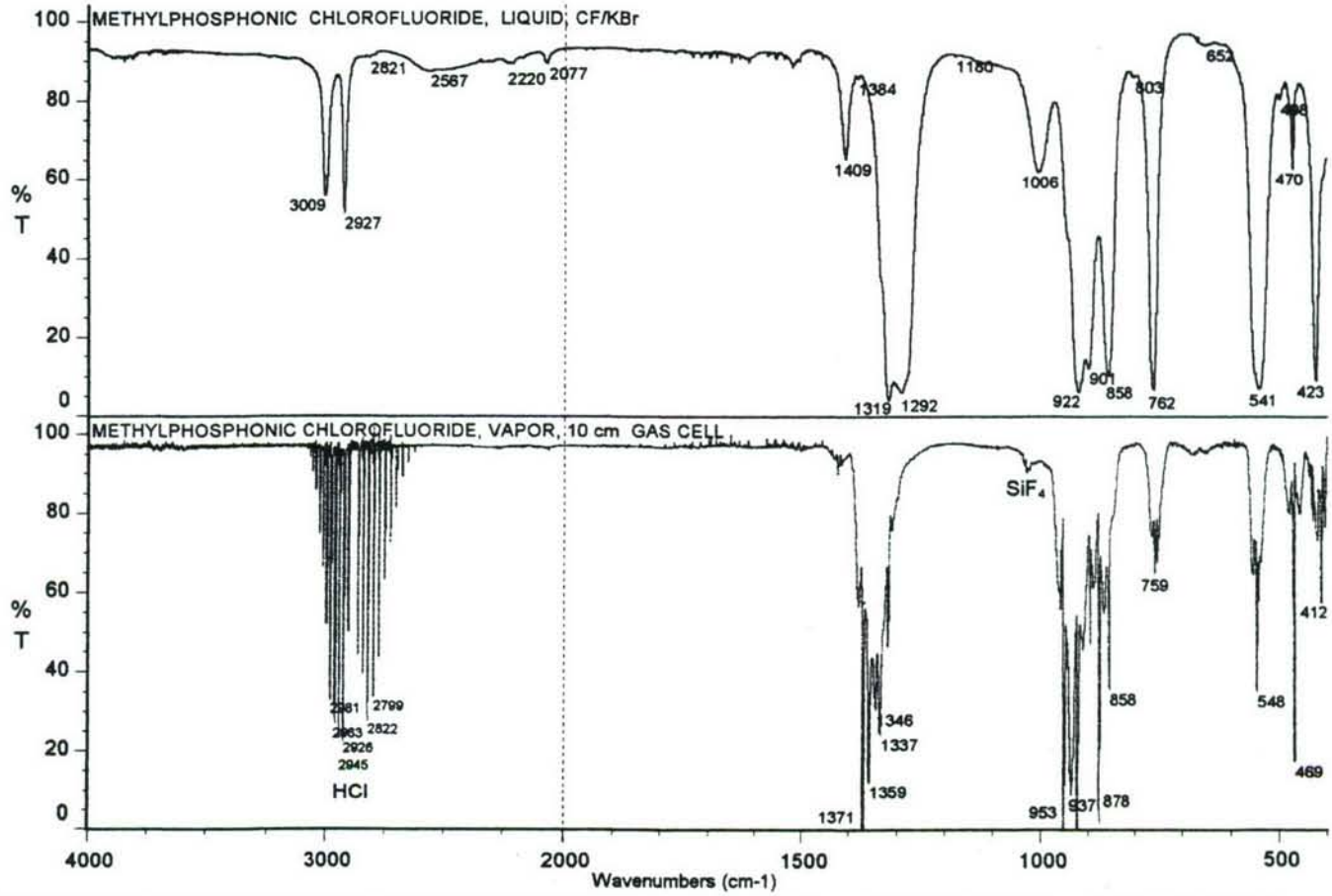


FIGURE 167 METHYLPHOSPHONIC CHLOROFLUORIDE, *UPPER SPECTRUM*--LIQUID, CF/KBr, *LOWER SPECTRUM*--VAPOR, 5 µL OF LIQUID INJECTED INTO A 10 cm PATHLENGTH GLASS BODY GAS CELL

3.5.7.2 Chloromethylphosphonic Dichloride $Cl\text{-}CH_2\text{-}P{=}O(Cl)_2$

The infrared spectrum of chloromethylphosphonic dichloride as a liquid film between KBr windows is given as ***Figure 168***. The band assignments are as follows: 2996 cm^{-1} m (ν_{as} CH_2), 2934 cm^{-1} m (ν_{sy} CH_2), 1389 cm^{-1} w (δ CH_2), 1278 cm^{-1} s (ν P=O), 1215 cm^{-1} m (ω CH_2-Cl), 1125 cm^{-1} w (CH_2-Cl), 967 cm^{-1} vw (ν P-OH), 817 cm^{-1} ms (CH_2 rock), 709 cm^{-1} ms (ν C-Cl), 573 cm^{-1} s (ν_{as} PCl_2), 511 and 489 cm^{-1} ms (ν_{sy} PCl_2), 425 cm^{-1} w (P=O deformation ?).

The effect of atmospheric moisture on chloromethylphosphonic dichloride is demonstrated by the infrared spectra reproduced in ***Figure 169***. After 18 hours of exposure to atmospheric moisture the spectrum

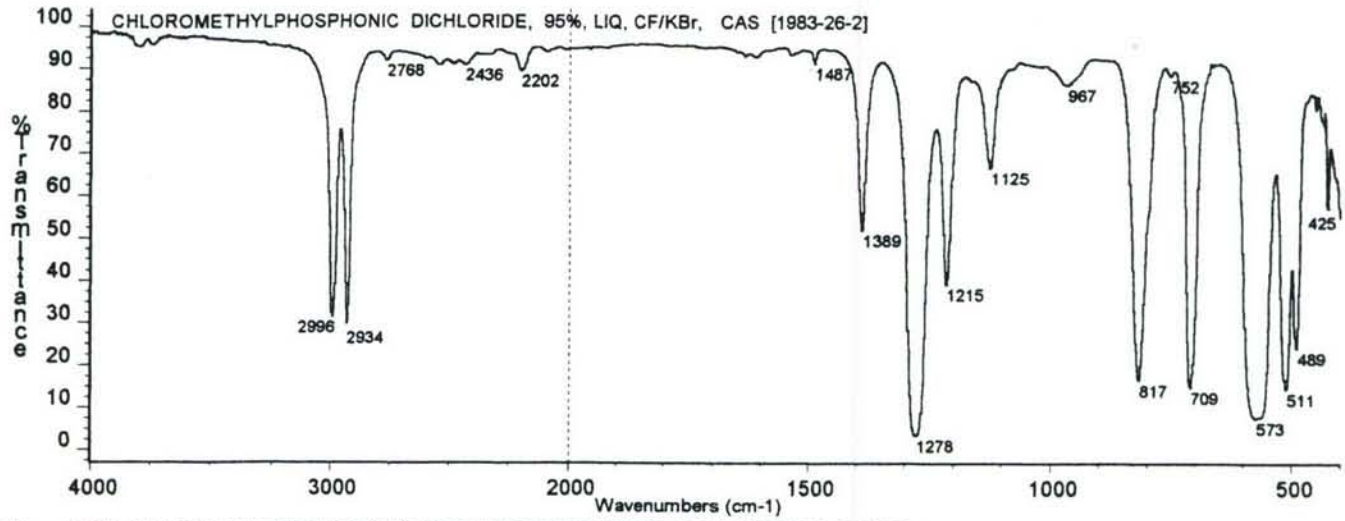


Figure 168 CHLOROMETHYLPHOSPHONIC DICHLORIDE, 95%, LIQUID, CF/KBr

shows the formation of bands near 2600, 2200 and 1620 cm^{-1} (POH) and near 970 cm^{-1} (ν P-OH). These bands are probably due to the formation of $ClCH_2$-P=O(OH)(Cl). With the progression of time these POH bands become more intense. The phosphoryl band begins to broaden and decrease in frequency, eventually reaching ca 1160 cm^{-1} after some 20 days of atmospheric exposure. The compound, chloromethylphosphonic acid, $ClCH_2P=O(OH)_2$, is believed to be formed. The hydrolysis of chloromethylphosphonic dichloride may be summarized as follows: $ClCH_2P=OCl_2$ -HOH→ $ClCH_2P=O(OH)(Cl)$ -HOH→ $ClCH_2P=O(OH)_2$.

3.5.7.3 Dichloromethylphosphonic dichloride Cl_2CH-P=OCl_2

The infrared spectrum of dichloromethylphosphonic acid as a liquid film between KBr windows is given in ***Figure 170***. The initial spectrum does show some hydrolysis as indicated by the presence of POH bands. The band assignments are as follows: 2952 cm^{-1} m (ν CH), ca 2560, ca 2230, ca 2120 and ca 1600 cm^{-1} w and broad (POH), 1282 cm^{-1} s (ν P=O), 1192 cm^{-1} vw (ν P=O of P-Acid from hydrolysis), 1010 cm^{-1} m (ν P-OH), 775 cm^{-1} ms and 672 cm^{-1} ms (ν_{as} and ν_{sy} CCl_2), 587 cm^{-1} s (ν_{as} PCl_2), 545 cm^{-1} m (ν_{sy} PCl_2).

3.5.7.4 Methylphosphonic Dichloride (**DC**, **Dichlor**) CH_3-P=OCl_2

The infrared spectrum of methylphosphonic dichloride (**DC**, **Dichlor**) as a liquid film between KBr windows is reproduced as ***Figure 171***. The compound is a precursor for the preparation of G-Agents. The

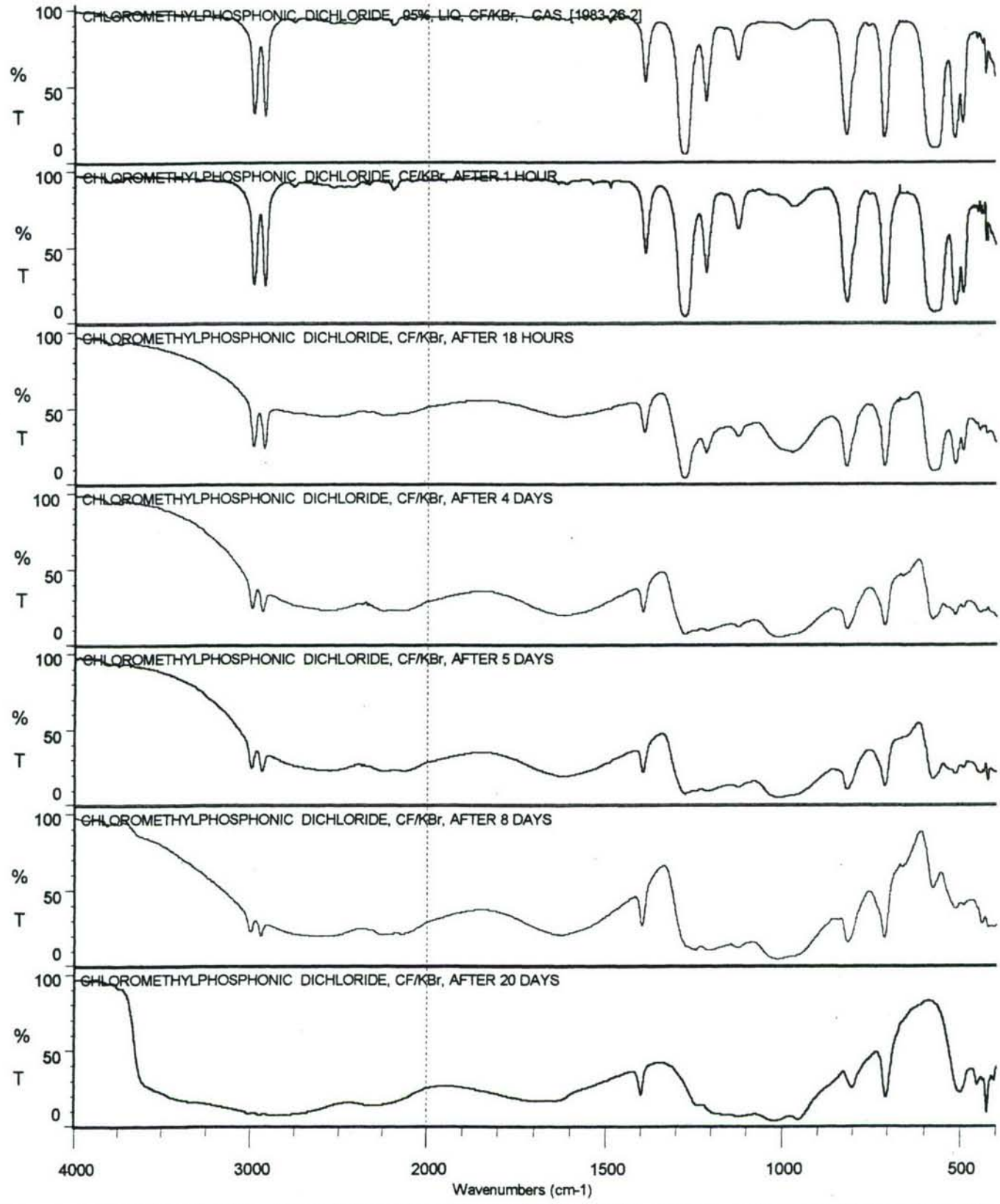


Figure 169 CHLOROMETHYLPHOSPHONIC DICHLORIDE, LIQUID, CF/KBr, SHOWING THE EFFECT OF EXPOSURE TO ATMOSPHERIC MOISTURE

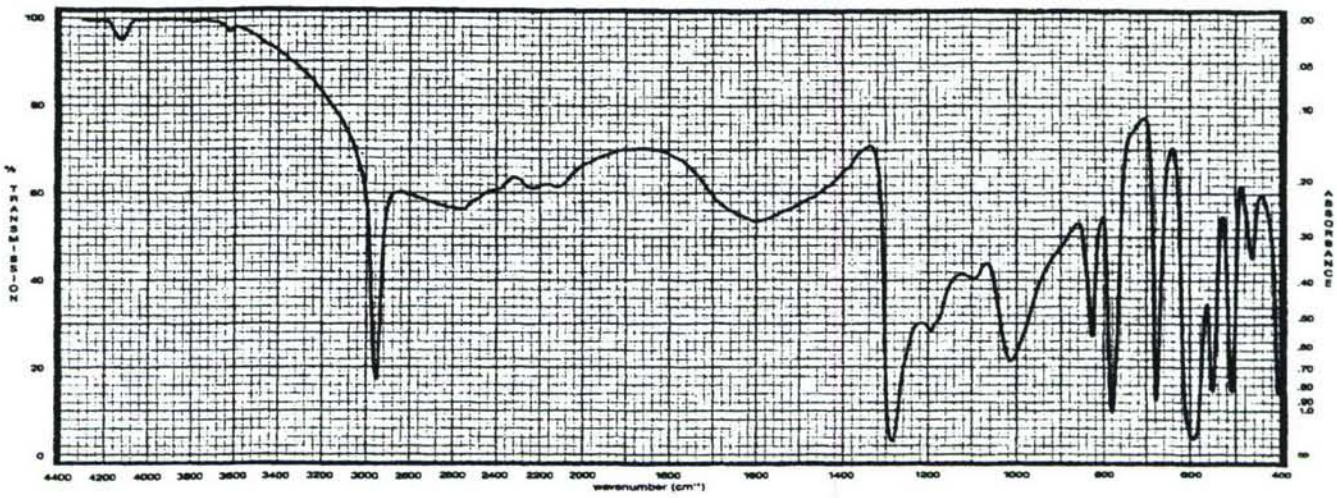


Figure 170 DICHLOROMETHYLPHOSPHONIC DICHLORIDE, LIQUID, CF/KBr (SHOWS SOME HYDROLYSIS TO THE ACID)

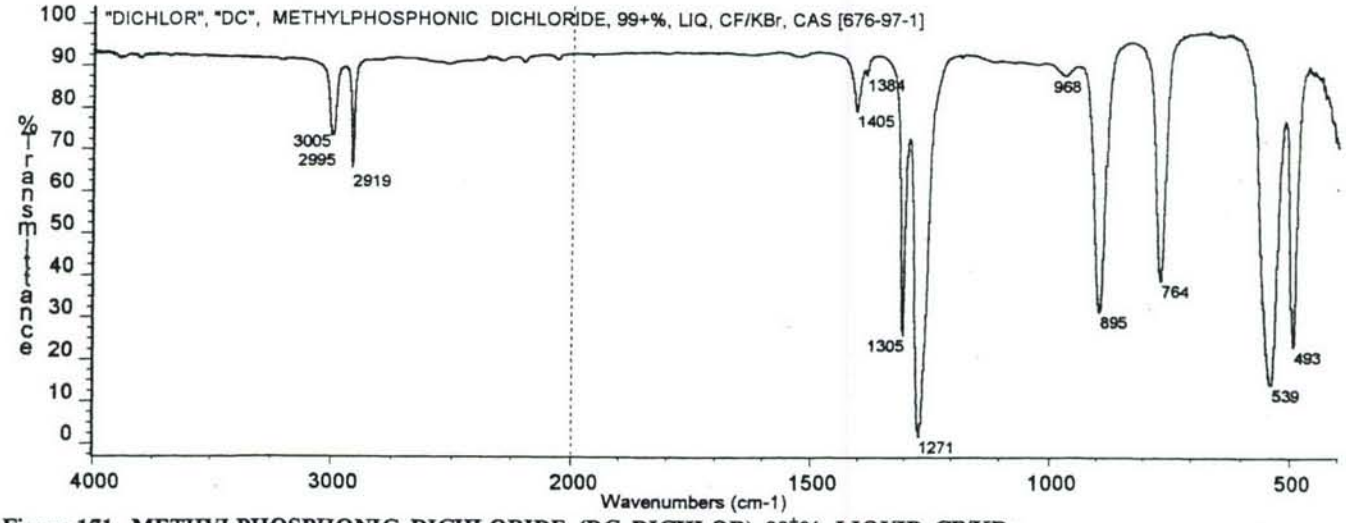


Figure 171 METHYLPHOSPHONIC DICHLORIDE (DC, DICHLOR), 99+%, LIQUID, CF/KBr

infrared spectrum has been previously reported by Durig et al.,[aa] and Piffath.[bb] The band assignments for the liquid film spectrum are as follows: 3005 and 2995 cm^{-1} w (ν_{as} CH_3), 2919 cm^{-1} w (ν_{sy} CH_3), 1405 cm^{-1} vw (δ_{as}

[aa] Durig, J.R., Block, F., and Levin, I.W., "Vibrational Spectra of CH_3PCl_2, CH_3POCl_2 and CH_3PSCl_2", Spectrochimica Acta, **21**, 1105 (1965).

[bb] Piffath, R.J., "Infrared Spectroscopic Observations On The Fate Of Organophosphorus Compounds Exposed To Atmospheric Moisture. Part I. G-Agents And Related Compounds", U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423. Approved For Public Release. (1999)
Piffath, R.J.,"Some Comments On The Infrared Spectra Of CH_3POF_2, CH_3PSF_2, CH_3PSCl_2, CH3POCl$_2$, CH3POClF, $CH_3PO(C{\equiv}N)(F)$, And $CH_3PO(C{\equiv}N)(OEt)$, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423. (In Preparation, 1999).

P-CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows used to contain the liquid film), 1305 cm^{-1} m (δ_{sy} P-CH_3), 1271 cm^{-1} s (ν P=O), 968 cm^{-1} vvw (impurity, hydrolysis product, P-OH or pyro P-O-P), 895 cm^{-1} m (P-CH_3 rock), 764 cm^{-1} m (ν P-C), 539 cm^{-1} ms (ν_{as} PCl_2), 493 cm^{-1} m (ν_{sy} PCl_2). The hydrolysis of **Dichlor** to methylphosphonic acid (**MPA**) is discussed in the references given in footnote [bb].

3.5.7.5 Methylphosphonic Difluoride (**DF, Difluor**) CH_3-P=OF_2

The infrared spectrum of methylphosphonic difluoride (**DF, Difluor**) as a liquid film between KBr windows and as a vapor is given is ***Figure 172***. The infrared spectrum of **DF** has been discussed by Durig et al.[cc], and Piffath.[bb] The band assignments for the liquid film are as follows: 3013 cm^{-1} w (ν_{as} CH_3), 2937 cm^{-1} w (ν_{sy} CH_3), 2623 cm^{-1} vvw (2 x 1312 = 2624 cm^{-1}), 2265 cm^{-1} vvw (1336 + 926 = 2262 cm^{-1}), 2088 cm^{-1} vvw (1336 + 755 = 2091 cm^{-1}), 1711 cm^{-1} vvw (2 x 857 = 1714 cm^{-1}), 1506 cm^{-1} vvw (2 x 755 = 1510 cm^{-1}), 1418 cm^{-1} w (δ_{as} P-CH_3), 1336 cm^{-1} s (ν P=O), 1312 cm^{-1} s (δ_{sy} P-CH_3), 944 and 926 cm^{-1} s (P-CH_3 rock), 882 cm^{-1} ms and 857 cm^{-1} m (ν_{as} and ν_{sy} PF_2), 755 cm^{-1} m (ν P-C), 469 cm^{-1} ms (PF_2 deformation ?), 415 and 407 cm^{-1} m (P=O deformation, PF_2 deformation ?).

The hydrolysis of **Difluor,** both as a liquid and as a vapor, by atmospheric moisture has been discussed by Piffath.[bb] Liquid **Difluor** was shown to hydrolyze to form the **Fluoro Acid**, methylphosphono-fluoridic acid, CH_3P=O(OH)(F), followed by further hydrolysis to form **MPA**, methylphosphonic acid, CH_3P=$O(OH)_2$. The effect of atmospheric moisture on vapor phase **Difluor,** in a *glass* body gas cell, was to produce SiF_4 , HCl, HBr and K_2SiF_6 (potassium hexafluorosilicate). When a Teflon body gas cell was used in place of the glass body cell, the HF produced in the hydrolysis could be visualized in the infrared spectrum. The hydrolysis products such as the **Fluor Acid** and the methylphosphonic acid and not volatile enough to appear in the vapor phase spectrum. This is especially true for methylphosphonic acid which is a solid. A more thorough

[cc] Durig, J.R., Mitchell, B.R., DiYorio, J.S., and Block, F., "Vibrational Spectra of Organophosphorus Compounds II. Infrared and Raman Spectra of CH_3POF_2 AND CH_3POFCl", EATR 4027, July 1966. U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423. Article also appeared in J. Phys. Chem. **70**, 3190 (1966).

discussion of the effect of atmospheric moisture on the vapor phase spectrum of **DF** is given by Piffath.[dd]

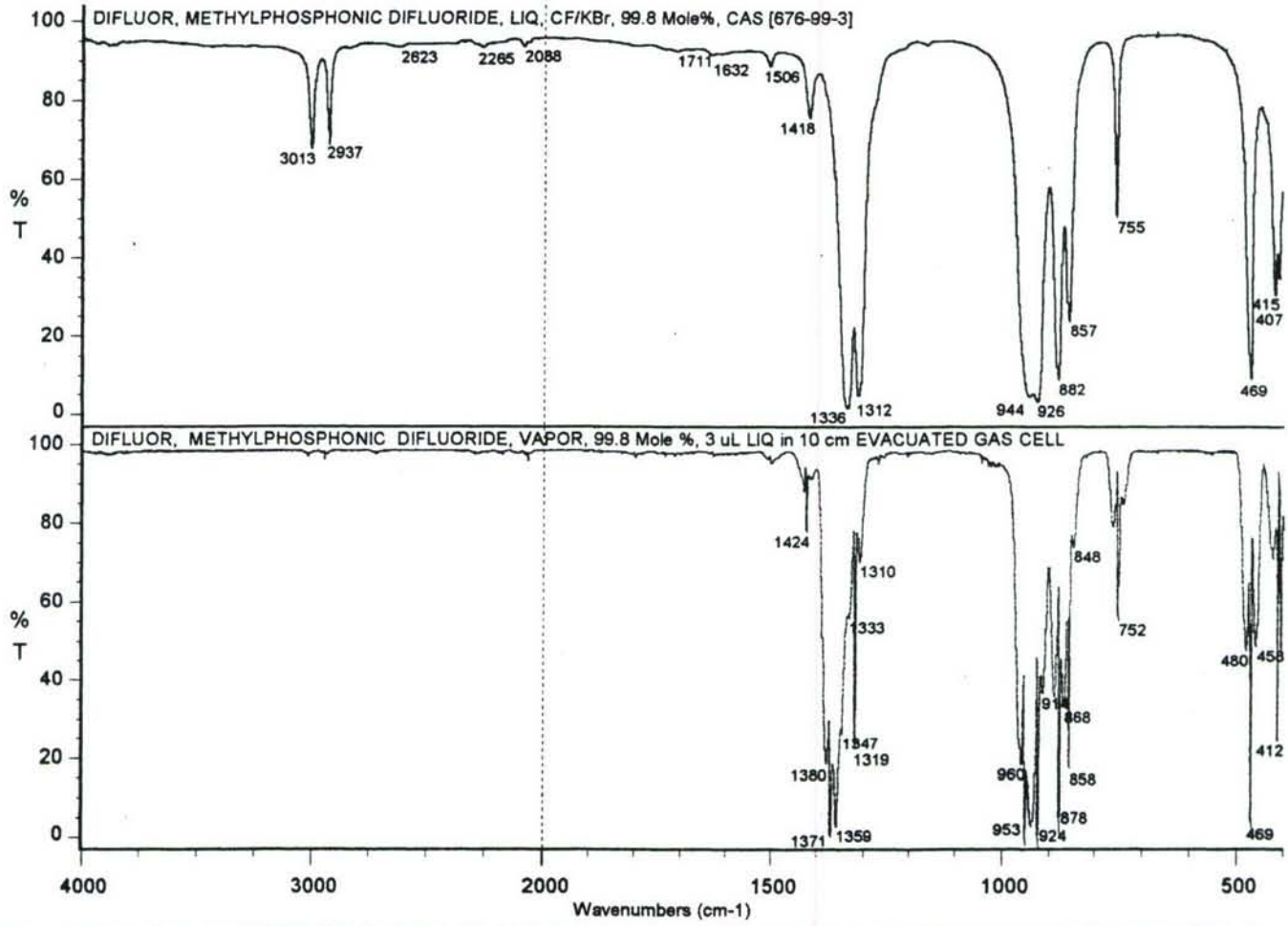


Figure 172 METHYLPHOSPHONIC DIFLUORIDE (DF, DIFLUOR), 99.8 MOLE %, *UPPER SPECTRUM*-- LIQUID, CF/KBr, *LOWER SPECTRUM*--VAPOR PHASE, 3 μL OF LIQUID INJECTED INTO A 10 cm EVACUATED GAS CELL

3.5.7.6 Methylphosphonocyanidic Fluoride $CH_3P{=}O(C{\equiv}N)(F)$

The infrared spectrum of methylphosphonocyanidic fluoride as a liquid is presented as ***Figure 173***. The spectrum as well as the effect of atmospheric moisture on the compound has been previously discussed by Piffath[dd]. The band assignments are as follows: 3174 cm^{-1} vw somewhat broad (ν H-C of H-C≡N), 3005 cm^{-1} (ν_{as} CH_3), 2924 cm^{-1} w (ν_{sy} CH_3), 2212 cm^{-1} ms (ν C≡N), 2090 cm^{-1} vw (ν C≡N of HC≡N), 1639 cm^{-1} vvw

[dd] Piffath, R.J., Some Comments On The Infrared Spectra Of CH_3POF_2, CH_3PSF_2, CH_3PSCl_2, CH3POCl$_2$, CH3POClF, $CH_3PO(C{\equiv}N)(F)$, And $CH_3PO(C{\equiv}N)(OEt)$, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423. (In Preparation)

(866 + 776 = 1642 cm^{-1} ?, 1549 cm^{-1} vvw (2 x 776 = 1552 cm^{-1}), 1405 cm^{-1} w (δ_{as} P-CH_3), 1323 cm^{-1} s (ν P=O), 1293 cm^{-1} s (δ_{sy} P-CH_3), 1009 cm^{-1} w (ν P-OH), 925 cm^{-1} s and 897 cm^{-1} ms (P-CH_3 rocking), 866 cm^{-1} ms (ν P-F), 776 cm^{-1} ms (ν P-C), 587 cm^{-1} m (PCN ?), 471 (PF, P=O deformation ?).

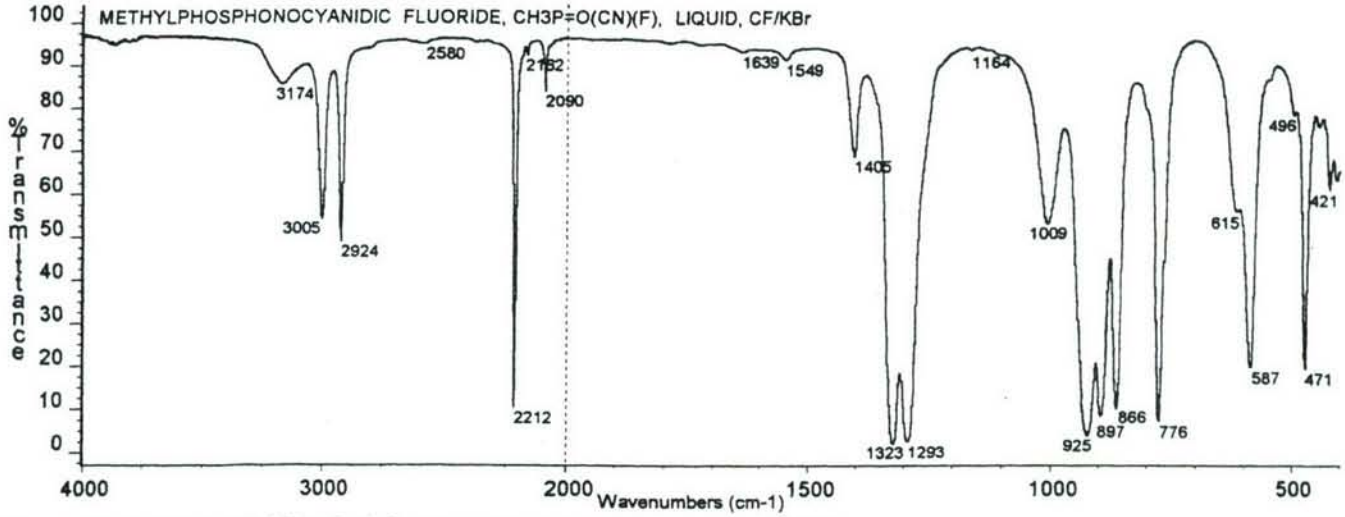


Figure 173 METHYLPHOSPHONOCYANIDIC FLUORIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on methylphosphonocyanidic fluoride has been discussed previously[dd]. The products of the hydrolysis were methylphosphonofluoridic acid, $CH_3P{=}O(OH)(F)$ and methylphosphonic acid, $CH_3P{=}O(OH)_2$.

3.5.7.7 Ethylphosphonic Dichloride CH_3CH_2-P=OCl_2

The infrared spectrum of ethylphosphonic dichloride as a liquid film between KBr windows is given in ***Figure 174***. The band assignments are as follows: 2987 cm^{-1} w (ν_{as} CH_3), 2946 cm^{-1} w (ν_{as} CH_2), 2919 cm^{-1} w (ν_{sy} CH_3), 2885 cm^{-1} vw (ν_{sy} CH_2), ca 2500 cm^{-1} vvw broad (POH ?), 1458 cm^{-1} m (δ_{as} CH_3), 1399 cm^{-1} w (δ P-CH_2), 1386 cm^{-1} vw (δ_{sy} CH_3), 1290 sh and 1277 cm^{-1} s (ν P=O isomers), 1247 cm^{-1} ms and 1228 cm^{-1} w (ω, τ CH_2 of P-Ethyl), 1034 cm^{-1} m and 1010 cm^{-1} w (ν C-C), 955 cm^{-1} vw (ν P-O-P pyro ?), 752 cm^{-1} m (CH_2 rock), 720 cm^{-1} ms (ν P-C), 659 vvw (pyro ?), 567 cm^{-1} s amd 539 cm^{-1} ms (ν_{as} PCl_2 isomers), 501 cm^{-1} m and 483 cm^{-1} m (ν_{sy} PCl_2 isomers). Note, the calculated value for the P=O stretch is 1262 cm^{-1} ; if the 1277 and 1247 band values are averaged the resultant value is 1262 cm^{-1}. The P-Ethyl group can cause some splitting of the P=O

band. The P-Ethyl group has two weak infrared bands in the region 1282-1227 cm^{-1} (ω and τ CH_2). When the P=O stretching vibration falls in this region, splitting of the P=O band *may* occur due to interaction. Thus, the presence of the P-Ethyl group should be suspected when this splitting occurs.[ee]

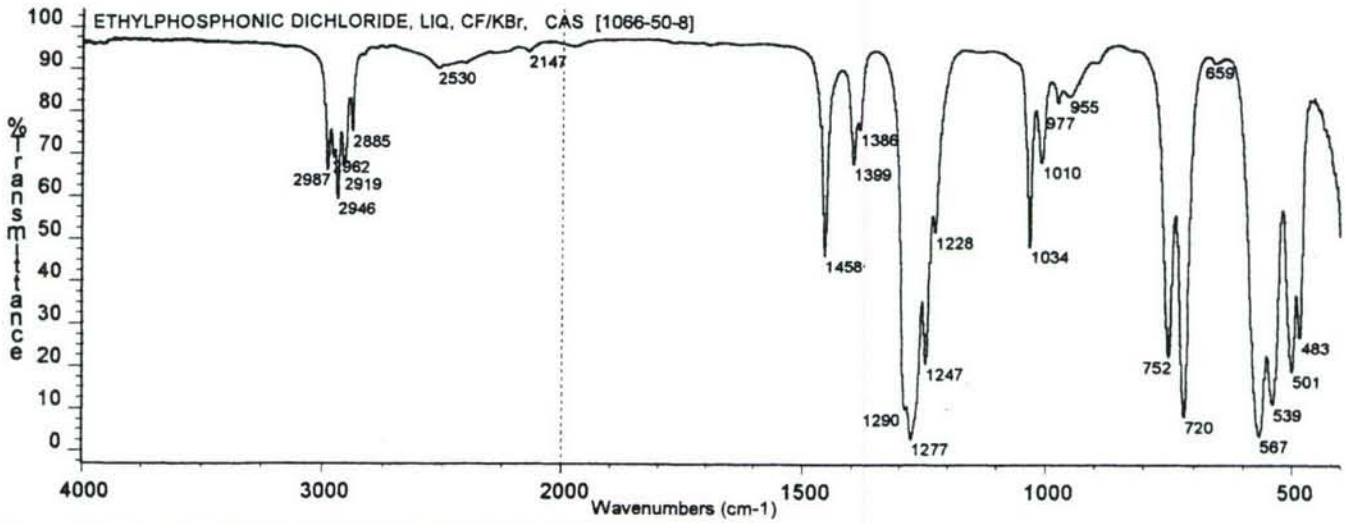


Figure 174 ETHYLPHOSPHONIC DICHLORIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on ethylphosphonic dichloride is illustrated by the infrared spectra presented in ***Figures 175A*** and ***175B***. The infrared spectrum for the compound after 3 hours of exposure to atmospheric moisture shows the formation of bands near 2500 cm^{-1} (POH), 955 cm^{-1} (ν P-O-P pyro and ν P-OH), and 657 cm^{-1} (pyro). After an exposure of 24 hours, the bands due to POH (2525, 2280,1650 and 950 cm^{-1}) have become stronger. The band near 950 cm^{-1} is strong and broad probably due to the fact that it may be composed of both ν P-O-P and ν P-OH. The P=O stretching band is still present at 1278 cm^{-1} as are the bands due to PCl_2 (570, 541, 503 and 485 cm^{-1}). The pyro compound Et(Cl)P(=O)-O-P(=O)(Cl)Et, has a calculated value of 1278 cm^{-1}. After 4 days of exposure to atmospheric moisture, the spectrum (***Figure 175B***) shows a lot of water near 3370 cm^{-1} and a shift of the ν P=O to a broad band near 1130 cm^{-1}. The bands due to the PCl_2 group are now gone from the spectrum. The original compound has hydrolyzed to ethylphosphonic acid, $CH_3CH_2P{=}O(OH)_2$. See ***Figure 113*** for the spectrum of ethylphosphonic acid.

[ee] Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p 97, Heyden & Son Ltd., London, 1974.

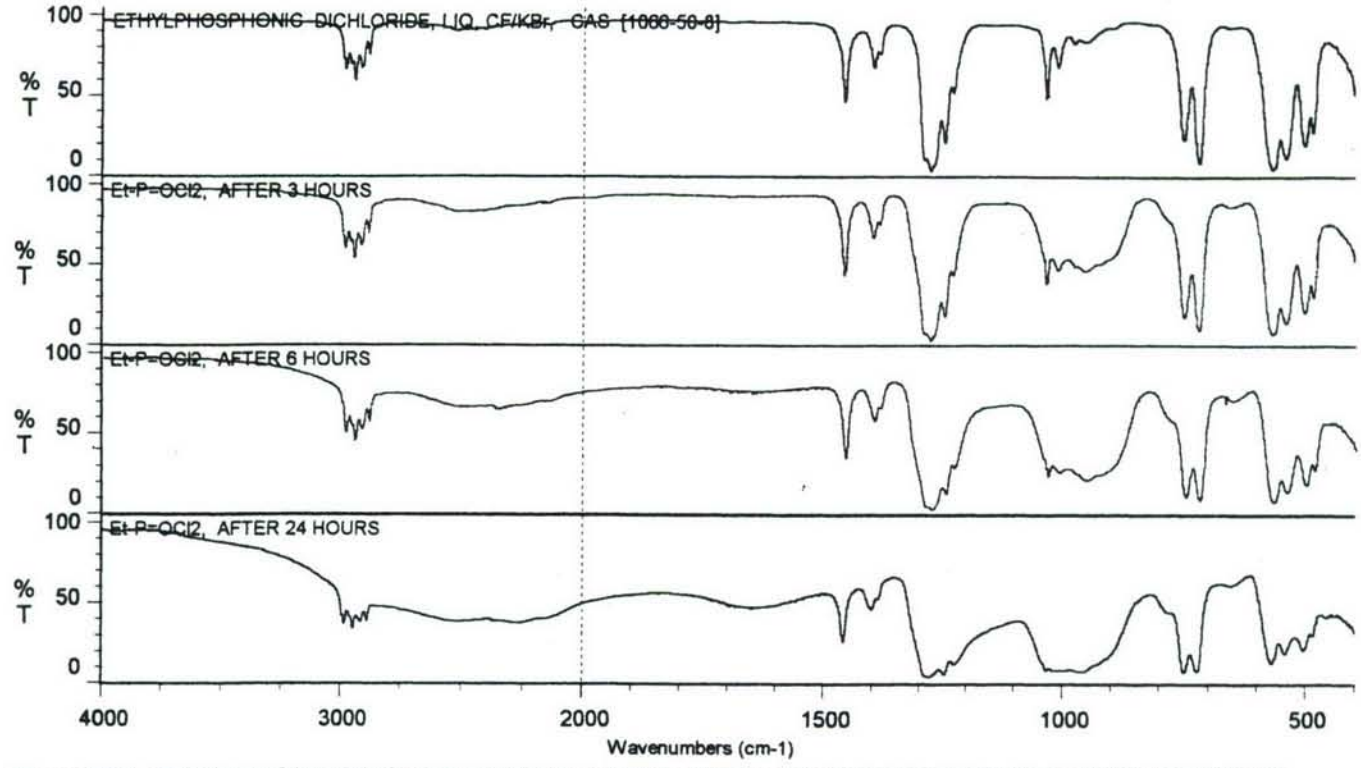


Figure 175A ETHYLPHOSPHONIC DICHLORIDE, LIQUID, CF/KBr, SHOWING THE EFFECT OF ATMOSPHERIC MOISTURE

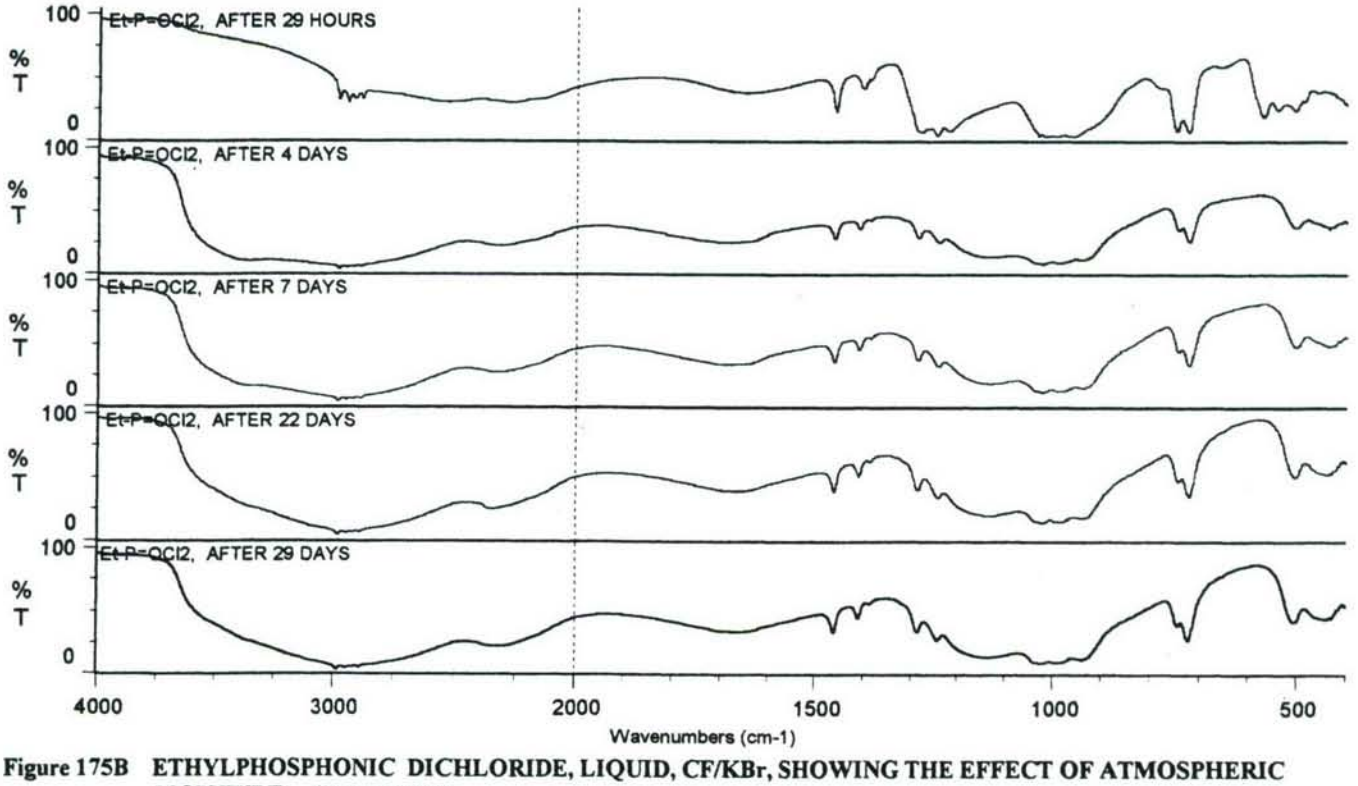


Figure 175B ETHYLPHOSPHONIC DICHLORIDE, LIQUID, CF/KBr, SHOWING THE EFFECT OF ATMOSPHERIC MOISTURE (CONTINUED)

3.5.7.8 Propylphosphonic Dichloride $CH_3CH_2CH_2\text{-}P{=}OCl_2$

The infrared spectrum of propylphosphonic dichloride as a liquid film between KBr windows is given in ***Figure 176***. The band assignments are as follows: 2973 cm^{-1} ms (ν_{as} CH_3), 2938 cm^{-1} m (ν_{as} CH_2), 2907 cm^{-1} w (ν_{sy} CH_3), 2880 cm^{-1} m (ν_{sy} CH_2), ca 2550 cm^{-1} vw broad (ν P-OH impurity, hydrolysis product), 1464 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1398 cm^{-1} m (δ P-CH_2), 1385 cm^{-1} sh (δ_{sy} CH_3), 1343 cm^{-1} w, 1303 cm^{-1} sh and 1223 cm^{-1} sh (ω, τ CH_2), 1078 and 1038 cm^{-1} m (ν C-C), 957 cm^{-1} w (possible pyro ν P-O-P), 767 cm^{-1} m (CH_2 rock or ν P-C), 723 and 700 cm^{-1} m (ν P-C or CH_2 rock), 564 cm^{-1} s and 541 cm^{-1} ms (ν_{as} PCl_2 doublet, isomers), 514 and 496 cm^{-1} ms (ν_{sy} PCl_2 doublet, isomers).

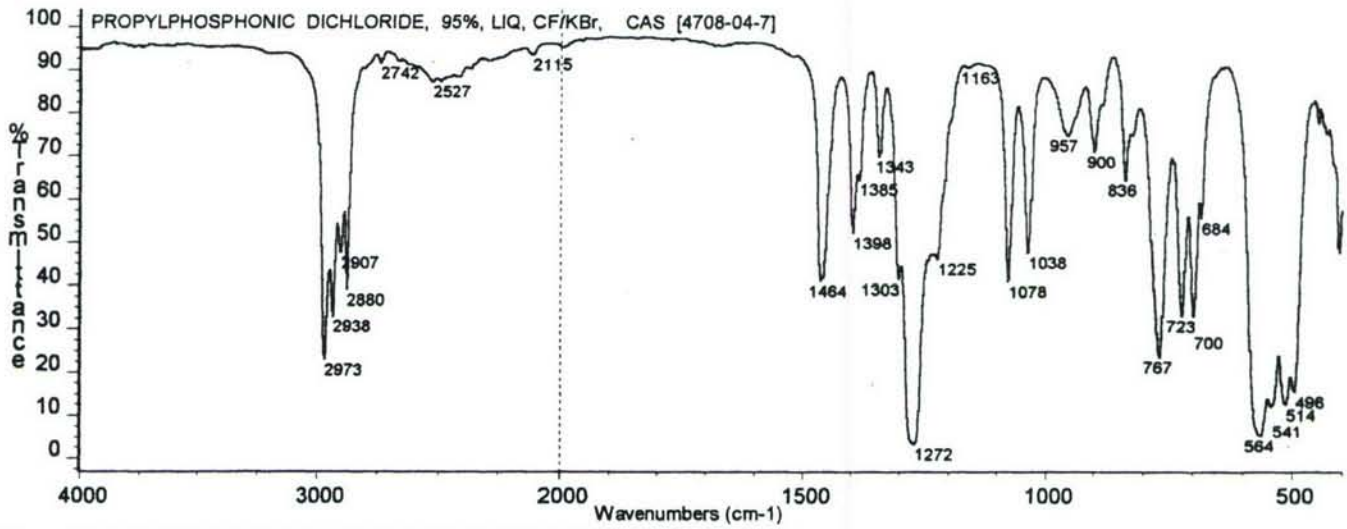


Figure 176 PROPYLPHOSPHONIC DICHLORIDE, 95%, LIQUID, CF/KBr

Figure 177 shows the effect of atmospheric moisture on the infrared spectrum of propylphosphonic dichloride. The band at ca 957 cm^{-1}, present in the sample originally, could be due to a pyro compound such as $H_7C_3(Cl)P(=O)\text{-}O\text{-}P=O(Cl)C_3H_7$. This pyro compound would have a calculated P=O stretching band of 1278 cm^{-1} which is close to the 1272 cm^{-1} band of the original compound. As the propylphosphonic dichloride begins to hydrolyze the bands near 2500 and 1650 cm^{-1}, indicative of the POH moiety, increase in intensity. Around the 8th day of exposure to atmospheric moisture the original compound has hydrolyzed to propylphosphonic acid, $CH_3CH_2CH_2P=O(OH)_2$.

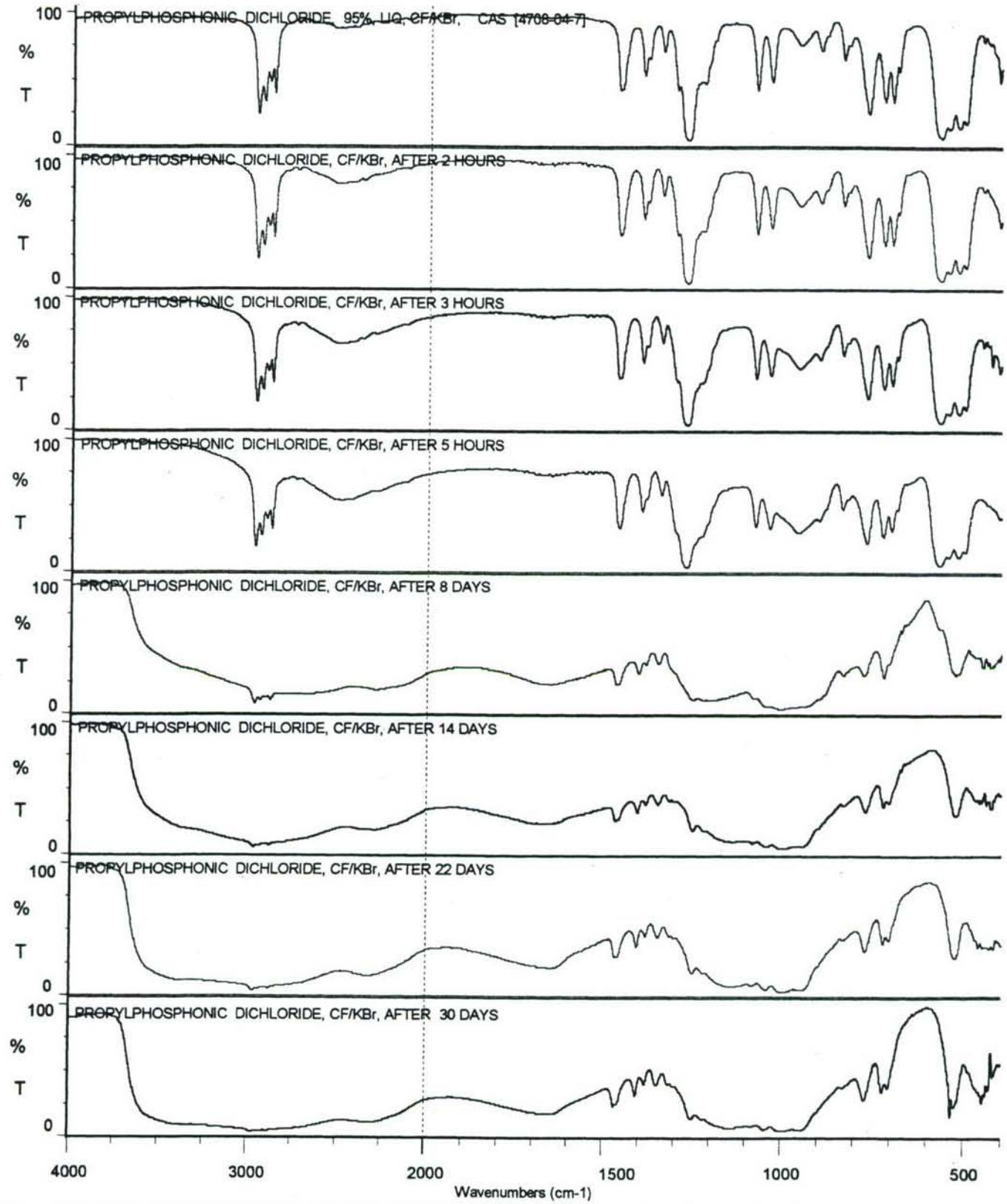


Figure 177 PROPYLPHOSPHONIC DICHLORIDE, 95%. LIQUID, CF/KBr, SHOWING THE EFFECT OF ATMOSPHERIC MOISTURE

3.5.7.9 *tert*-Butylphosphonic Difluoride $(CH_3)_3C\text{-}P{=}OF_2$

The infrared spectrum of *tert*-butylphosphonic difluoride as a liquid film between KBr windows is presented as ***Figure 178***. The band assignments are as follows: 3396 cm^{-1} vw (H_2O), 2980 cm^{-1} m (ν_{as} CH_3), 2946 cm^{-1} sh (1480 + 1468 = 2948 cm^{-1}), 2915 or 2883 cm^{-1} w (ν_{sy} CH_3), 1480 and 1468 cm^{-1} m (δ_{as} CH_3), 1406 and 1374 cm^{-1} w (δ_{sy} CH_3), 1326 cm^{-1} s (ν P=O), 1230 cm^{-1} w (*t*-butyl skeletal), 946 cm^{-1} vw (CH_3 rock ?), 819 cm^{-1} w (*t*-butyl moiety), 642 cm^{-1} m (ν P-C), 483 cm^{-1} ms, 464 cm^{-1} m (P=O, PF_2 deformations ?).

The potential hydrolysis product of *tert*-butylphosphonic difluoride is *tert*-butylphosphonic acid, $(CH_3)_3C\text{-}P{=}O(OH)_2$. The infrared spectrum of the acid was given earlier as ***Figure 123***.

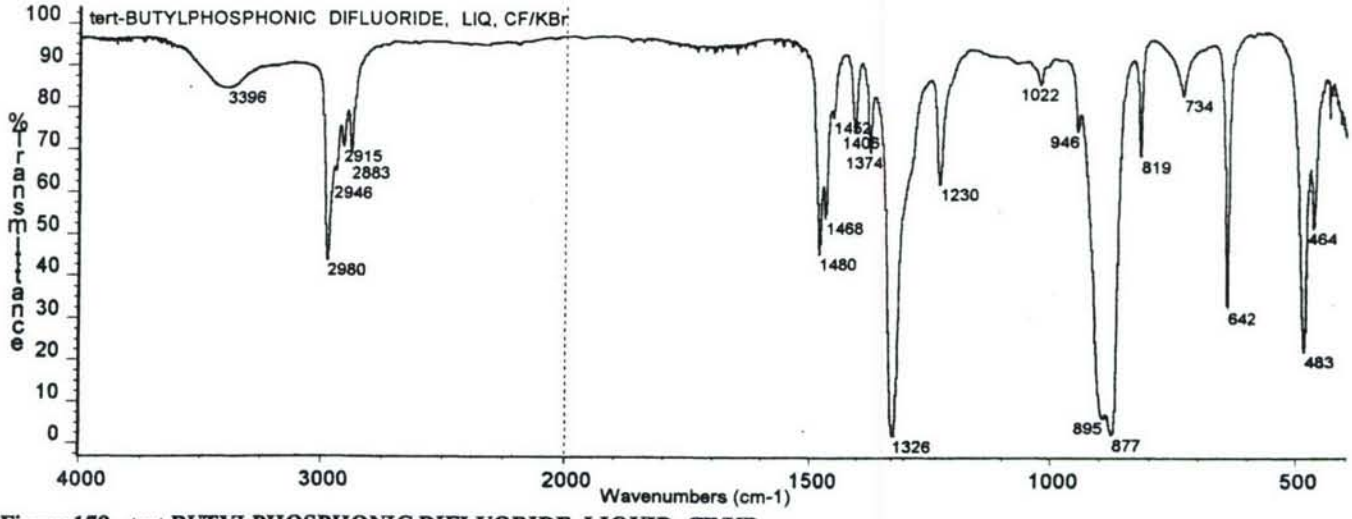


Figure 178 ***tert*-BUTYLPHOSPHONIC DIFLUORIDE, LIQUID, CF/KBr**

3.5.7.10 Phenylphosphonic Dichloride $C_6H_5\text{-}P{=}OCl_2$

The infrared spectrum of phenylphosphonic dichloride as a liquid film between KBr windows is given as ***Figure 179***. The band assignments are as follows: 3062 cm^{-1} vw (ν C-H aromatic), 1587 cm^{-1} w, 1484 cm^{-1} vw and 1440 cm^{-1} m (aromatic ring), 1274 cm^{-1} ms (ν P=O), 1185, 1162, 1142 1069, 1027 cm^{-1} all vvw and 998 cm^{-1} vw (β C-H mono-substituted aromatic ring), 1109 cm^{-1} m (phenyl-P), 749 cm^{-1} m (γ C-H mono-substituted aromatic ring), 687 cm^{-1} m (δ mono-substituted aromatic ring), 562 cm^{-1} ms (ν_{as} PCl_2) and 541 cm^{-1} s (ν_{sy} PCl_2).

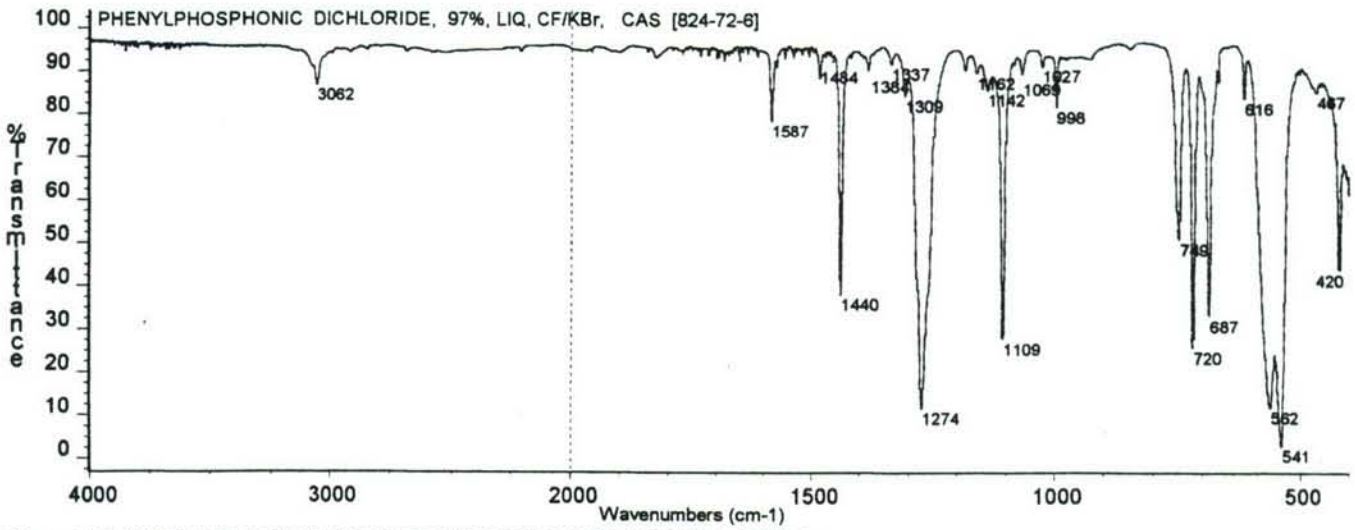


Figure 179 PHENYLPHOSPHONIC DICHLORIDE, 97%, LIQUID, CF/KBr

Infrared spectra depicting the effect of atmospheric moisture on phenylphosphonic dichloride are reproduced in ***Figures 180A*** and *180B*. After an exposure to atmospheric moisture of 1 day, the infrared spectrum (***Figure 180A***) shows a weak band near 960 cm^{-1} which may be due to a pyro compound (ν P-O-P). Perhaps a pyro compound such as $(Cl)C_6H_5P(=O)\text{-}O\text{-}P(=O)C_6H_5(Cl)$, having a calculated ν P=O of 1282 cm^{-1}, is forming. Also, a broad band is forming near 2500 cm^{-1}, signifying a POH moiety. The PCl_2 bands near 562 and 541 cm^{-1} appear to remain until some time around the 135th day where they are absent from the spectrum (***Figure 180B***). The compound has hydrolyzed to phenylphosphonic acid as indicated by the POH bands near 2700, 2250 cm^{-1} (POH) and near 1010 cm^{-1} and 950 cm^{-1} (ν P-OH). An infrared spectrum for an authentic sample of phenylphosphonic acid was presented earlier as ***Figure 135***.

3.5.8 **Phosphonates** $R\text{-}P{=}O(OR)_2$

3.5.8.1 Dimethyl Hydrogenphosphonate (Dimethyl Phosphite) $H\text{-}P{=}O(OCH_3)_2$

The infrared spectrum of dimethyl hydrogenphosphonate (dimethyl phosphonate, dimethyl phosphite) as a liquid film between KBr windows and as a vapor is given in ***Figure 181***. The band assignments for the liquid phase are as follows: 3000 cm^{-1} vw, 2958 cm^{-1} w (ν_{as} CH_3), 2854 cm^{-1} vw (ν_{sy} CH_3), 2428 cm^{-1} vw (ν P-H), 1465 cm^{-1} w ($\delta_{as}$and δ_{sy} CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1267 cm^{-1} s (ν P=O), 1187

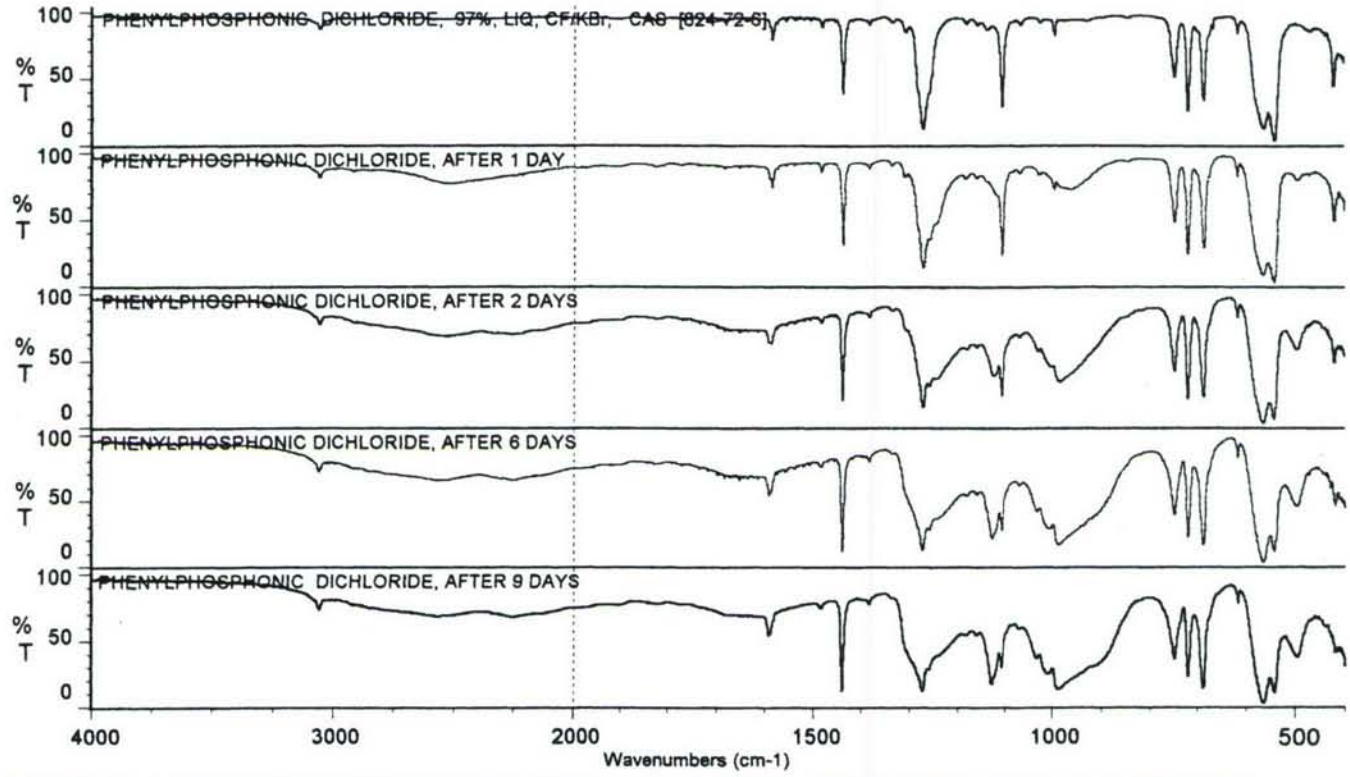


FIGURE 180A PHENYLPHOSPHONIC DICHLORIDE. LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

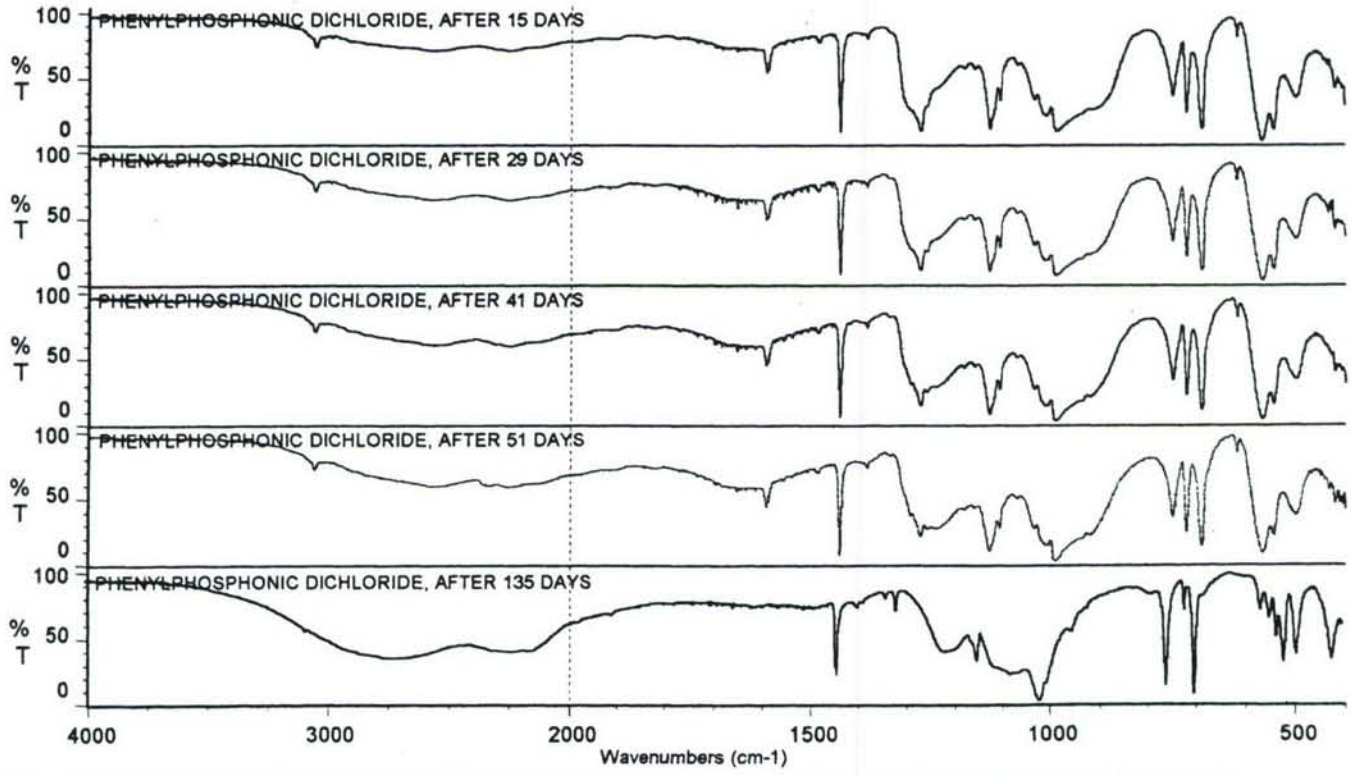


Figure 180B PHENYLPHOSPHONIC DICHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

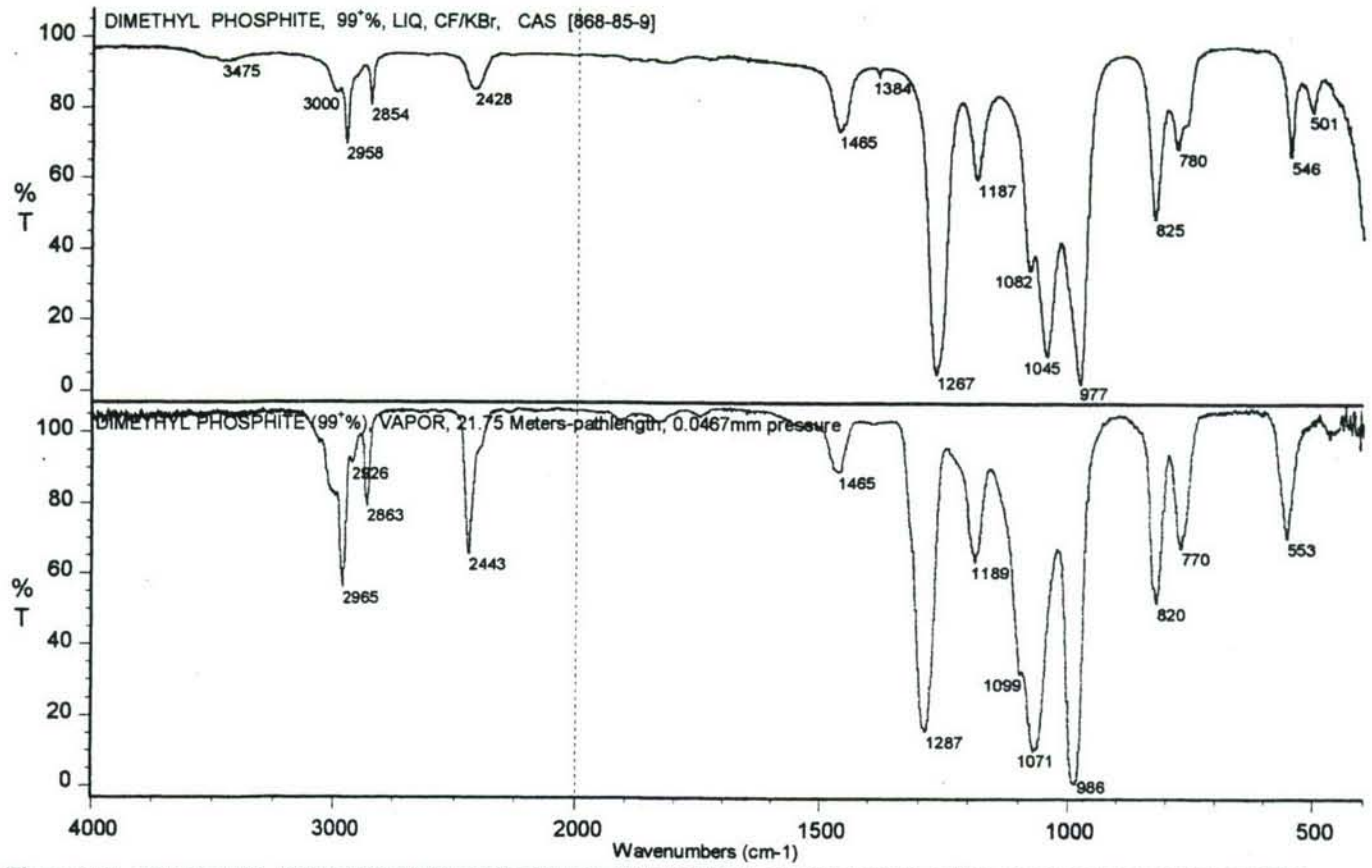


Figure 181 DIMETHYL HYDROGENPHOSPHONATE (DIMETHYL PHOSPHITE), 99+%, *UPPER SPECTRUM*--LIQUID, CF/KBr, *LOWER SPECTRUM*--VAPOR PHASE, 21.75 METERS PATHLENGTH, 0.0467 mm PRESSURE

cm^{-1} w (CH_3 rock, characteristic of $POCH_3$), 1082 cm^{-1} m and 1045 cm^{-1} ms (ν P-O-C), 977 cm^{-1} s (P-H deformation). 825 cm^{-1} m and 780 cm^{-1} w (POC), 546 cm^{-1} w (P=O deformation), 501 cm^{-1} vw (POC).

The effect of atmospheric moisture on a liquid film of dimethyl hydrogenphosphonate is illustrated by the infrared spectra reproduced in ***Figures 182A*** and ***182B***. The infrared spectrum is essentially unchanged up to the 44 hour time period. After 6 days have passed, the spectrum dramatically changes to that resembling a P-acid moiety as indicated by the broad POH bands near 2850, 2300 and 1650 cm^{-1}. Other bands occur near 2435 cm^{-1} (ν P-H), 1150 cm^{-1} m and broad (ν P=O), 1010 cm^{-1} s (ν P-OH, and P-H deformation), 939 cm^{-1} m (ν P-OH) and 524 cm^{-1} w (P=O deformation). By the 41 day period no bands of the OCH_3 moiety are present in the spectrum. The final spectrum in the series (***Figure 182B***) appears to be consistent with that for phosphorous acid, $P(OH)_3$, that is, $HP{=}O(OH)_2$, phosphonic acid.

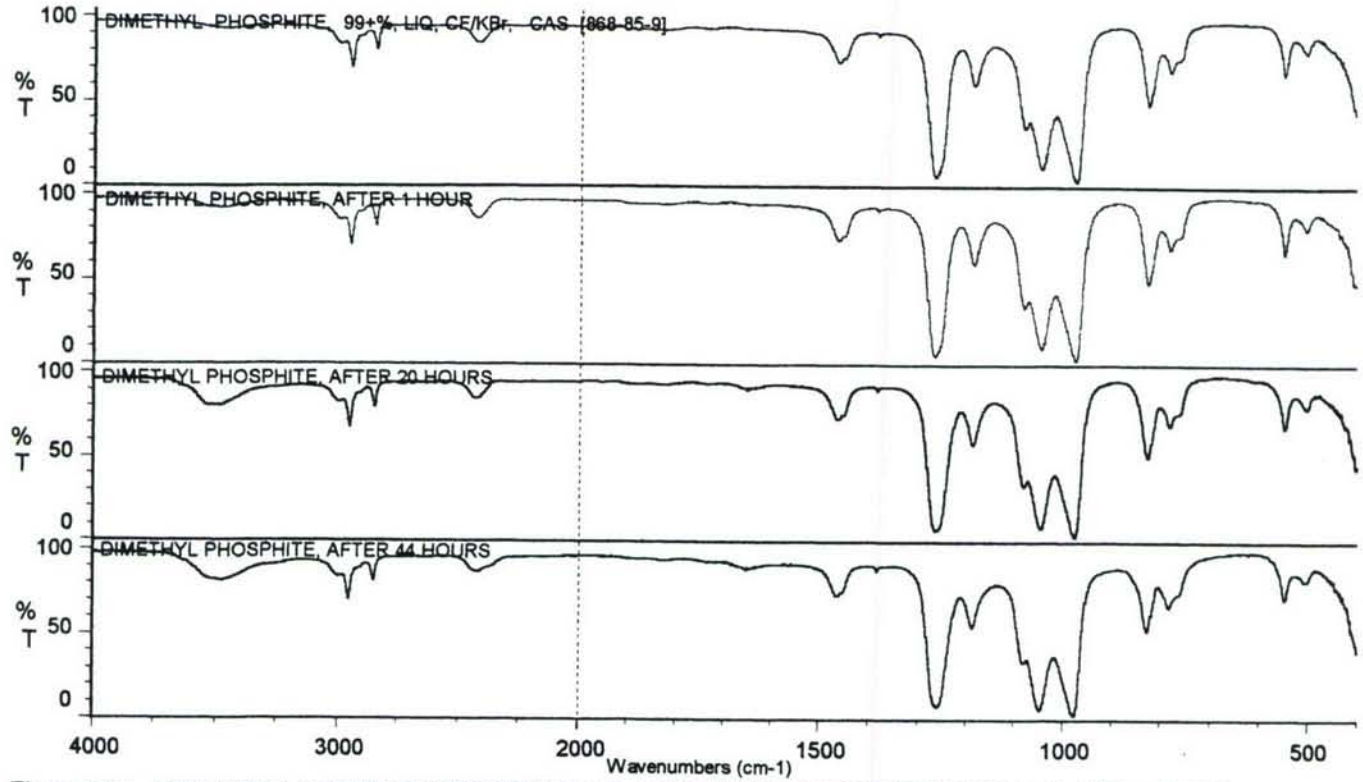


Figure 182A DIMETHYL HYDROGENPHOSPHONATE (DIMETHYL PHOSPHITE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

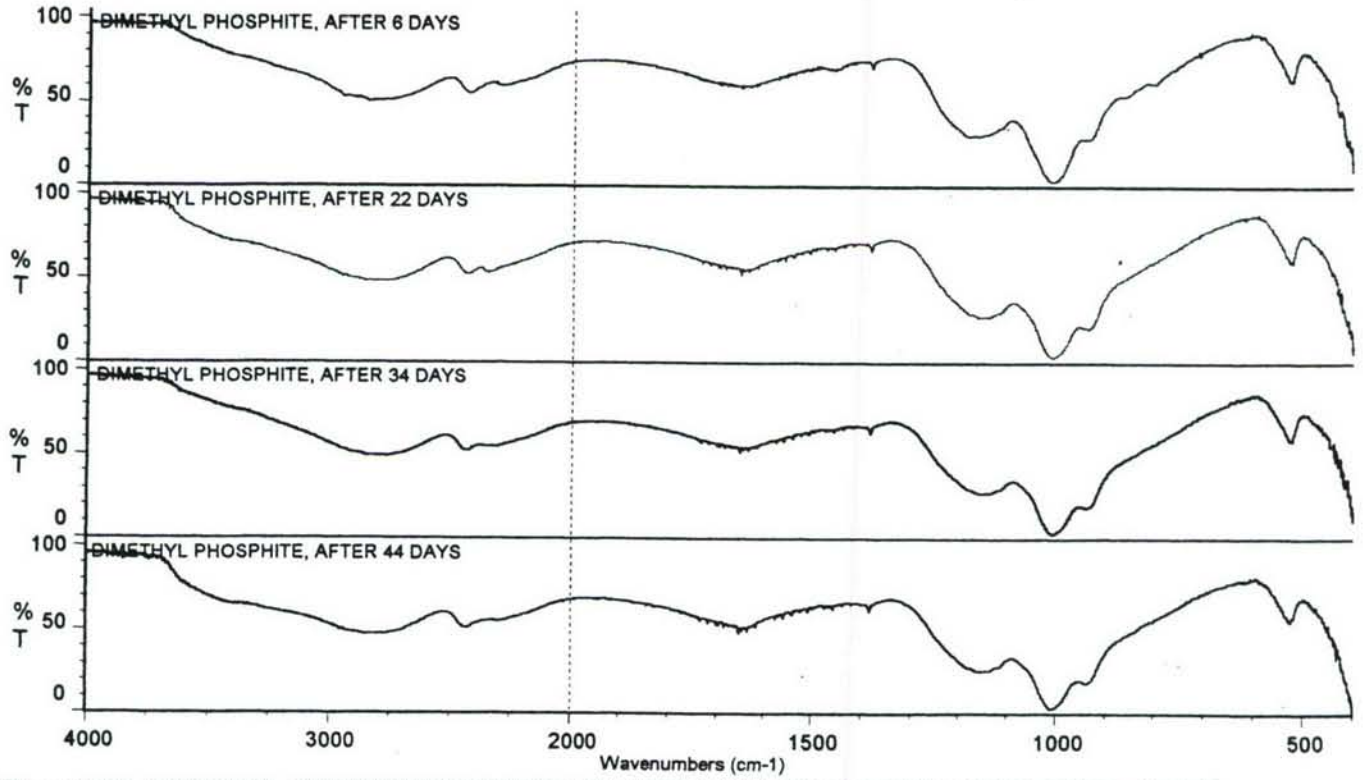


Figure 182B DIMETHYL HYDROGENPHOSPHONATE (DIMETHYL PHOSPHITE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.5.8.2 Diethyl Hydrogenphosphonate (Diethyl Phosphite) $H\text{-}P{=}O(OCH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl hydrogenphosphonate (diethyl phosphonate, diethyl phosphite) as a liquid film between KBr discs (windows) is reproduced as ***Figure 183***. The band assignments are as follows: 3447 cm^{-1} vw (H_2O), 2985 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), 2909 cm^{-1} m (ν_{sy} CH_3), 2873 cm^{-1} w (ν_{sy} CH_2), 2426 cm^{-1} w (ν P-H), 1480 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1393 cm^{-1} m (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1260 cm^{-1} ms (ν P=O), 1165 and 1100 cm^{-1} m (CH_3 rock, characteristic of POEt), 1077 cm^{-1} m and 1045 cm^{-1} ms (ν P-O-C), 977 cm^{-1} s (P-H deformation and ν C-C of POEt), 791 cm^{-1} m (POC), 549 cm^{-1} m (P=O deformation), 514 cm^{-1} w (POC).

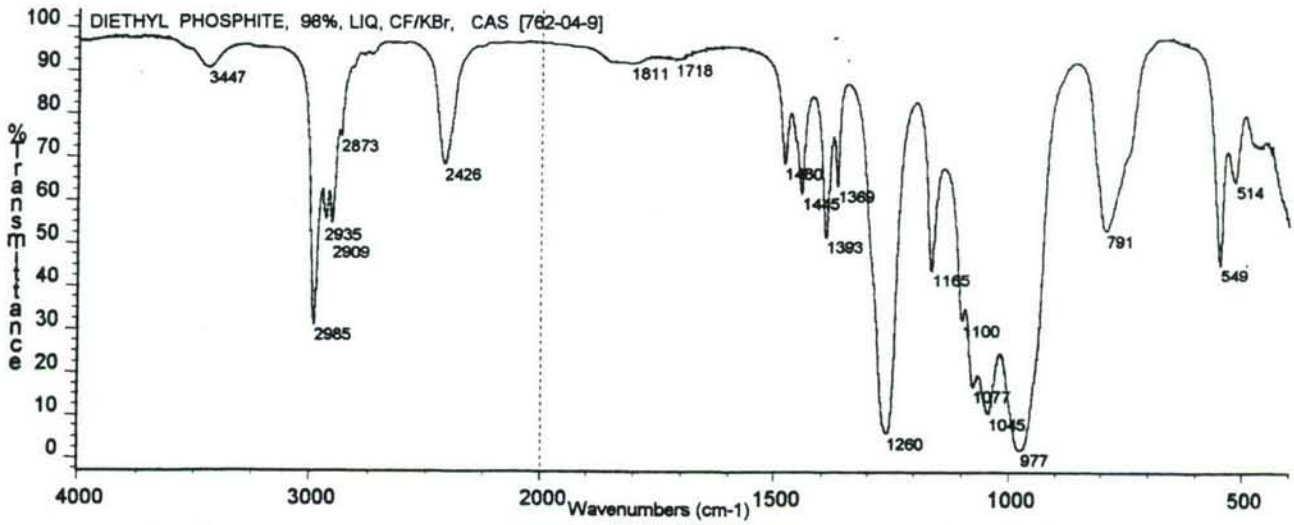


Figure 183 DIETHYL HYDROGENPHOSPHONATE (DIETHYL PHOSPHITE), 98%, LIQUID, CF/KBr

The effect of atmospheric moisture on the liquid film of diethyl hydrogenphosphonate is illustrated by the infrared spectra presented in ***Figures 184A*** and ***184B***. The compound appears to remain intact for the first 3 days of exposure to atmospheric moisture. At the 7th day the spectrum is that of mainly a P-acid with only some very weak residual POEthyl bands still visible (bands due to CH_3, CH_2 and a POEt band at 1166 cm^{-1}) and a P-H stretching band at 2445 cm^{-1}. After 13 days to the end of the study (56 days) the spectrum appears to be that of phosphonic acid, $H\text{-}P{=}O(OH)_2$. The hydrolysis of diethyl hydrogenphosphonate may be summarized as follows:

$H\text{-}P{=}O(OCH_2CH_3)_2$ $\xrightarrow{-HOH}$ $H\text{-}P{=}O(OH)(OCH_2CH_3)$ $\xrightarrow{-HOH}$ $H\text{-}P{=}O(OH)_2$.

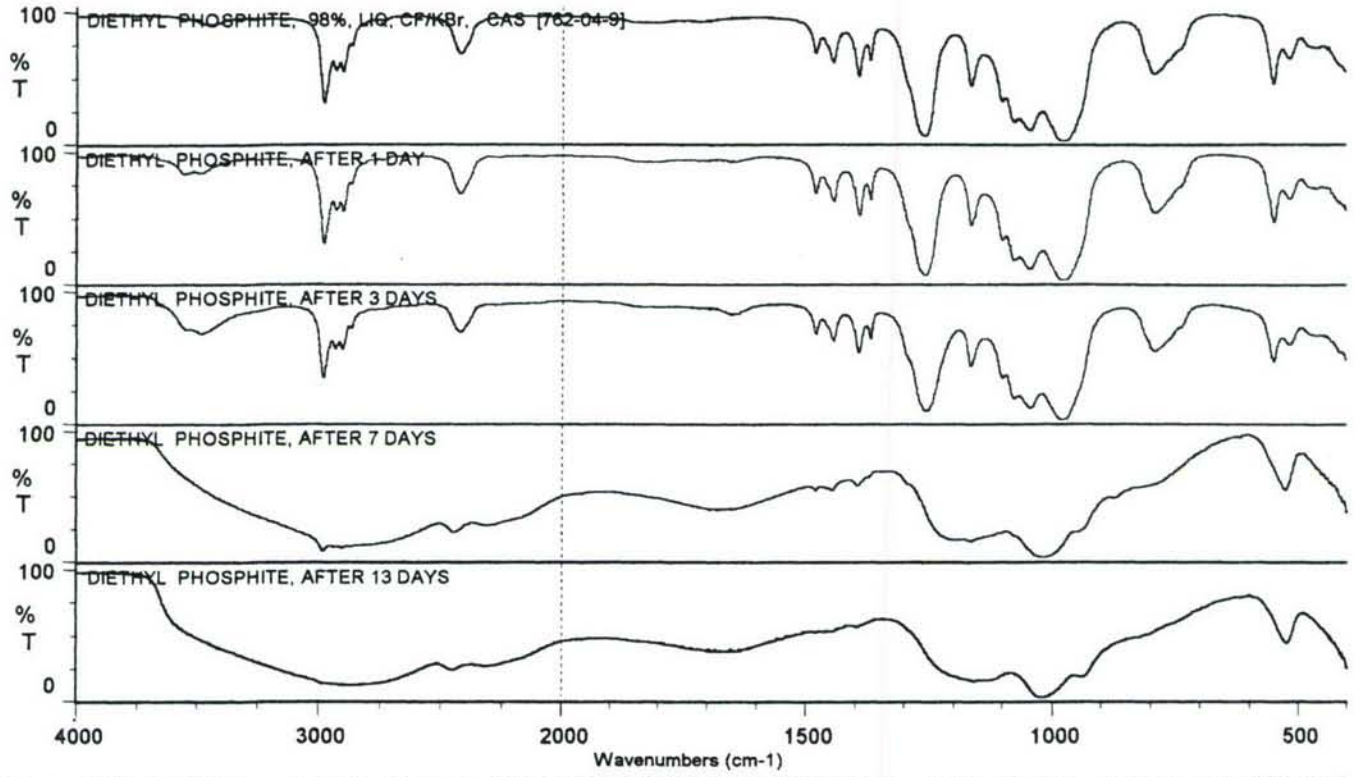


Figure 184A DIETHYL HYDROGENPHOSPHONATE (DIETHYL PHOSPHITE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

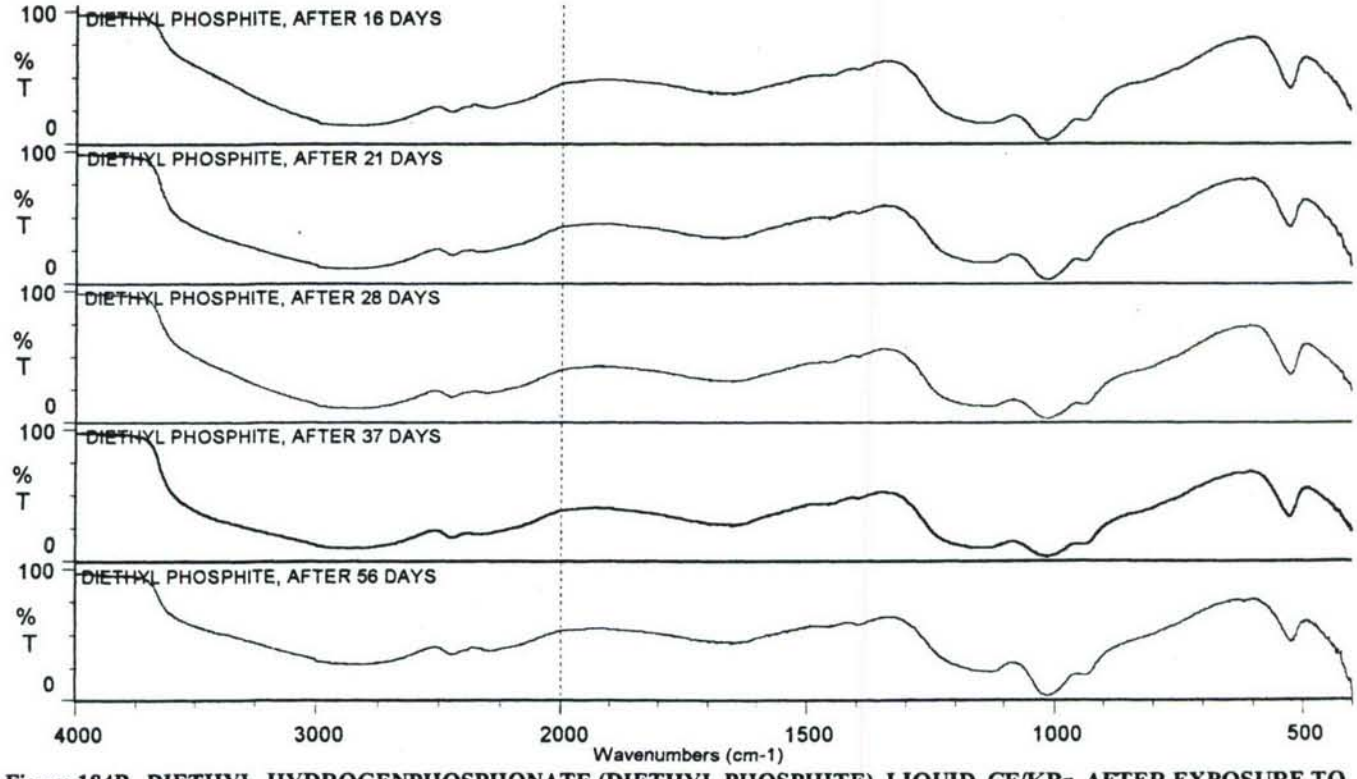


Figure 184B DIETHYL HYDROGENPHOSPHONATE (DIETHYL PHOSPHITE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.5.8.3 Diisopropyl Hydrogenphosphonate (Diisopropyl Phosphite) $H\text{-}P{=}O[OCH(CH_3)_2]_2$

The infrared spectrum of diisopropyl hydrogenphosphonate (diisopropyl phosphite) as a liquid and as a vapor is given in ***Figure 185***. The band assignments of the liquid phase are as follows: 3446 cm^{-1} vw (H_2O), 2981 cm^{-1} m (ν_{as} CH_3), 2936 cm^{-1} w (ν -C-H), 2878 cm^{-1} vw (ν_{sy} CH_3), 2423 cm^{-1} w (ν P-H), 1468 and 1456 cm^{-1} w (δ_{as} CH_3), 1387 and 1377 cm^{-1} m (δ_{sy} CH_3), ca 1350 cm^{-1} sh (δ -C-H), 1259 cm^{-1} ms (ν P=O), 1179, 1143 and 1110 cm^{-1} w-m (three bands characteristic of P-O-isopropyl), 1050 cm^{-1} sh, 974 cm^{-1} s (ν P-O-C and P-H deformation), 895, 886 cm^{-1} vw (CH_3 rock ?), 768 cm^{-1} w (POC), 555 cm^{-1} w (P=O deformation).

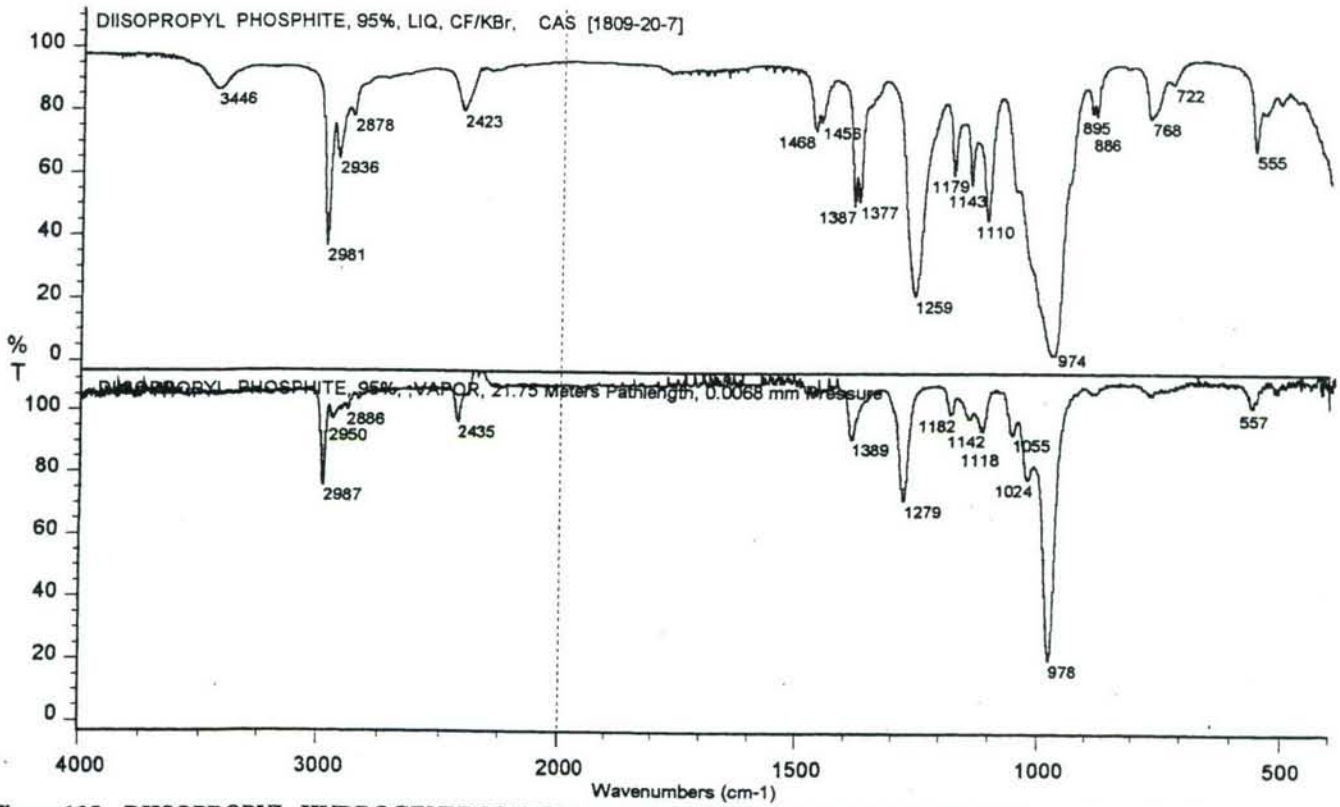


Figure 185 DIISOPROPYL HYDROGENPHOSPHONATE (DIISOPROPYL PHOSPHITE), 95%, *UPPER SPECTRUM*--LIQUID, CF/KBr, *LOWER SPECTRUM*--VAPOR PHASE, 21.75 Meters Pathlength, 0.0068 mm Pressure

The effect of atmospheric moisture on a liquid film of diisopropyl hydrogenphosphonate is illustrated by the infrared spectra given in ***Figures 186A*** and ***186B***. After 6 days, the spectrum (***Figure 186A***) shows bands due to the POH moiety near 2700, 2280 and 1650 cm^{-1}. The P=O stretching vibration has fallen to 1225 cm^{-1}. By the 13th day the presence of the P-acid is even more pronounced, with a further decrease in the P=O frequency

to ca 1200 cm^{-1}. The bands indicative of the P-O-isopropyl moiety have greatly decreased in intensity. After 19 days of exposure to atmospheric moisture, the spectrum shows a further decrease in the P=O frequency to 1167 cm^{-1} and the almost total absense of bands indicative of the P-O-isopropyl moiety. As time progresses toward the last period of exposure, namely 90 days, the spectrum shows only bands indicative of the PH, POH and P=O groups. The final compound in the hydrolysis being represented as $H\text{-}P{=}O(OH)_2$, phosphonic acid.

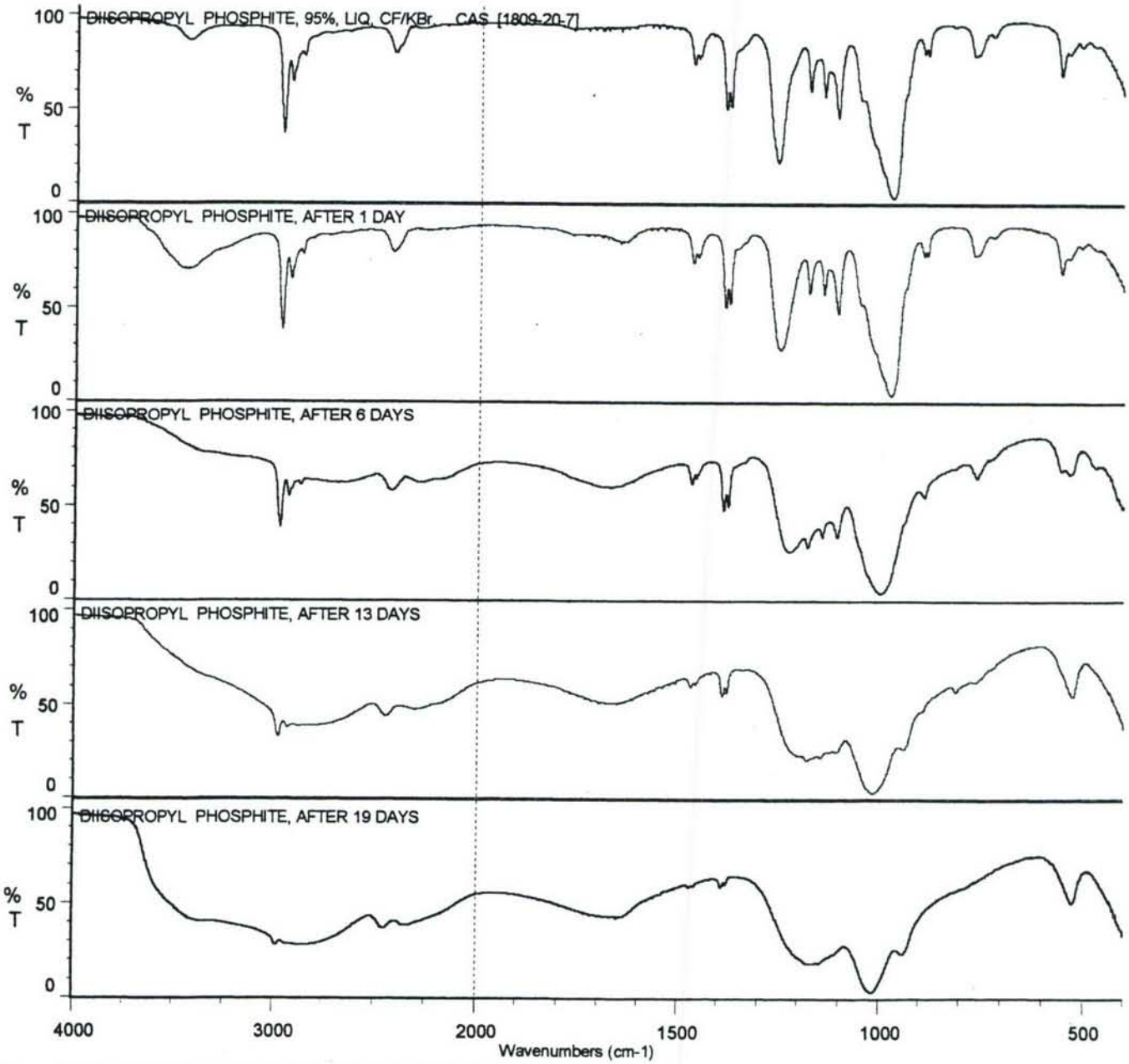


Figure 186A DIISOPROPYL HYDROGENPHOSPHONATE (DIISOPROPYL PHOSPHITE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

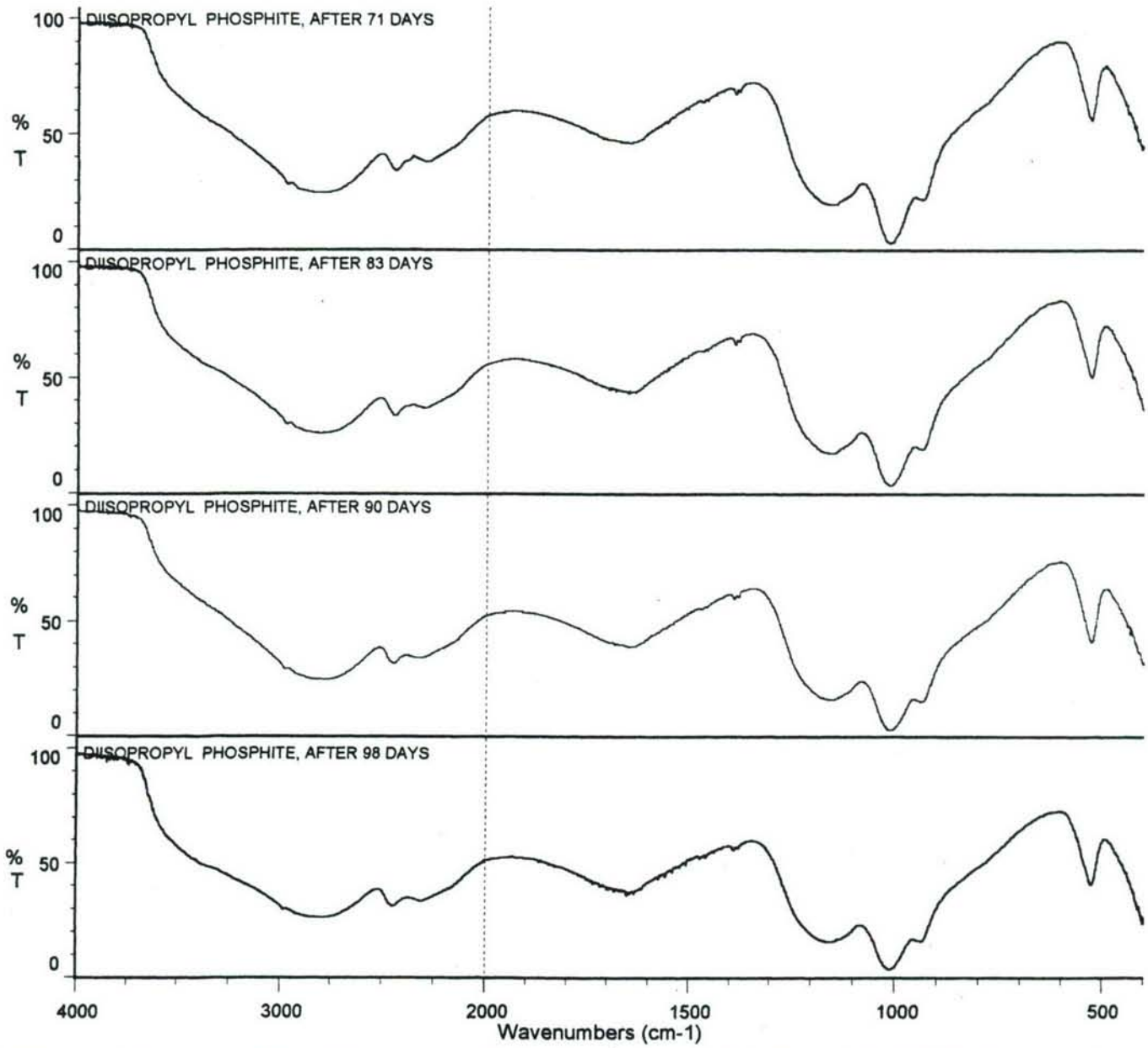


Figure 186B DIISOPROPYL HYDROGENPHOSPHONATE (DIISOPROPYL PHOSPHITE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.5.8.4 Dibutyl Hydrogenphosphonate (Dibutyl Phosphite) $H\text{-}P{=}O(O\text{-}C_4H_9)_2$

The infrared spectrum of dibutyl hydrogenphosphonate (dibutyl phosphite) as a liquid film and as a vapor is given in ***Figure 187***. The band assignments of the liquid phase are as follows: 3453 cm^{-1} vvw (H_2O), 2961 cm^{-1} ms (ν_{as} CH_3), 2936 cm^{-1} m (ν_{as} CH_2), ca 2910 cm^{-1} sh (ν_{sy} CH_3), 2875 cm^{-1} m (ν_{sy} CH_2), 2425 cm^{-1} vw (ν P-H), 1466 cm^{-1} w (δ CH_2 and δ_{as} CH_3), 1383 cm^{-1} (δ_{sy} CH_3), 1261 cm^{-1} ms (ν P=O), 1165 cm^{-1} sh and 1150

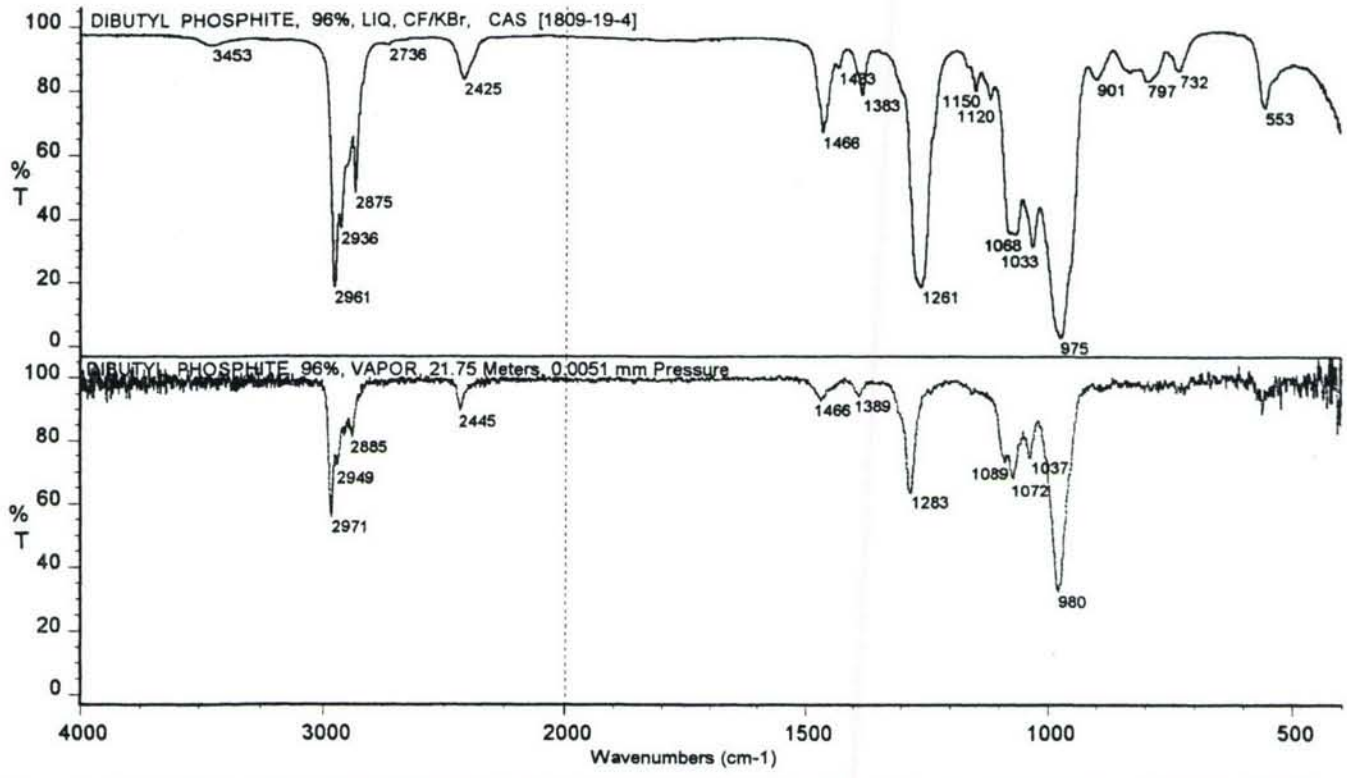


Figure 187 DIBUTYL HYDROGENPHOSPHONATE (DIBUTYL PHOSPHITE), 96%, *UPPER SPECTRUM*--LIQUID, CF/KBr, *LOWER SPECTRUM*--VAPOR PHASE, 21.75 Meters Pathlength, 0.0051 mm Presssure

and 1120 cm^{-1} vw (possible triplet characteristic of P-O-Butyl ?), 1080, 1066, 1033 cm^{-1} m (part of ν P-O-C), 975 cm^{-1} s (partly ν P-O-C and P-H deformation), 797 and 732 cm^{-1} vw (POC), 553 cm^{-1} w (P=O deformation).

The effect of atmospheric moisture on dibutyl hydrogenphosphonate (dibutyl phosphite) is illustrated by the infrared spectra reproduced as ***Figure 188***. After 5-8 days of exposure to atmospheric moisture the spectra of the compound show a gradual formation of POH bands near 2730, 2200 and 1650 cm^{-1}. By the 8th day the P=O stretching band has decreased to 1235 cm^{-1}, the P-H is still present near 2424 cm^{-1} and the CH bands due to the butyl moiety are decreasing in intensity. As time progresses the P-acid bands become more predominant in the spectra and the P=O stretching band decreases in value to near 1200 cm^{-1}. After some 307 days the CH bands due to the butyl group are still evident in the spectrum, possibly due to the presence of butanol. The spectrum after some 40 days of exposure, despite the butyl group CH bands, appears to resemble the phosphinic acid, $H\text{-}P{=}O(OH)_2$, which based on the previous phosphonates would be the expected hydrolysis product.

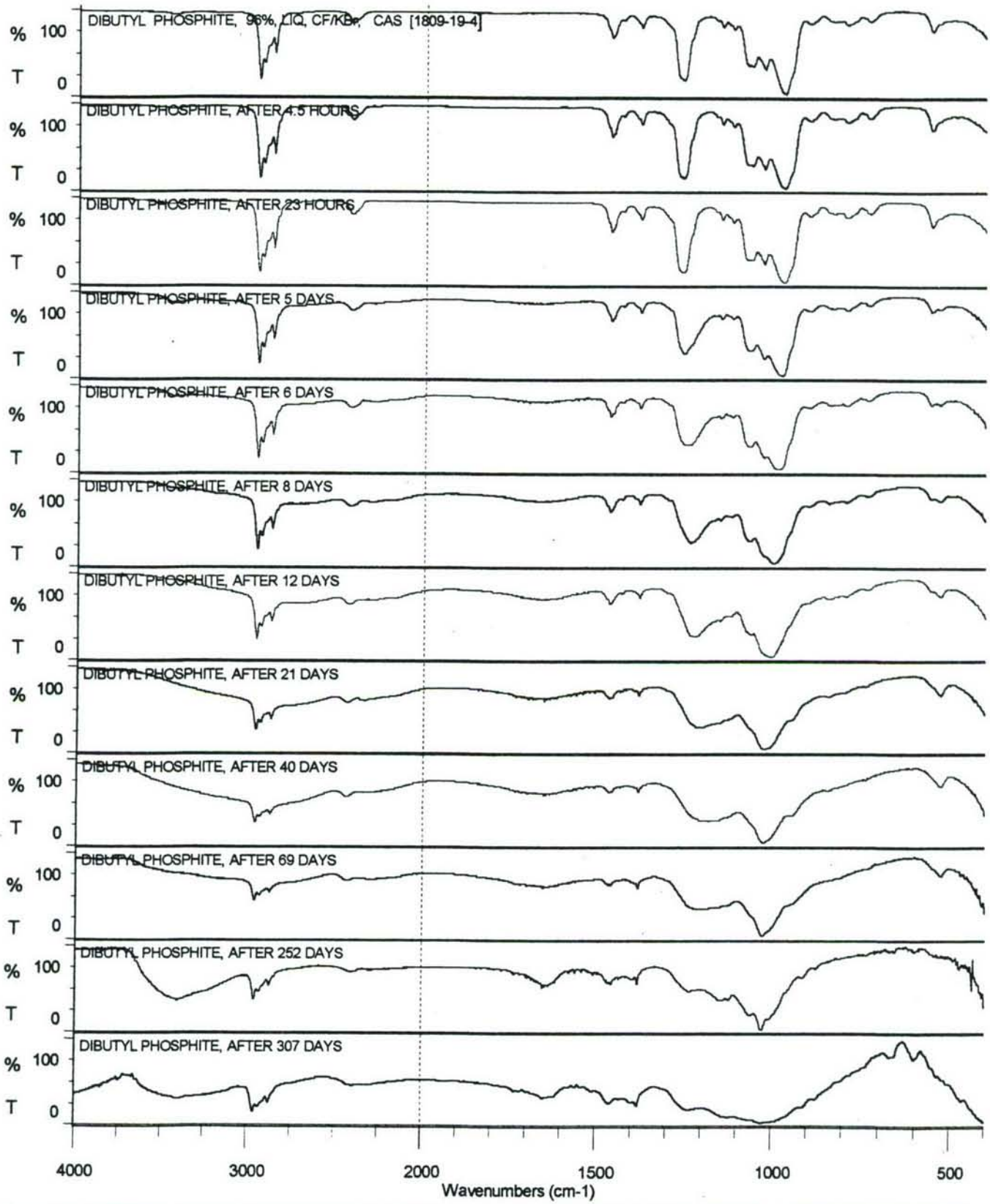


Figure 188 DIBUTYL HYDROGENPHOSPHONATE (DIBUTYL PHOSPHITE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.8.5 Di-*tert*-Butyl Hydrogenphosphonate (Di-*tert*-Butyl Phosphite) $H\text{-}P{=}O[OC(CH_3)_3]_2$

The infrared spectra of a liquid film of di-*tert*-butyl hydrogenphosphonate (di-*tert*-butyl phosphonate, di-*tert*-butyl phosphite) between KBr windows is presented in ***Figure 189***. The band assignments are as follows: 2981 cm^{-1} ms, 2937 cm^{-1} m and 2877 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 2415 cm^{-1} w (ν P-H), 1477 cm^{-1} w (δ_{as} CH_3), 1395 cm^{-1} m and 1371 cm^{-1} ms (δ_{sy} CH_3, *t*-butyl group), 1268 cm^{-1} s (ν P=O), 1175 cm^{-1} m (*t*-butyl skeletal), 1071 and 1041 cm^{-1} m (ν C-C), 970 cm^{-1} s (ν P-O-C and P-H deformation), 920 cm^{-1} m (CH_3 rock, 824 cm^{-1} w (POC), 699 cm^{-1} w (*t*-butyl moiety), 565 cm^{-1} w (P=O deformation ?).

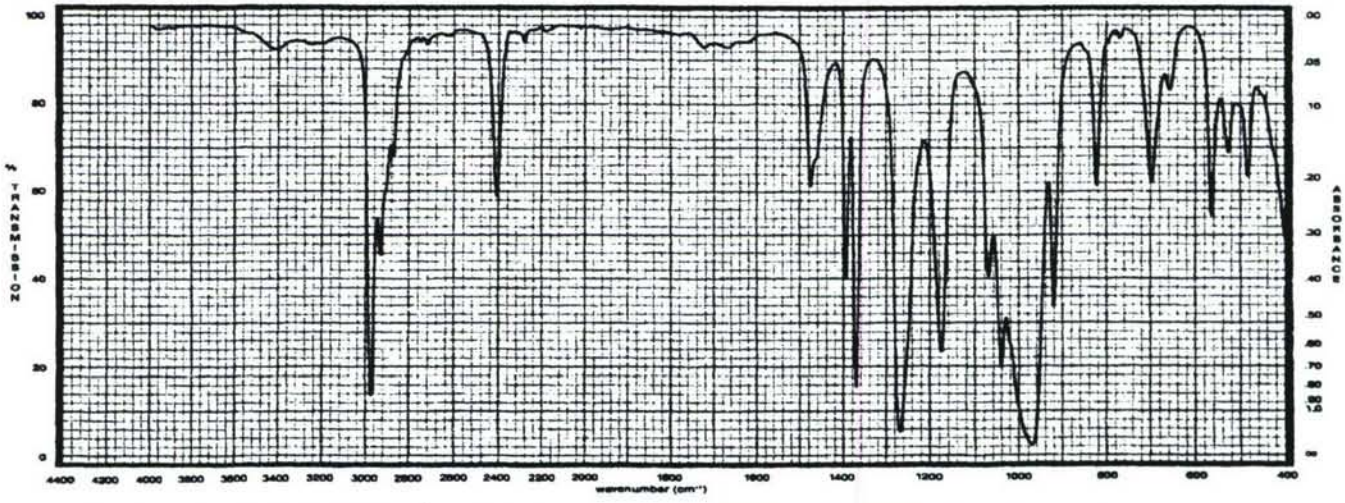


Figure 189 DI-*tert*-BUTYL HYDROGENPHOSPHONATE (DI-*tert*-BUTYL PHOSPHITE), LIQUID, CF/KBr

The effect of moisture on a liquid film of di-*tert*-butyl hydrogenphosphonate is illustrated by the infrared spectra given in ***Figures 190A*** and ***190B***. The infrared spectrum, after 14 days of exposure to atmospheric moisture (***Figure 190A***) , shows a decrease in the intensity of the P-H stretching band at 2413 cm^{-1} and the appearance of broad bands near 2700, 2300 and 1670 cm^{-1} due to the POH moiety. The P=O stretching band has broadened somewhat and fallen slightly to 1260 cm^{-1}. The ν POC/P-H deformation band now occurs near 997 cm^{-1}. After some 53 days of exposure to atmospheric moisture, the spectrum (***Figure 190B***) shows some residual CH bands from the *tert*-butyl group. Mainly, the spectrum is that of a P-acid, which should be phosphonic acid, $H\text{-}P{=}O(OH)_2$.

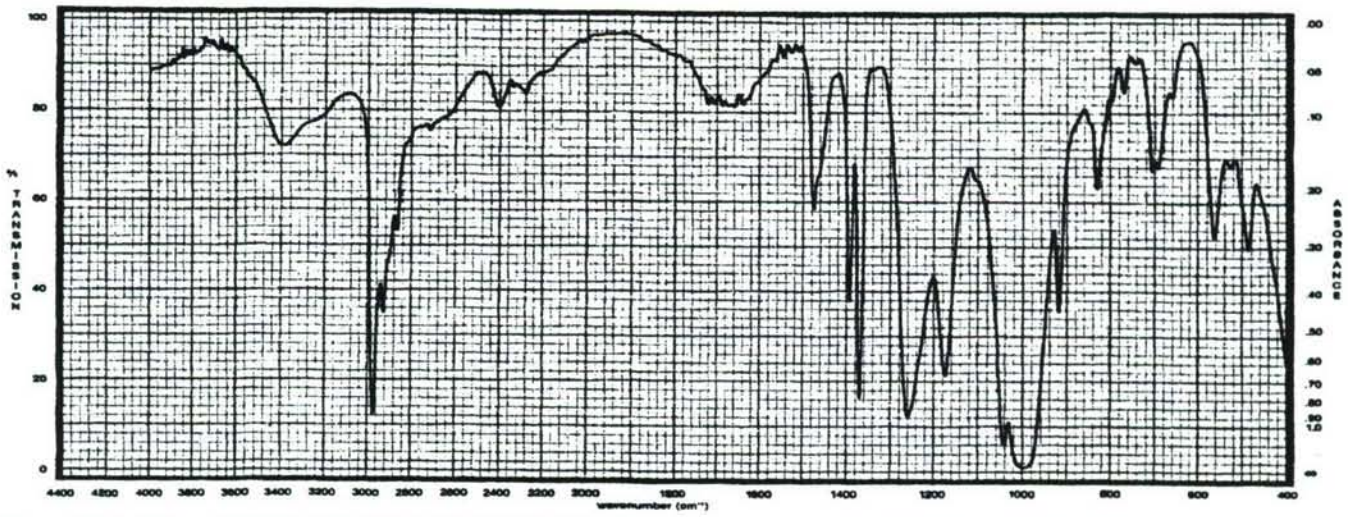


Figure 190A DI-*tert*-BUTYL HYDROGENPHOSPHONATE (DI-*tert*-BUTYL PHOSPHITE), LIQUID, CF/KBr, AFTER 14 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

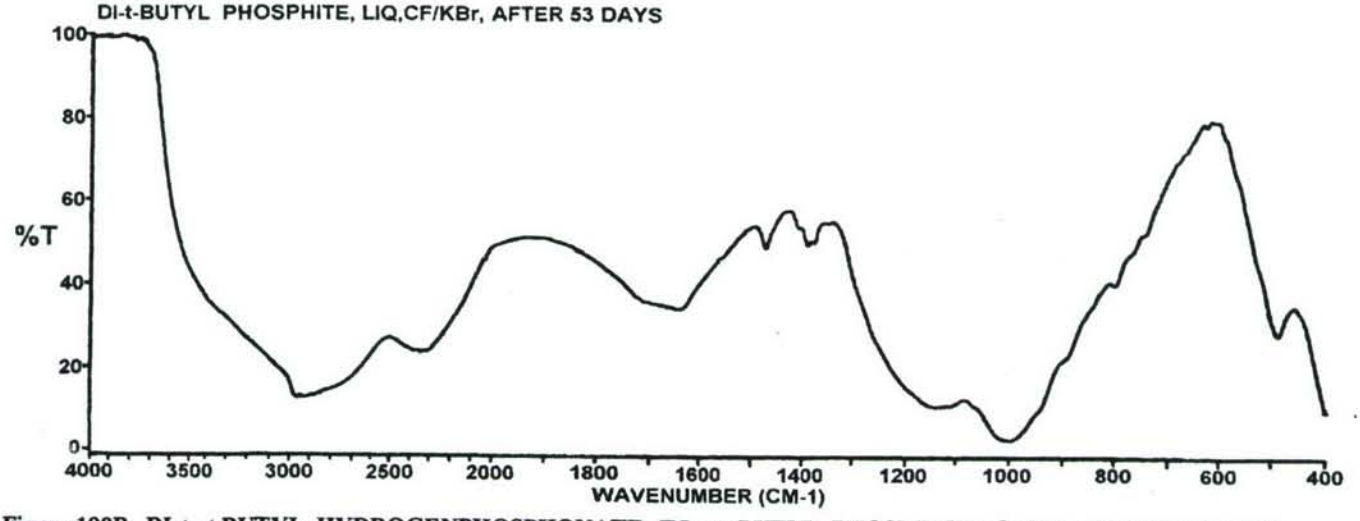


Figure 190B DI-*tert*-BUTYL HYDROGENPHOSPHONATE (DI-*tert*-BUTYL PHOSPHITE), CF/KBr, AFTER 53 DAYS EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.8.6 Bis(2-Ethylhexyl Hydrogenphosphonate [**BIS**, Bis(2-Ethylhexyl Phosphite]

$$H\text{-}P{=}O[\text{-}O\text{-}CH_2\text{-}HC(CH_2CH_3)\text{-}(CH_2)_3\text{-}CH_3]_2$$

The infrared spectrum of bis(2-ethylhexyl hydrogenphosphonate [**BIS**, bis(2-ethylhexyl phosphite] as a liquid film between KBr discs (windows) is reproduced as ***Figure 191***. The band assignments are as follows: 3462 cm^{-1} vw (H_2O), 2960 cm^{-1} s (ν_{as} CH_3), 2931 cm^{-1} s (ν_{as} CH_2), 2873 cm^{-1} ms (ν_{sy} CH_3), 2861 cm^{-1} ms (ν_{sy} CH_2), 2424 cm^{-1} w (ν P-H), 1463 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1381 cm^{-1} w (δ_{sy} CH_3), 1262 cm^{-1} ms (ν P=O),

1148 and 1113 cm^{-1} vw (CH_3 rock), 1073 cm^{-1} sh and 1041 cm^{-1} ms (ν P-O-C) , 976 cm^{-1} s ((ν P-O-C and P-H deformation), 778 cm^{-1} vw (POC), 728 cm^{-1} vw (CH_2 rock), 542 cm^{-1} w (P=O deformation),

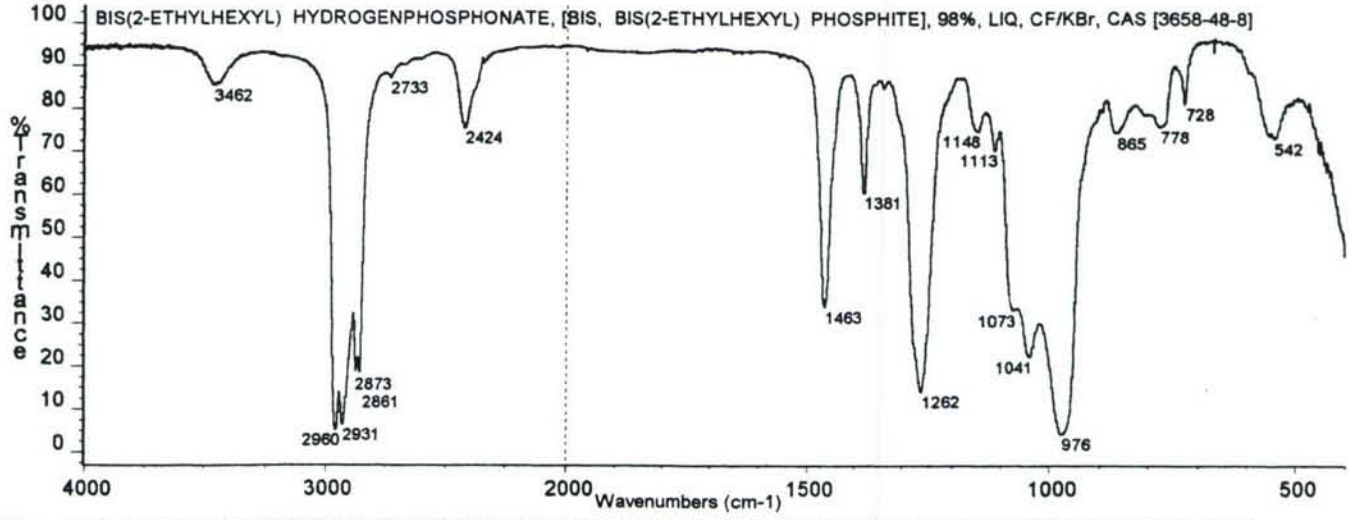


Figure 191 BIS(2-ETHYLHEXYL) HYDROGENPHOSPHONATE, [BIS, BIS(2-ETHYLHEXYL) PHOSPHITE], 98%, LIQUID, CF/KBr

The effect of atmospheric moisture on **BIS** is illustrated by the spectra presented in ***Figures 192A-C.***

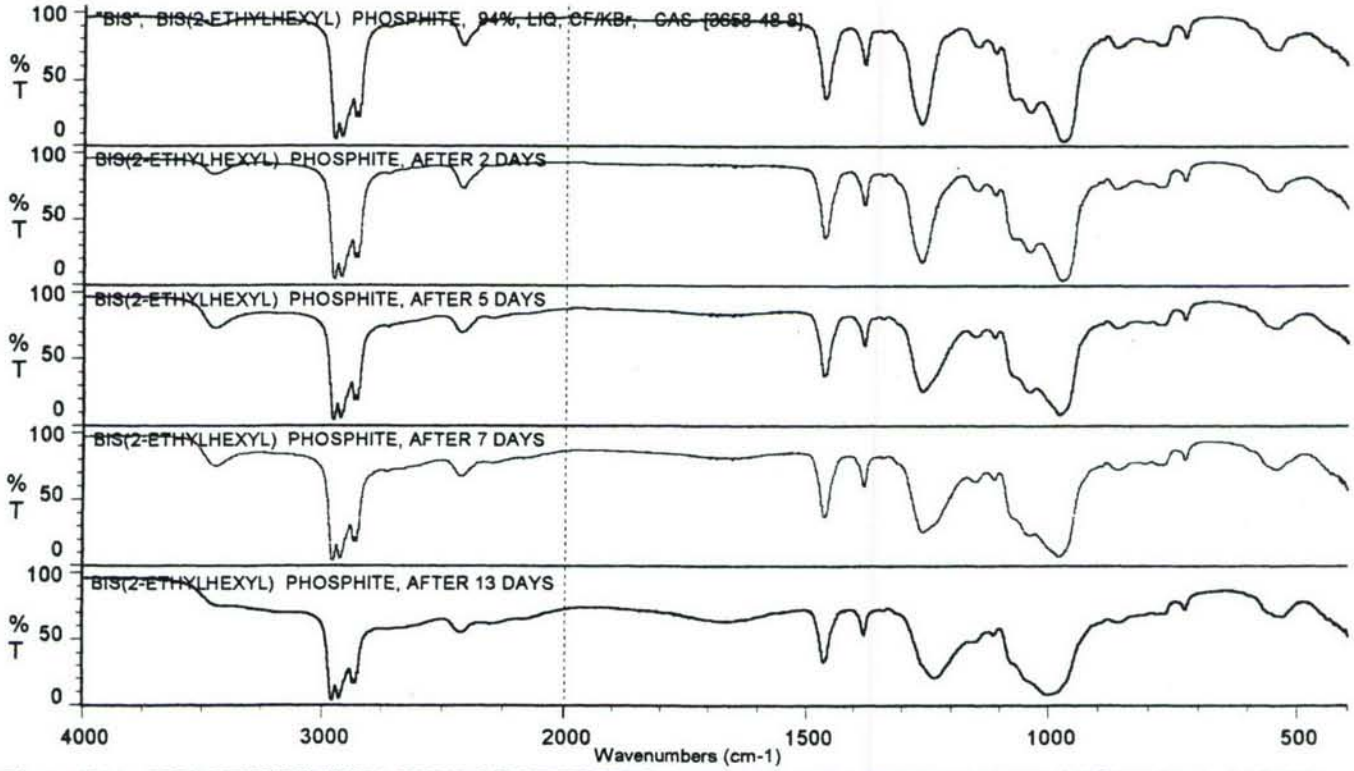


Figure 192A BIS(2-ETHYLHEXYL) HYDROGENPHOSPHONATE [BIS, BIS(2-ETHYLHEXYL) PHOSPHITE], LIQUID, CF/KBr AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

The infrared spectrum after 5 days of exposure (***Figure 192A***) shows the formation of bands near 2750, 2300 and 1660 cm^{-1}. These bands increase in intensity as time progresses and the P=O stretching band broadens and decreases in value to 1229 cm^{-1} by the 19th day (***Figure 192B***) of exposure to atmospheric moisture. The compound 2-ethylhexyl hydrogen phosphonate, H-P=O(OH)[O-CH2-CH(C_2H_5)-(CH_2)$_3$-CH_3], (2-ethylhexyl phosphonic acid) has probably formed from the hydrolysis of the original compound. As the time of exposure to atmospheric moisture increases the bands indicatve of the 2-ethylhexyl moiety continue to decrease in strength. By the 90th day of exposure (***Figure 192C***) the bands from the 2-ethyhexyl moiety are quite weak. The spectrum is mainly that of phosphonic acid, H-P=O($OH)_2$. The last spectrum is that taken after 223 days of exposure to atmospheric moisture and shows large amounts of water (3400, 1630 and near 600 cm^{-1}) plus some bands due to the phosphonic acid (2449, 1143 cm^{-1}).

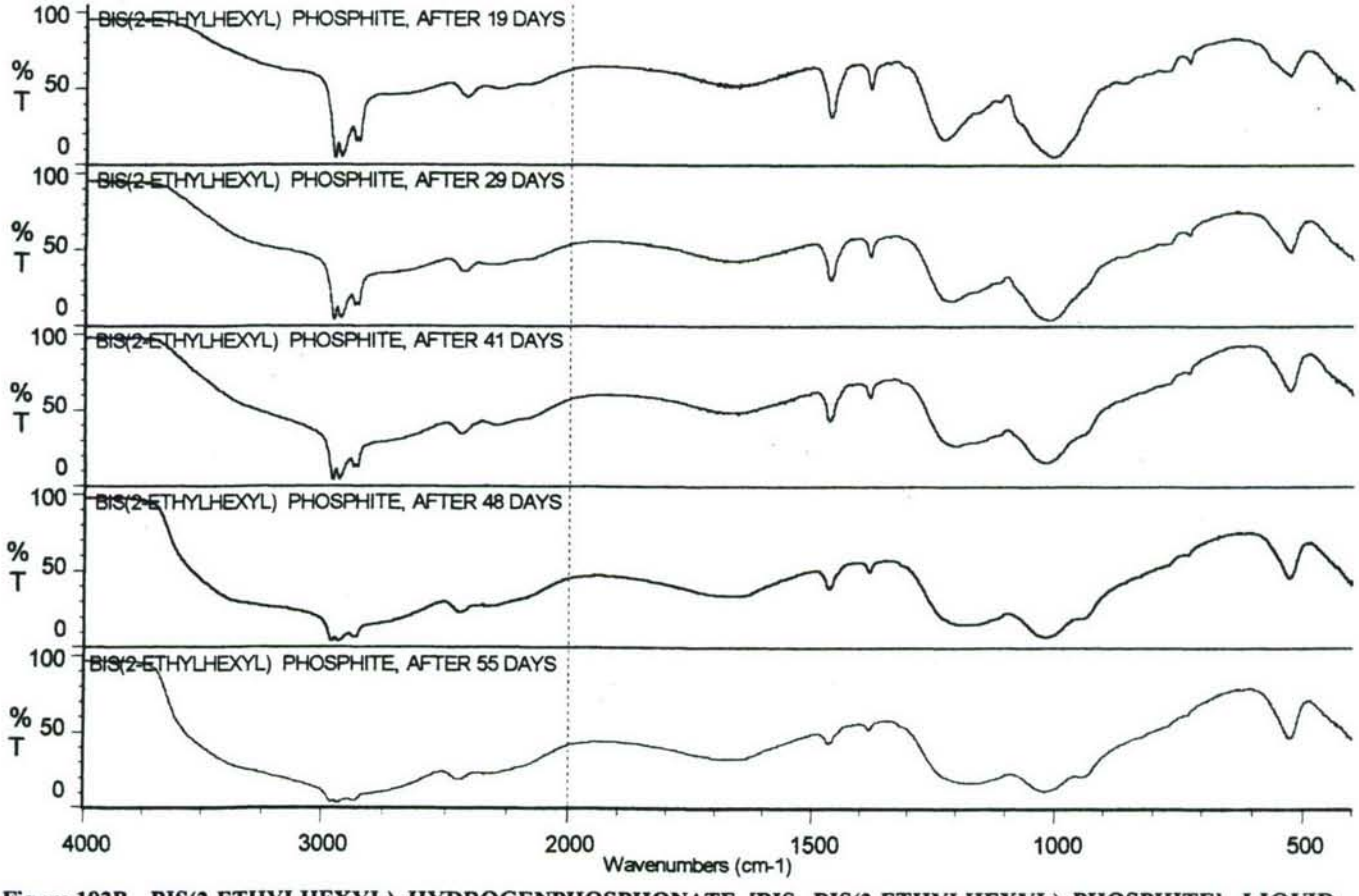


Figure 192B BIS(2-ETHYLHEXYL) HYDROGENPHOSPHONATE [BIS, BIS(2-ETHYLHEXYL) PHOSPHITE], LIQUID, CF/KBr AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

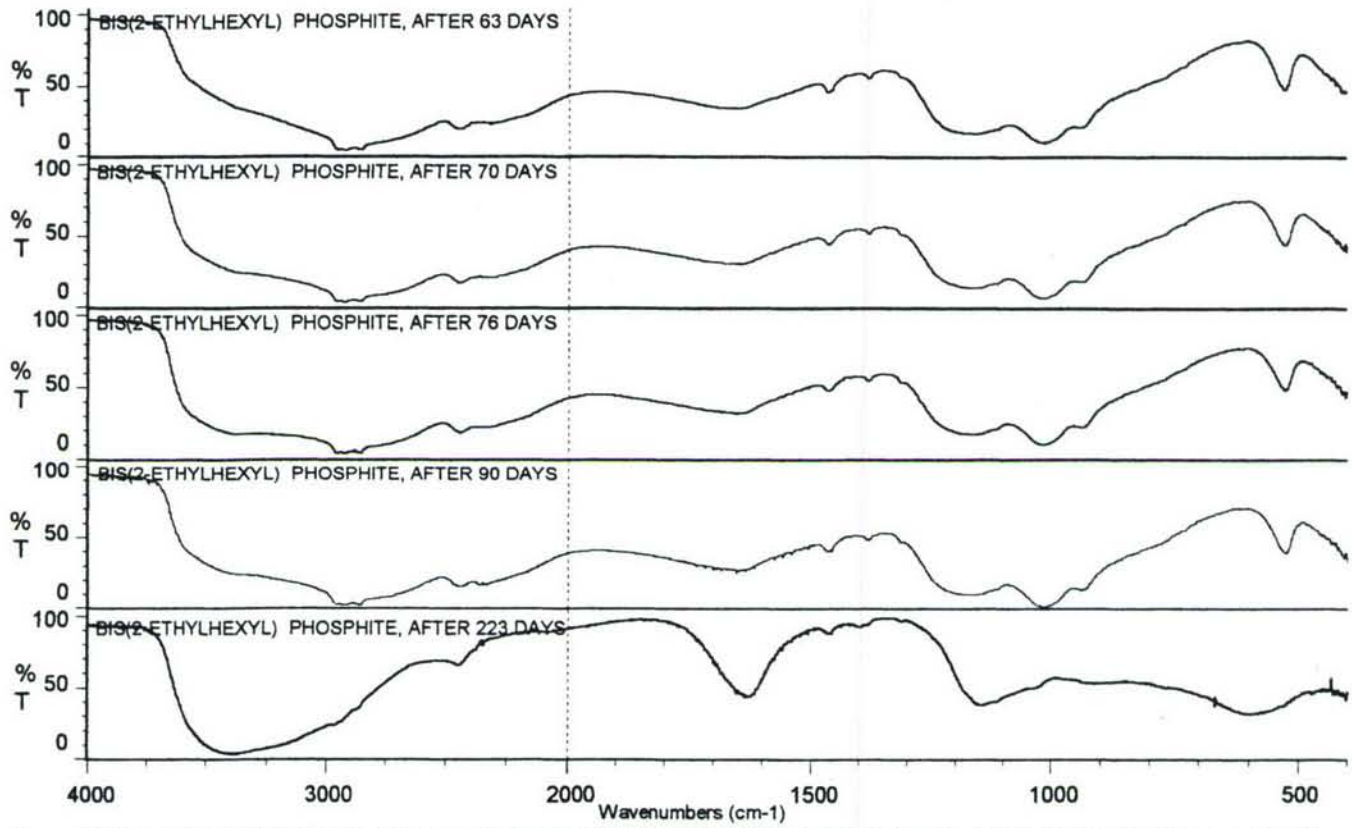


Figure 192C BIS(2-ETHYLHEXYL) HYDROGENPHOSPHONATE [BIS, BIS(2-ETHYLHEXYL) PHOSPHITE], LIQUID, CF/KBr AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.5.8.7 Dilauryl Hydrogenphosphonate (Dilauryl Phosphite) $H\text{-}P{=}O[O\text{-}(CH_2)_{11}\text{-}CH_3]_2$

The infrared spectrum of dilauryl hydrogenphosphonate (dilauryl phosphite) as a liquid film between KBr discs (windows) is presented as ***Figure 193***. The band assignments are as follows: 3455 cm^{-1} vw (H_2O), 2955 cm^{-1} sh (ν_{as} CH_3), 2925 cm^{-1} s (ν_{as} CH_2), ca 2870 cm^{-1} sh (ν_{sy} CH_3), 2854 cm^{-1} ms (ν_{sy} CH_2), 2428 cm^{-1} vw (ν P=O), 1467 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1378 cm^{-1} vw (δ_{sy} CH_3), 1262 cm^{-1} ms (ν P=O), 1083 and 1053 cm^{-1} m (ν P-O-C), 975 cm^{-1} ms (P-H deformation, ν P-O-C ?), 804 cm^{-1} vvw (POC), 721 cm^{-1} w (CH_2 rock), 554 cm^{-1} w (P=O deformation).

The effect of atmospheric moisture on dilauryl hydrogenphosphonate is illustrated by the infrared spectra presented in ***Figure 194***. After two days of exposure to atmospheric moisture, the infrared spectrum shows new bands near 2700, 2300 and 1650 cm^{-1} due to the formation of POH. The P=O stretching band is decreasing to 1243 cm^{-1}. As time progresses to longer exposure times the POH bands grow in intensity and the

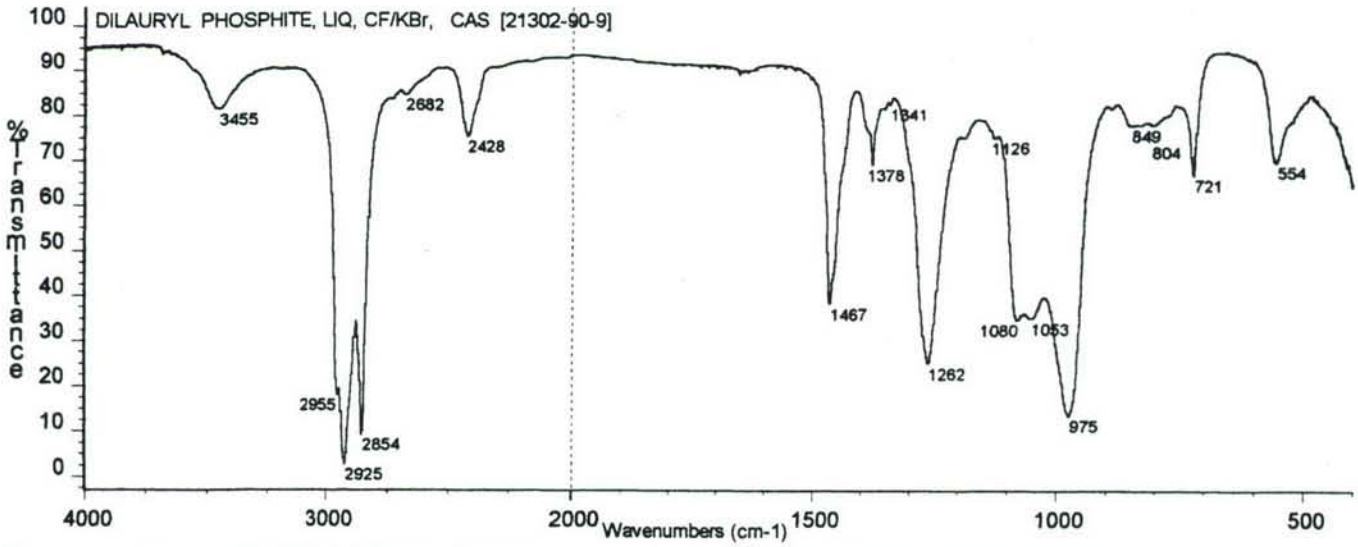


Figure 193 DILAURYL HYDROGENPHOSPHONATE (DILAURYL PHOSPHITE), LIQUID, CF/KBr

P=O band decreasess in value to near 1200 cm^{-1} by the 21st day. The ν POC and PH deformation bands have merged into a single broad band near 1020 cm^{-1}. The C-H bands from the lauryl moiety have decreased in intensity as the compound hydrolyses. The spectrum by day 70 may be due in part to the presence of lauryl alcohol (1-dodecanol) and lauryl hydrogen phosphonate, H-P=O(OH) [O-$(CH_2)_{11}$-CH_3], and perhaps some phosphonic acid, H-P=O$(OH)_2$.

3.5.8.8 Diallyl Hydrogenphosphonate (Diallyl Phosphite) H-P=O(O-CH_2-CH=$CH_2)_2$

The infrared spectrum of a liquid film of diallyl hydrogenphosphonate (diallyl phosphite) between CsI discs (windows) is given in ***Figure 195***. The band assignments are as follows: 3446 cm^{-1} (H_2O), 3087 cm^{-1} vw (ν_{as} =CH_2), 3022 cm^{-1} vw (ν =C-H), 2985 cm^{-1} vw (ν_{sy} =CH_2), 2949 cm^{-1} w (ν_{as} CH_2), 2887 cm^{-1} w (ν_{sy} CH_2), 2434 cm^{-1} w (ν P-H), 1879 cm^{-1} vvw (2 x =CH_2 wag, near 930 cm^{-1} ?), 1650 cm^{-1} w (ν C=C), 1460 cm^{-1} w (δ OCH_2), 1426 cm^{-1} m (δ =CH_2), 1262 cm^{-1} ms (ν P=O), 1065 cm^{-1} sh and 1035 cm^{-1} ms (ν P-O-C), 979 cm^{-1} s [P-H deformation, *trans* =C-H in phase wag and =CH_2 wag (ca 930 cm^{-1} sh ?)] , 857 and 804 cm^{-1} w (POC), 630 cm^{-1} vw (*cis* =C-H in phase wag ?), 545 cm^{-1} w (P=O deformation).

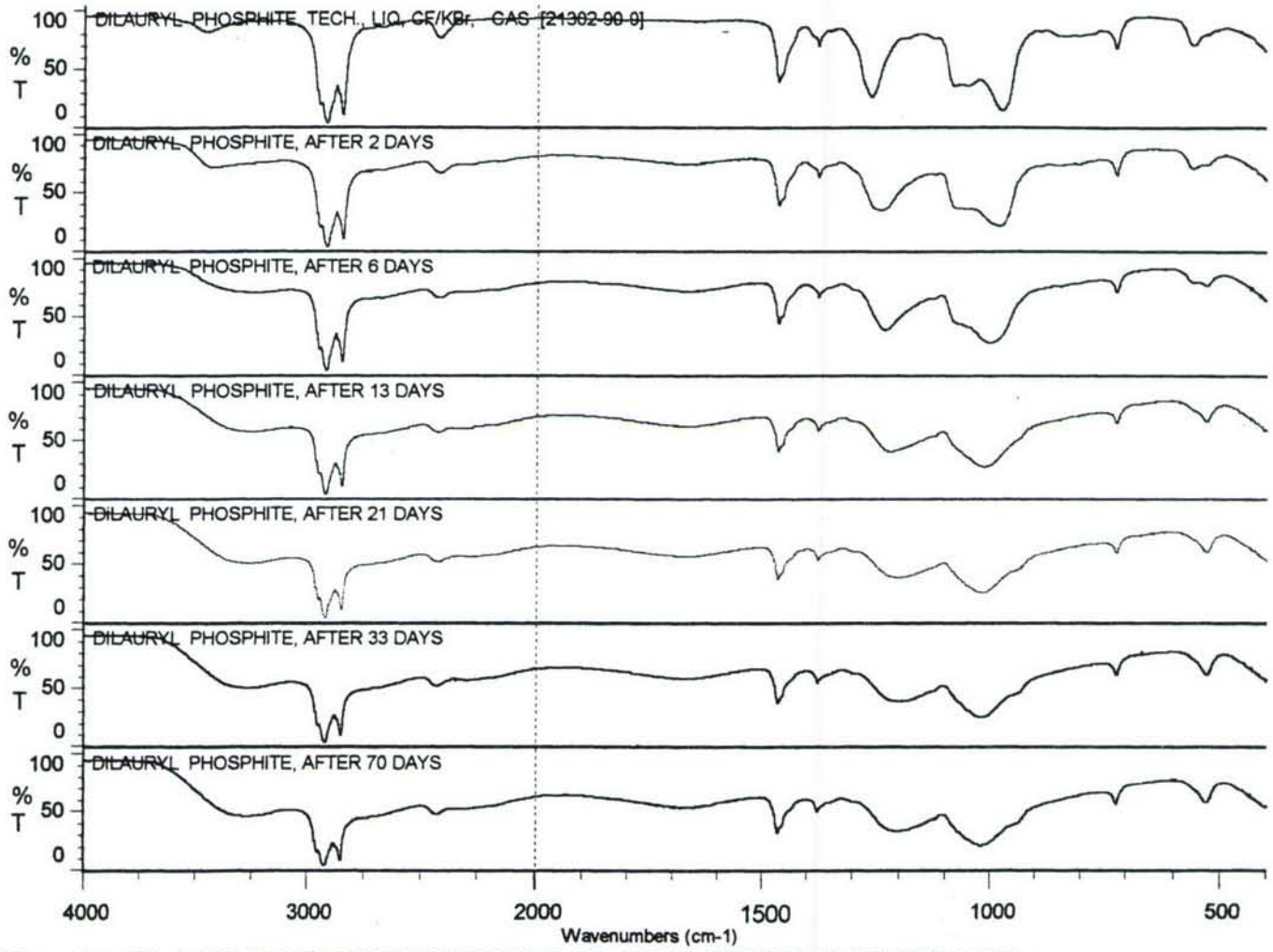


Figure 194 DILAURYL HYDROGENPHOSPHONATE (DILAURYL PHOSPHITE), LIQUID, CF/KBr

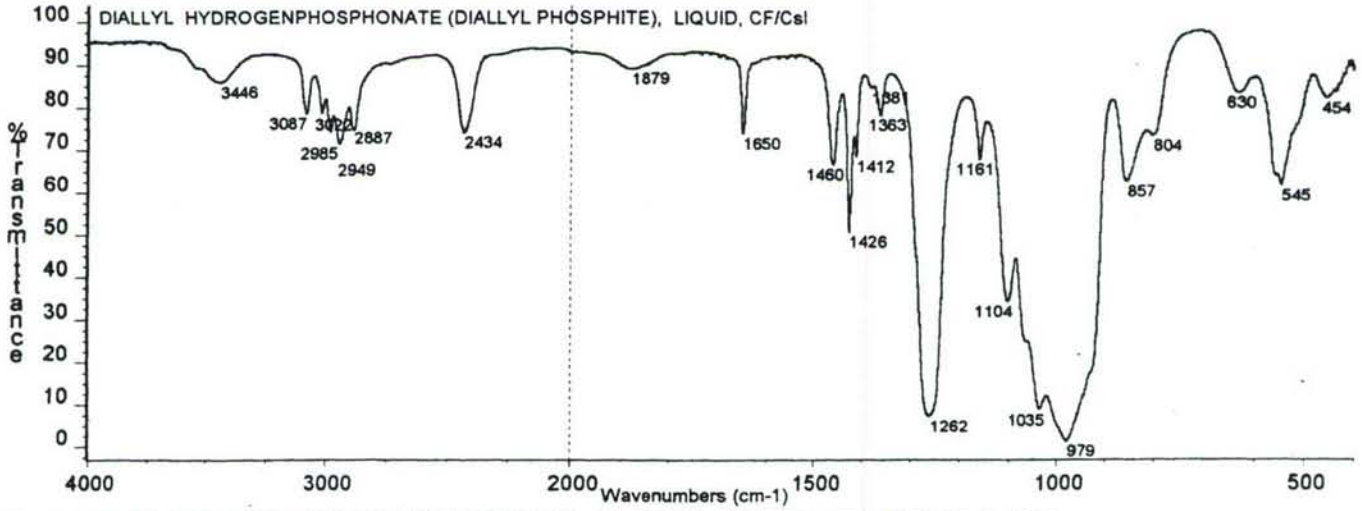


Figure 195 DIALLYL HYDROGENPHOSPHONATE (DIALLYL PHOSPHITE), LIQUID, CF/CsI

3.5.8.9 Diphenyl Hydrogenphosphonate (Diphenyl Phosphite) $H\text{-}P{=}O(O\text{-}C_6H_5)_2$

The infrared spectrum of diphenyl hydrogenphosphonate (diphenyl phosphite) as a liquid film between KBr windows is presented as ***Figure 196***. The sample as determined contained 10-15% phenol. The band assignments for diphenyl hydrogenphosphonate are as follow: 3324 cm^{-1} m (ν OH from phenol), 3066 and 3042 cm^{-1} w (ν C-H aryl), 2447 cm^{-1} w (ν P-H), 1943, 1865, 1784 and 1725 cm^{-1} vw-w (summation bands mono-substituted benzene ring), 1592 cm^{-1} ms, 1490 cm^{-1} s and 1456 cm^{-1} m (aromatic ring), 1280 cm^{-1} ms (ν P=O), 1193 cm^{-1} s (ν C-O), 1164, 1071, 1025 and 1010 cm^{-1} w-m (β C-H mono-substituted aromatic ring), 946 cm^{-1} s (ν P-O), 763 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 689 cm^{-1} ms (δ mono-substituted aromatic ring), 616 cm^{-1} w (mono-substituted aromatic ring ?), 499 cm^{-1} m (P=O deformation ?).

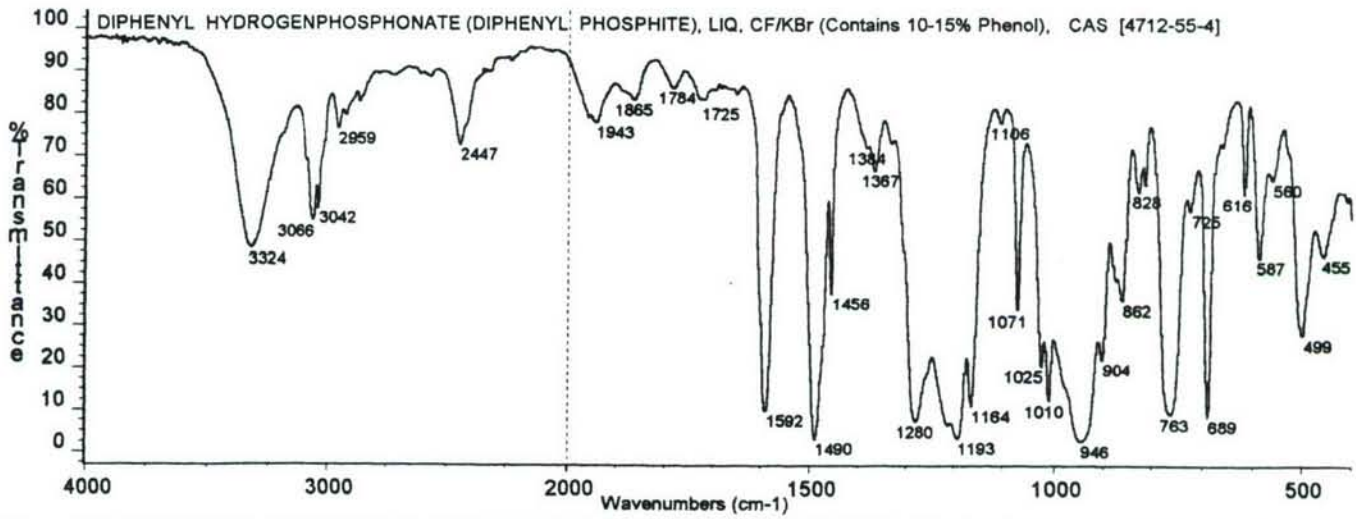


Figure 196 DIPHENYL HYDROGENPHOSPHONATE (DIPHENYL PHOSPHITE), CONTAINS 10-15% PHENOL, LIQUID, CF/KBr

The effect of atmospheric moisture on the thin liquid film of diphenyl hydrogenphosphonate is illustrated by the infrared spectra in ***Figure 197***. After 1 day of exposure to atmospheric moisture, the spectrum of the compound shows an increase in the intensity of the OH band at 3332 cm^{-1}. This is due to the hydrolysis of the original compound to produce phenol, C_6H_5-OH. The P=O stretch has decreased to 1259 cm^{-1} and the P-H stretching band has increased to 2460 cm^{-1}. As time progresses through 1.5 days to 5 days of exposure to atmospheric moisture the band near 3000 cm^{-1} becomes very broad due to the formation of OH (phenol) and POH

from the hydrolyis of the compound. Broad POH bands also occur near 2300 and 1650 cm^{-1}. By the 5th day of exposure to atmospheric moisture the P=O stretch has fallen in value to about 1180 cm^{-1}. The following compounds are being formed, H-P=O(OH)(O-C_6H_5) and H-P=O$(OH)_2$, along with phenol, C_6H_5OH.

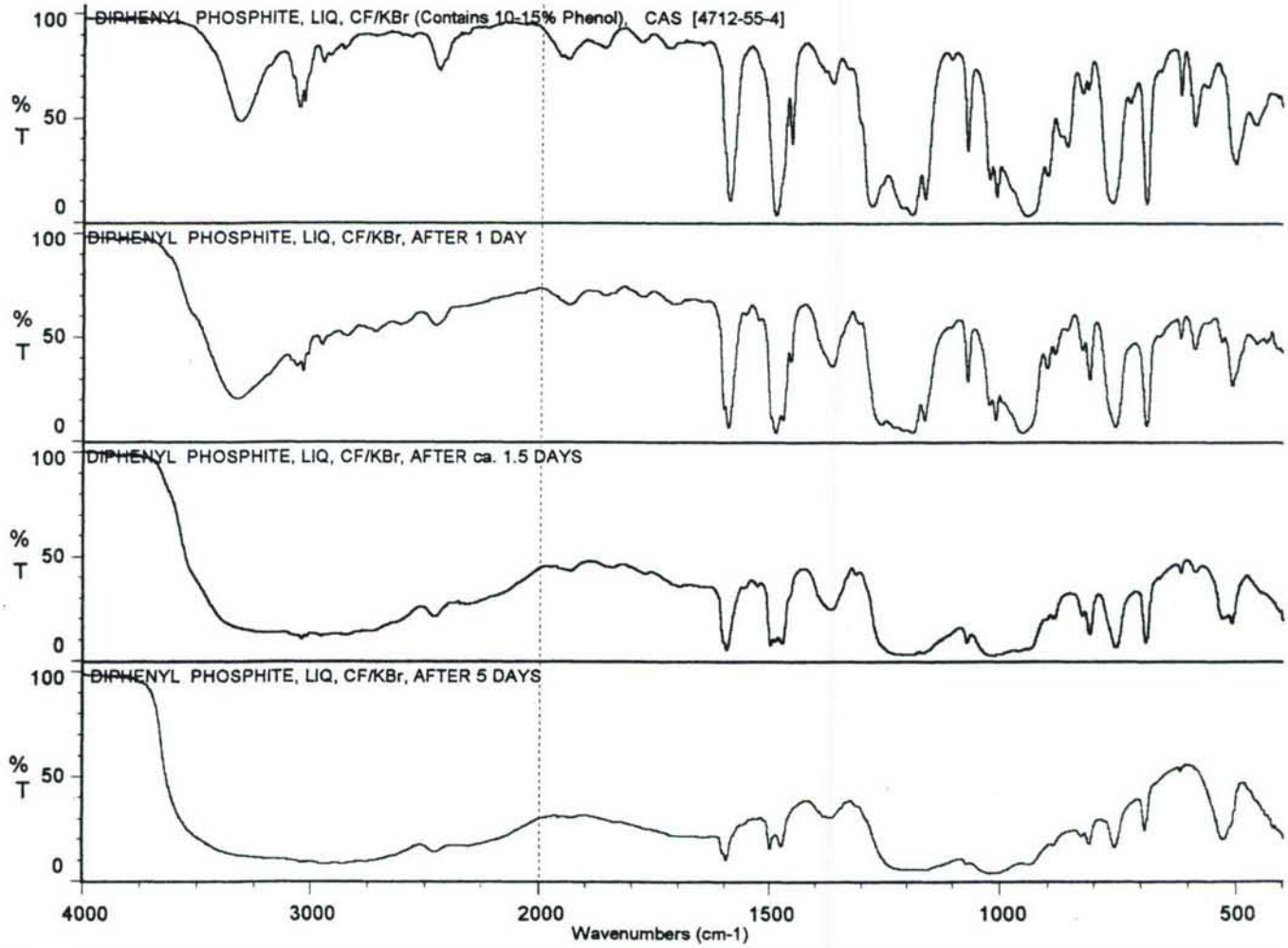


Figure 197 DIPHENYL HYDROGENPHOSPHONATE (DIPHENYL PHOSPHITE), CONTAINS 10-15% PHENOL, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.8.10 Dibenzyl Hydrogenphosphonate (Dibenzyl Phosphite) H-P=O(O-CH_2-C_6H_5)$_2$

The infrared spectrum of dibenzyl hydrogenphosphonate (dibenzyl phosphite) as a liquid film between CsI windows is reproduced as ***Figure 198***. The band assignments are as follows: 3443 cm^{-1} vw (H_2O), 3090 cm^{-1} vvw, 3064 cm^{-1} vw and 3033 cm^{-1} vw (ν C-H aryl), 2955 cm^{-1} vw (ν_{as} CH_2), 2893 cm^{-1} vw (ν_{sy} CH_2), 2436 cm^{-1} vw (ν P-H), 1587 cm^{-1} vvw, 1497 cm^{-1} w and 1456 cm^{-1} m (aromatic ring), 1380 cm^{-1} vw (ω OCH_2),

1259 cm^{-1} ms (ν P=O), 1214 cm^{-1} w (benzyl moiety ?), 1158, 1082, 1024 and 1004 cm^{-1} vvw (β C-H mono-substituted aromatic ring), 1035 cm^{-1} sh (ν P-O-C ?), 960 cm^{-1} s (P-H deformation, ν P-O-C ?), 822 and 801 cm^{-1} vw (POC), 736 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 697 cm^{-1} ms (δ mono-substituted aromatic ring).

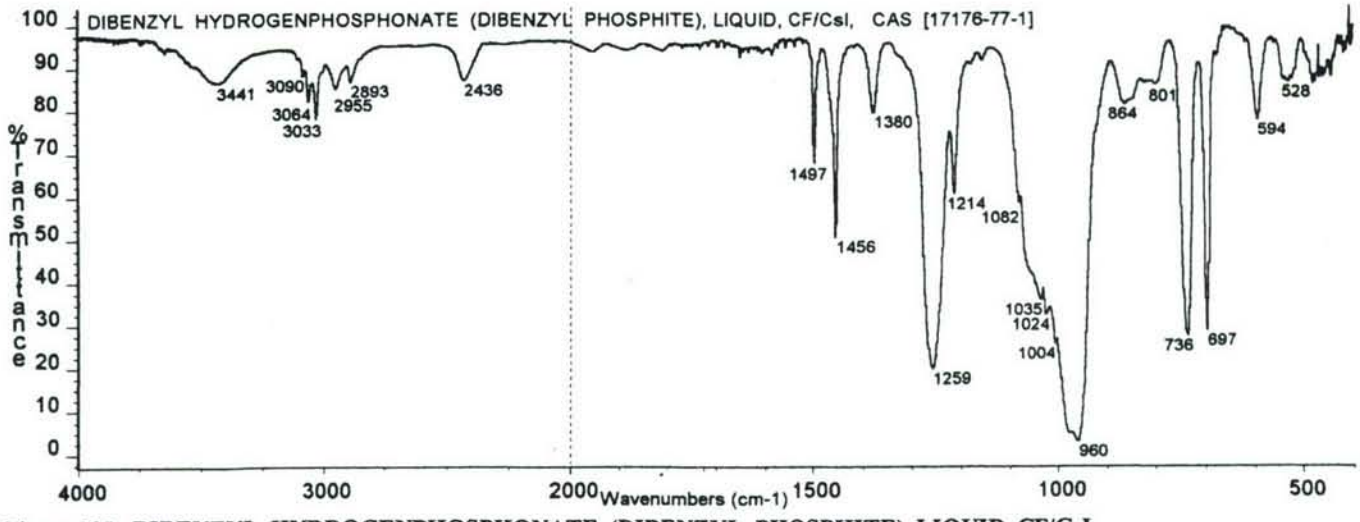


Figure 198 DIBENZYL HYDROGENPHOSPHONATE (DIBENZYL PHOSPHITE), LIQUID, CF/CsI

3.5.8.11 Dimethyl Methylphosphonate $CH_3\text{-}P{=}O(OCH_3)_2$

The infrared spectrum for dimethyl methylphosphonate (**DMMP**) as a liquid film and as a vapor is given in ***Figure 199***. Dimethyl methylphosphonate is a G-Agent precursor. The band assignments for the liquid film are as follows: 2994 cm^{-1} vw (ν_{as} CH_3), 2956 cm^{-1} w (ν_{as} CH_3-O), 2926 cm^{-1} vvw (ν_{sy} CH_3), 2852 cm^{-1} vw (ν_{sy} CH_3-O), 1844 cm^{-1} vvw (1058 + 788 + 1846; 1032 + 819 = 1851), 1465 cm^{-1} vw (δ OCH_3), 1420 cm^{-1} vvw (δ_{as} P-CH_3), 1313 cm^{-1} m (δ_{sy} P-CH_3), 1245 cm^{-1} ms (ν P=O), 1185 cm^{-1} w (CH_3 rock of P-OCH_3, characteristic), 1058 cm^{-1} ms and 1032 cm^{-1} s (ν P-O-C), 914 m cm^{-1} m (P-CH_3 rock), 819 and 788 cm^{-1} m (POC), 713 cm^{-1} w (ν P-C), 501 cm^{-1} w (P=O deformation).

The infrared spectrum for the vapor phase spectrum shows the ν P=O at 1276 cm^{-1}, an increase of 31 cm^{-1} over the liquid phase spectrum. The POC stretch for the vapor phase also occurs at higher frequencies than that for the liquid phase (1076, 1056 and 1050 cm^{-1} compared to 1058 and 1032 cm^{-1}). The δ_{sy} P-CH_3 occurs at the same value (1313 cm^{-1}) for both the liquid and vapor phases.

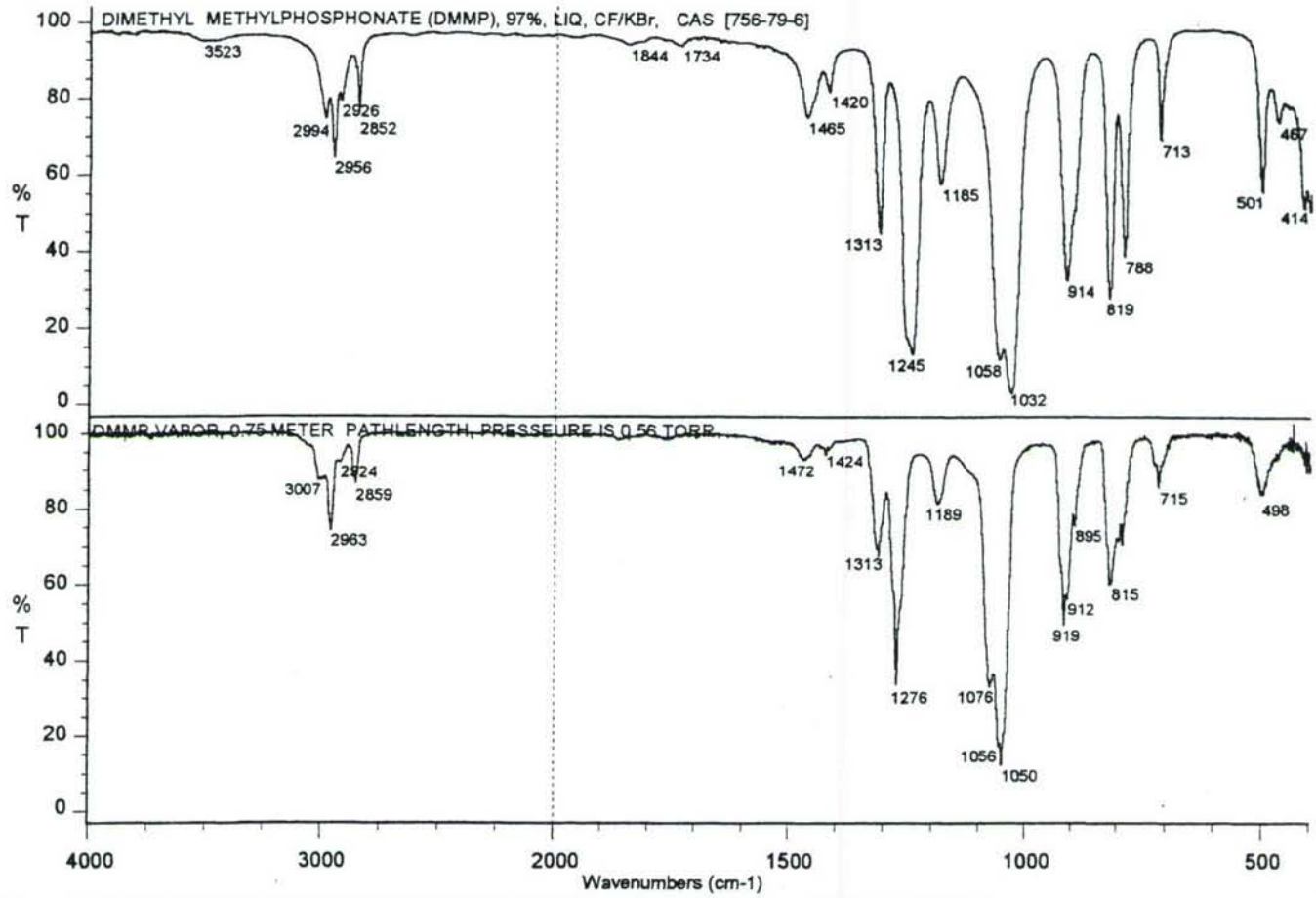


Figure 199 DIMETHYL METHYLPHOSPHONATE 97%, *UPPER SPECTRUM*--LIQUID, CF/KBr, *LOWER SPECTRUM*--VAPOUR PHASE, 0.75 METER GAS CELL, PRESSURE=0.56 TORR

The effect of atmospheric moisture on a liquid film of dimethyl methylphosphonate (**DMMP**) between KBr windows has been discussed before[ff] and will be presented here in a somewhat shortened version by ***Figure 200***. By the 7th day of exposure the sample has picked up water (3470 and 1650 cm^{-1}) and the P=O stretch has decreased from 1246 to 1238 cm^{-1}. Very broad bands are visible near 2800 and 237O cm^{-1} and indicate the presence of a P-acid (POH bands). These bands increase in intensity with time. By the 14th day the acid POH bands are quite evident in the spectrum at ca 2800, 2370, 1650 and 995 cm^{-1}. The P=O stretching band has decreased to ca 1200 cm^{-1}. The $POCH_3$ moiety is still present as indicated by the bands at 1187 and 1037

[ff] Piffath, R.J., "Infrared Spectroscopic Observations On The Fate Of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part I. G-Agents And Related Compounds", 1999, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423. Approved for Public Release.

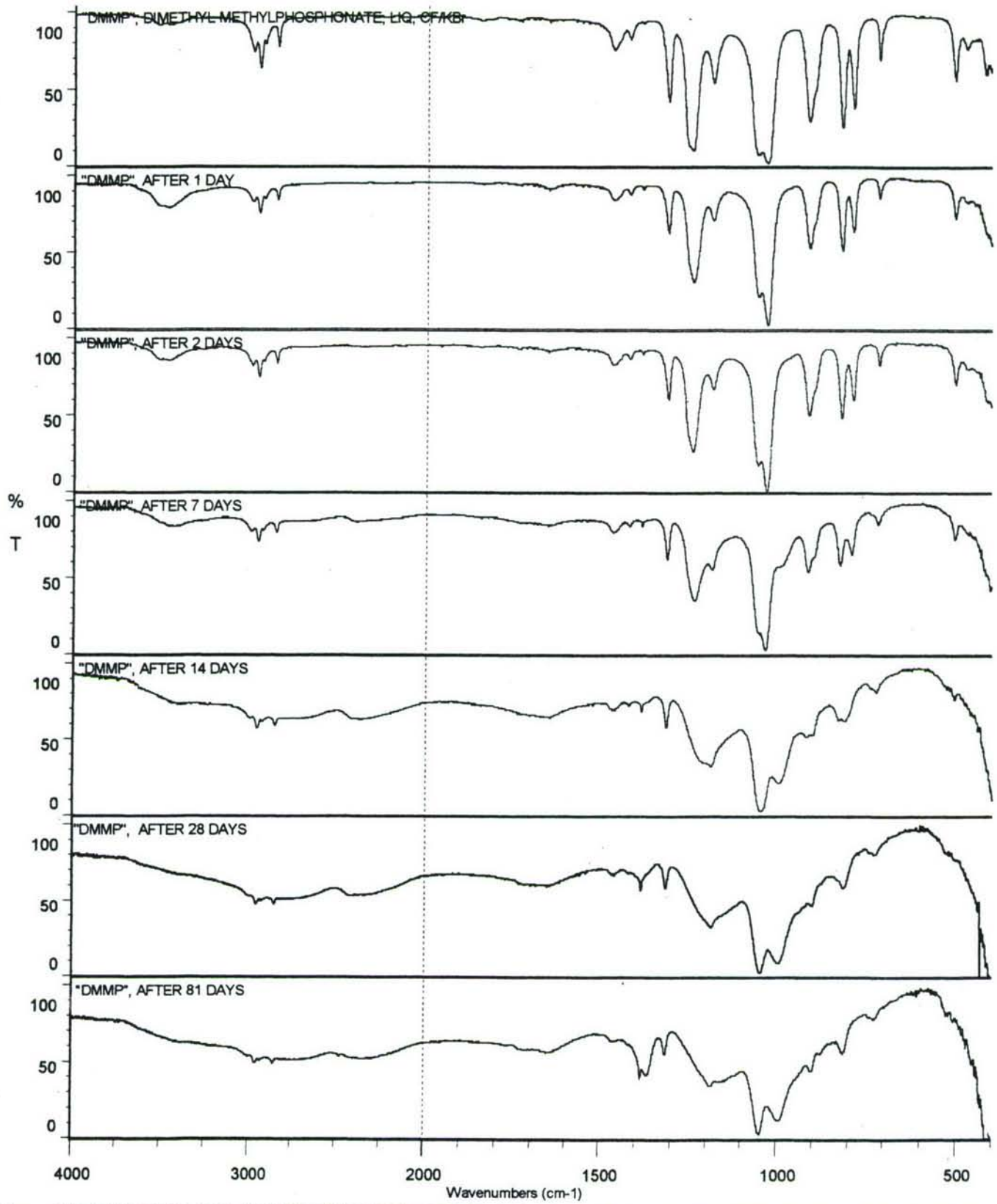


Figure 200 DIMETHYL METHYLPHOSPHONATE (DMMP), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

cm^{-1}. The species now present may be methyl hydrogen methylphosphonate, CH_3-P=O(OH)(OCH_3). As time progresses through the 28th to 81st days the hydrolysis may be continuing as indicated by the slight broadening of the band below 1186 cm^{-1}. Another compound such as methylphosphonic acid, CH_3-P=O$(OH)_2$, may be forming.

3.5.8.12 Ethyl Methyl Methylphosphonate (**EMMP**) CH_3-P=O(OCH_3)(OCH_2CH_3)

The infrared spectrum of ethyl methyl methylphosphonate (**EMMP**) as a liquid film between KBr windows is given as ***Figure 201***. The band assignments are as follows: 3530 and 3476 cm^{-1} vvw (H_2O), 2986 cm^{-1} m (ν_{as} CH_3), 2955 cm^{-1} w (ν CH_3O), 2928 cm^{-1} vvw (ν CH_2), 2910 cm^{-1} sh (ν C_2H_5), 2851 cm^{-1} vw (ν OCH_3), 1836 cm^{-1} vvw (1059 + 778 = 1837 cm^{-1}, 1031 + 814 = 1845 cm^{-1}), 1740 cm^{-1} vvw (1245 + 502 = 1747 cm^{-1}), 1457 cm^{-1} sh (δ OCH_2), 1447 cm^{-1} vw (δ_{as} CH_3), 1419 cm^{-1} vw (δ_{as} P-CH_3), 1392 cm^{-1} vw (ω OCH_2), 1368 cm^{-1} vvw (δ_{sy} CH_3), 1313 cm^{-1} m (δ_{sy} P-CH_3), 1245 cm^{-1} ms (ν P=O), 1184 cm^{-1} w (CH_3 rock of $POCH_3$, characteristic), 1165 and 1098 cm^{-1} w (CH_3 rock of POEthyl, characteristic), 1059 cm^{-1} ms and 1031 cm^{-1} s (ν P-O-C, mainly ν C-O),[gg] 965 cm^{-1} m (ν C-C of POEthyl), 907 cm^{-1} ms (P-CH_3 rock), 814 cm^{-1} m and 778 cm^{-1} m (POC, mainly ν P-O),[gg] 714 cm^{-1} w (ν P-C), 502 cm^{-1} m (P=O deformation).

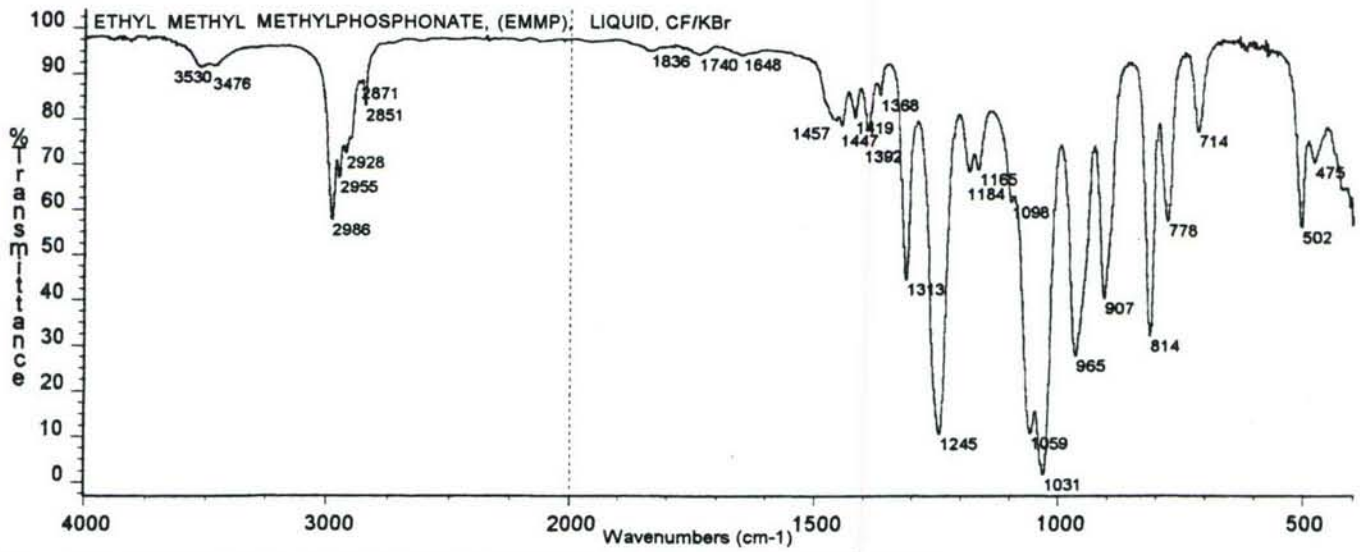


Figure 201 ETHYL METHYL METHYLPHOSPHONATE (EMMP), LIQUID, CF/KBr

[gg] Lin-Vien, D., Colthup, N.B., Fateley, W.G. and Grasselli, J.G., "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules", p 270, Academic Press, Inc., San Diego, CA, 1991.

3.5.8.13 Ethyl Methylphosphonocyanidate CH_3-P=O(C≡N)(OCH_2CH_3)

The infrared spectrum of ethyl methylphosphonocyanidate as a liquid film between KBr windows is presented in ***Figure 202***. The band assignments are as follows: ca 3100 cm^{-1} sh (ν H-C from H-C≡N), 2992 cm^{-1} w (ν_{as} CH_3), 2921 cm^{-1} w (ν_{sy} CH_3), 2201 cm^{-1} m (ν C≡N), 2083 cm^{-1} vvw (ν C≡N from HCN), 1478 cm^{-1} vw (δ OCH_2), 1446 cm^{-1} vw (δ_{as} CH_3), 1407 cm^{-1} sh (δ_{as} P-CH_3), 1396 cm^{-1} w (ω OCH_2), 1371 cm^{-1} vw (δ_{sy} CH_3), 1314 cm^{-1} ms (δ_{sy} P-CH_3), 1262 cm^{-1} s (ν P=O), 1164 and 1099 cm^{-1} w (CH_3 rock of POEthyl, characteristic), 1030 cm^{-1} s (ν P-O-C), 979 cm^{-1} m (ν C-C of POEt), 891 cm^{-1} m (P-CH_3 rock), 799 cm^{-1} m (POC), 749 cm^{-1} w (ν P-C), 576 cm^{-1} m (PC≡N ?), 499 cm^{-1} w (P=O deformation ?).

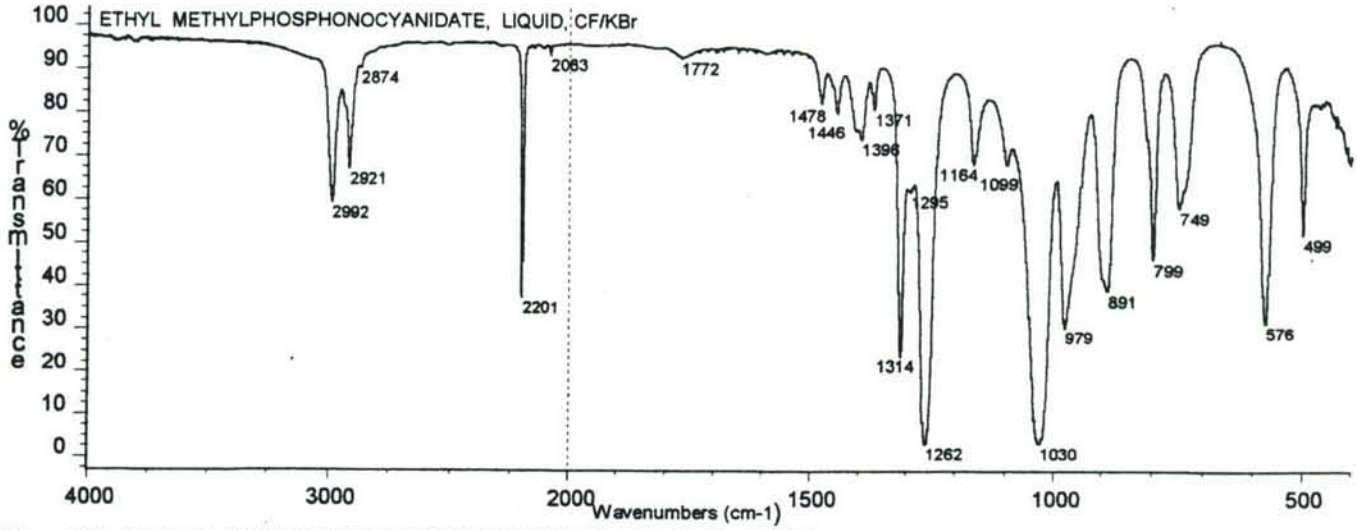


Figure 202 ETHYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/KBr

The effect of atmospheric moisture on a liquid film of ethyl methylphosphonocyanidate is illustrated by the infrared spectra in ***Figures 203A*** and ***203B***. After 4 hours of exposure to atmospheric moisture a slight increase in the amount of HCN is evident by the bands at 3089 and 2083 cm^{-1}. After 3 days of exposure, the C≡N band at 2201 cm^{-1} was absent from the spectrum. Bands occur at 1261 cm^{-1}, 946 and 655 cm^{-1} and are assigned to the P=O stretch and POP of the pyro compound, diethyl dimethypyrophosphonate, $CH_3(OEt)P(=O)$-O-$P=O(OEt)CH_3$. Some POH is present as evidenced by the bands near 2700, 2300 and 1680 cm^{-1}. A small amount of HCN is evident at 2083 cm^{-1}. After 4 days of exposure (***Figure 203B***) , the amount of

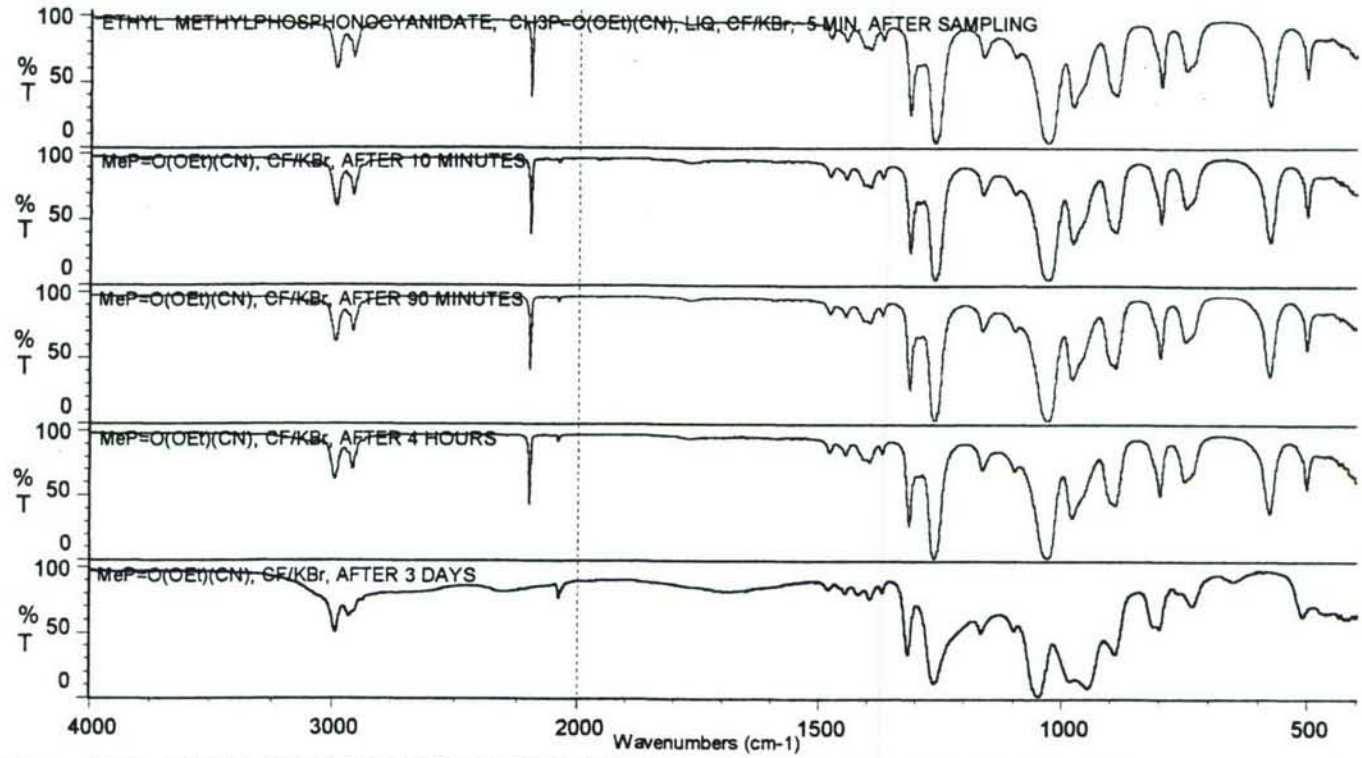


Figure 203A ETHYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

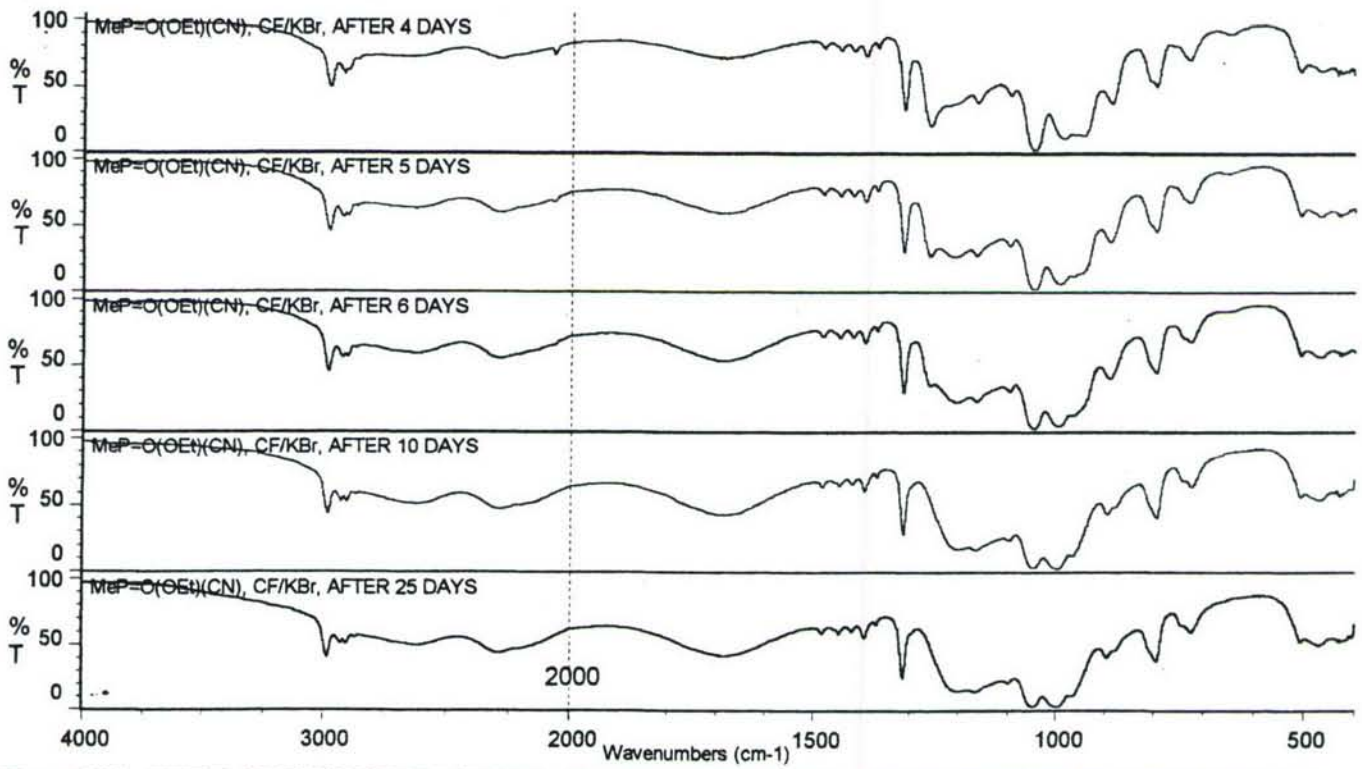


Figure 203B ETHYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

P-acid increased, while the HCN and pyro bands decreased. After 5-6 days, the P-acid moiety has become more predominant and the pyro entity has decreased further. After 10 days of exposure, the spectrum was essentially that of the P-acid, ethyl methylphosphonic acid (**EMPA**), $CH_3P{=}O(OH)(OEt)$. See Figure 143 for an authentic sample of **EMPA**.

3.5.8.14 Diethyl Methylphosphonate (**DEMP, TRO**) $CH_3\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl methylphosphonate (**DEMP, TRO**) as a liquid film and as a vapor is presented in ***Figure 204***. The band assignments for the liquid phase are as follows: 3526 and 3475 cm^{-1} vw (H_2O), 2984 cm^{-1} ms (ν_{as} CH_3), 2931 cm^{-1} m (ν_{as} CH_2), 2907 cm^{-1} m (ν_{sy} CH_3), 2873 cm^{-1} w (ν_{sy} CH_2), 1480 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1420 cm^{-1} vw (δ_{as} P-CH_3), 1392 cm^{-1} m (ω OCH_2), 1368 cm^{-1} w (δ_{sy} CH_3), 1314 cm^{-1} ms (δ_{sy} P-CH_3), 1245 cm^{-1} s (ν P=O), 1164 and 1098 cm^{-1} m (CH_3 rock, characteristic of POEthyl), 1058 and 1031 cm^{-1} s (ν P-O-C), 964 cm^{-1} s (ν C-C of POEthyl), 899 cm^{-1} m (P-CH_3 rock), 804 cm^{-1} ms and 771 cm^{-1} m (POC), 713 cm^{-1} w (ν P-C), 502 cm^{-1} m (P=O deformation).

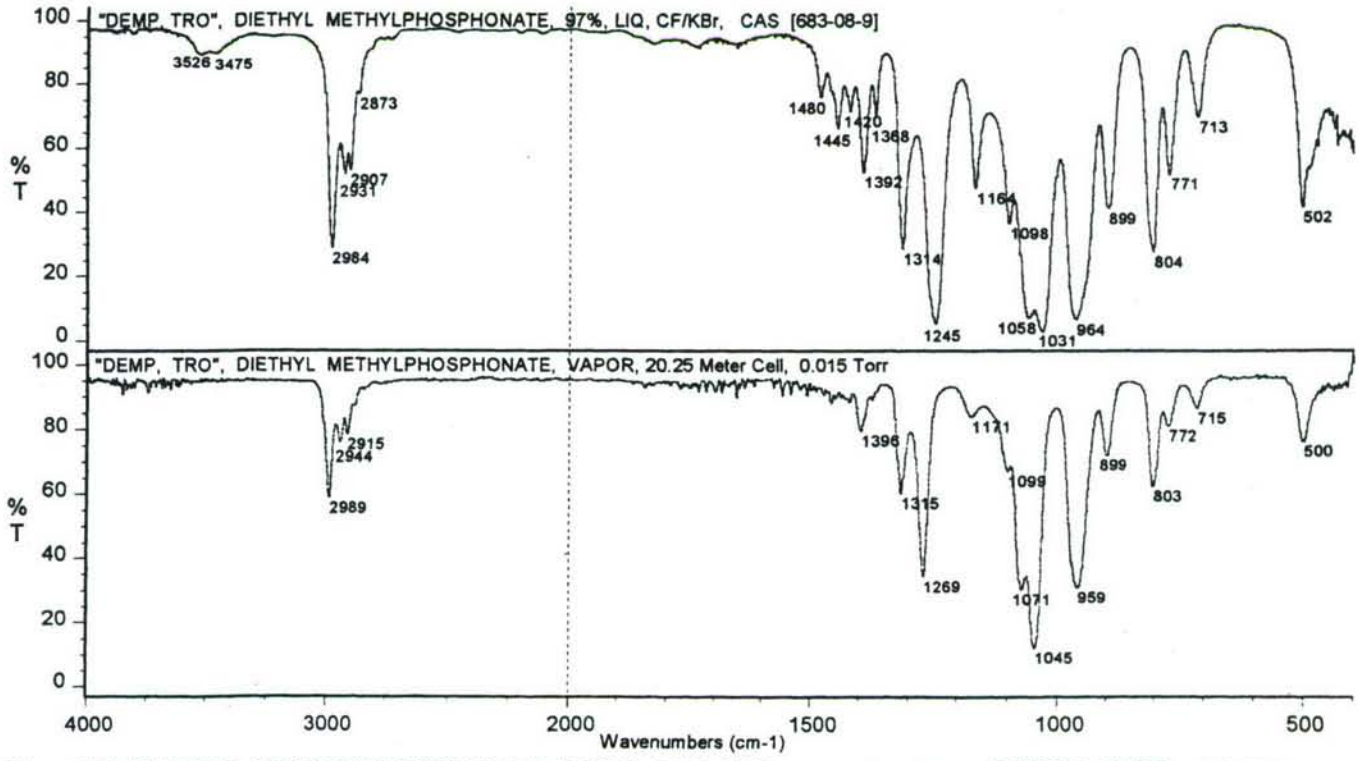


Figure 204 DIETHYL METHYLPHOSPHONATE (DEMP, TRO), 97%, *UPPER SPECTRUM*--LIQUID, CF/KBr, *LOWER SPECTRUM*--VAPOR PHASE, 20.25 Meter PATHLENGTH, 0.015 Torr PRESSURE

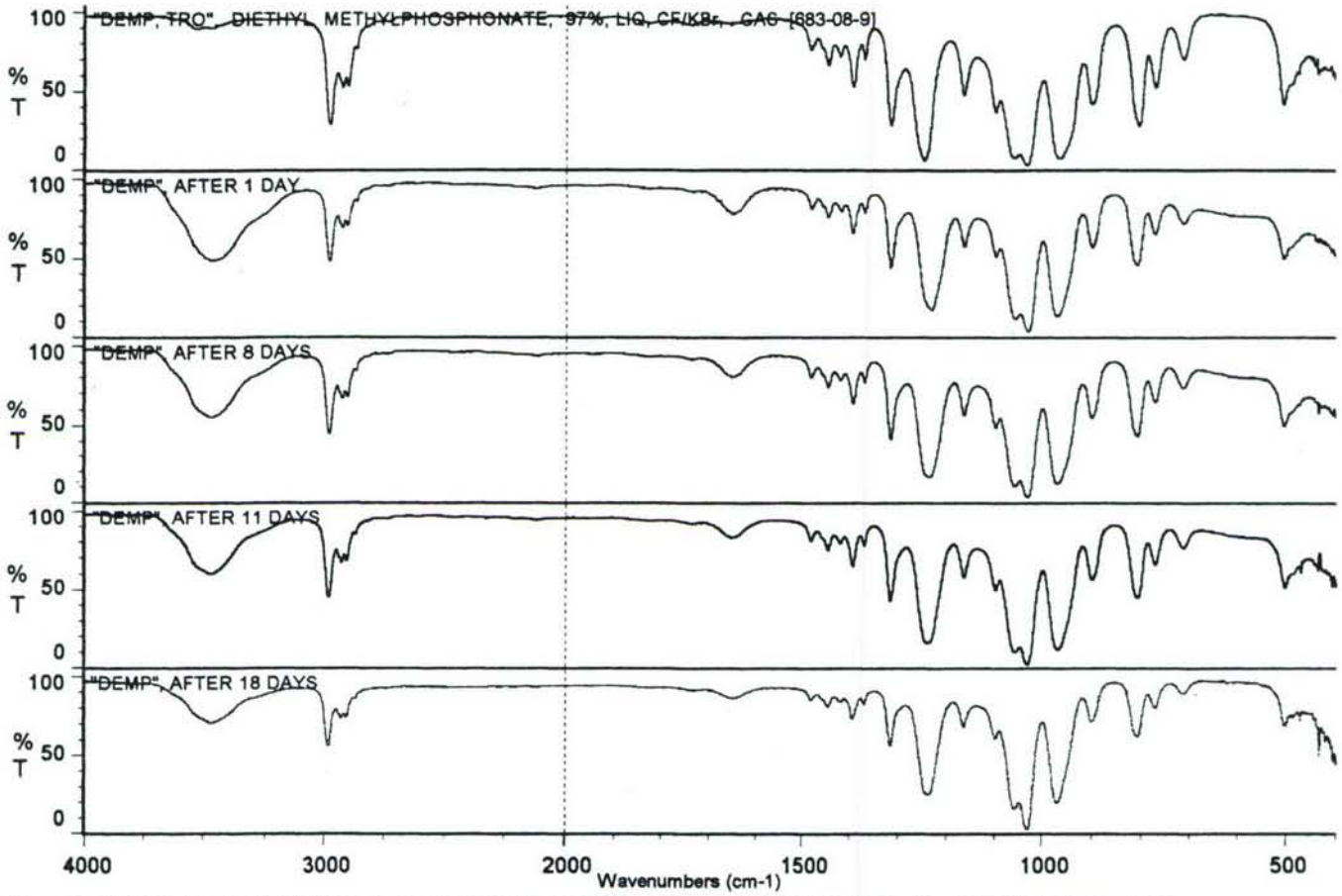


Figure 205 DIETHYL METHYLPHOSPHONATE (DEMP, TRO), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

The effect of moisture on a liquid film of diethyl methylphosphonate (**DEMP**, **TRO**) is shown in ***Figure 205***. Over the 18 days of exposure to atmospheric moisture the film of **DEMP** shows only the effect of water on the position of the P=O stretching vibration. The P=O band varies as follows: day 0 (1245 cm^{-1}), 1 days (1232 cm^{-1}), 8 days (1236 cm^{-1}), 11 days (1241 cm^{-1}), 18 days (1240 cm^{-1}). When the amount of water in the spectrum is the largest, as in day 1, the P=O band occurs at the lowest value, 1232 cm^{-1}.

3.5.8.15 Ethyl 2,2-Dichlorovinyl Methylphosphonate CH_3-P=O(O-CH_2-CH3)(O-HC=CCl_2)

The infrared spectrum of ethyl 2,2,-dichlorovinyl methylphosphonate as as liquid film between KBr windows is presented as ***Figure 206***. The band assignments are as follows: 3487 cm^{-1} vvw (H_2O), 3261 cm^{-1} vvw (ν OH alcohol ?), 3070 cm^{-1} w (ν =C-H), 2989 cm^{-1} w, 2928 cm^{-1} w, 2870 cm^{-1} vvw (ν CH_3 and CH_2), 1643

cm^{-1} w (ν C=C), 1479 cm^{-1} vw (δ OCH_2), 1444 cm^{-1} vw (δ_{as} CH_3), 1416 cm^{-1} vw (δ_{as} P-CH_3), 1394 cm^{-1} vw (ω OCH_2), 1369 cm^{-1} vw (δ_{sy} CH_3), 1316 cm^{-1} m (δ_{sy} P-CH_3), 1256 cm^{-1} ms (ν P=O), 1148 cm^{-1} s (ν PO-C=), 1098 cm^{-1} vw (CH_3 rock of POEt, the higher band near 1165 cm^{-1} in covered over by the 1148 cm^{-1} POC band), 1037 cm^{-1} ms (ν P-O-C), 975 cm^{-1} s (ν C-C of POEt and ν P-OC=C), 903 cm^{-1} m (P-CH_3 rock), 818 cm^{-1} m (ν_{as} CCl_2), 787 cm^{-1} w (POC), 733 cm^{-1} w (ν P-C), 655 cm^{-1} w (ν_{sy} CCl_2 ?), 497 cm^{-1} sh (P=O deformation ?).

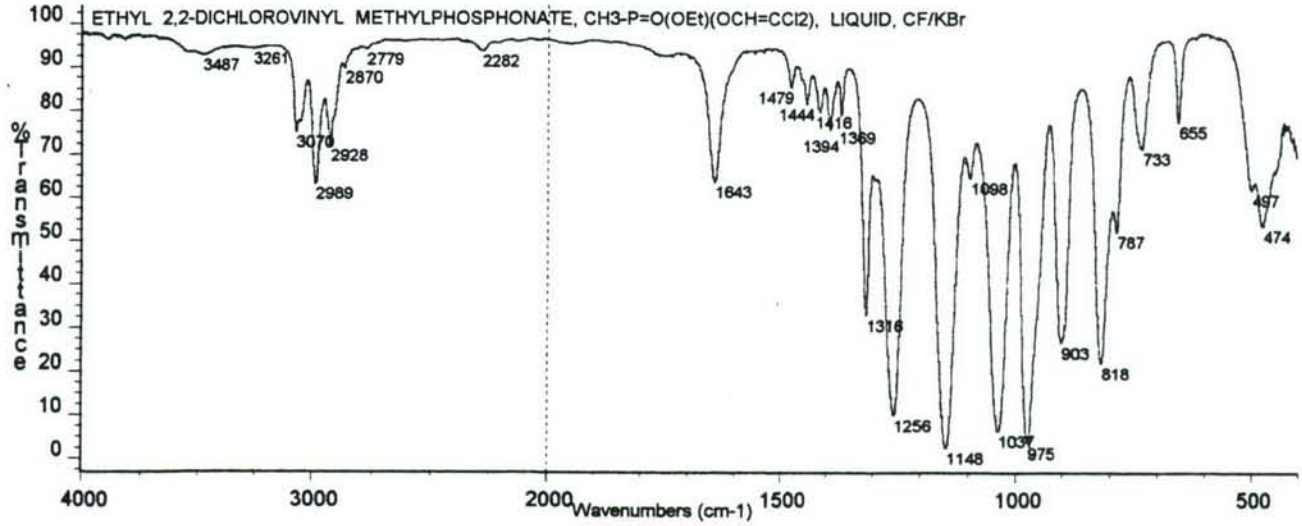


Figure 206 ETHYL 2,2-DICHLOROVINYL METHYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.16 Diisopropyl Methylphosphonate (**DIMP**) CH_3-P=O[O-CH(CH_3)$_2$]$_2$

The infrared spectrum of diisopropyl methylphosphonate (**DIMP**) as a liquid film between CsI windows and as a vapor is presented as ***Figure 207***. The band assignments for the liquid phase spectrum are: 2979 cm^{-1} m (ν_{as} CH_3), 2934 cm^{-1} w (ν -C-H), 2877 cm^{-1} vw (ν_{sy} CH_3), 1468 cm^{-1} w, 1456 cm^{-1} sh (δ_{as} CH_3), 1419 cm^{-1} vw (δ_{as} P-CH_3), 1386 and 1375 cm^{-1} m (δ_{sy} P-CH_3), 1356 cm^{-1} sh (δ -C-H), 1311 cm^{-1} m (δ_{sy} P-CH_3), 1245 cm^{-1} ms (ν P=O), 1178, 1142 and 1110 cm^{-1} w-m (triplet characteristic of POisopropyl), 1012 cm^{-1} ms and 983 cm^{-1} s (ν P-O-C), 917 and 899 cm^{-1} m (P-CH_3 rock and CH_3 rock of isopropyl group), 791 cm^{-1} m and 751 cm^{-1} vw (POC), 719 cm^{-1} w (ν P-C), 504 cm^{-1} m (P=O deformation).

Figure 208 shows the effect of moisture on the infrared spectrum of **DIMP**. By the 9th day of exposure to atmospheric moisture the P=O stretching band has decreased in value from 1245 to 1230 cm^{-1}.

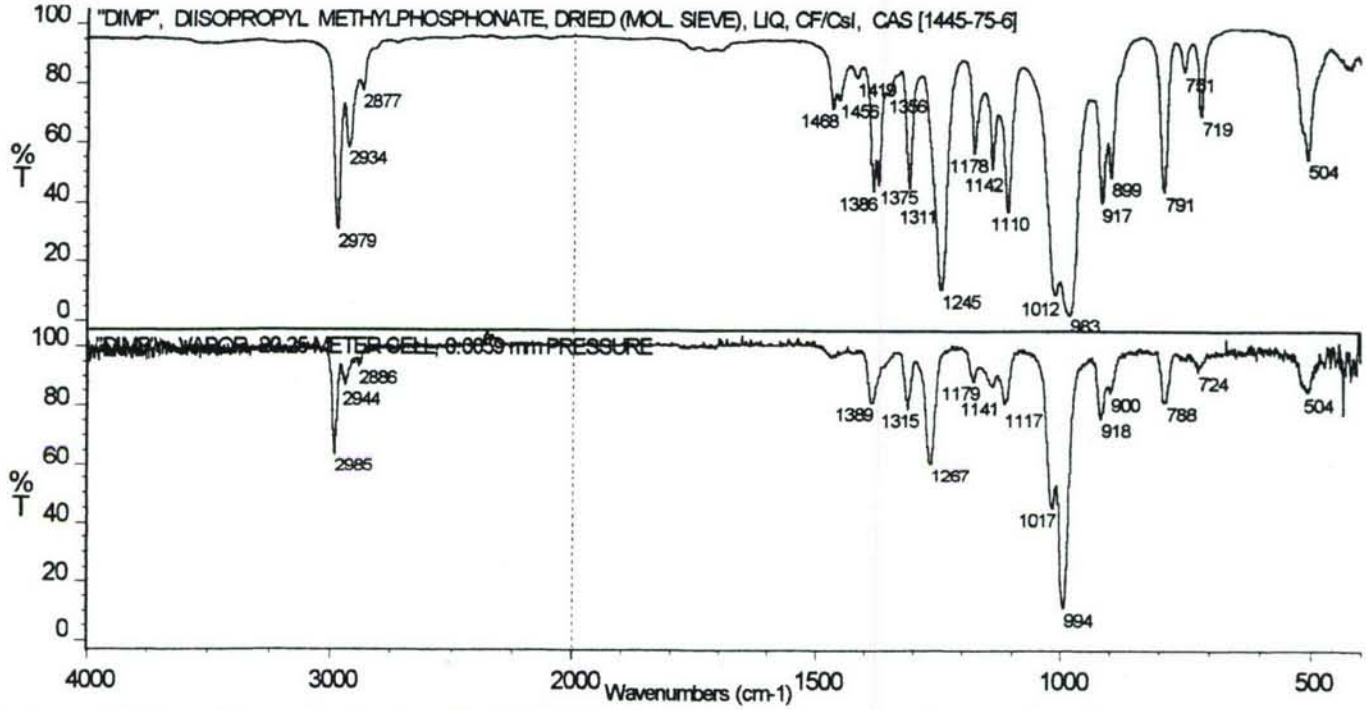


Figure 207 DIISOPROPYL METHYLPHOSPHONATE (DIMP), 98%, *UPPER SPECTRUM*--LIQUID, CF/KBr, *LOWER SPECTRUM*--VAPOR, 20.25 METER PATHLENGTH, 0.0059 MM PRESSURE

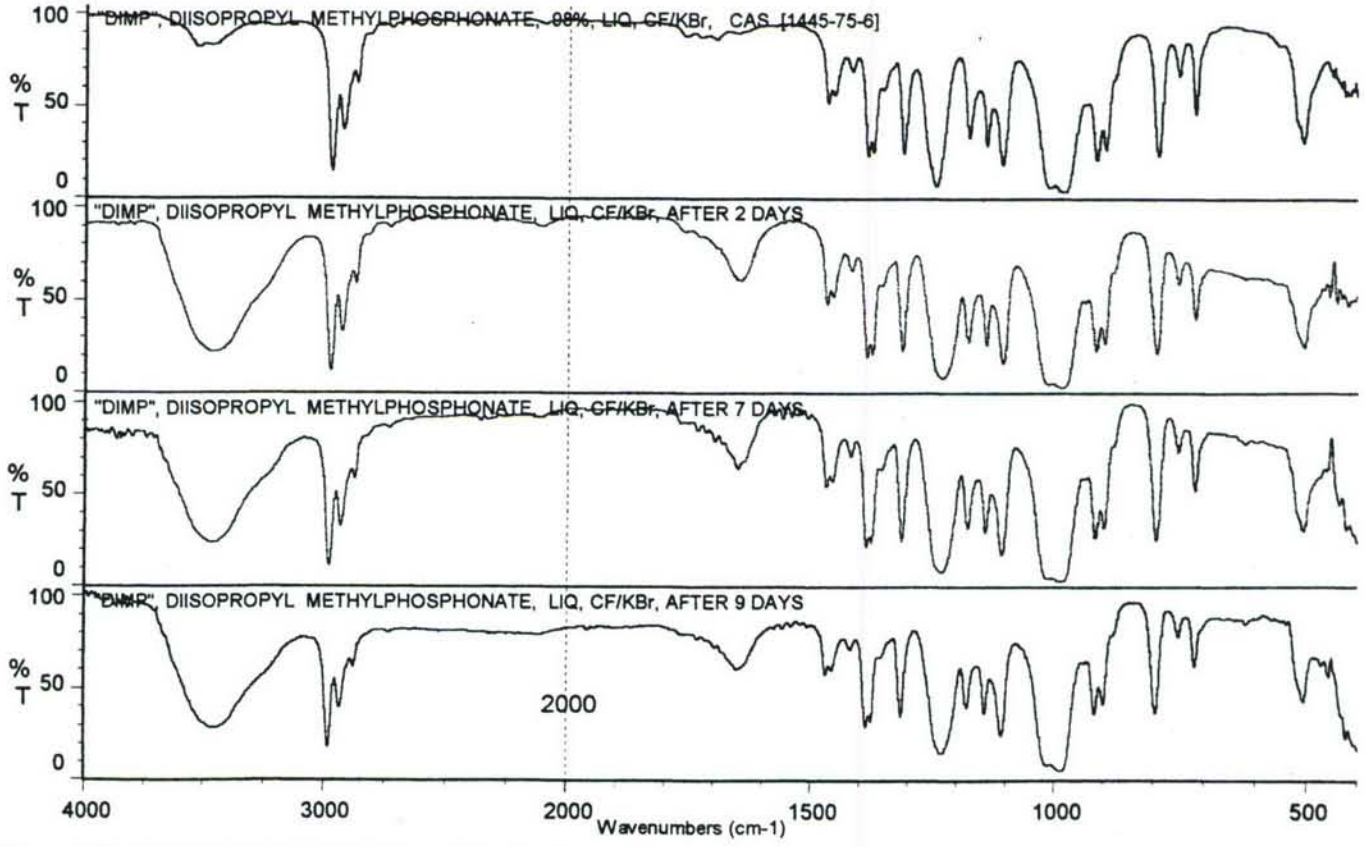


Figure 208 DIISOPROPYL METHYLPHOSPHONATE (DIMP), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.8.17 Dipinacolyl Methylphosphonate (**DPMP**), [Bis(1,2,2-trimethylpropyl) Methyphosphonate]

CH_3-P=O[O-CH(CH_3)-C(CH_3)$_3$]$_2$

The infrared spectrum of a liquid film of dipinacolyl methylphosphonate (**DPMP**) or Bis(1,2,2-trimethylpropyl) methylphosphonate, between CsI windows is given as ***Figure 209***. The band assignments are as follows: 3532 and 3469 cm^{-1} vw and 1650 cm^{-1} vvw (H_2O), 3216 cm^{-1} vvw (ν OH alcohol ?), 2962 cm^{-1} ms, 2912 cm^{-1} w and 2874 cm^{-1} m (ν CH_3), 1481 cm^{-1} m and 1464 cm^{-1} w (δ_{as} CH_3), 1417 cm^{-1} vw (δ_{as} P-CH_3), 1396 and 1378 cm^{-1} m [δ_{sy} CH_3 from C(CH_3)$_3$] , 1365 cm^{-1} m (δ_{sy} CH_3), 1307 cm^{-1} m (δ_{sy} P-CH_3), 1248 cm^{-1} ms (ν P=O), 1211 cm^{-1} w (*t*-butyl skeletal), 1115 cm^{-1} w, 1081 cm^{-1} ms, 1052 cm^{-1} w, 1021 and 1006 cm^{-1} ms (pinacolyl moiety, CH_3 rock, ν C-C ?), 971 cm^{-1} s (ν P-O-C), 934 cm^{-1} m (pinacolyl moiety), 907 and 894 cm^{-1} w (P-CH_3 rock and CH_3 rock of *t*-butyl moiety), 867, 811, and 750 cm^{-1} w-m (pinacolyl moiety), 727 cm^{-1} vw (ν P-C ?), 515 cm^{-1} m (P=O deformation).

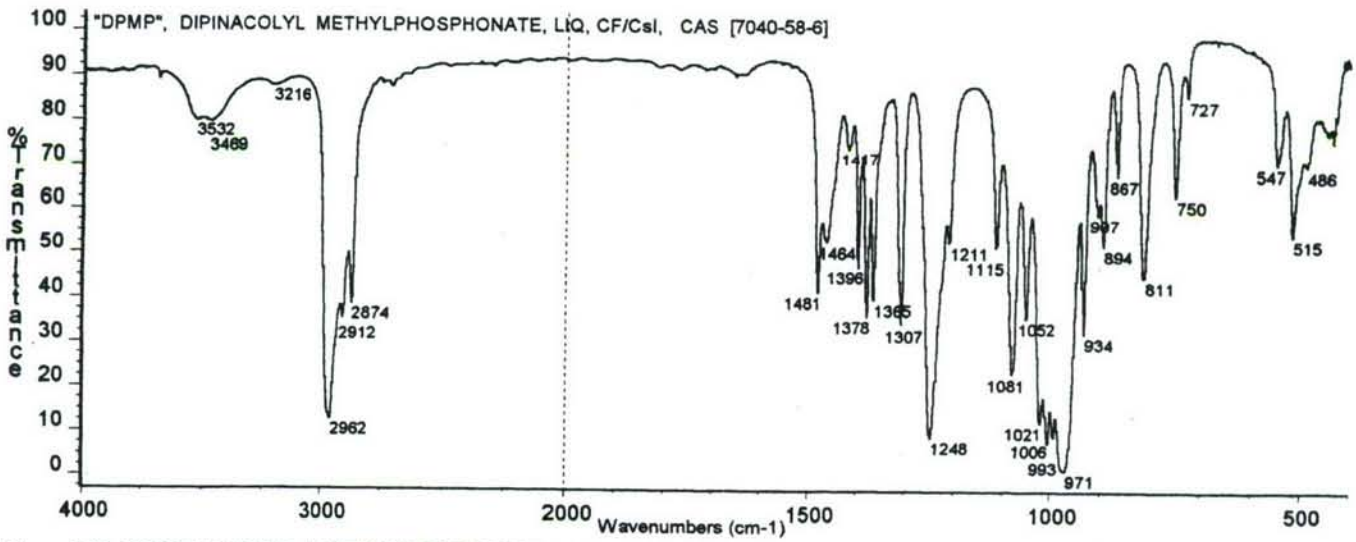


Figure 209 DIPINACOLYL METHYLPHOSPHONATE (DPMP), [BIS(1,2,2-TRIMETHYLPROPYL) METHYLPHOSPHONATE], LIQUID, CF/CsI.

3.5.8.18 Benzyl Isopropyl Methylphosphonate CH_3-P=O(O-CH_2-C_6H_5)[O-CH(CH_3)$_2$]

The infrared spectrum of benzyl isopropyl methylphosphonate as a liquid film between KBr windows is reproduced as ***Figure 210***. The band assignments are as follows: 3090, 3065 and 3033 cm^{-1} vw (ν =C-H aromatic), 2978 cm^{-1} m, 2934 cm^{-1} w, 2877 cm^{-1} vw (ν CH_3, CH_2), 1607 and 1587 cm^{-1} vvw, 1498 cm^{-1} vw

(aromatic ring) 1466 cm^{-1} sh, 1456 cm^{-1} w (δ_{as} CH_3, and aromatic ring), 1418 cm^{-1} vvw (δ_{as} P-CH_3), 1385 and 1375 cm^{-1} w (δ_{sy} CH_3 isopropyl goup), ca 1355 cm^{-1} sh (δ -C-H), 1311 cm^{-1} m (δ_{sy} P-CH_3), 1244 cm^{-1} ms (ν P=O), 1215 cm^{-1} vw (CH_2, benzyl moiety; dibenzyl phosphite, ***Figure 198***, had a band at 1214 cm^{-1}), 1178, 1142 and 1108 cm^{-1} vw-w (triplet characteristic of POisopropyl group), 1081 and 1024 cm^{-1} vw (β C-H of mono-substituted aromatic ring), 992 cm^{-1} s (ν P-O-C), 918 cm^{-1} m and 898 cm^{-1} w (P-CH_3 rock and CH_3 rock of isopropyl group), 819 cm^{-1} w (POC), 740 cm^{-1} w (γ C-H mono-substituted aromatic ring), 697 cm^{-1} w (δ mono-substituted aromatic ring), ca 480 cm^{-1} w (P=O deformation ?).

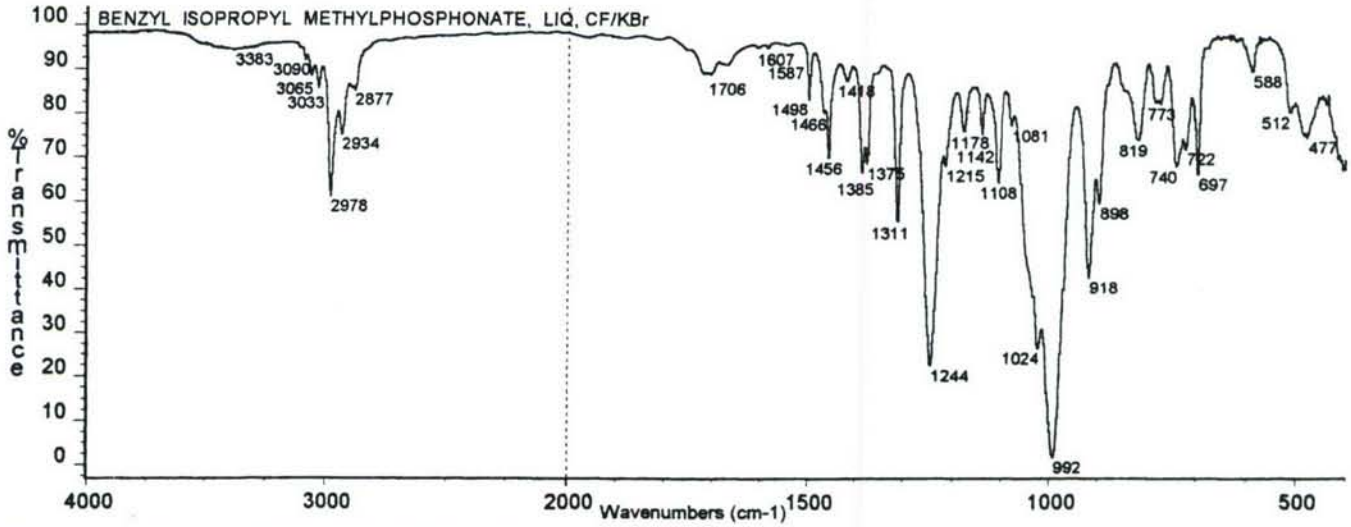


Figure 210 BENZYL ISOPROPYL METHYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.19 Dibenzyl Methylphosphonate CH_3-P=O(O-CH_2-C_6H_5)

The infrared spectrum of dibenzyl methylphosphonate as a liquid film between KBr windows is presented as ***Figure 211***. The band assignments are as follows: 3455 cm^{-1} vw (H_2O), 3089 cm^{-1} vvw, 3064 cm^{-1} vw, 3033 cm^{-1} vw (ν =C-H aromatic), 2952 cm^{-1} vw, 2925 cm^{-1} vvw, 2891 cm^{-1} vw (ν CH_3, CH_2), 1607 and 1587 cm^{-1} vvw, 1498 cm^{-1} w and 1456 cm^{-1} m (aromatic ring), 1416 cm^{-1} vw (δ_{as} P-CH_3), 1380 cm^{-1} w (ω O-CH_2), 1311 cm^{-1} m (δ_{as} P-CH_3), 1243 cm^{-1} ms (ν P=O), 1215 w (CH_2, benzyl moiety, see ***Figures 198*** and ***210***), 1181 and 1158 cm^{-1} vvw, 1081 cm^{-1} w an 1035 cm^{-1} sh (β C-H mono-substituted aromatic ring), 922 cm^{-1} ms (P-CH_3 rock, benzyl moiety), 827 cm^{-1} w (POC), 733 cm^{-1} m (γ C-H mono-substituted aromatic ring), 697 cm^{-1} m (δ

mono-substituted aromatic ring), 466 cm^{-1} w (P=O deformation ?).

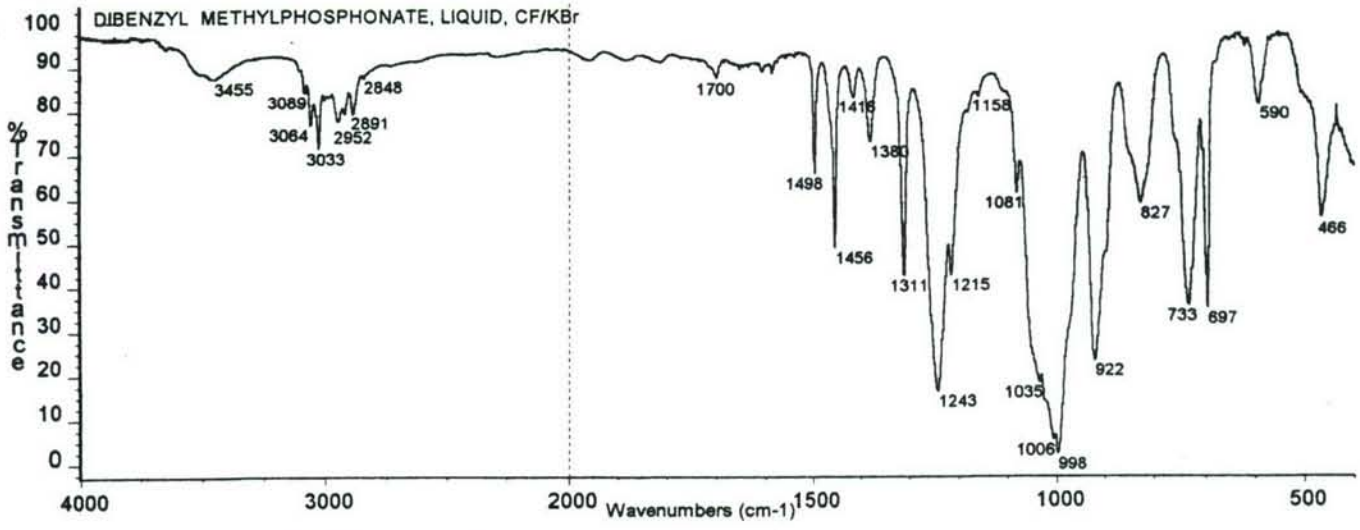


Figure 211 DIBENZYL METHYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.20 Pinacolyl 2,2-Dichlorovinyl Methylphosphonate CH_3-P=O[O-HC=C$(Cl)_2$][O-HC(CH_3)-C$(CH_3)_3$]

The infrared spectrum of pinacolyl 2,2-dichlorovinyl methylphosphonate [1,2,2-trimethylpropyl 2,2-dichlorovinyl methylphosphonate] as a liquid between KBr windows is given in ***Figure 212***. The band assignments are as follows: 3071 and 3051 cm^{-1} vw (ν =C-H), 2969 cm^{-1} m (ν_{as} CH_3), 2874 cm^{-1} w (ν_{sy} CH_3), 1643 cm^{-1} w (ν C=C), 1481 cm^{-1} w and 1464 cm^{-1} vw (δ_{as} CH_3), 1415 cm^{-1} vvw (δ_{as} P-CH_3), 1398 cm^{-1} vw and 1381 cm^{-1} w (δ_{sy} CH_3 *t*-butyl), 1366 cm^{-1} w (δ_{sy} CH_3), 1314 cm^{-1} m (δ_{sy} P-CH_3), 1257 cm^{-1} ms (ν P=O), 1211 cm^{-1} sh, 1117 cm^{-1} sh, 1077 cm^{-1} m , 1048 cm^{-1} sh , 996 cm^{-1} sh (pinacolyl moiety), 1150 cm^{-1} ms (ν P-O-C=), 1011 cm^{-1} ms (P-O-C=, or pinacolyl moiety ?), 974 cm^{-1} s (ν P-O-C, pinacolyl), 935 and 870 cm^{-1} w (pinacolyl moiety ?), 909 and 894 cm^{-1} m (P-CH_3 rock, CH_3 rock from *t*-butyl), 815 cm^{-1} m (ν_{as} CCl_2), 756 cm^{-1} w (POC), 657 cm^{-1} (ν_{sy} CCl_2 ?), 498 cm^{-1} w (P=O deformation ?).

The effect of atmospheric moisture on pinacolyl 2,2-dichlorovinyl methylphosphonate [1,2,2-trimethylpropyl 2,2-dichlorovinyl methylphosphonate] as a liquid film is presented in ***Figure 213***. After some 98 days of exposure to atmospheric moisture the spectrum of the compound shows the formation of POH bands near 2650, 2300 and 1670 cm^{-1}. The P=O stretch has been lowered to 1209 cm^{-1}. The bands due to the 2,2-dichlorovinyl moiety are absent from the spectrum, while those bands indicative of the pinacolyl group are still evident in

the spectrum. The compound has been hydrolyzed to a phosphonic acid, namely, pinacolyl methylphosphonic acid, $CH_3P{=}O(OH)[OCH(CH_3)C(CH_3)_3]$, for which an authentic spectrum has been presented as ***Figure 146***.

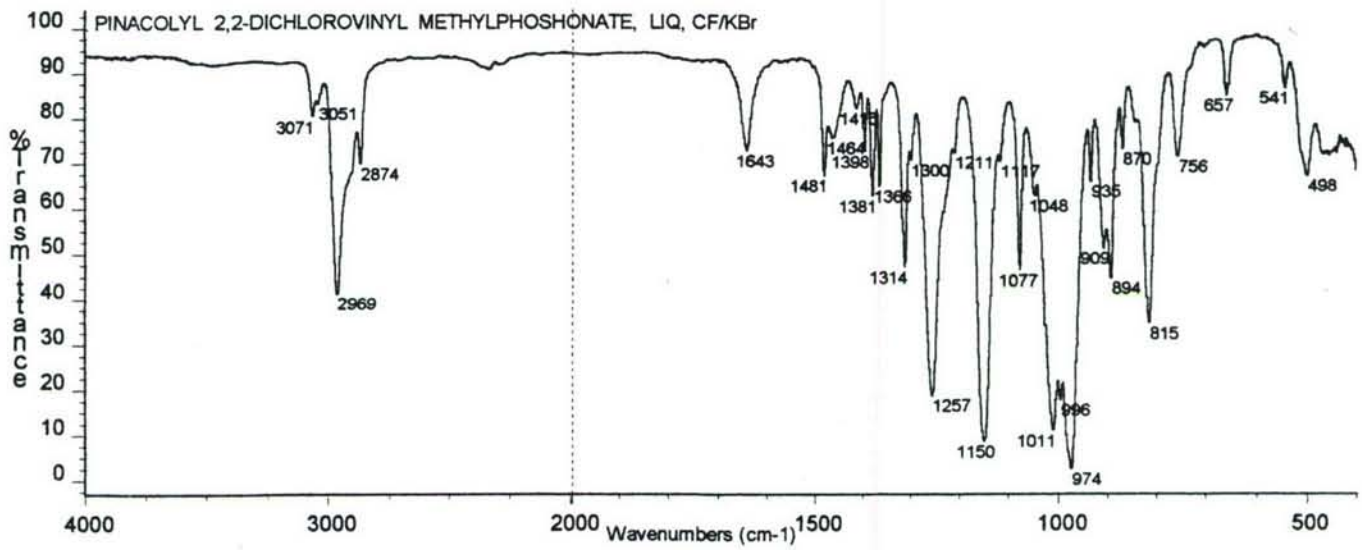


Figure 212 PINACOLYL 2,2-DICHLOROVINYL METHYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.21 Ethyl 2-Diisopropylaminoethyl Methylphosphonate (**QLO**, **QB**)

$CH_3P{=}O(OCH_2CH_3)[OCH_2CH_2N(i\text{-}C_3H_7)_2$

The infrared spectrum of ethyl 2-diisopropylaminoethyl methylphosphonate as a liquid film between KBr windows is presented as ***Figure 214***. The compound is a possible impurity in **VX**, ethyl S-(2-diisopropyl-aminoethyl) methylphosphonothiolate. The band assignments of **QLO** (**QB**) are as follows: 3477 cm^{-1} w and 1650 cm^{-1} vw (H_2O), 2968 cm^{-1} s, 2932 cm^{-1} m, 2907 cm^{-1} sh and 2874 cm^{-1} m (ν CH_3 and CH_2), 1466 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1418 cm^{-1} vw (δ_{as} P-CH_3), 1392 cm^{-1} m (ω OCH_2 and δ_{sy} CH_3), 1363 cm^{-1} m (δ_{sy} CH_3), 1312 cm^{-1} ms (δ_{sy} P-CH_3), 1246 cm^{-1} s (ν P=O), 1162 cm^{-1} sh and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1150 and 1121 cm^{-1} w (ν C-N ?, isopropyl skeletal), 1054, 1033 and 1011 cm^{-1} s (ν P-O-C), 963 cm^{-1} ms (ν C-C of POEt), 912 cm^{-1} m and 895 cm^{-1} sh (P-CH_3 rock and isopropyl CH_3 rock), 800 cm^{-1} m (POC), 713 cm^{-1} w (ν P-C), 501 cm^{-1} m (P=O deformation).

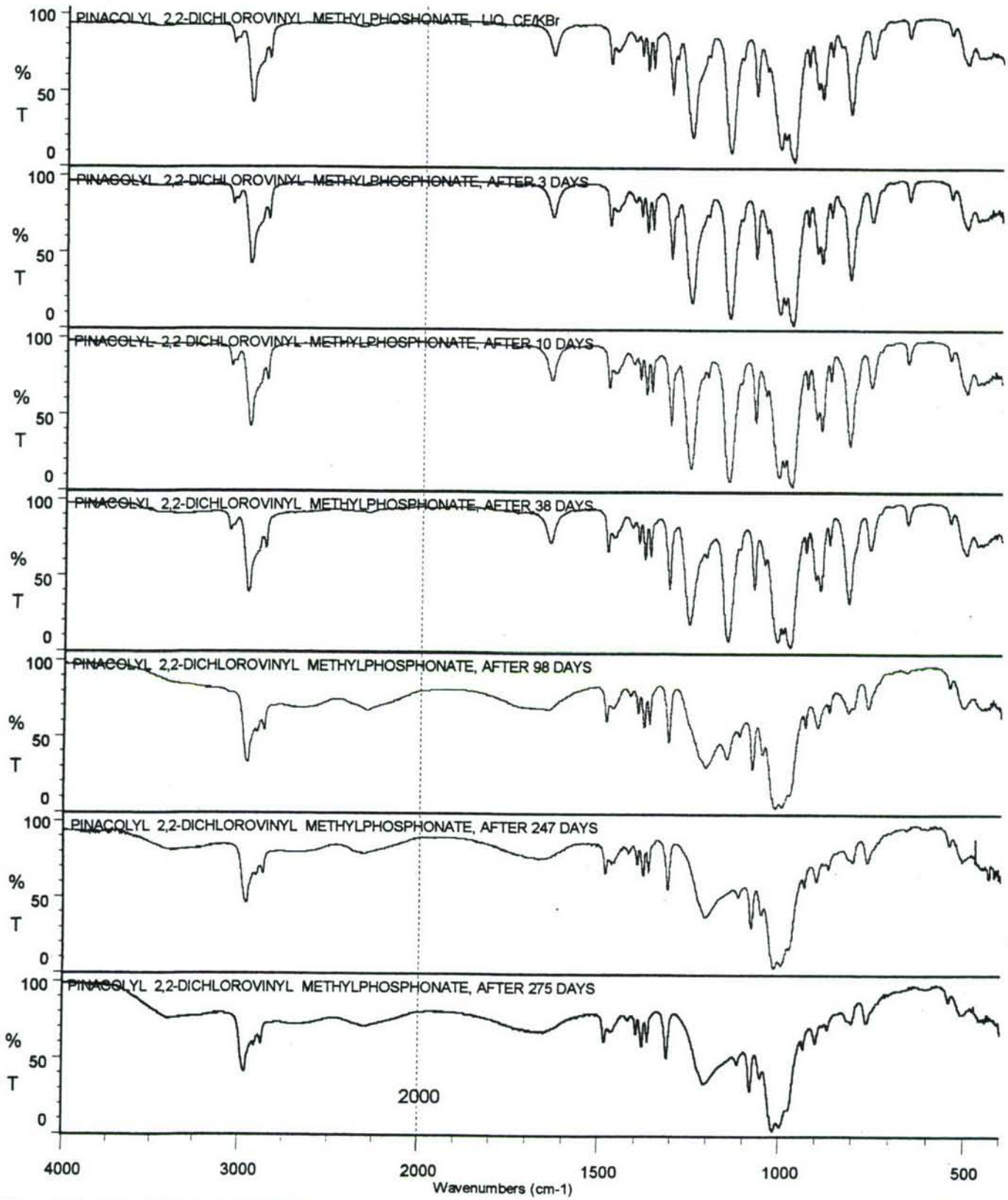


Figure 213 PINACOLYL 2,2-DICHLOROVINYL METHYLPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

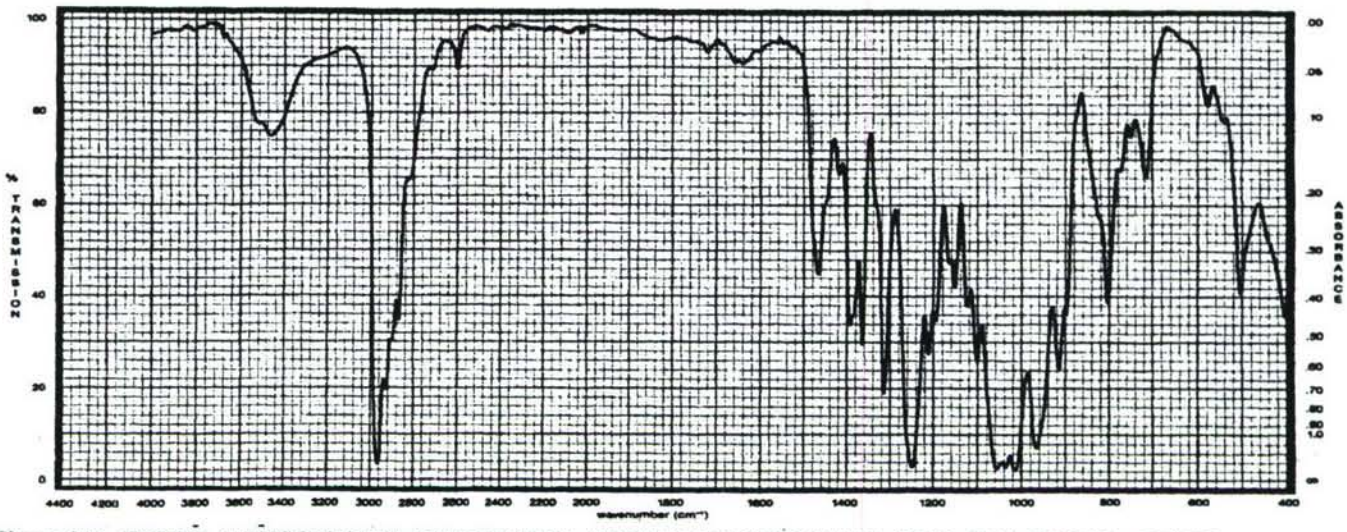


Figure 214 ETHYL 2-DIISOPROPYLAMINOETHYL METHYLPHOSPHONATE (QLO, QB), LIQUID, CF/CsI

3.5.8.22 Bis(2-diisopropylaminoethyl) Methylphosphonate (**LTO, LTA**) $CH_3P{=}O[OCH_2CH_2N(i\text{-}C_3H_7)_2]_2$

The infrared spectrum of bis(2-diisopropylaminoethyl) methylphosphonate (**LTO, LTA**) as a liquid between KBr windows is given in ***Figure 215***. The band assignments are as follows: ca 3460 cm^{-1} w (H_2O), 2967 cm^{-1} s, 2933 cm^{-1} sh, 2874 cm^{-1} ms and 2836 cm^{-1} sh (ν CH_3 and ν CH_2), 2719 cm^{-1} vw and 2608 cm^{-1} vw [these two bands seem to appear when the N(isopropryl)$_2$ moiety is present], 1466 cm^{-1} m (δ CH_3 and δ CH_2), 1416 cm^{-1} sh (δ_{as} P-CH_3), 1381 cm^{-1} ms and 1362 cm^{-1} ms (δ_{sy} CH_3), 1310 cm^{-1} ms (δ_{sy} P-CH_3), 1246 cm^{-1} s (ν P=O), 1208 cm^{-1} m (ν C-N ?), 1149 cm^{-1} and 1122 cm^{-1} m (isopropyl skeletal ?), 1037 cm^{-1} and 1001 cm^{-1} s (ν P-O-C), 923 cm^{-1} ms (CH_3 rock of isopropyl and P-CH_3), 827 cm^{-1} w and 796 cm^{-1} w (POC), 713 cm^{-1} w (ν P-C), 498 cm^{-1} w (P=O deformation ?).

Figure 216 shows **LTO** after exposure to atmospheric moisture for 44 hours. The spectrum shows only an increase in the water bands near 3450 cm^{-1} and 1650 cm^{-1}. The very weak band near 1960 cm^{-1} in both ***Figures 215*** and ***216*** is instrumental in origin and should be disregarded.

3.5.8.23 Diethyl Chloromethylphosphonate $Cl\text{-}CH_2\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of a liquid film of diethyl chloromethylphosphonate between KBr windows is presented as ***Figure 217***. The band assignments are as follows: 3480 cm^{-1} vvw (H_2O), 2987 cm^{-1} ms (ν_{as} CH_3),

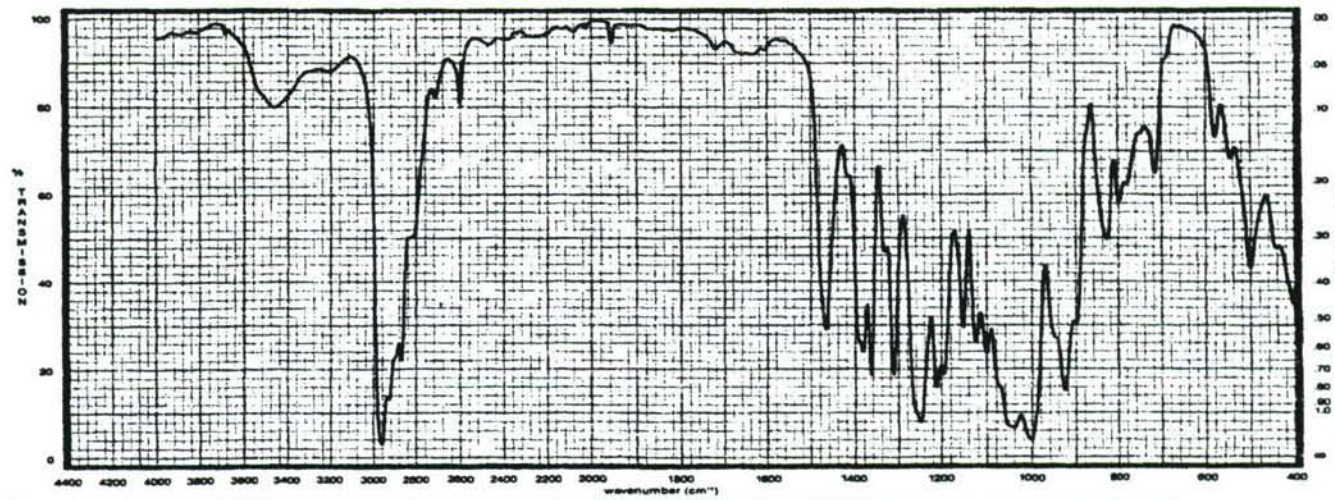


Figure 215 BIS(2-DIISOPROPYLAMINOETHYL) METHYLPHOSPHONATE (LTO, LTA), LIQUID, CF/KBr

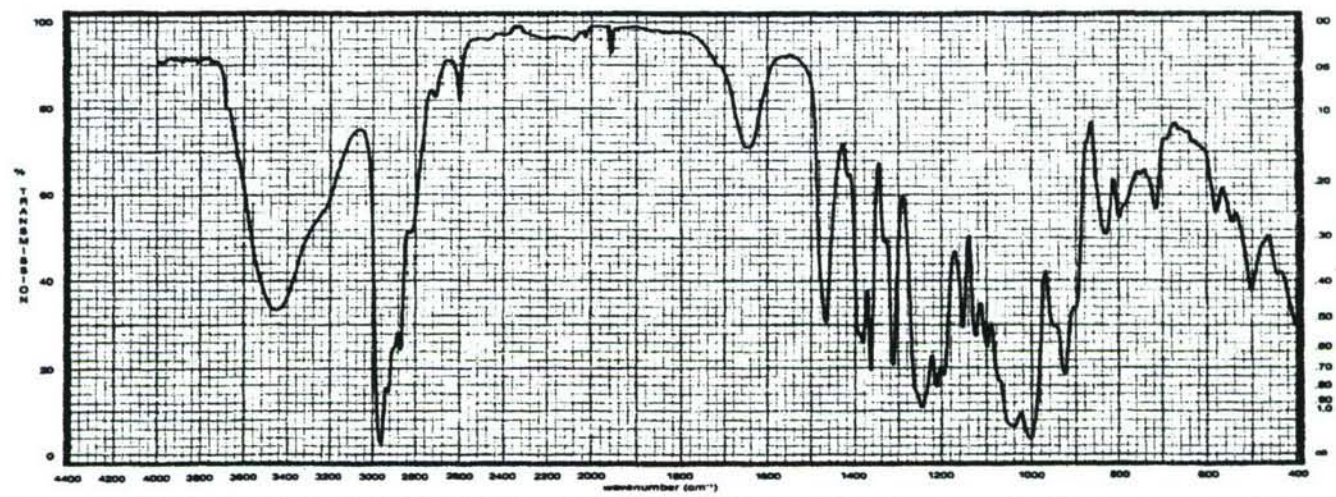


Figure 216 BIS(2-DIISOPROPYLAMINOETHYL) METHYLPHOSPHONATE (LTO, LTA), LIQUID, CF/KBr AFTER 44 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

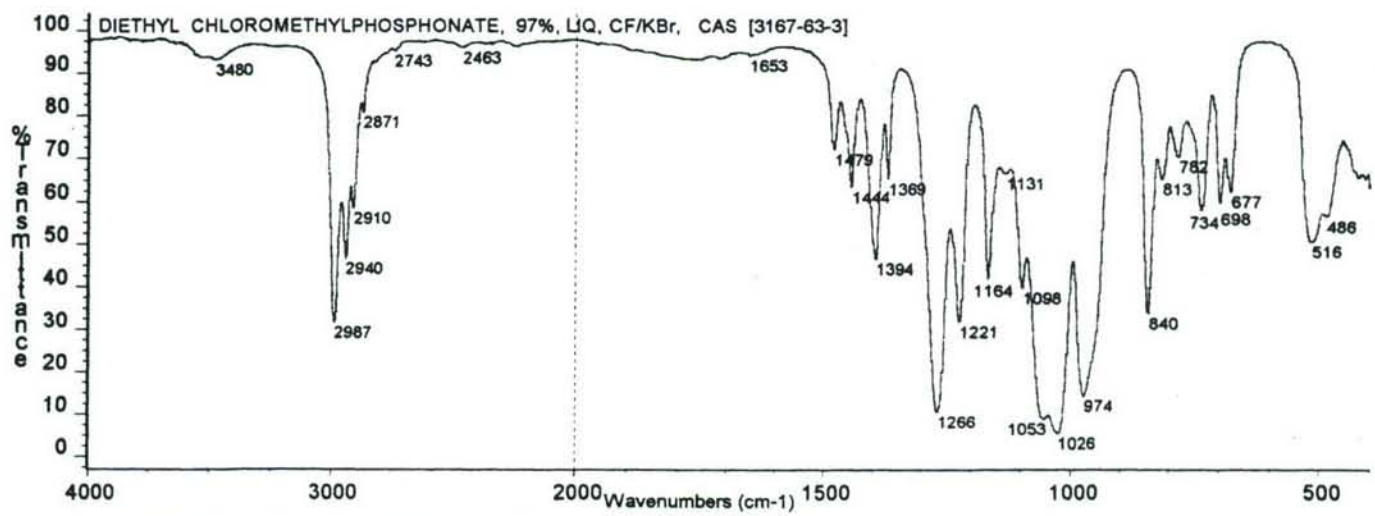


Figure 217 DIETHYL CHLOROMETHYLPHOSPHONATE, 97%, LIQUID, CF/KBr

2940 cm^{-1} m (ν_{as} CH_2), 2910 cm^{-1} w (ν_{sy} CH_3), 2871 cm^{-1} vw (ν_{sy} CH_2), 1479 w (δ OCH_2), 1444 cm^{-1} w (δ_{as} CH_3), 1394 cm^{-1} m (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1266 cm^{-1} ms (ν P=O), 1221 cm^{-1} m (ω CH_2Cl), 1164 and 1098 cm^{-1} m (CH_3 rock of POEt, characteristic), 1053 and 1026 cm^{-1} s (ν P-O-C), 974 cm^{-1} ms (ν C-C of POEt), 840 cm^{-1} m (POC), 734 cm^{-1} w (CH_2 rock ?), 689 and 677 cm^{-1} w (ν C-Cl, ν P-C), 516 cm^{-1} m (δ P=O.

The effect of atmospheric moisture on the thin film of diethyl chloromethylphosphonate is illustrated by ***Figures 218A and 218B***. The spectra show very little change even after 49 days of exposure to atmospheric moisture. The major difference is the increase in water as indicated by the bands near 3480 and 1650 cm^{-1}. The phosphoryl stretching vibration shows only a small decrease to 1263 cm^{-1} from the original value of 1266 cm^{-1}.

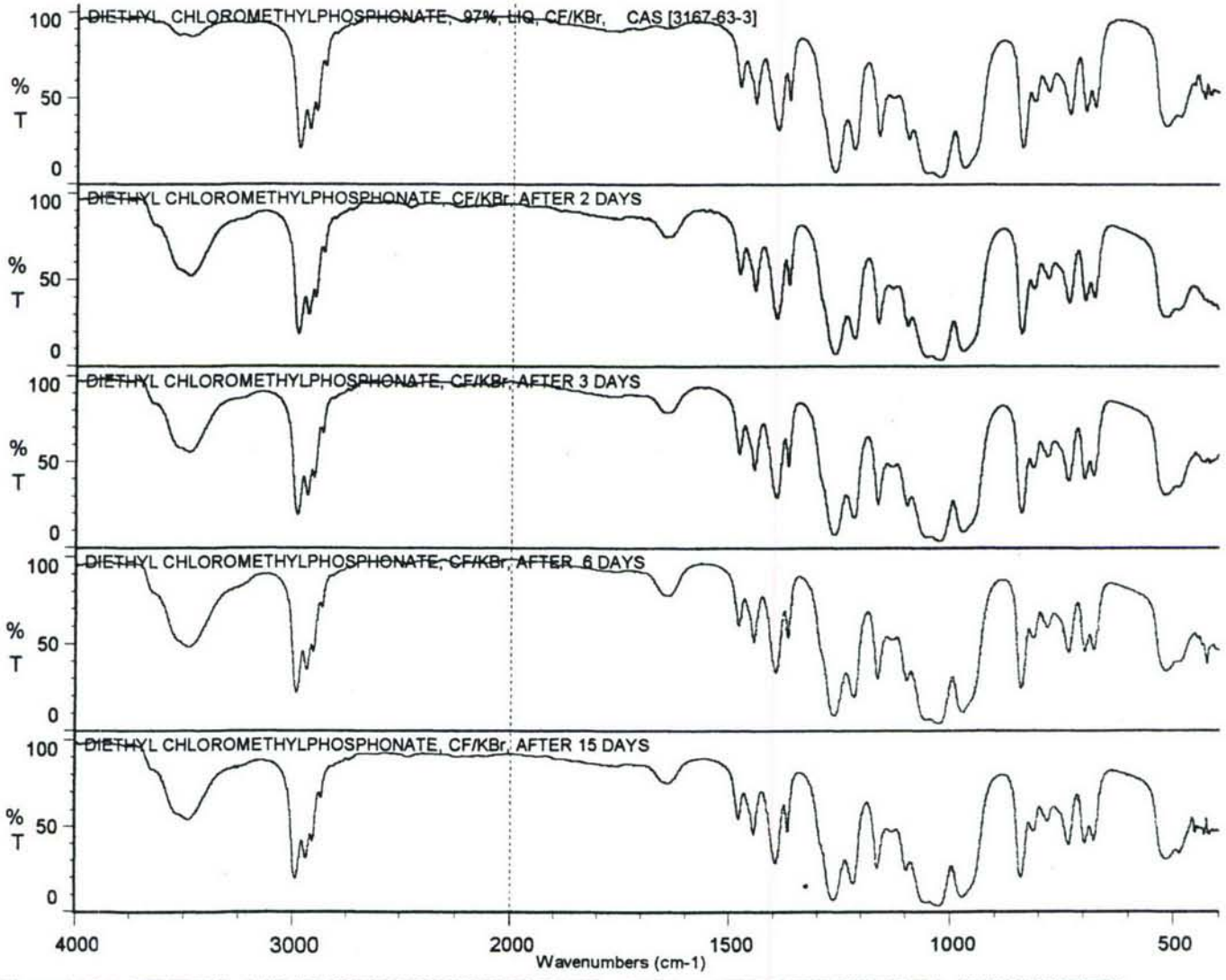


Figure 218 A DIETHYL CHLOROMETHYLPHOSPHONATE , CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

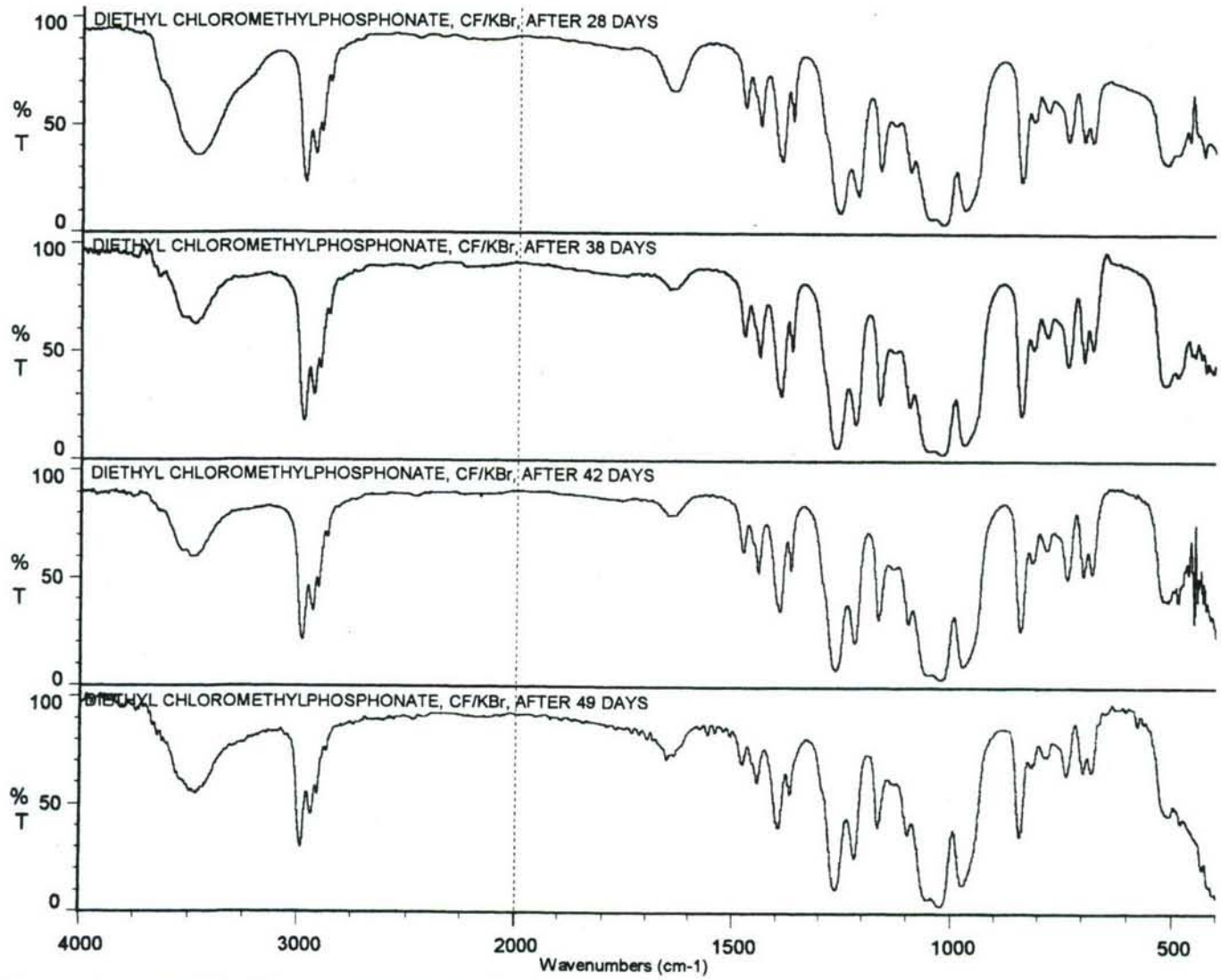


Figure 218B DIETHYL CHLOROMETHYLPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.5.8.24 Diethyl Hydroxymethylphosphonate $HO\text{-}CH_2\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl hydroxymethylphosphonate as a liquid between KBr windows is reproduced as ***Figure 219***. The band assignments are as follows: 3313 cm^{-1} ms (ν OH), 2985 cm^{-1} ms (ν_{as} CH_3), 2933 cm^{-1} w (ν_{as} CH_2), 2909 cm^{-1} m (ν_{sy} CH_3), 2827 cm^{-1} w (ν_{sy} CH_2), 1480 cm^{-1} w (δ OCH_2), 1444 cm^{-1} m (δ_{as} CH_3), 1426 cm^{-1} sh (δ P-CH_2), 1393 cm^{-1} m (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1293 cm^{-1} w (β OH ?), 1236 cm^{-1} ms (ν P=O), 1165 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), ca 1065 cm^{-1} sh (ν C-O alcohol), 1048 and 1027 cm^{-1} s (ν P-O-C), 972 cm^{-1} ms (ν C-C of POEt), 874 cm^{-1} w (CH_2 rock ?), 805 and 777 cm^{-1} m (POC),

713 cm^{-1} vw (ν P-C ?), 651 cm^{-1} vw broad (γ OH), 532 cm^{-1} m (δ P=O ?).

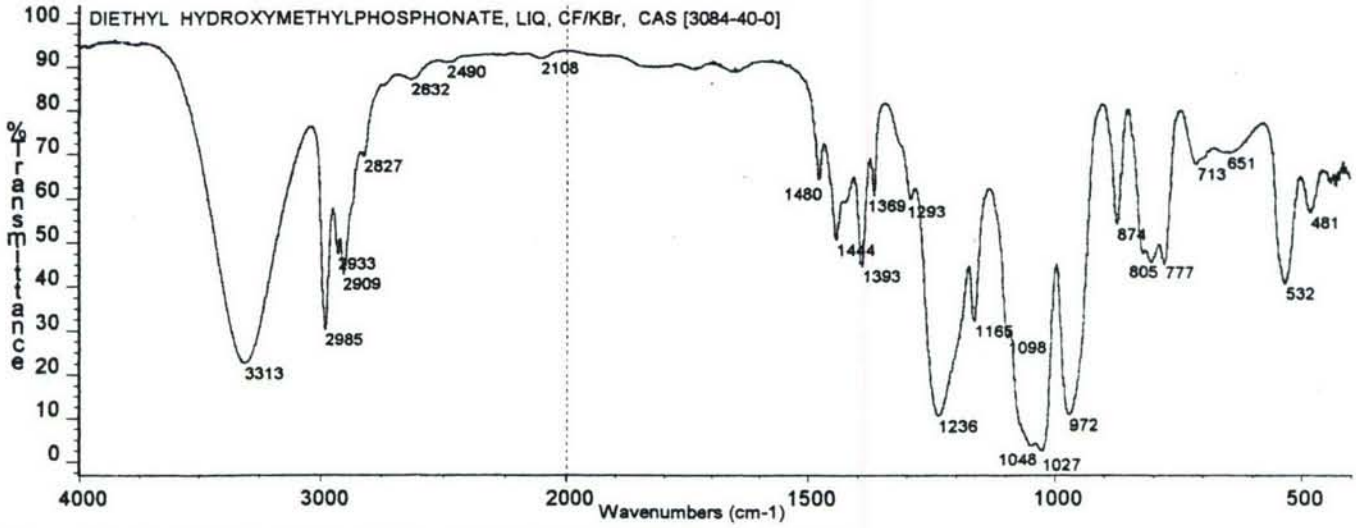


Figure 219 DIETHYL HYDROXYMETHYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.25 Diethyl Cyanomethylphosphonate $N\equiv C\text{-}CH_2\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl cyanomethylphosphonate as a liquid film between KBr windows is given as Figure ***220***. The band assignments are as follows: 3485 cm^{-1} vw (H_2O), 3204 cm^{-1} vvw (2256 + ca 950 = 3206 cm^{-1} ?), 2987 cm^{-1} m, 2963 cm^{-1} sh, 2932 cm^{-1} sh and 2910 cm^{-1} m (ν CH_3 and CH_2), 2256 cm^{-1} m (ν C≡N), 1480 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1394 cm^{-1} m (ω OCH_2), 1370 cm^{-1} w (δ_{sy} CH_3), 1270 cm^{-1} ms (ν P=O), ca 1232 cm^{-1} sh (ω CH_2 ?), 1164 and 1098 cm^{-1} m (CH_3 rock of POEt, characteristic), 1051 and 1023 cm^{-1} s (ν P-O-C), 979 cm^{-1} ms (ν C-C of POEt), ca 950 cm^{-1} sh (ν C-C of $P\text{-}CH_2\text{-}C\equiv N$?), 845 cm^{-1} m (CH_2 rock ?), 803 and 777 cm^{-1} m (POC), 708 cm^{-1} w (ν P-C), 563 cm^{-1} m (related to $P\text{-}CH_2\text{-}C\equiv N$), 487 cm^{-1} w (δ P=O).

The effect of moisture on the liquid film of diethyl cyanomethylphosphonate is illustrated by the spectra presented in ***Figures 221A*** and ***221B***. Even after 271 days of exposure to atmospheric moisture no changes were observed in the spectra save for the gradual increase in water as shown by the bands near 3450 and 1650 cm^{-1}. A slight decrease in the phosphoryl frequency (from 1270 to 1267 cm^{-1}) was observed by the 271st day of exposure to atmospheric moisture.

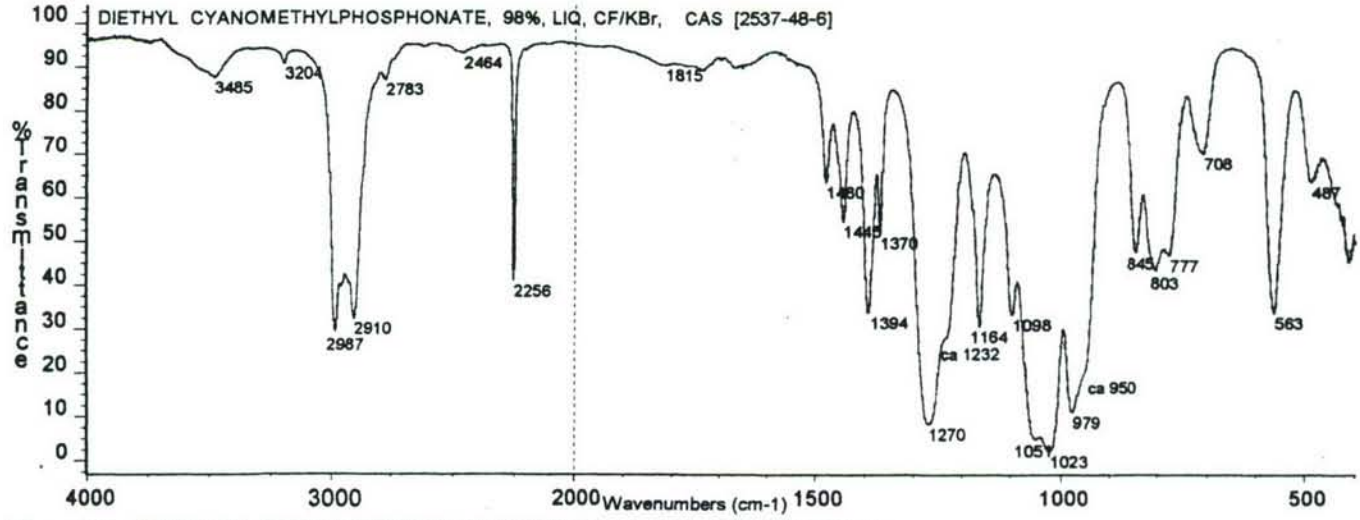


Figure 220 DIETHYL CYANOMETHYLPHOSPHONATE, 98%, LIQUID, CF/KBr

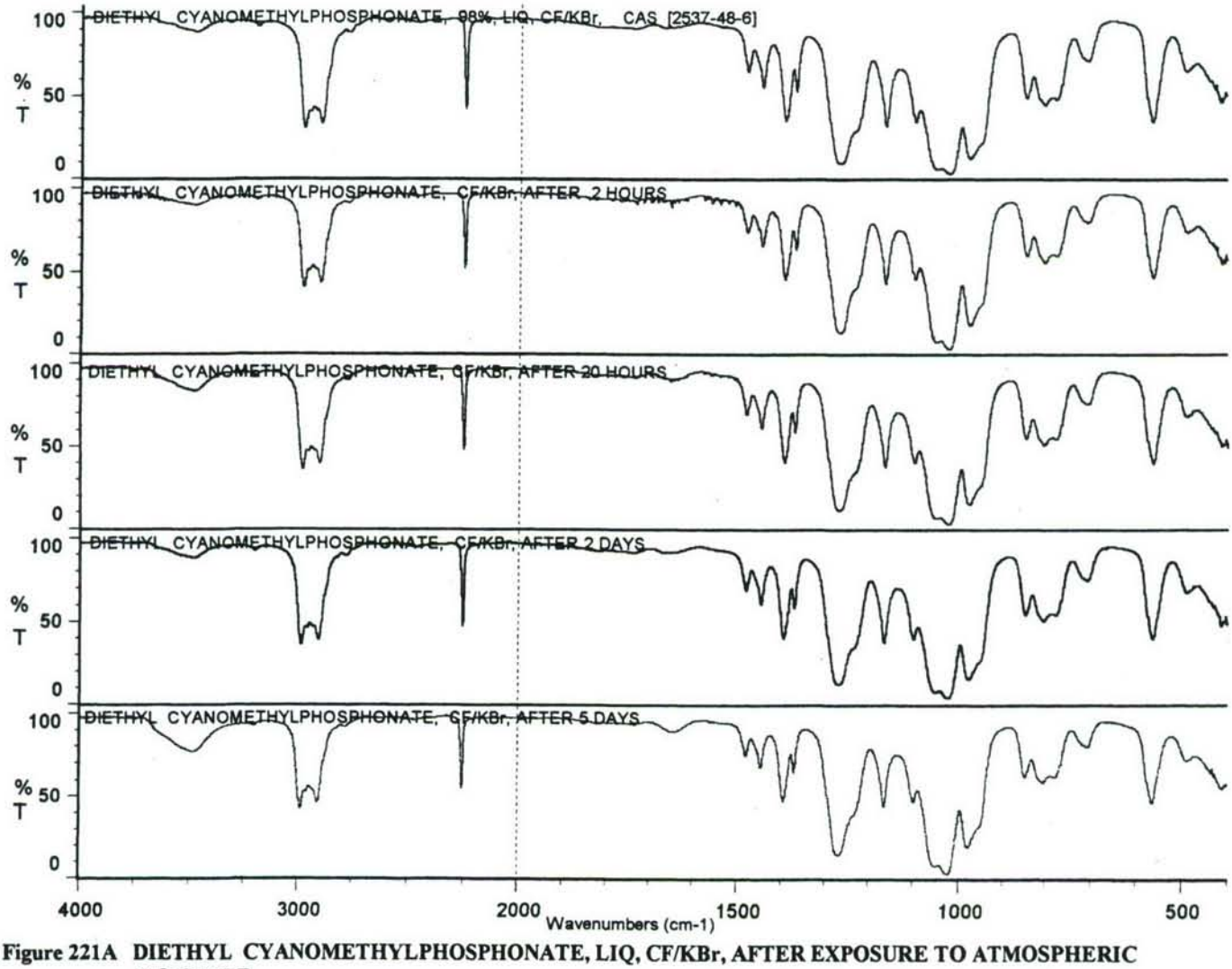


Figure 221A DIETHYL CYANOMETHYLPHOSPHONATE, LIQ, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

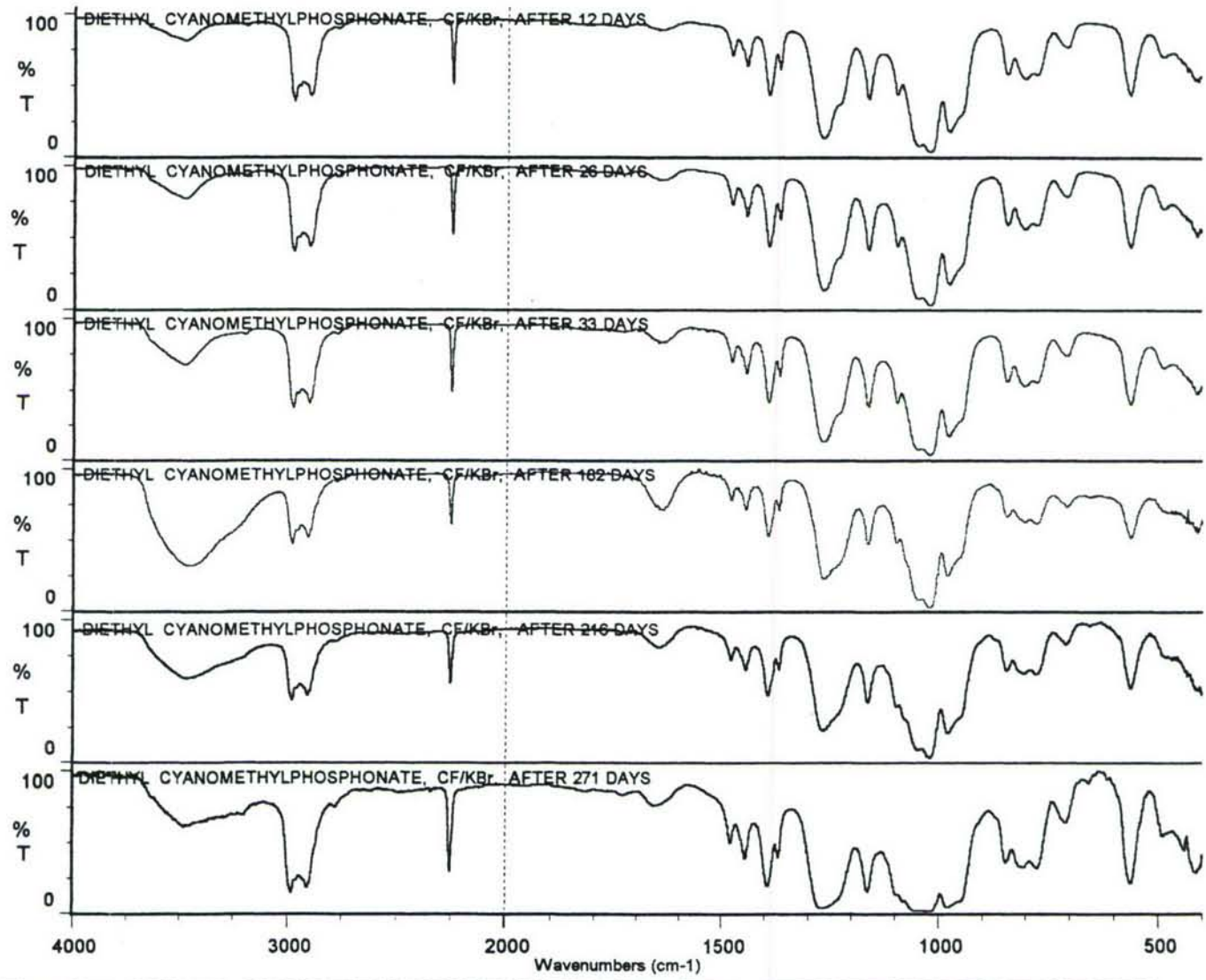


Figure 221B DIETHYL CYANOMETHYLPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.5.8.26 Diethyl Isocyanomethylphosphonate $C{\equiv}N\text{-}CH_2\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of a liquid film of diethyl isocyanomethylphosphonate between KBr windows is presented as ***Figure 222***. The band assignments are as follows: 3275 cm^{-1} vvw (ν N-H ?), 2985 cm^{-1} m, 2928 cm^{-1} m and 2873 cm^{-1} vw (ν CH_3 and CH_2), 2153 cm^{-1} ms (ν C≡N-), 1687 cm^{-1} vw (ν C=O hydrolysis product), ca 1543 cm^{-1} vvw (δ N-H ?), 1479 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1420 cm^{-1} w (δ_{as} P-CH_2), 1394 cm^{-1} m (ω OCH_2), 1370 cm^{-1} w (δ_{sy} CH_3), 1294 cm^{-1} sh (ω CH_2), 1262 and 1254 cm^{-1} ms (ν P=O), 1164 and 1098 cm^{-1} m (CH_3 rock of POEt, characteristic), 1052 and 1024 cm^{-1} s (ν P-O-C), 980 cm^{-1} ms (ν C-C of POEt),

Figure 222 DIETHYL ISOCYANOMETHYLPHOSPHONATE, LIQUID, CF/KBr

863 cm^{-1} w (CH_2 rock), 803 and 772 cm^{-1} m (POC), 703 cm^{-1} w (ν P-C), 540 cm^{-1} m (P-CH_2-NC ?), 487 vw (δ P=O).

The effect of atmospheric moisture on a thin liquid film of diethyl isocyanomethylphosphonate is depicted by the infrared spectra presented in ***Figures 223A*** through ***223G***. The first spectrum (***Figure 222***) showed vw-w bands near 3275 and 1687 and 1543 cm^{-1} which were assigned to N-H stretching, C=O stretching and δ N-H respectively. These bands gradually increase with time, as does the water content (3480, 1640 cm^{-1}). As time progresses the sample becomes black in color, the isocyano band near 2153 cm^{-1} decreases in intensity

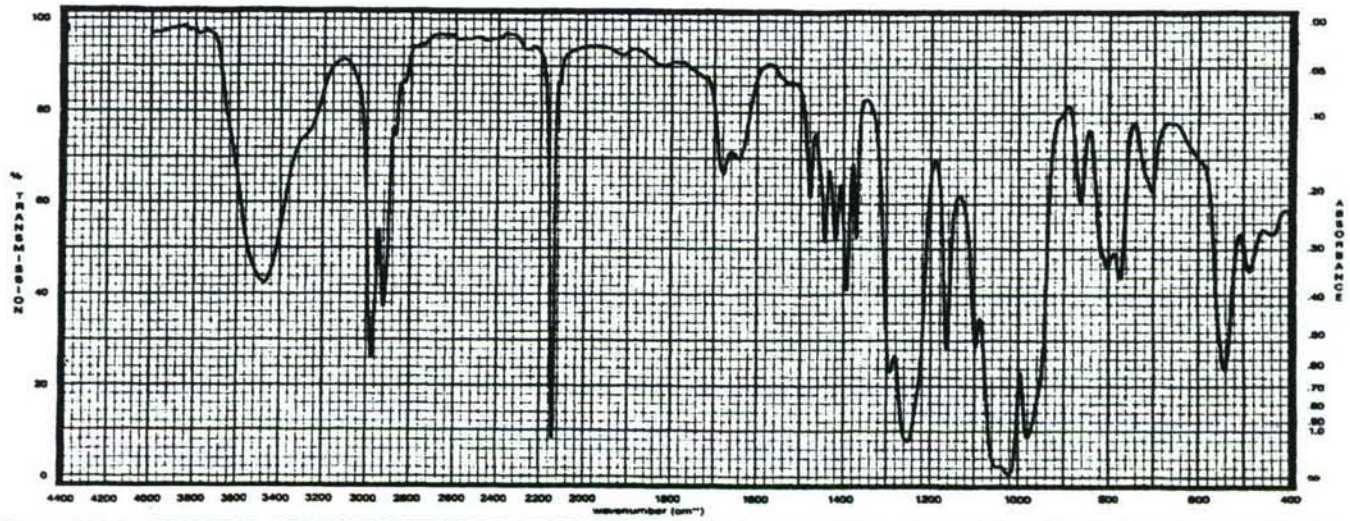


Figure 223 A DIETHYL ISOCYANOMETHYLPHOSPHONATE, LIQUID, CF/KBr, AFTER 21 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

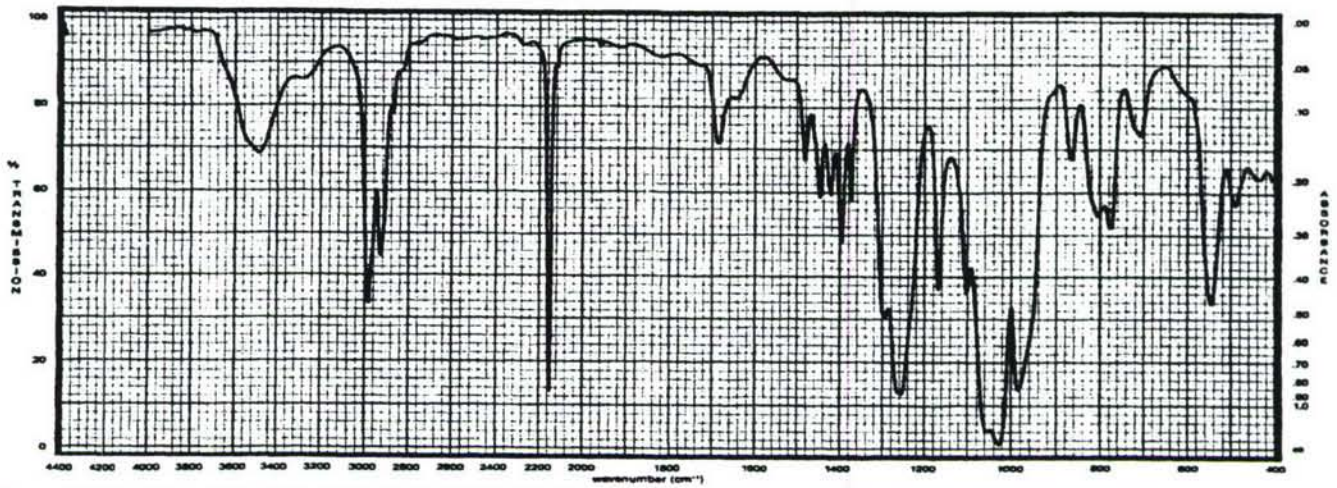


Figure 223B DIETHYL ISOCYANOMETHYLPHOSPHONATE, CF/KBr, AFTER 9 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

Figure 223C DIETHYL ISOCYANOMETHYLPHOSPHONATE, CF/KBr, AFTER 29 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

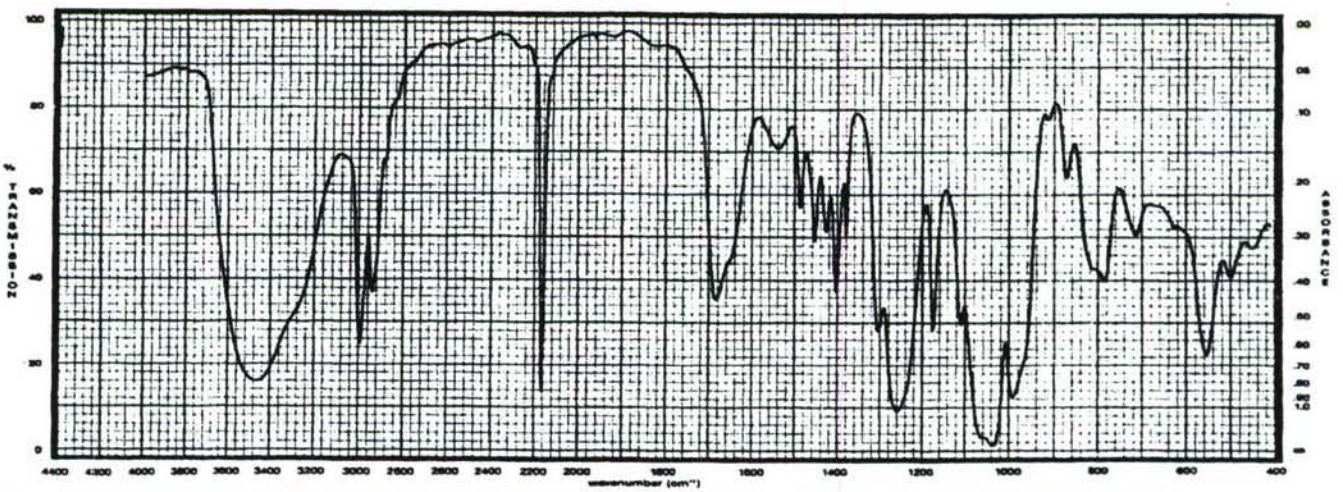


Figure 223D DIETHYL ISOCYANOMETHYLPHOSPHONATE, CF/KBr, AFTER 61 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

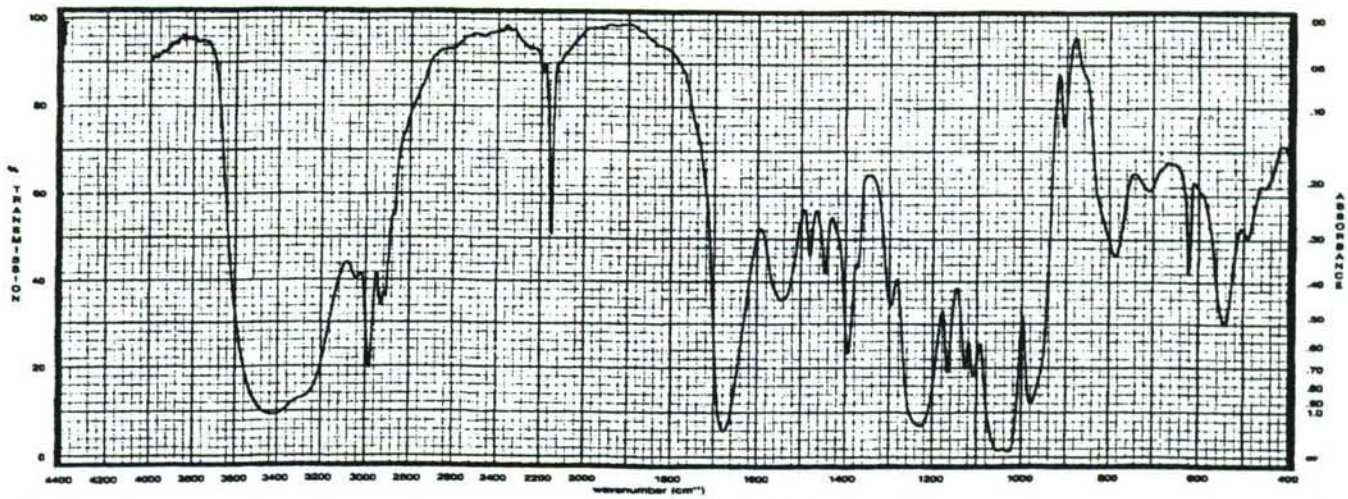


Figure 223E DIETHYL ISOCYANOMETHYLPHOSPHONATE, CF/KBr, AFTER 153 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

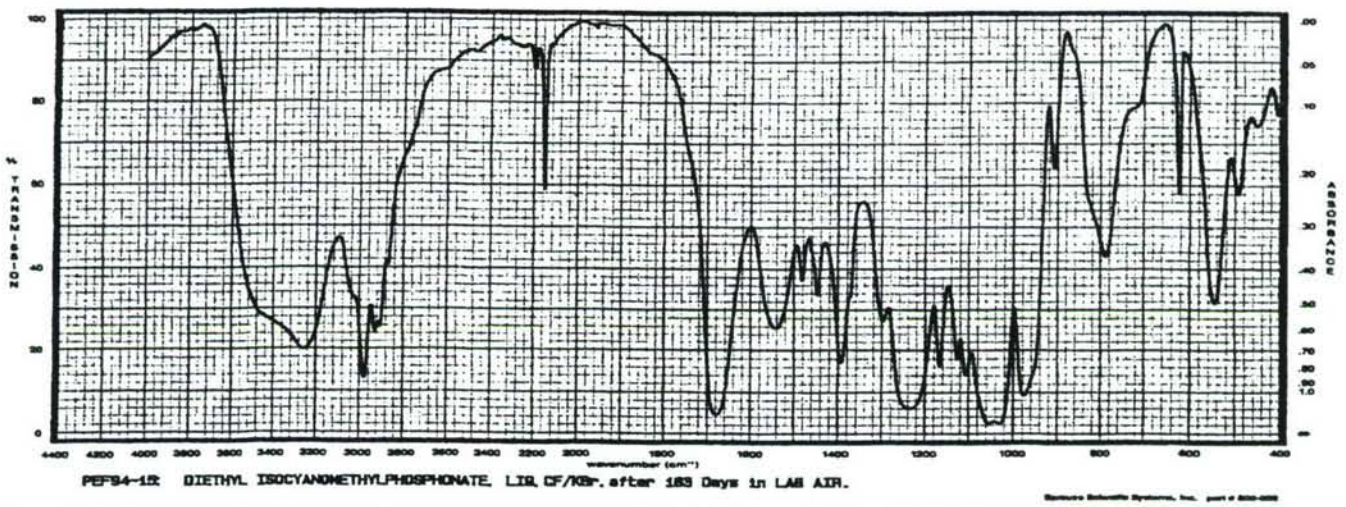


Figure 223F DIETHYL ISOCYANOMETHYLPHOSPHONATE, CF/KBr, AFTER 183 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

and bands indicative of a secondary amide become predominant in the spectra. After 183 days (***Figure 223F***) of exposure to atmospheric moisture the spectrum shows the following: ca 3400 cm^{-1} sh (H_2O), 3264 cm^{-1} ms (ν N-H), ca 3036 cm^{-1} sh (2 x 1542 = 3084 cm^{-1}), 2984 cm^{-1} ms, 2932 and 2912 cm^{-1} m and 2873 cm^{-1} sh (ν CH_3 and CH_2), 2152 cm^{-1} w (ν C≡N-), 1680 cm^{-1} s (ν C=O, Amide I band), 1542 cm^{-1} m (CNH, δ NH and ν C-N, Amide II band), 1480 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1392 cm^{-1} m (ω OCH_2, the band may be partly due to δ C-H from a secondary formamide, H-C=ONHR), ca 1370 cm^{-1} sh (δ_{sy} CH_3), 1296 cm^{-1} w (CNH, Amide III band), 1235 cm^{-1} s (ν P=O), 1164 and 1105 cm^{-1} w (CH_3 rock of POEt, characteristic), 1051 and 1027 cm^{-1} s

(ν P-O-C), 973 cm^{-1} ms (ν C-C of POEt), 784 cm^{-1} m (POC), ca 717 cm^{-1} sh (Amide V band ?), 618 w (Amide IV, VI bands ?). The hydrolysis of diethyl isocyanomethylphosphonate may be summarized as follows:

$C\equiv N\text{-}CH_2\text{-}P{=}O(OCH_2CH_3)_2$ -HOH→ $H\text{-}C(=O)\text{-}NH\text{-}CH_2\text{-}P{=}O(OCH_2CH_3)_2$.

3.5.8.27 Dimethyl Methylthiomethylphosphonate $CH_3\text{-}S\text{-}CH_2\text{-}P{=}O(OCH_3)_2$

The infrared spectrum of a liquid film of dimethyl methylthiomethylphosphonate between CsI windows is presented as ***Figure 224***. The band assignments are as follows: 3434 cm^{-1} vvw (H_2O), 2993 cm^{-1} w, 2955 cm^{-1} m, 2922 cm^{-1} w and 2852 cm^{-1} w (ν CH_3 and ν CH_2), 1462 cm^{-1} w and 1446 cm^{-1} w (δ CH_3), 1426 cm^{-1} sh (δ P-CH_2 or δ S-CH_2, δ_{as} S-CH_3), 1379 cm^{-1} vw (δ S-CH_2-P ?), 1321 cm^{-1} vw (δ_{sy} S-CH_3), 1253 cm^{-1} ms (ν P=O, the ω S-CH_2 may occur at 1270-1220 cm^{-1}), 1187 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1055 and 1031 cm^{-1} s (ν P-O-C), 975 cm^{-1} w (S-CH3 rock), 842 and 819 cm^{-1} ms (POC), 745 cm^{-1} vw (ν P-C ?), 712, 685 cm^{-1} vw (ν C-S-C), 519 cm^{-1} m (δ P=O).

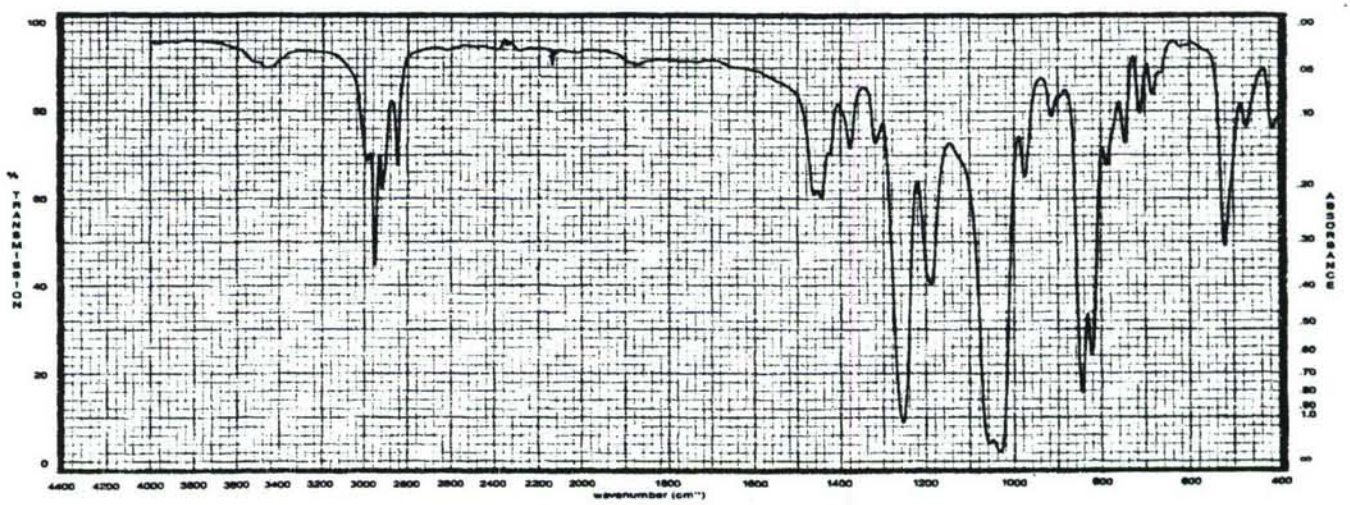


Figure 224 DIMETHYL METHYLTHIOMETHYLPHOSPHONATE, LIQUID, CF/CsI

3.5.8.28 Diethyl Methylthiomethylphosphonate $CH_3\text{-}S\text{-}CH_2\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl methylthiomethylphosphonate as a liquid film between KBr windows is given as ***Figure 225***. The band assignments are as follows: 3528 and 3475 cm^{-1} w (H_2O), 2982 cm^{-1} m,2924 and 2908 cm^{-1} m, 2870 cm^{-1} w and 2834 cm^{-1} vw (ν CH_3 , ν CH_2), 1478 cm^{-1} w (δ OCH_2), 1443 cm^{-1} m (δ_{as} CH_3),

1425 cm^{-1} w (δ CH_2, δ S-CH_3), 1391 cm^{-1} m (ω OCH_2), 1378 cm^{-1} sh (S-CH_2-P ?), 1368 cm^{-1} w (δ_{sy} CH_3), 1321 cm^{-1} w (δ_{sy} S-CH_3), 1290 cm^{-1} sh (ω S-CH_2 ?), 1251 cm^{-1} ms (ν P=O), 1164 and 1098 cm^{-1} m (CH_3 rock of POEt, characteristic), 1054 and 1027 cm^{-1} s (ν P-O-C), 963 cm^{-1} ms (ν C-C of POEt), 824 cm^{-1} m (POC), 737 cm^{-1} w (ν P-C), 714 and 685 cm^{-1} w (ν C-S-C), 523 cm^{-1} m (δ P=O).

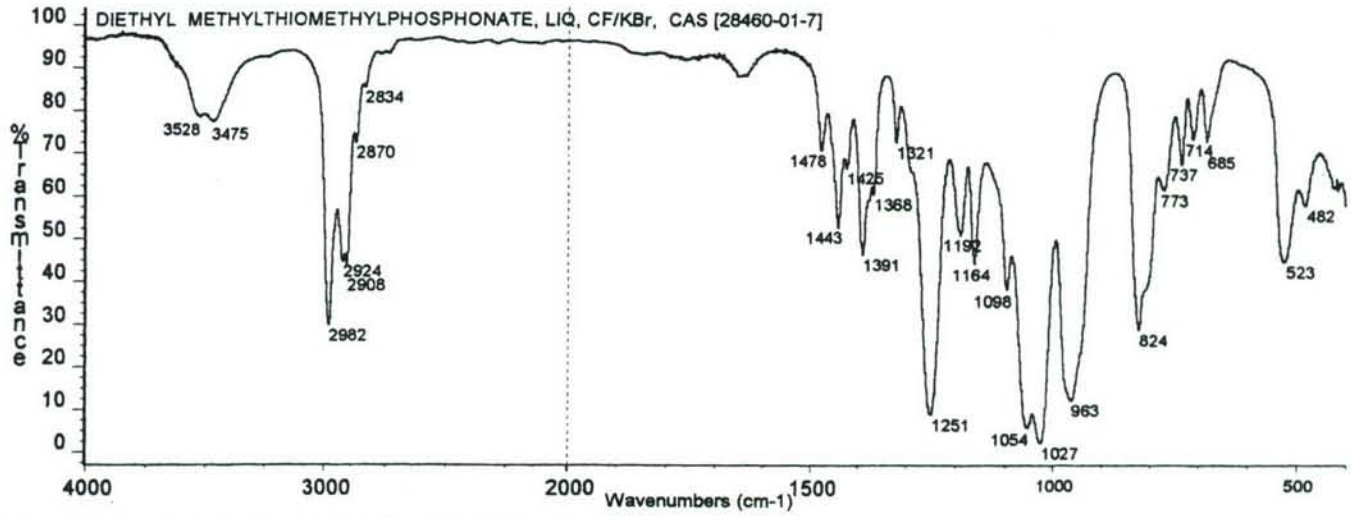


Figure 225 DIETHYL METHYLTHIOMETHYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.29 Diethyl Ethylthiomethylphosphonate CH_3-CH_2-S-CH_2-P=O(O-CH_2-CH_3)$_2$

The infrared spectrum of a liquid film of diethyl ethylthiomethylphosphonate between KBr windows is reproduced as ***Figure 226***. The band assignments are as follows: 3478 cm^{-1} vvw (H_2O), 2979 cm^{-1} m (ν_{as}

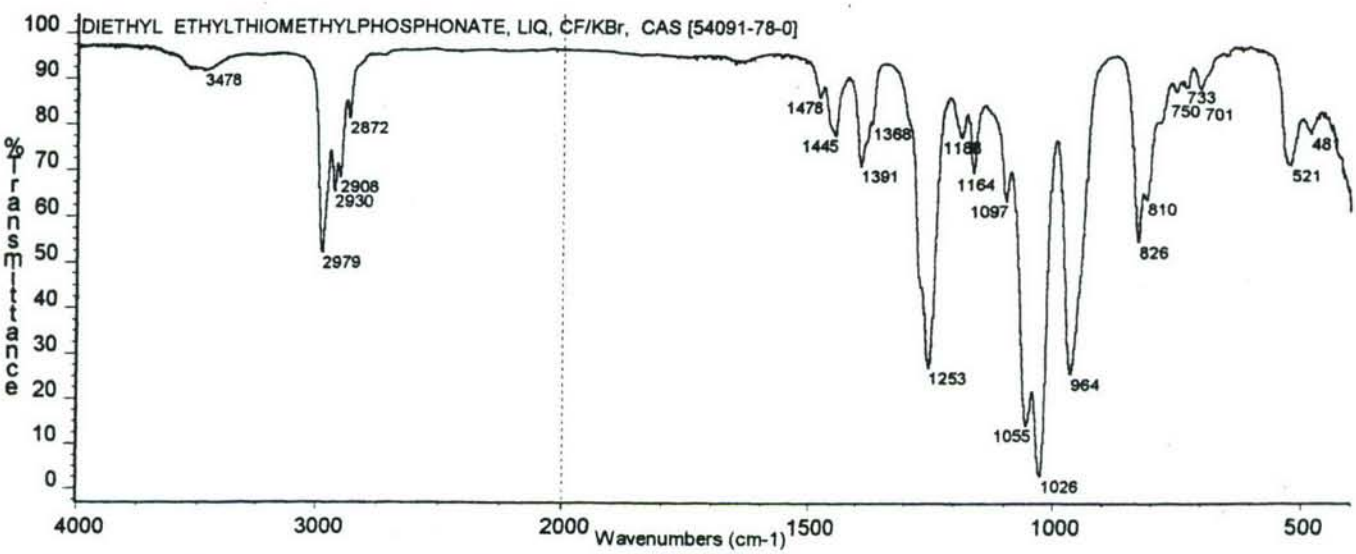


Figure 226 DIETHYL ETHYLTHIOMETHYLPHOSPHONATE, LIQUID, CF/KBr

CH_3), 2930 cm^{-1} w (ν_{as} CH_2), 2908 cm^{-1} w (ν_{sy} CH_3), 2872 cm^{-1} vw (ν_{sy} CH_2), 1478 cm^{-1} vvw (δ OCH_2), 1445 cm^{-1} vw (δ_{as} CH_3), 1391 cm^{-1} (ω OCH_2), 1368 cm^{-1} sh (δ_{sy} CH_3), ca 1269 cm^{-1} sh (ω S-CH_2), 1253 cm^{-1} ms (ν P=O), 1164 and 1097 cm^{-1} w (CH_3 rock of POEt, characteristic), 1055 and 1026 cm^{-1} s (ν P-O-C), 964 cm^{-1} ms (ν C-C of POEt), 826 cm^{-1} m and 810 cm^{-1} w (POC), 750 cm^{-1} vvw (CH_2 rock ?), 733 cm^{-1} vvw (ν P-C ?), 701 cm^{-1} vvw (ν C-S-C), 521 cm^{-1} w (P=O deformation).

3.5.8.30 Diethyl Phenylthiomethylphosphonate C_6H_5-S-CH_2-P=O(O-CH_2-CH_3)$_2$

The infrared spectrum of a liquid film of diethyl phenylthiomethylphosphonate between KBr windows is given in ***Figure 227***. The band assignments are as follows: 3470 cm^{-1} vvw (H_2O), 3057 cm^{-1} vw (ν C-H aromatic), 2981 cm^{-1} m (ν_{as} CH_3), 2928 cm^{-1} vw (ν_{as} CH_2), 2907 cm^{-1} w (ν_{sy} CH_3), 2868 cm^{-1} vvw (ν_{sy} CH_2), 1582 cm^{-1} w, 1481 and 1439 cm^{-1} m (aromatic ring), 1392 cm^{-1} w (ω OCH_2), 1368 cm^{-1} w (δ_{sy} CH_3), ca 1290 cm^{-1} sh (ω S-CH_2), 1255 cm^{-1} ms (ν P=O), 1189 cm^{-1} w (CH_2),[hh] 1163 and 1097 cm^{-1} w (CH_3 rock of POEt, characteristic), 1088 cm^{-1} sh (phenyl-S), 1053 and 1025 cm^{-1} s (ν P-O-C), 967 cm^{-1} ms (ν C-C of POEt), 827 and 809 cm^{-1} m (POC), 742 cm^{-1} m (γ C-H mono-substituted aromatic ring), 691 cm^{-1} m (δ mono-substituted aromatic ring),

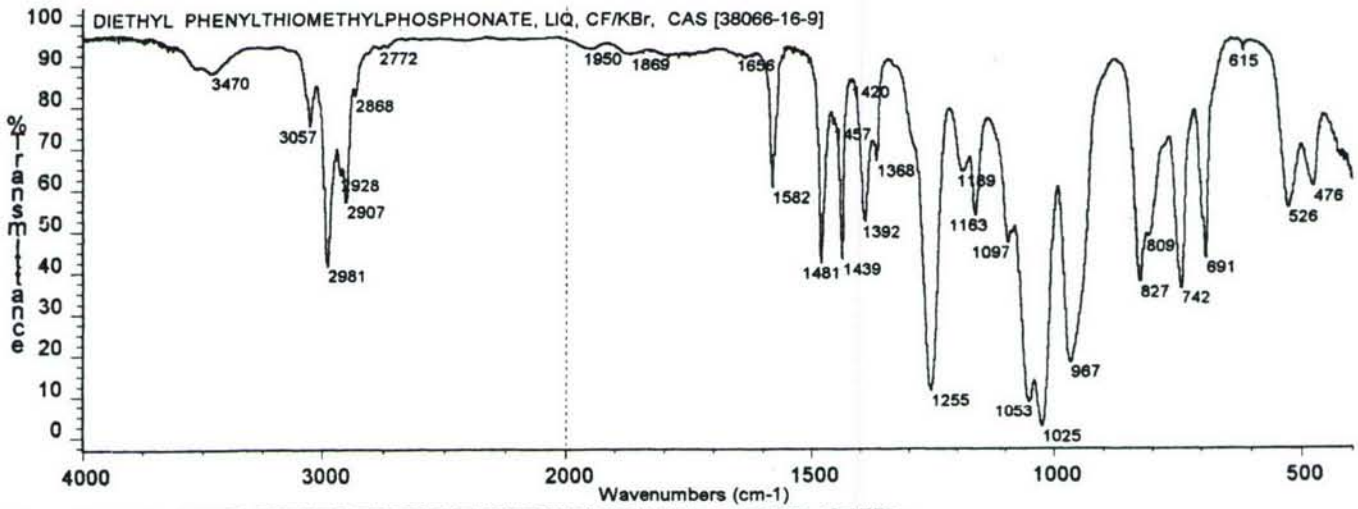


Figure 227 DIETHYL PHENYLTHIOMETHYLPHOSPHONATE, LIQUID, CF/KBr

[hh] The three compounds comprising ***Figures 225, 226*** and ***227*** containing the S-CH_2-P=O$(OEt)_2$ moiety have a weak band in the range 1192-1188 cm^{-1}. This band is in addition to the two bands due to the CH_3 rock of the POEt moiety near 1165 and 1100 cm^{-1}. Too few compounds have been examined to see if this is characteristic. However,this band would fall in the range of the CH_3 rock from a $POCH_3$ moiety (1190-1170 cm^{-1}) as is the case for the compound represented by ***Figure 224***, which contains the P$(OCH_3)_2$ entity.

3.5.8.31 Diethyl Pyrrolidinomethylphosphonate $C_4H_8N\text{-}CH_2\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum for diethyl pyrrolidinomethylphosphonate as a liquid film between KBr windows is given as ***Figure 228***. The band assignments are as follows: 2976 cm^{-1} ms, 2934 cm^{-1} sh, 2908 cm^{-1} sh, 2877 cm^{-1} m (ν CH_3 and ν CH_2), 2786 cm^{-1} m (ν N-CH_2), 1479 cm^{-1} w (δ OCH_2), 1461 and 1444 cm^{-1} w (δ CH_2 and δ_{as} CH_3), 1413 cm^{-1} w (δ P-CH_2), 1391 cm^{-1} m (ω OCH_2), 1366 cm^{-1} w (δ_{sy} CH_3), 1259 cm^{-1} ms (ν P=O), 1164 and 1097 cm^{-1} m (CH_3 rock of POEt, characteristic), 1058 and 1029 cm^{-1} s (ν P-O-C), 964 cm^{-1} ms (ν C-C of POEt), 809 and 780 cm^{-1} m (POC), 543 cm^{-1} m (P=O deformation).

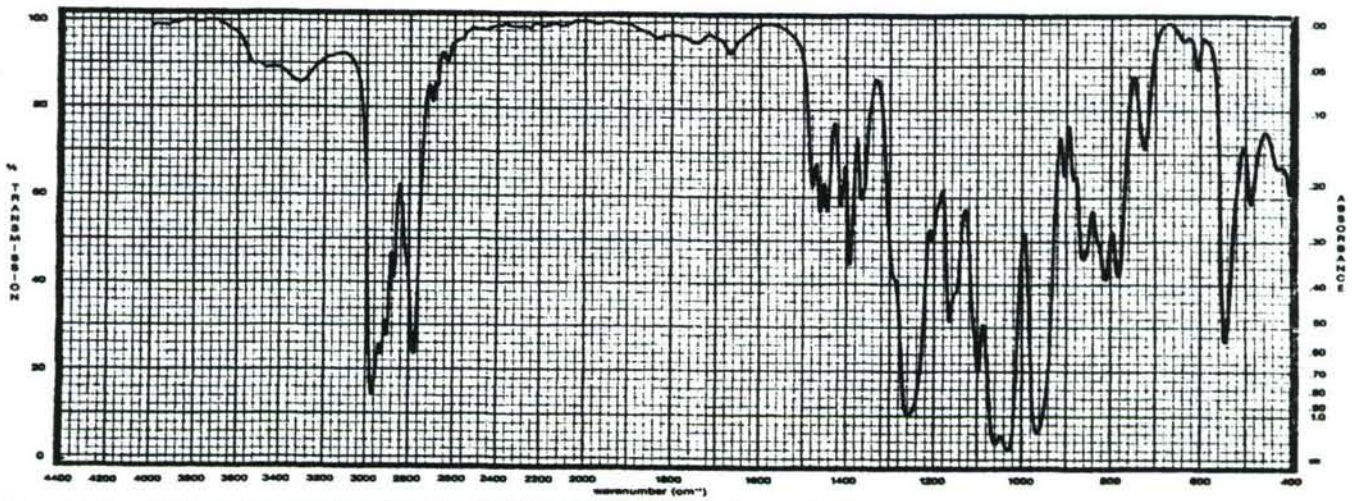


Figure 228 DIETHYL PYRROLIDINOMETHYLPHOSPHONATE, 96%, LIQUID, CF/KBr

3.5.8.32 Bis(2,2,2-trifluoroethyl) (Methoxycarbonylmethyl)phosphonate $CH_3O\text{-}C(=O)\text{-}CH_2\text{-}P{=}O(O\text{-}CH2\text{-}CF_3)$

The infrared spectrum of bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate as a liquid film between KBr windows is presented as ***Figure 229***. The band assignments are as follows: 3470 cm^{-1} vw (H_2O), 3010 cm^{-1} sh, 2975 cm^{-1} m, 2938 cm^{-1} sh, 2854 cm^{-1} vw (ν CH_3 and ν CH_2), 1745 cm^{-1} s (ν C=O), 1456 cm^{-1} sh and 1441 cm^{-1} ms (δ_{as} and δ_{sy} CH_3), 1420 ms (δ CH_2), 1402 cm^{-1} sh (ω OCH_2 ?), 1299 cm^{-1} s (CF_3), 1266 cm^{-1} s (ν P=O and ν C-O ester), 1174 cm^{-1} s (CF_3), 1102 and 1073 cm^{-1} s (ν P-O-C), 964 cm^{-1} ms (ν C-C), 880 and 845 cm^{-1} m (POC), 657 cm^{-1} m (CF_3 ?), 555 cm^{-1} m (P=O deformation).

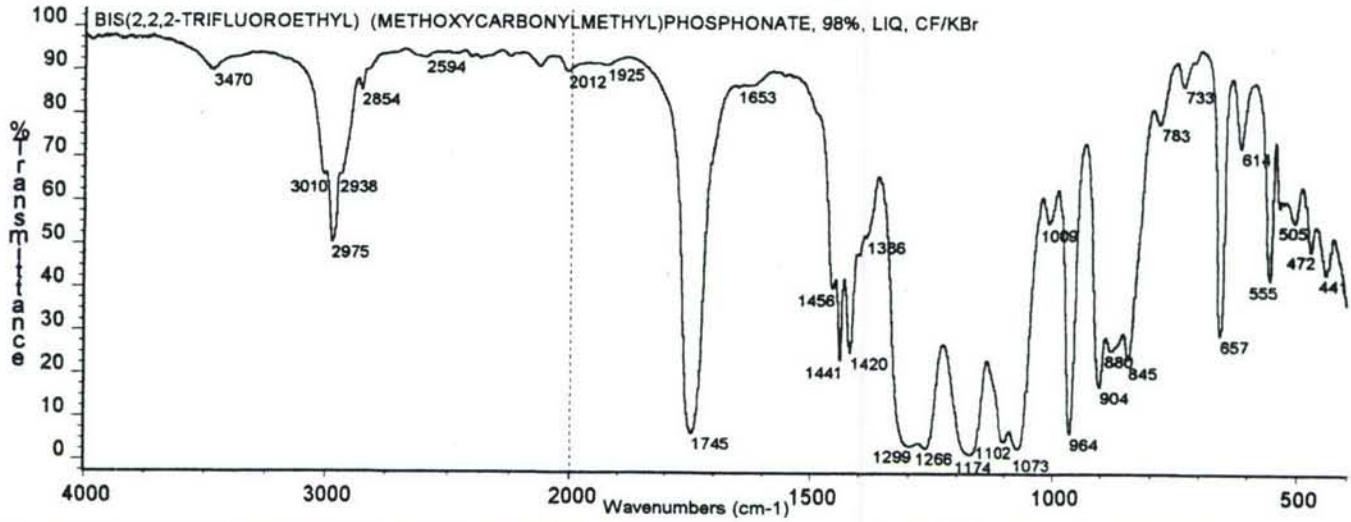


Figure 229 BIS(2,2,2-TRIFLUOROETHYL) (METHOXYCARBONYLMETHYL)PHOSPHONATE, 98%, LIQUID, CF/KBr

3.5.8.33 Diethyl (Trimethylsilyloxycarbonylmethyl)phosphonate $(CH_3)_3Si\text{-}O\text{-}C(=O)\text{-}CH_2\text{-}P=O(OCH_2CH_3)_2$

The infrared spectrum of diethyl (trimethylsilyloxycarbonylmethyl)phosphonate (or trimethylsilyl P,P-diethylphosphonoacetate), as a liquid film between KBr windows, is given in ***Figure 230***. The band assignments are as follows: 3410 cm^{-1} vw (H_2O), 2983 cm^{-1} ms, 2964 cm^{-1} sh, 2934 cm^{-1} sh, 2908 cm^{-1} m and 2874 cm^{-1} sh (ν CH_3 and ν CH_2), 2634 and 2503 cm^{-1} vw (together with some broadness in the 3000 cm^{-1} region indicates COOH, carboxylic acid from hydrolysis), 1721 cm^{-1} s (ν C=O), 1480 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1394 cm^{-1} m (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1287 cm^{-1} s (δ_{sy} $SiCH_3$), 1255 cm^{-1} (ν P=O), 1215 cm^{-1} w (ω CH_2 ?), 1165 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1056 and 1028 cm^{-1} s (ν P-O-C), 969 cm^{-1} ms (ν C-C of POEt), 853 cm^{-1} s and 765 cm^{-1} m [CH_3 rock and ν Si-C fron $Si(CH_3)_3$].

The effect of atmospheric moisture on diethyl (trimethylsilyloxycarbonylmethyl)phosphonate is illustrated by the spectra in ***Figures 231A*** through ***231C***. After 22 hours of exposure to atmospheric moisture the spectrum (***Figure 231A***) shows an increase in the intensities of the COOH bands near 3000, 2633 and 2527 cm^{-1}, while the bands indicative of the $Si(CH_3)_3$ moiety (1287, 853 and 765 cm^{-1}) show a corresponding decrease in intensity. By 27 hours of exposure (***Figure 231B***), the bands indicative of a carboxylic acid moiety are even more pronounced. A broad band near 1235 cm^{-1} has replaced the original two bands at 1297 and 1255 cm^{-1}. This

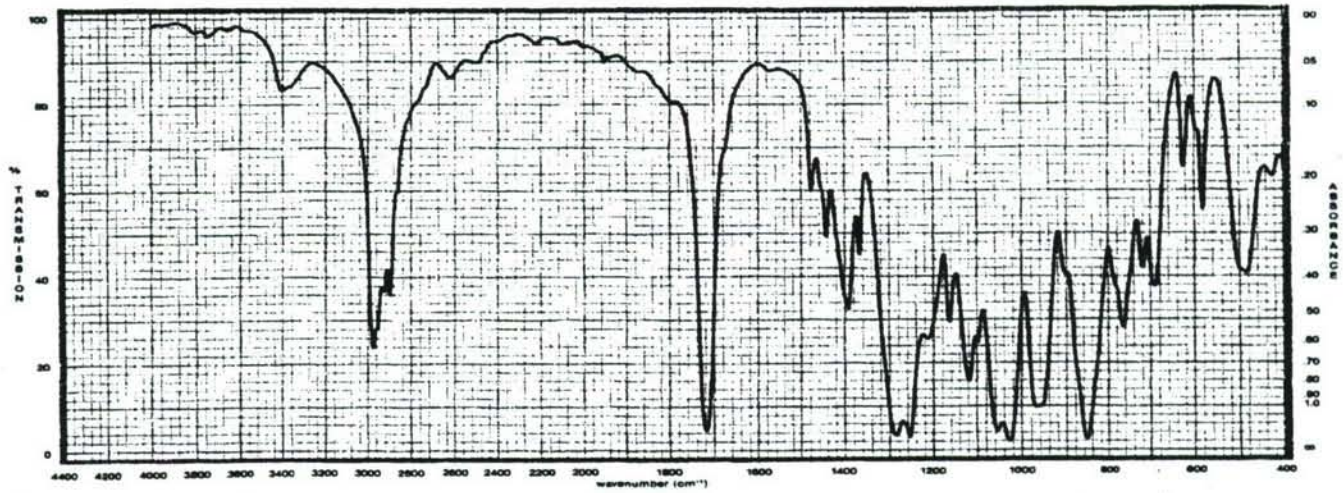


Figure 230 DIETHYL (TRIMETHYLSILYLOXYCARBONYLMETHYL)PHOSPHONATE, LIQUID, CF/KBr

Figure 231A DIETHYL (TRIMETHYLSILYLOXYCARBONYLMETHYL)PHOSPHONATE, LIQUID, CF/KBr, AFTER 22 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

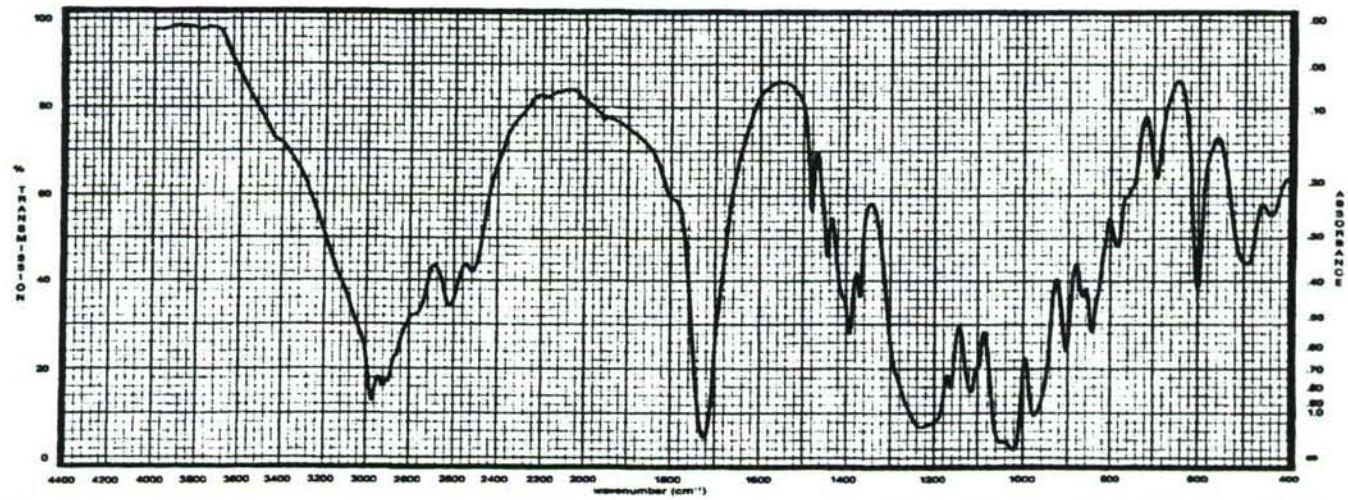


Figure 231B DIETHYL (TRIMETHYLSILYLOXYCARBONYLMETHYL)PHOSPHONATE, LIQUID, CF/KBr, AFTER 27 HOURS OF EXPOSURE TO ATMOSPHERIC MOISTURE

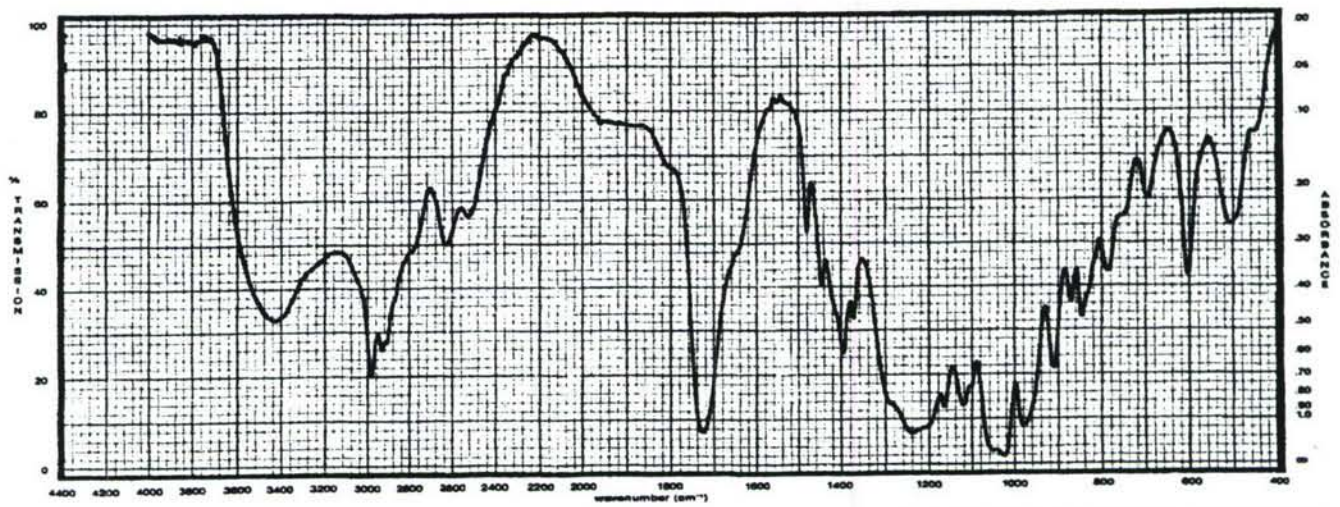


Figure 231C DIETHYL (TRIMETHYLSILYLOXYCARBONYLMETHYL)PHOSPHONATE, LIQUID, CF/KBr, AFTER 116 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

broad band may be assigned in part to the P=O stretching vibration and the carboxylic acid C-O stretch. After 116 days of exposure to atmospheric moisture (***Figure 231C***) the spectrum still shows the presence of a carboxylic acid moiety together with the $-P=O(OEt)_2$ moiety along with a larger amount of water (ca 3420 and ca 1650 cm^{-1}). The hydrolysis may be depicted as follows:

$(CH_3)_3Si\text{-}O\text{-}C(=O)\text{-}CH_2\text{-}P=O(OCH_2CH_3)_2$ $\xrightarrow{-HOH}$ $HO\text{-}C(=O)\text{-}CH_2\text{-}P=O(OCH_2CH_3)_2 + (CH_3)_3Si\text{-}OH$

3.5.8.34 Diisopropyl Cyanomethylphosphonate $N\equiv C\text{-}CH_2\text{-}P=O[O\text{-}CH(CH_3)_2]_2$

The infrared spectrum of a liquid film of diisopropyl cyanomethylphosphonate between KBr windows is given as ***Figure 232***. The band assignments are as follows: 3481 cm^{-1} vw (H_2O), 3204 cm^{-1} vvw (2254 + 952 = 3206 cm^{-1} ?), 2983 cm^{-1} ms, 2936 cm^{-1} m and 2904 cm^{-1} w (ν CH_3 and ν C-H), 2254 cm^{-1} w (ν C≡N), 1467 and 1455 cm^{-1} w (δ CH_2 and δ_{as} CH_3 1388 and 1378 cm^{-1} ms (δ_{sy} CH_3), 1356 cm^{-1} vw (δ -C-H), 1268 cm^{-1} ms (ν P=O), 1231 cm^{-1} (ω CH2), 1179 and 1143 cm^{-1} w and 1104 cm^{-1} m (triplet characteristic of POisopropyl), 995 cm^{-1} s (ν P-O-C), 952 cm^{-1} w (ν C-C of $N\equiv C\text{-}CH_2\text{-}P$?), 901 and 889 cm^{-1} w (CH_3 rock, isopropyl group), 795 and 774 cm^{-1} w (POC), 707 cm^{-1} w (ν P-C), 559 cm^{-1} w (P=O deformation).

The effect of atmospheric moisture on diisopropyl cyanomethylphosphonte is depicted in ***Figure 233***.

The spectrum after 205 days of exposure to atmospheric moisture is essentially the same as that of the first scan except for the water pick-up as indicated by the bands at 3472 and 1650 cm^{-1}.

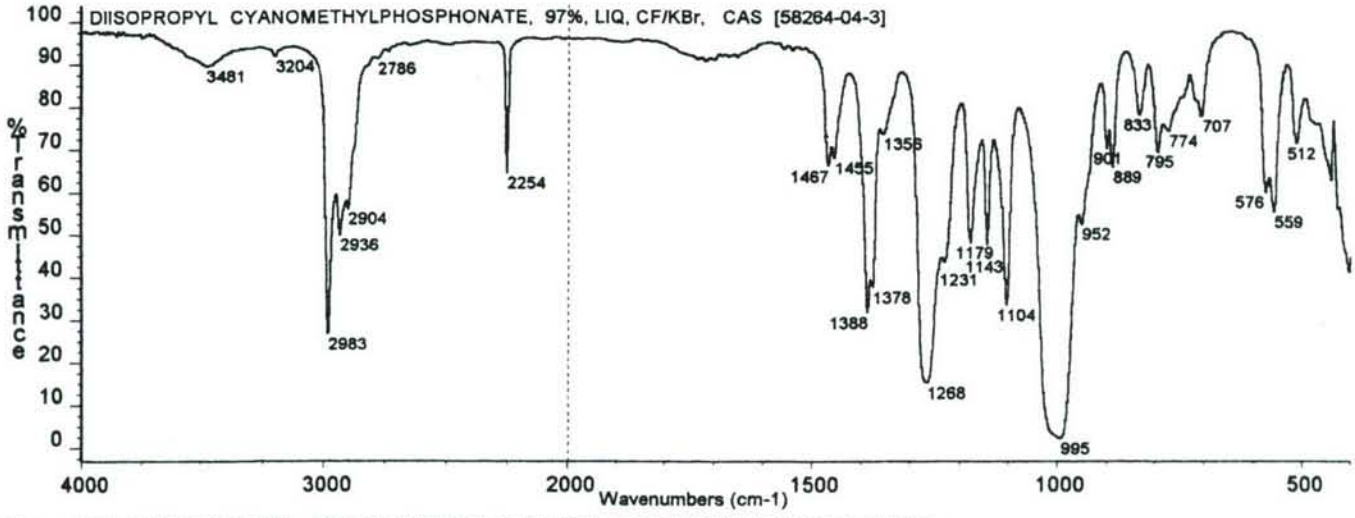


Figure 232 DIISOPROPYL CYANOMETHYLPHOSPHONATE, 97%, LIQUID, CF/KBr

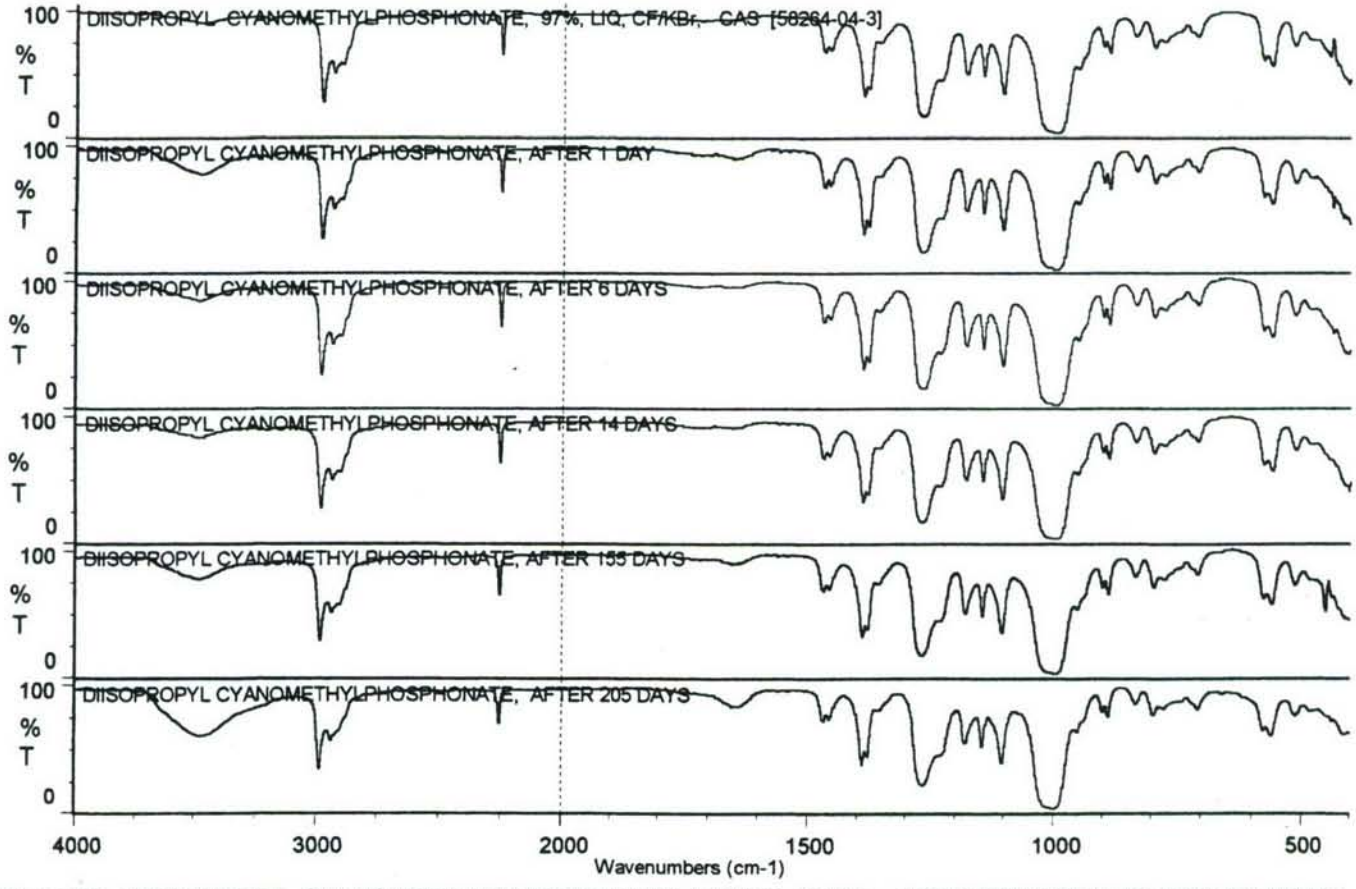


Figure 233 DIISOPROPYL CYANOMETHYLPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.8.35 Dimethyl 2-Hydroxyethylphosphonate $HO\text{-}CH_2\text{-}CH_2\text{-}P{=}O(O\text{-}CH_3)_2$

The infrared spectrum of dimethyl 2-hydroxyethylphosphonate as a liquid film between KBr discs (windows) is reproduced as ***Figure 234***. The band assignments are as follows 3376 cm^{-1} ms (ν O-H), 2957 cm^{-1} m, 2892 cm^{-1} vw and 2854 cm^{-1} w (ν CH_3 and ν CH_2), 1463 cm^{-1} w (δ CH_3), 1397 cm^{-1} vw (δ CH_2, β OH), 1310 cm^{-1} vw (ω CH_2), 1243 cm^{-1} ms (ν P=O), 1186 cm^{-1} w (CH_3 rock of $POCH_3$, characteristic), 1037 cm^{-1} s (ν P-O-C and ν C-O, alcohol), 843 and 821 cm^{-1} m (POC), 642 cm^{-1} vw (γ OH), 546 cm^{-1} m (P=O deformation).

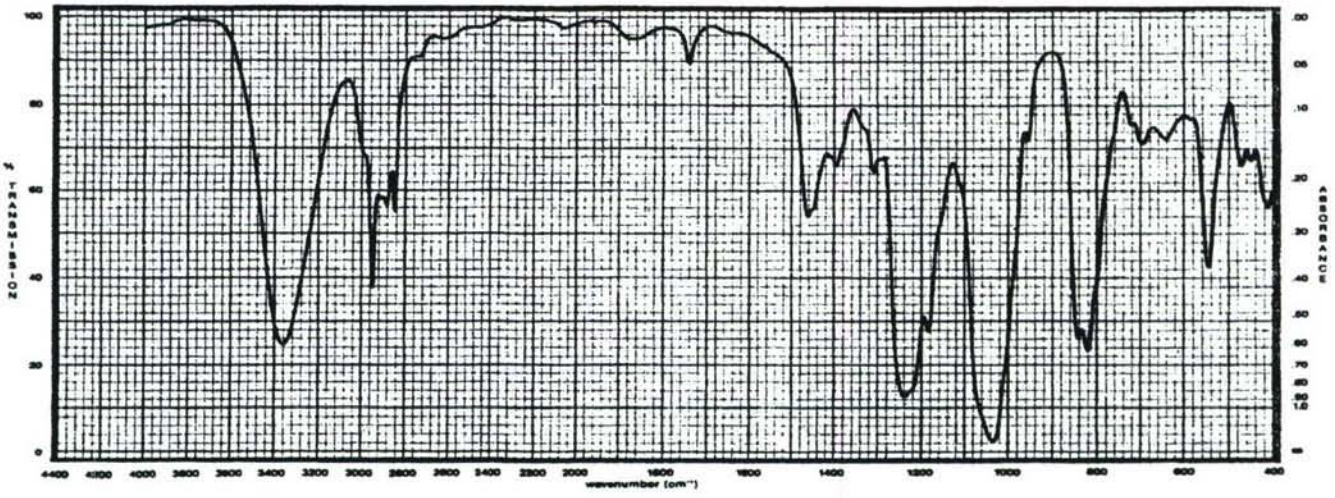


Figure 234 DIMETHYL 2-HYDROXYETHYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.36 Diethyl Trichloromethylphosphonate $Cl_3C\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of a liquid film of diethyl trichloromethylphosphonate between KBr windows is given in ***Figure 235***. The band assignments are as follows: 2984 cm^{-1} w (ν_{as} CH_3), 2933 cm^{-1} vw (ν_{as} CH_2), 2914 cm^{-1} vw (ν_{sy} CH_3), 2870 cm^{-1} vvw (ν_{sy} CH_2), 1477 cm^{-1} vw (δ OCH_2), 1443 cm^{-1} vw (δ_{as} CH_3), 1393 cm^{-1} w (ω OCH_2), 1370 cm^{-1} vw (δ_{sy} CH_3), 1277 cm^{-1} ms (ν P=O), 1163 and 1097 cm^{-1} w (CH_3 rock of POEt, characteristic), 1050 and 1022 cm^{-1} s (ν P-O-C), 982 and 970 w (ν C-C of POEt), 810 cm^{-1} vw (POC), 764 cm^{-1} m (ν CCl_3), 555 cm^{-1} m (P=O deformation).

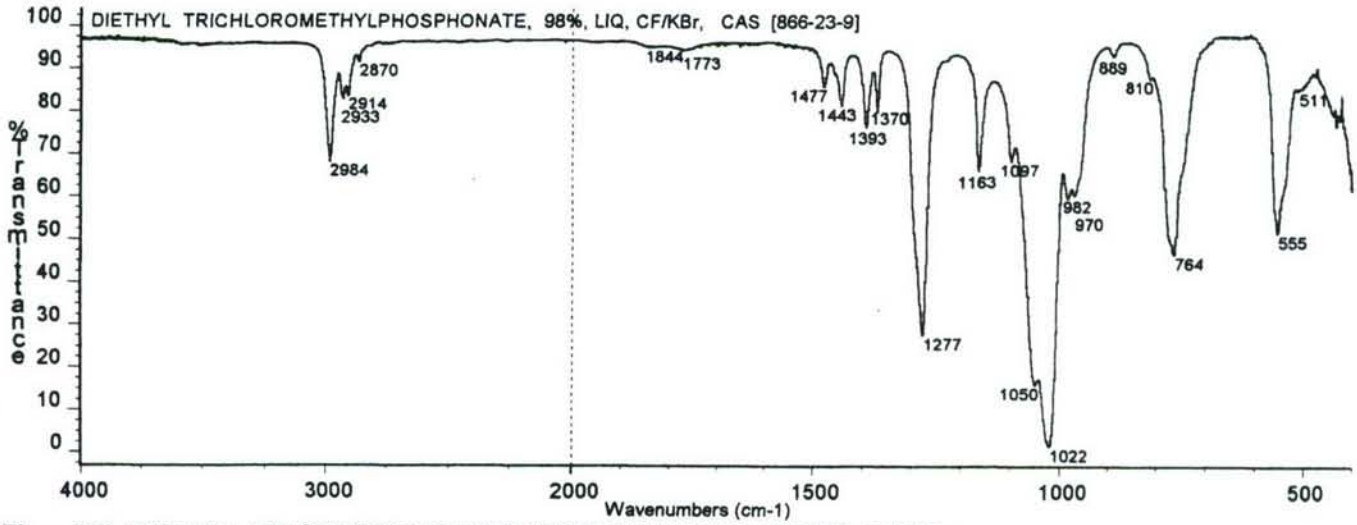


Figure 235 DIETHYL TRICHLOROMETHYLPHOSPHONATE, 98%, LIQUID, CF/KBr

3.5.8.37 Diethyl Cyanophosphonate (Diethylphosphoryl Cyanide) $N\equiv C-P=O(O-CH_2-CH_3)_2$

The infrared spectrum of a liquid film of diethyl cyanophosphonate (diethylphosphoryl cyanide) between KBr windows is presented as ***Figure 236***. The band assignments are as follows: 2990 cm^{-1} m (ν_{as} CH_3), 2941 cm^{-1} w (ν_{as} CH_2), 2914 cm^{-1} w (ν_{sy} CH_3), 2874 cm^{-1} vw (ν_{sy} CH_2), 2208 cm^{-1} m (ν C≡N), 2084 cm^{-1} vvw (ν C≡N of HCN), 1830 cm^{-1} vw (1027 + 798 = 1825 cm^{-1} ?), 1792 cm^{-1} vw (1027 + 761 = 1788 cm^{-1} ?), 1479 cm^{-1} w (δ OCH_2), 1446 cm^{-1} w (δ_{as} CH_3), 1395 cm^{-1} m (ω OCH_2), 1378 cm^{-1} m (δ_{sy} CH_3), 1304 cm^{-1} ms (ν P=O), 1165 and 1101 cm^{-1} m (CH_3 rock of POEt, characteristic), 1027 cm^{-1} s (ν P-O-C), 971 cm^{-1} sh (ν C-C of POEt), 798 and 761 cm^{-1} m (POC), 649 cm^{-1} sh and 619 cm^{-1} m (ν P-C, O=P-C≡N bending ?).

The effect of atmospheric moisture on a thin film of diethyl cyanophosphonate is illustrated by the infrared spectra given in ***Figures 237A***, ***237B*** and ***237C***. After a period of 1-6 hours of exposure to atmospheric moisture, the spectra show the formation of POH bands near 2600, 2300 and 1680 cm^{-1}. By 24-29 hours of exposure the ν C≡N band at 2208 cm^{-1} has become extremely weak and the spectrum resembles that of mainly a P-acid, with the P=O stretching band having decreased to 1234 cm^{-1}. By 24 hours of exposure (***Figure 237B***), the spectrum shows the absence of any C≡N, and resembles that of a P-acid, probably $HO-P=O(OEt)_2$. The spectra through the 48 days of exposure to atmospheric moisture (***Figure 237C***) remain relatively unchanged

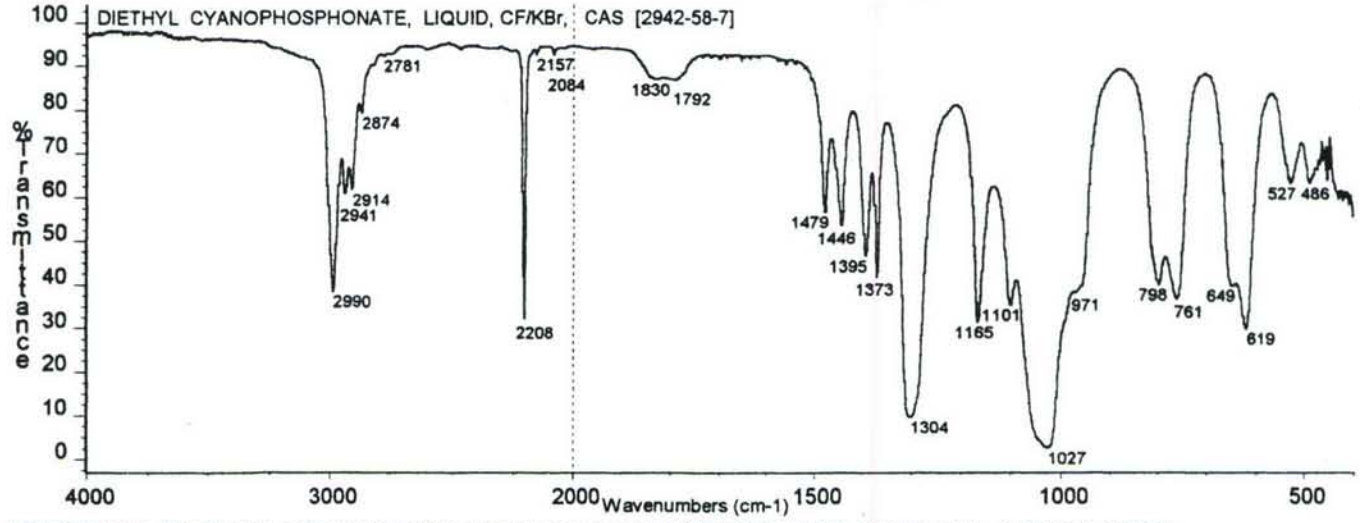


FIGURE 236 DIETHYL CYANOPHOSPHONATE (DIETHYLPHOSPHORYL CYANIDE), LIQUID, CF/KBr

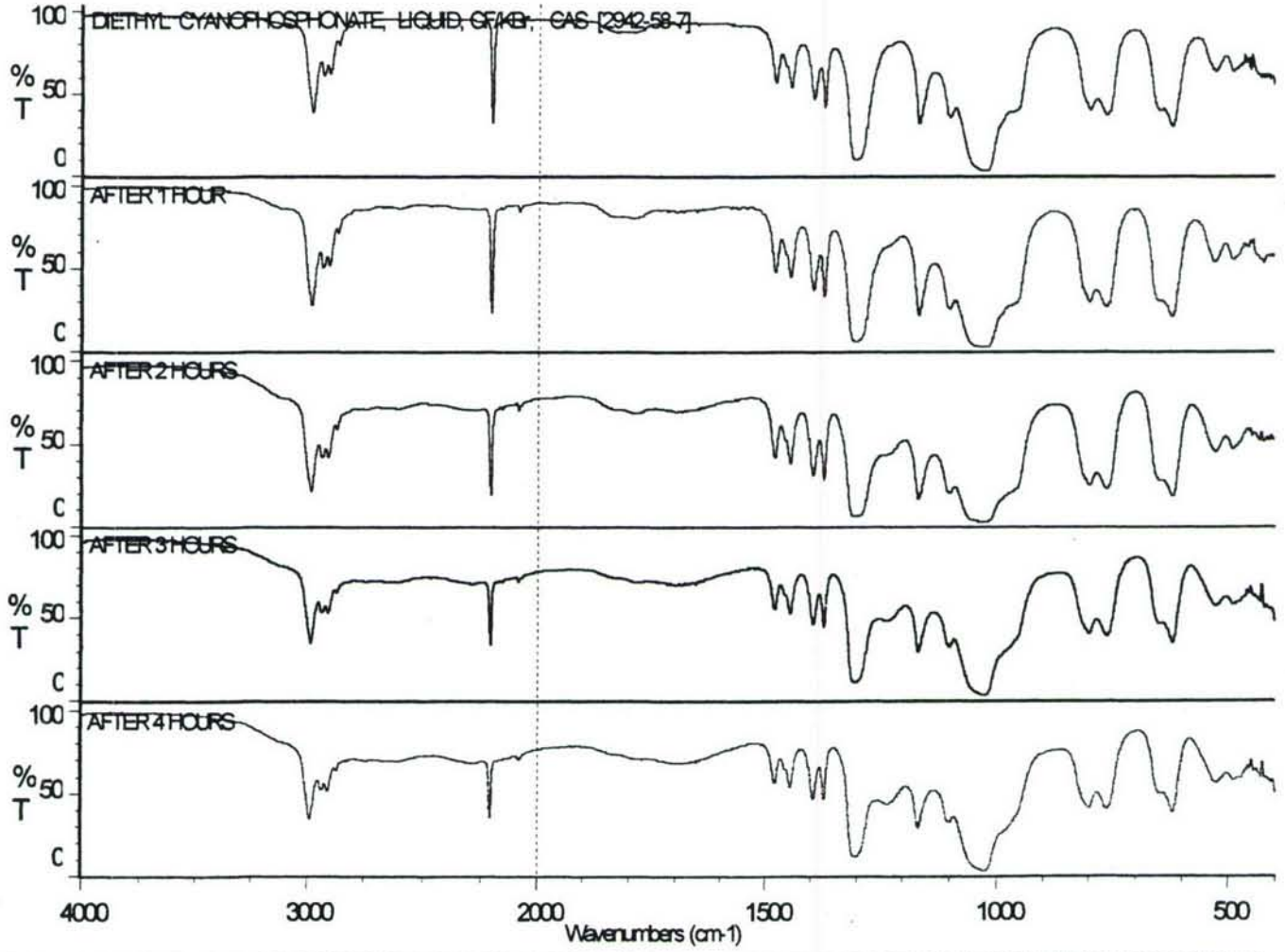


Figure 237A DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

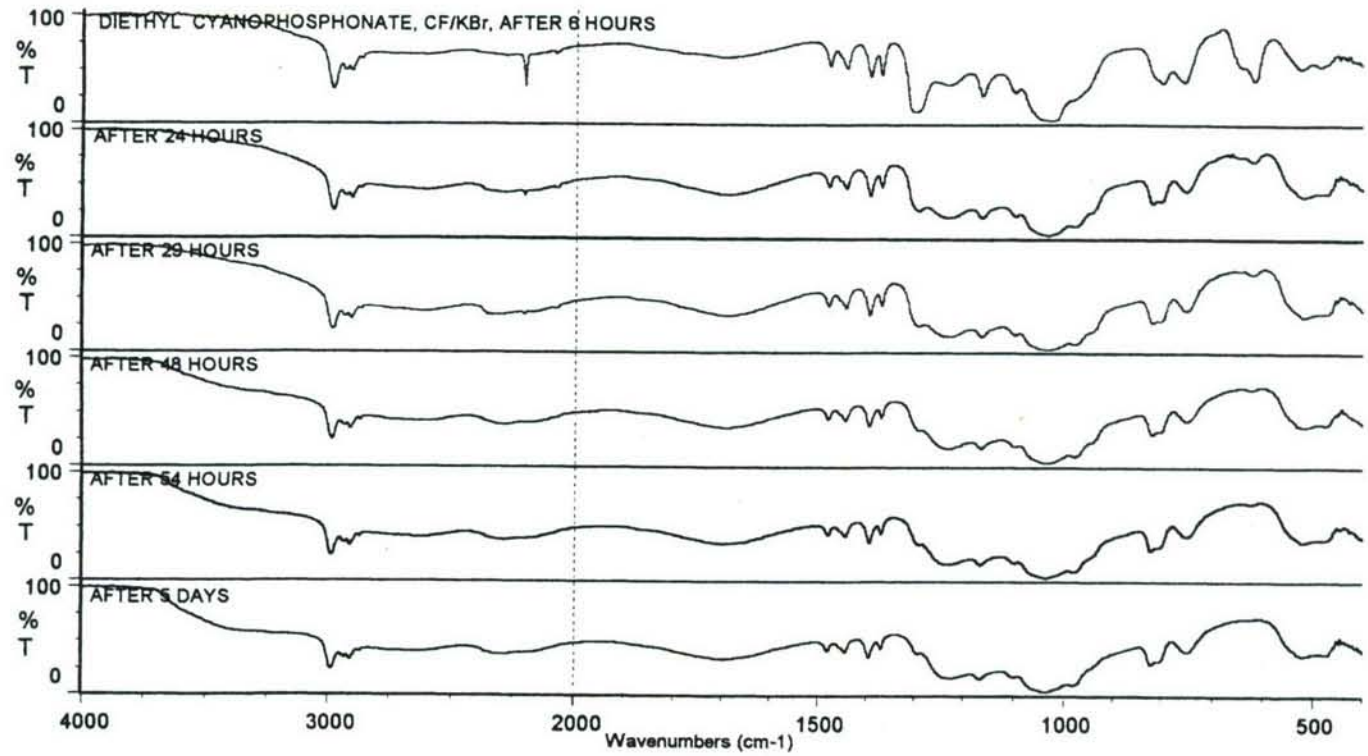


Figure 237B DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

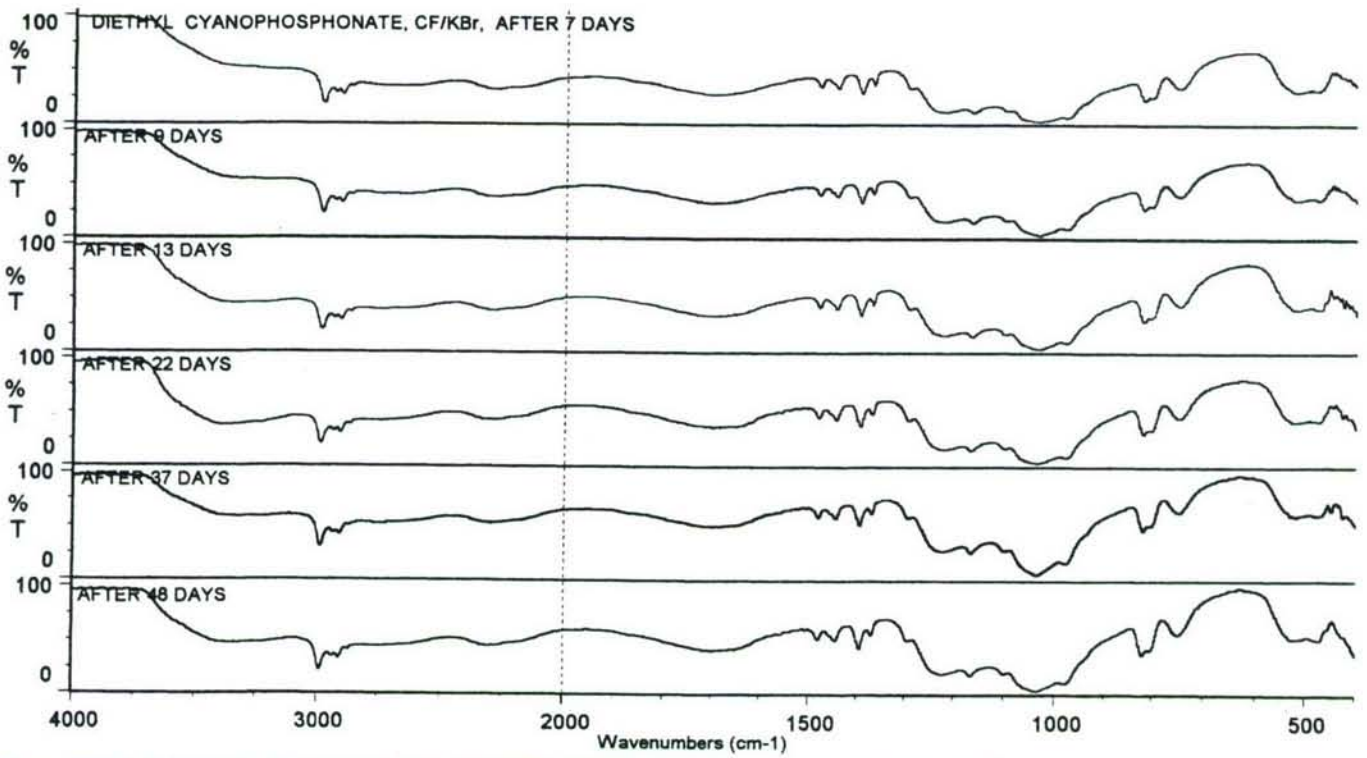


Figure 237C DIETHYL CYANOPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

with the P-acid being the predominant compound. However, a weak band occurs at 1294 cm^{-1} which could possibly be from a pyro compound such as $(EtO)_2P(=O)\text{-}O\text{-}P=O(OEt)_2$, which would have a calculated P=O stretch of 1290 cm^{-1}.

3.5.8.38 Diethyl Ethylphosphonate (**DEEP**) $CH_3\text{-}CH_2\text{-}P=O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of a liquid film of diethyl ethylphosphonate (**DEEP**) between KBr discs (windows) is reproduced as ***Figure 238***. The band assignments are as follows: 3419 cm^{-1} vw (H_2O), 2981 cm^{-1} m (ν_{as} CH_3), 2942 cm^{-1} w (ν_{as} CH_2), 2908 cm^{-1} w (ν_{sy} CH_3), 2887 cm^{-1} w (ν_{sy} CH_2), 1479 cm^{-1} vw (δ OCH_2), 1461 and 1445 cm^{-1} w (δ_{as} CH_3), 1410 cm^{-1} vw (δ CH_2-P), 1392 cm^{-1} w (ω OCH_2), 1368 cm^{-1} vw (δ_{sy} CH_3), 1282 and 1290 cm^{-1} w (ω, τ CH_2), 1251 and 1229 cm^{-1} ms (ν P=O and CH_2), 1164 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1061, 1043, 1026 and 1008 cm^{-1} s (ν P-O-C and ν C-C of P-Ethyl), 959 cm^{-1} ms (ν C-C of POEt), 794 cm^{-1} m (POC), 744 cm^{-1} vw (CH_2 rock of P-Ethyl), 699 cm^{-1} w (ν P-C), 520 and 503 cm^{-1} w (O=P-O bending).

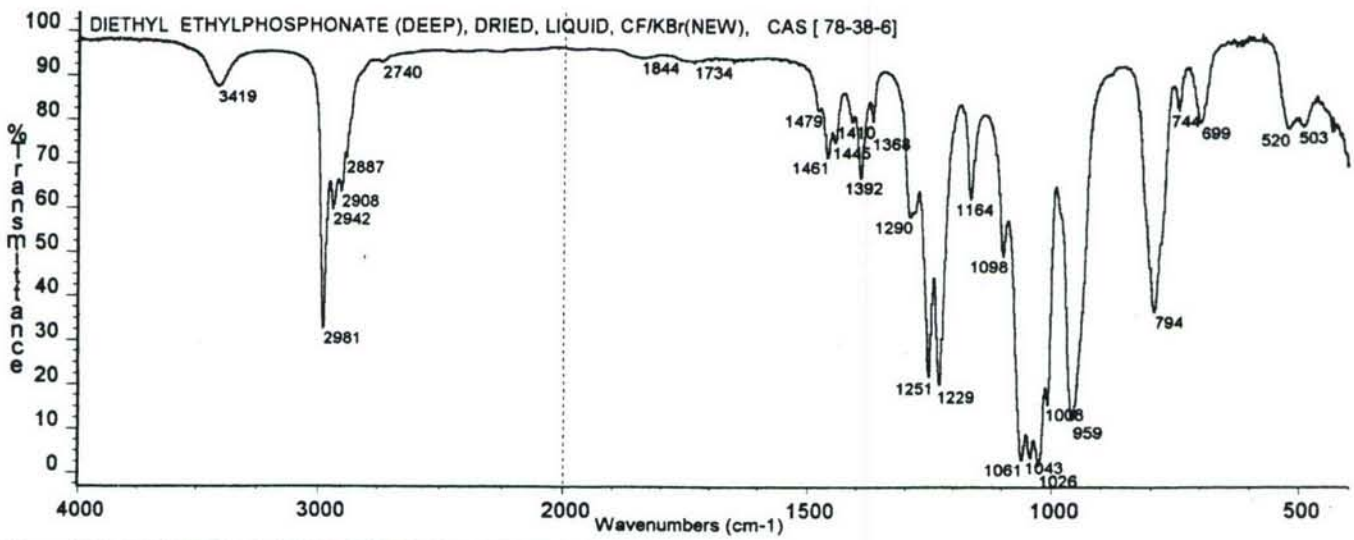


Figure 238 DIETHYL ETHYLPHOSPHONATE (DEEP), LIQUID, CF/KBr

The effect of atmospheric moisture on diethyl ethylphosphonate (**DEEP**) is illustrated by the infrared spectra presented in ***Figures 239A*** and ***239B***. After 13 days of exposure to atmospheric moisture the infrared spectrum (***Figure 239B***) shows some POH bands near 2750 and 2350 cm^{-1}. By the 34th day of exposure, the

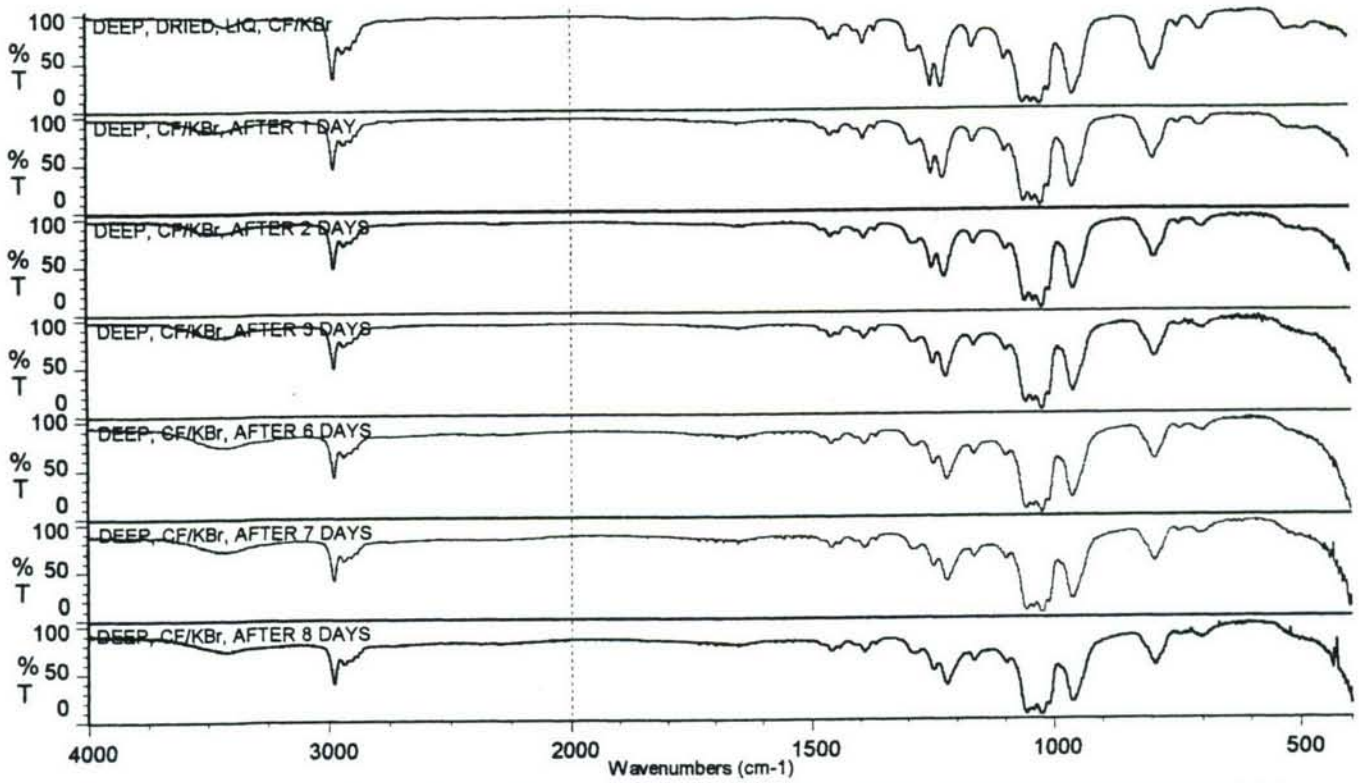


Figure 239A DIETHYL ETHYLPHOSPHONATE (DEEP), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

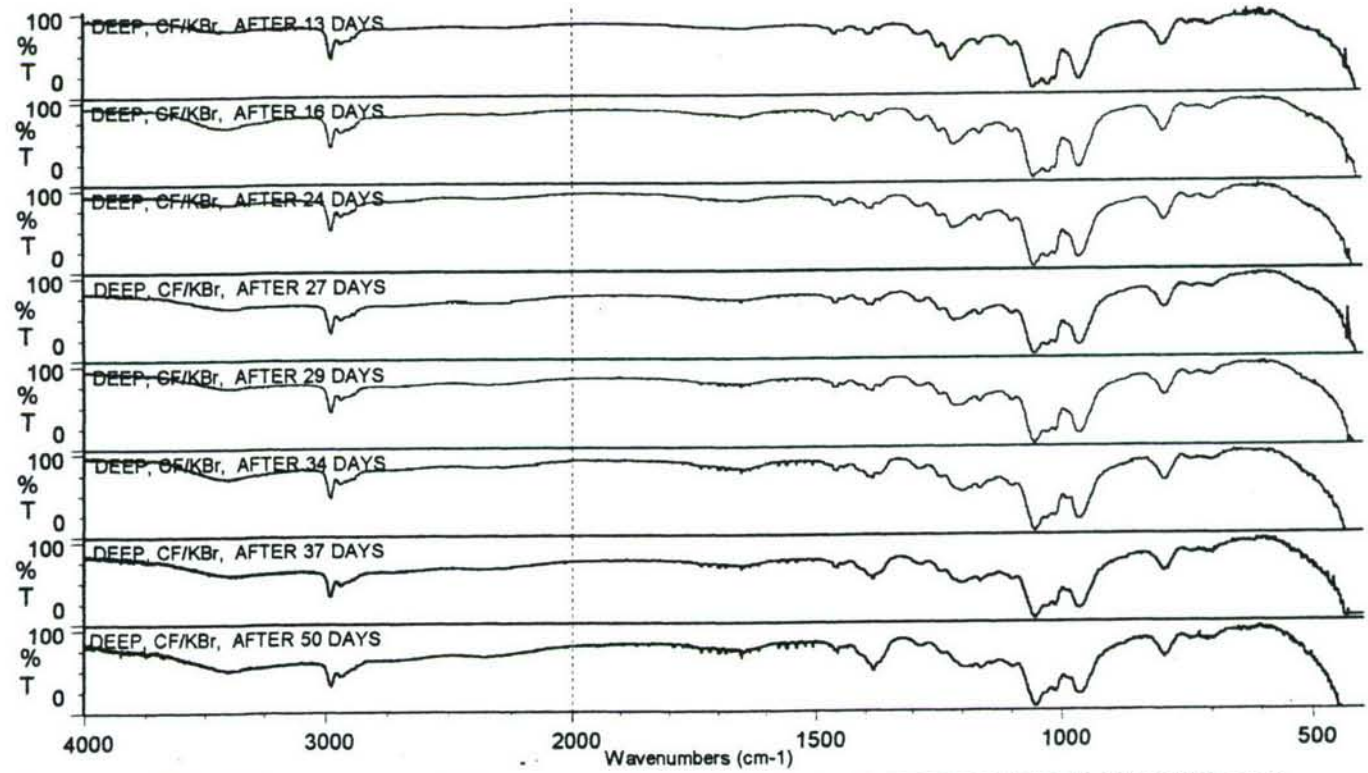


Figure 239B DIETHYL ETHYLPHOSPHONATE (DEEP), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

the infrared spectrum (***Figure 239B***) shows the same POH bands but now the P=O band is more clearly defined near 1201 cm^{-1} as are the P-Et bands near 1287 and 1241 cm^{-1}. A weak shoulder near 986 cm^{-1} may be assigned to the P-O(H) stretch. By the 50th day of exposure to atmospheric moisture the spectrum shows definite POH bands near 2750 and 2350 cm^{-1}, as well as a P=O stretch near 1195 cm^{-1} and the P-O(H) band near 983 cm^{-1}. Bands assignable to the P-Et moiety are visible as 1287 and 1241 cm^{-1}. The compound, **DEEP**, although evaporating while between the KBr windows, does show some hydrolysis to CH_3CH_2-P=O(OH)(OCH_2CH_3), ethyl hydrogen ethylphosphonate (ethyl ethylphosphonic acid). This acid would have a calculated P-O(H) stretching frequency of 984 cm^{-1} (983 cm^{-1} observed value after 50 days). For compounds of the type RP=O(OH)(OR'), Thomas[ii] lists a range of 1225-1170 cm^{-1} for the P=O stretching vibration. The observed P=O stretch of 1195 cm^{-1} is within this range.

3.5.8.39 Dimethyl *n*-Propylphosphonate CH_3-CH_2-CH_2-P=O(O-CH_3)$_2$

The infrared spectrum of dimethyl *n*-propylphosphonate as a liquid film between KBr windows is reproduced as ***Figure 240***. The band assignments are as follows: 3529 and 3476 cm^{-1} w (H_2O), 2962 cm^{-1} ms (ν_{as} CH_3), 2910 cm^{-1} sh (ν_{as} CH_2), 2877 cm^{-1} m (ν_{sy} CH_3), 2851 cm^{-1} m (ν_{sy} CH_2), 1465 cm^{-1} m (δ_{as} CH_3), 1408 cm^{-1} w (δ P-CH_2), 1381 cm^{-1} vw (δ_{sy} CH_3), 1258 and 1238 cm^{-1} ms (ν P=O and CH_2 wag, twist, the CH_2-CH_2-P

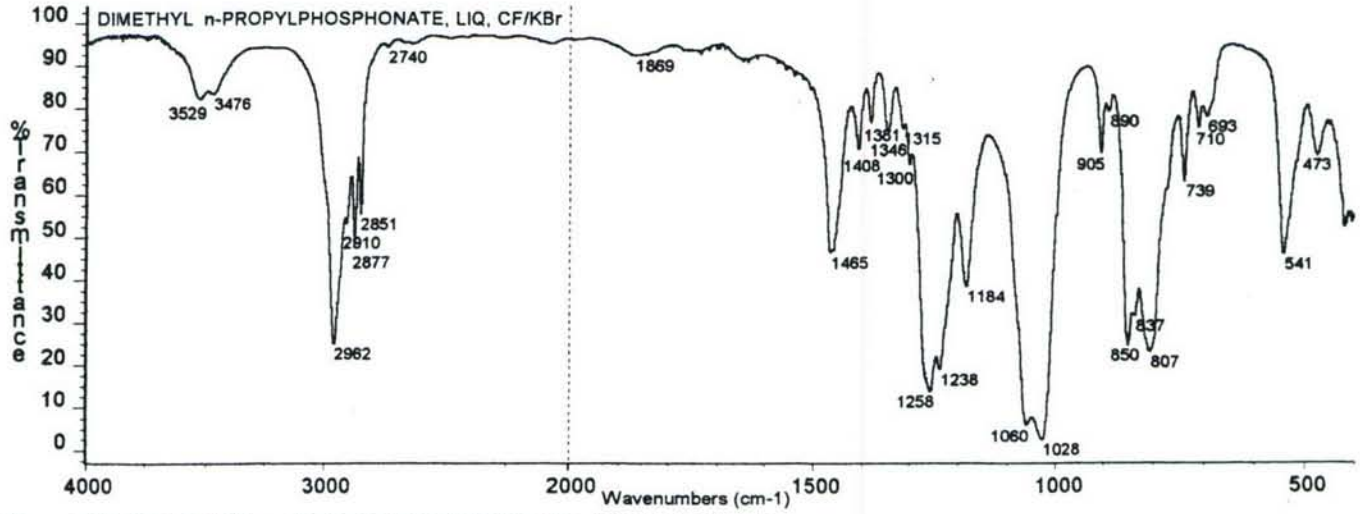


Figure 240 DIMETHYL *n*-PROPYLPHOSPHONATE, LIQUID, CF/KBr

[ii] Thomas, L.C. "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p 13, Heyden & Son Ltd., London, 1974.

moiety may cause the P=O stretching band to split as is the case with P-Et. The calculated value of the ν P=O is 1242 cm^{-1}. The average value for the 1258 and 1238 cm^{-1} bands is 1248 cm^{-1}.), 1184 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1060 and 1028 cm^{-1} s (ν P-O-C and ν C-C of P-propyl), 850 cm^{-1} ms (CH_2 rock), 807 cm^{-1} ms (POC), 710 cm^{-1} vw (ν P-C ?), 541 cm^{-1} m (O=P-X bending ?).

3.5.8.40 Diethyl *n*-Propylphosphonate CH_3-CH_2-CH_2-P=O(O-CH_2-CH_3)$_2$

The infrared spectrum of diethyl *n*-propylphosphonate as a liquid film between KBr windows is given as ***Figure 241***. The band assignments are as follows: 3532 and 3471 cm^{-1} vw (H_2O), 2979 and 2966 cm^{-1} m (ν_{as} CH_3), 2935 cm^{-1} w (ν_{as} CH_2), 2907 cm^{-1} w (ν_{sy} CH_3), 2876 cm^{-1} w (ν_{sy} CH_2), 1478 cm^{-1} sh (δ OCH_2), 1467, 1457 and 1445 cm^{-1} w(δ CH_2, δ_{as} CH_3), 1406 cm^{-1} sh (P-CH_2), 1391 cm^{-1} w (ω OCH_2(, 1368 cm^{-1} vw (δ_{sy} CH_3), 1298 cm^{-1} vw (CH_2), 1255 and 1235 cm^{-1} m (ν P=O and with the 1298 cm^{-1} band ω, τ of CH_2; the calculated value for the ν P=O is 1238 cm^{-1}; the average value of the 1255 and 1235 cm^{-1} bands is 1245 cm^{-1}, this splitting is caused by the P-propyl group), 1164 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1059 and 1026 cm^{-1} s (ν P-O-C), 959 cm^{-1} ms (ν C-C of POEt), 843 cm^{-1} vw (CH_2 rock ?), 803 and 781 cm^{-1} w (POC), 702 cm^{-1} vw (ν P-C), 536 cm^{-1} w (O=P-X bending ?).

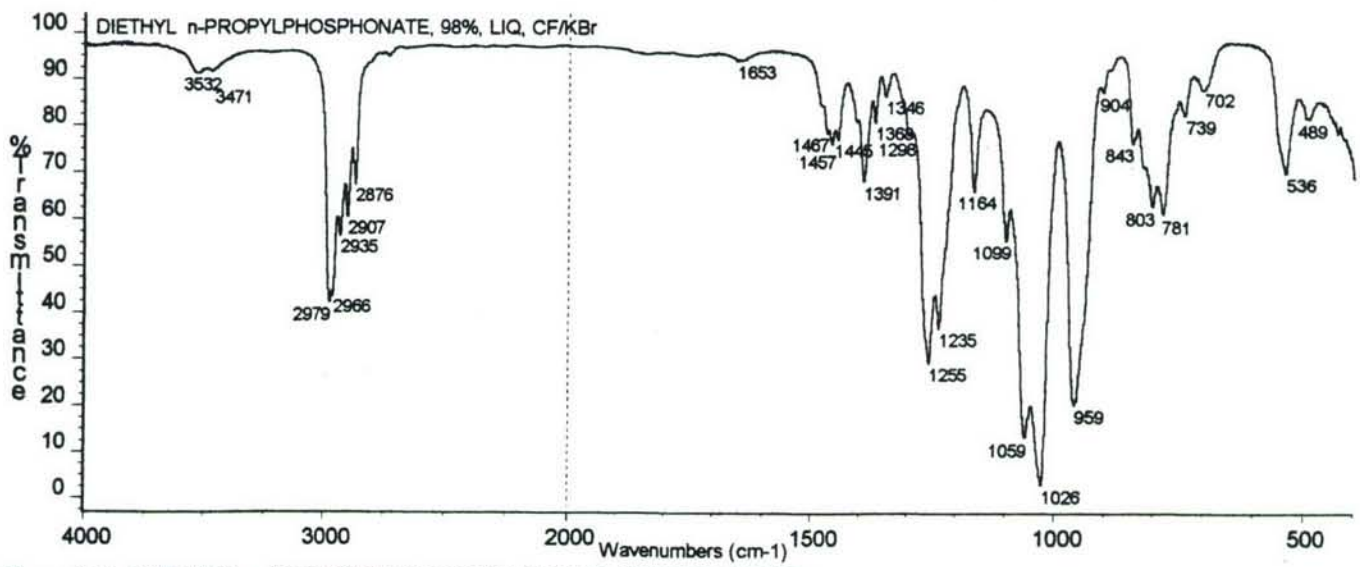


Figure 241 DIETHYL *n*-PROPYLPHOSPHONATE, 98%, LIQUID, CF/KBr

3.5.8.41 Diethyl Isopropylphosphonate $(CH_3)_2CH\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl isopropylphosphonate as a liquid film between KBr windows and as a vapor sample is given as ***Figure 242***. The band assignments for the liquid phase are as follows: 3526 and 3472 cm^{-1} vw (H_2O), 2980 cm^{-1} m (ν_{as} CH_3), 2936 cm^{-1} w (ν_{as} CH_2), 2907 cm^{-1} w (ν_{sy} CH_3), 2877 cm^{-1} w (ν_{sy} CH_2),

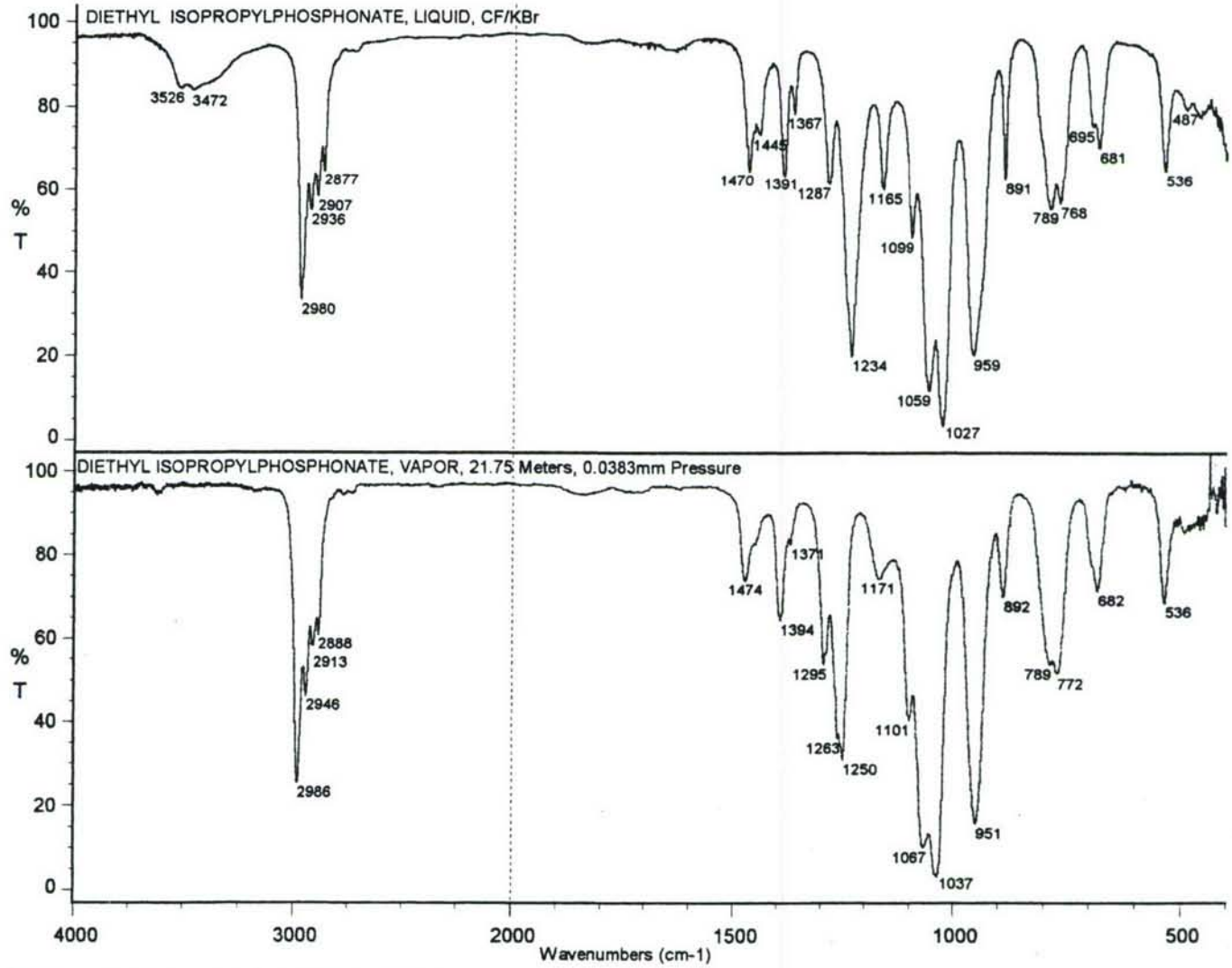


Figure 242 DIETHYL ISOPROPYLPHOSPHONATE, LIQUID, CF/KBr

1470 cm^{-1} w (δ OCH_2), 1445 cm^{-1} vw (δ_{as} CH_3), 1391 cm^{-1} w (ω OCH_2 and δ_{sy} CH_3, isopropyl), 1367 cm^{-1} vw (δ_{sy} CH_3, isopropyl), 1287 cm^{-1} w (P-isopropyl ?), 1234 cm^{-1} ms (ν P=O), 1165 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1059 and 1027 cm^{-1} s (ν P-O-C), 959 cm^{-1} ms (ν C-C of POEt), 891 cm^{-1} w (CH_3 rock of the isopropyl group), 789 and 768 cm^{-1} w (P-O-C), 681 cm^{-1} w (ν P-C), 536 cm^{-1} w (O=P-X bending).

3.5.8.42 Dibutyl Butylphosphonate (**DBBP**) $(H_9C_4\text{-}n)\text{-}P{=}O(O\text{-}n\text{-}C_4H_9)_2$

The infrared spectrum of dibutyl butylphosphonate (**DBBP**) as a liquid film between KBr windows is presented as ***Figure 243***. The band assignments are as follows: 3531 and 3431 cm^{-1} vw (H_2O), 2959 cm^{-1} s (ν_{as} CH_3), 2935 cm^{-1} ms (ν_{as} CH_2), ca 2910 cm^{-1} sh (ν_{sy} CH_3), 2874 cm^{-1} m (ν_{sy} CH_2), 1467 w (δ_{as} CH_3, δ OCH_2 ?), 1434 cm^{-1} vvw (δ CH_2), 1407 cm^{-1} vvw (δ P-CH_2), 1381 cm^{-1} vw (δ_{sy} CH_3, ω OCH_2 ?), 1351 vvw, 1310 vw and 1278 cm^{-1} vw (ω, τ CH_2 from P-butyl), 1249 cm^{-1} ms and 1220 cm^{-1} w (ν P=O and CH_2 deformation, the presence of P-butyl may again cause the ν P=O to split as is the case of P-ethyl.[jj] The calculated value of the ν P=O is 1238 cm^{-1}, while the average of 1249 and 1220 is 1235 cm^{-1}), 1166 cm^{-1} vvw, 1150 and 1119 cm^{-1} vw (CH_3 rock, the three bands may be characteristic of the P-O-*n*-butyl group), 1071 cm^{-1} ms, 1025 cm^{-1} s, 1002 cm^{-1} sh and 977 cm^{-1} ms (ν P-O-C, may also be a contribution from ν C-C of P-butyl), 910 cm^{-1} w (ν C-C ?), 840 cm^{-1} w (CH_2 rock, P-butyl ?), 819 and 803 cm^{-1} w (POC), 732 cm^{-1} w (CH_2 rock), 545 cm^{-1} w (O=P-O bending ?).

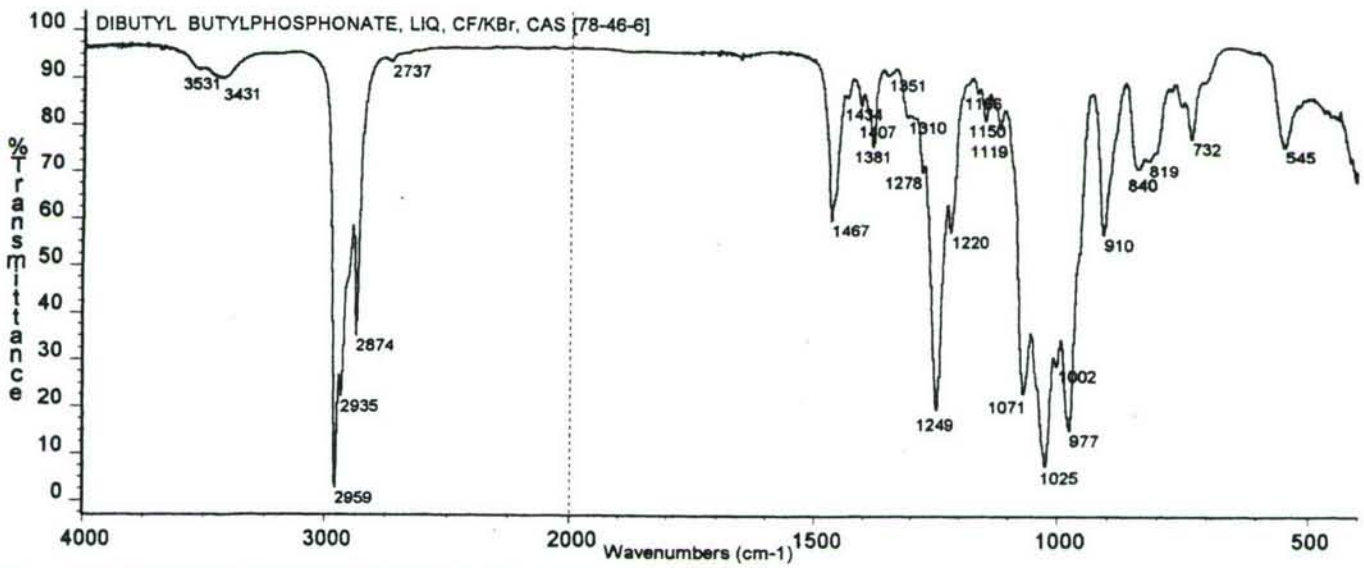


Figure 243 DIBUTYL BUTYLPHOSPHONATE (DBBP), LIQUID, CF/KBr

[jj] Thomas, L.C. in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 97,98, Heyden & Son Ltd., London, 1974, reports that the P-Ethyl group, has two weak bands between 1282 and 1227 cm^{-1}, one band occurring each side of 1250 cm^{-1}, denoting CH_2 wag and twist. This is the case when the P=O group is absent or falls outside the 1300-1200 cm^{-1} region. When a P=O occurs in this region, splitting may occur because of interaction with the CH_2 vibration and thus may indicate the presence of the O=P-Ethyl moiety. This occurs in diethyl ethylphosphonate (***Figure 238***) and also appears to occur in dimethyl *n*-propylphosphonate (***Figure 240***), diethyl *n*-propylphosphonate (***Figure 241***) and now in dibutyl butylphosphonate (***Figure 243***). See also ***Figure 244*** (diethyl hexylphosphonate).

3.5.8.43 Diethyl Hexylphosphonate CH_3-$(CH_2)_5$-P=O$(O$-CH_2-$CH_3)_2$

The infrared spectrum of a liquid film of diethyl hexylphosphonate between KBr windows is given in ***Figure 244***. The band assignments are as follows: 2956 cm^{-1} ms (ν_{as} CH_3), 2932 cm^{-1} ms (ν_{as} CH_2), 2872 cm^{-1} m (ν_{sy} CH_3), 2861 cm^{-1} m (ν_{sy} CH_2), 1467 and 1459 cm^{-1} w (δ OCH_2 and δ CH_2), 1445 cm^{-1} vw (δ_{as} CH_3), 1407 cm^{-1} vw (δ P-CH_2), 1391 cm^{-1} w (ω OCH_2), 1368 cm^{-1} vw (δ_{sy} CH_3), 1291 and 1237 cm^{-1} w (ω, τ CH_2), 1250 and 1237 cm^{-1} s (ν P=O and δ CH_2, average value is 1244 cm^{-1}, the ν P=O band is split by the P-hexyl moiety (see previous footnote [ii]), 1164 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1058 and 1032 cm^{-1} s (ν P-O-C), 959 cm^{-1} ms (ν C-C of POEt), 792 cm^{-1} w (POC), 743 and 727 cm^{-1} vw (CH_2 rock ?), 541 cm^{-1} w (P=O deformation).

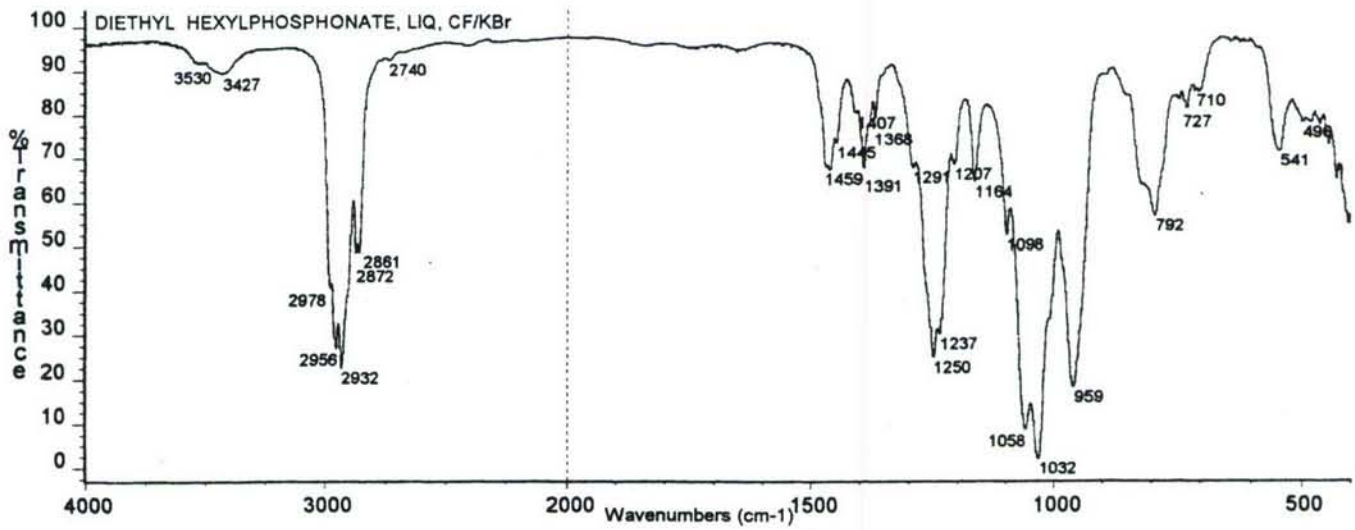


Figure 244 DIETHYL HEXYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.44 Diethyl *n*-Heptylphosphonate CH_3-$(CH_2)_6$-P=O$(O$-CH_2-$CH_3)_2$

The infrared spectrum of diethyl *n*-heptylphosphonate as a liquid film between KBr discs (windows) is presented as ***Figure 245***. The band assignments are as follows: 2955 cm^{-1} sh (ν_{as} CH_3), 2930 cm^{-1} ms (ν_{as} CH_2), 2871 cm^{-1} sh (ν_{sy} CH_3), 2857 cm^{-1} m (ν_{sy} CH_2), 1467 and 1458 cm^{-1} w (δ OCH_2 and δ CH_2), 1444 cm^{-1} w (δ_{as} CH_3), 1405 cm^{-1} sh (δ P-CH_2), 1391 cm^{-1} w (ω OCH_2), 1368 cm^{-1} vw (δ_{sy} CH_3), 1254 and 1244 cm^{-1} ms (ν P-O and CH_2 deformation, there is a slight shouder near 1230 cm^{-1} which could be the CH_2 deformation ?), 1164 and

1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1059 and 1033 cm^{-1} s (ν P-O-C), 959 cm^{-1} ms (ν C-C of POEt), 806 and 785 cm^{-1} w (POC), 725 cm^{-1} vw (CH_2 rock), 704 cm^{-1} vw (ν P-C), 546 cm^{-1} w (O=PX bending),

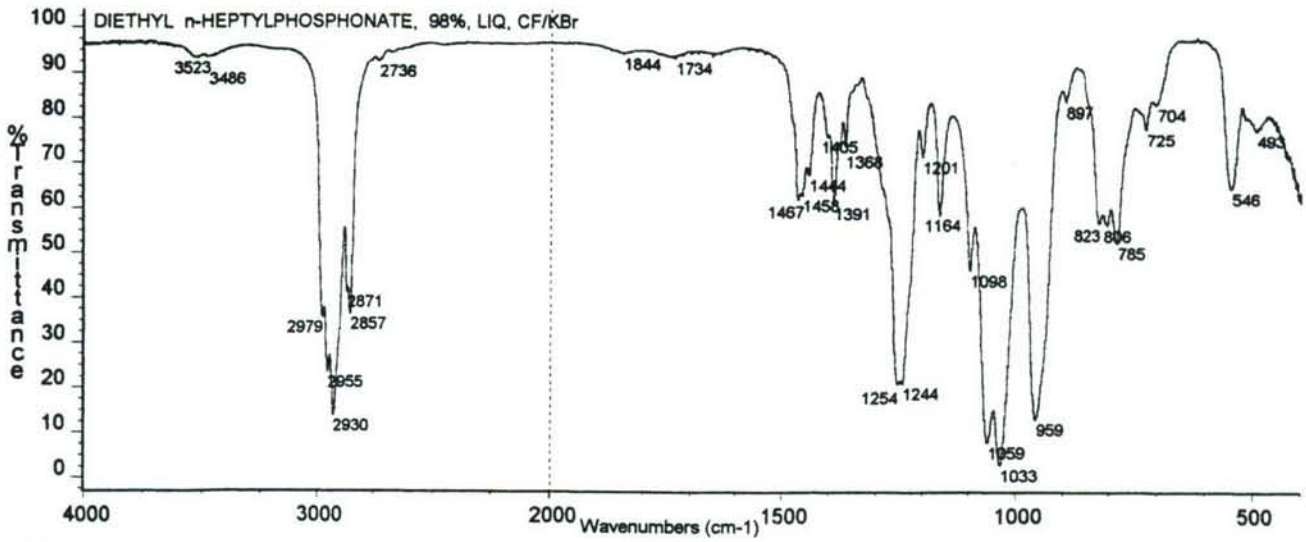


Figure 245 DIETHYL *n*-HEPTYLPHOSPHONATE, 98%, LIQUID, CF/KBr

3.5.8.45 Dimethyl Vinylphosphonate $H_2C{=}CH\text{-}P{=}O(O\text{-}CH_3)_2$

The infrared spectrum of dimethyl vinylphosphonate as a thin liquid film between KBr windows is given in ***Figure 246***. The band assignments are as follows: 3530 and 3477 cm^{-1} w (H_2O), 3086 cm^{-1} vw (ν_{as} $=CH_2$), 3007 cm^{-1} w (ν =CH and ν_{sy} $=CH_2$), 2956 cm^{-1} m (ν_{as} CH_3), 2853 cm^{-1} m (ν_{sy} CH_3), 1854 cm^{-1} vw (ca

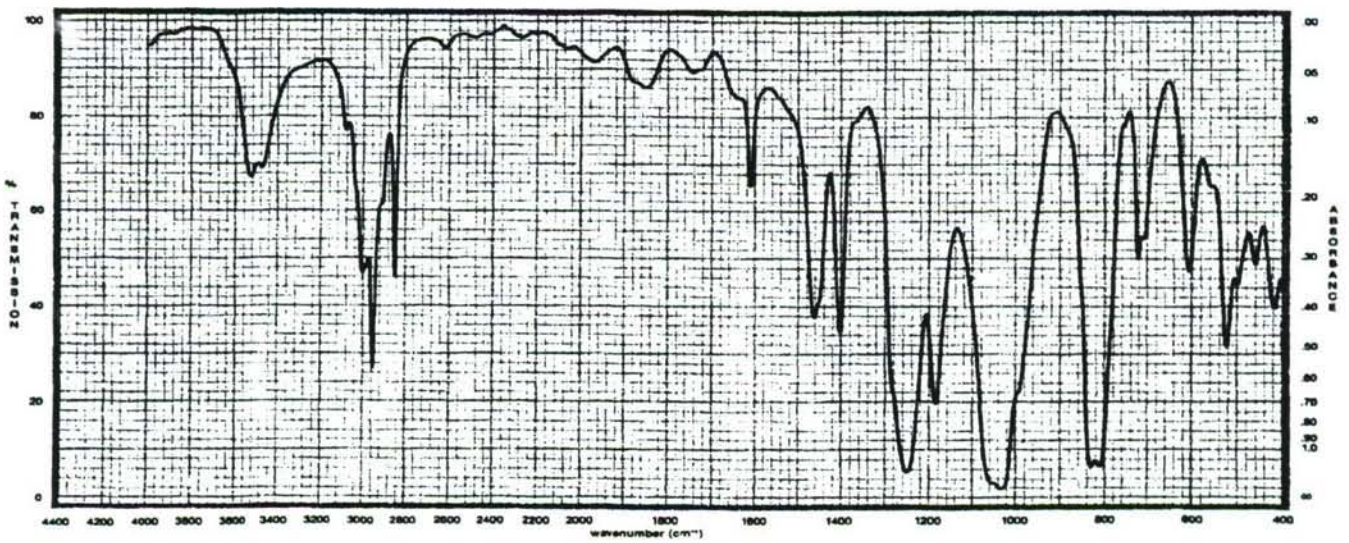


Figure 246 DIMETHYL VINYLPHOSPHONATE, LIQUID, CF/KBr

1050 + 809 = 1859 cm^{-1} , 1031 + 828 = 1859 cm^{-1}), 1612 cm^{-1} w (ν C=C lowered by heavy P atom ?)[kk], 1463 cm^{-1} m (δ_{as} and δ_{sy} CH_3), 1402 cm^{-1} m (δ =CH_2), ca 1280 cm^{-1} sh (δ =C-H), 1251 cm^{-1} s (ν P=O)[kk], 1185 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), ca 1050 cm^{-1} sh and 1031 cm^{-1} s (ν P-O-C), ca 990 cm^{-1} sh (*trans* =C-H wag), 828 and 809 cm^{-1} s (POC), 720 cm^{-1} w (ν P-C), 604 cm^{-1} w (*cis* H-C=C-H wag), 522 cm^{-1} w (O=P-X bending).

3.5.8.46 Diethyl Vinylphosphonate $H_2C=CH-P=O(O-CH_2-CH_3)_2$

The infrared spectrum of a liquid film of diethyl vinylphosphonate between KBr windows is given as ***Figure 247***. The band assignments are as follows: 3531 and 3476 cm^{-1} vvw (H_2O), 3087 cm^{-1} vvw (ν_{as} =CH_2), 3039 cm^{-1} vvw (ν =C-H and ν_{sy} =CH_2), 2983 cm^{-1} m (ν_{as} CH_3), 2934 cm^{-1} w (ν_{as} CH_2), 2907 cm^{-1} w (ν_{sy} CH_3), 2872 cm^{-1} vw (ν_{sy} CH_2), 1844 cm^{-1} vvw (1056 + 788 = 1844 cm^{-1}), 1613 cm^{-1} w (ν C=C)[kk], 1480 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1396 cm^{-1} m (ω OCH_2 and δ =CH_2), 1368 cm^{-1} w (δ_{sy} CH_3), 1279 cm^{-1} sh (δ =C-H), 1250 cm^{-1} ms (ν P=O), 1165 and 1098 cm^{-1} m (CH_3 rock of POEt, characteristic), 1056 and 1028 cm^{-1} s

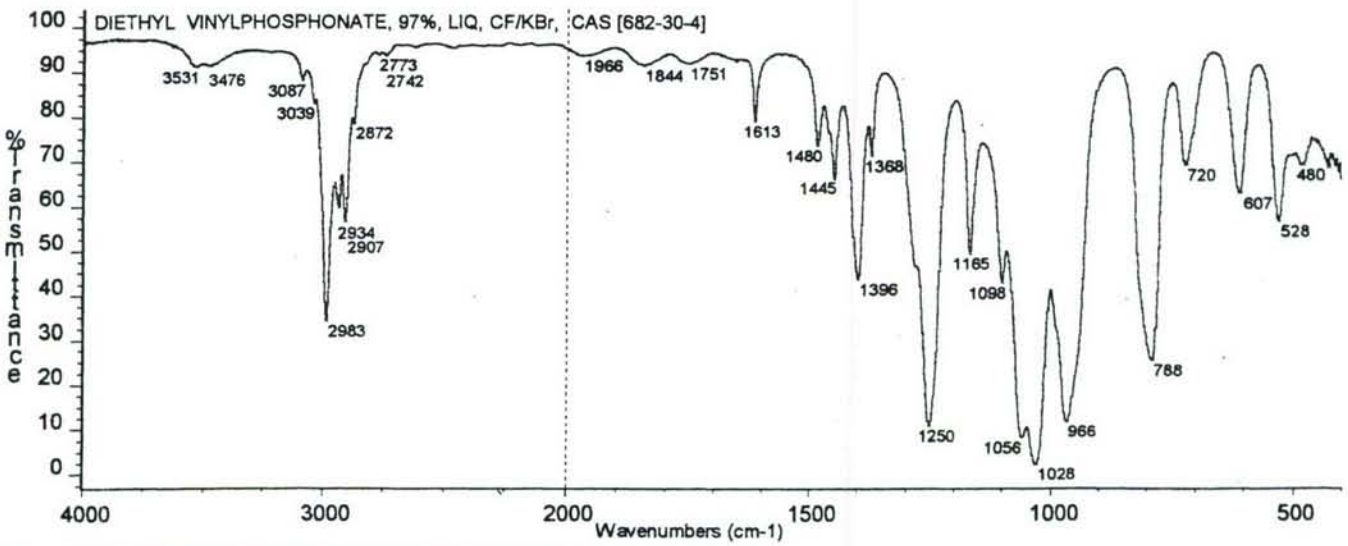


Figure 247 DIETHYL VINYLPHOSPHONATE, 97%, LIQUID, CF/KBr

[kk] The C=C vibration in α-unsaturated organophosphorus compounds occurs at lower frequencies (1645-1605 cm^{-1}) than in the β-unsaturatead organophosphorus compounds (1661-1631 cm^{-1}). This is the case despite the claim that no conjugation exists between the phosphorus atom and α-unsaturated bonds. Also, there is no lowering of the P=O frequency as occurs in the case of the corresponding C=O compounds. See Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 18,102, Heyden and Son Ltd., 1974, and the references therein.

(ν P-O-C), 990 cm^{-1} sh (*trans* =C-H wag), 788 cm^{-1} m (POC), 720 cm^{-1} w (ν P-C), 607 cm^{-1} w (*cis* H-C=C-H wag), 528 cm^{-1} w (O=P-X bending).

3.5.8.47 Diethyl Allylphosphonate $H_2C=CH-CH_2-P=O(O-CH_2-CH_3)_2$

The infrared spectrum of diethyl allylphosphonate as a liquid film between KBr discs (windows) is presented as ***Figure 248***. The band assignments are as follows: 3534 and 3474 cm^{-1} vw (H_2O), 3084 cm^{-1} vw (ν_{as} $=CH_2$), 2983 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), 2908 cm^{-1} m (ν_{sy} CH_3), 2873 cm^{-1} sh (ν_{sy} CH_2), 1640 cm^{-1} w (ν C=C), 1480 cm^{-1} vw (δ OCH_2), 1445 cm^{-1} (δ_{as} CH_3), 1422 cm^{-1} w (δ $=CH_2$), 13 94 cm^{-1} m (ω OCH_2, δ P-CH_2 ?), 1369 cm^{-1} vw (δ_{sy} CH_3), 1255 cm^{-1} ms (ν P=O), 1164 and 1099 cm^{-1} m (CH_3 rock of POEt, characteristic), 1054 and 1029 cm^{-1} s (ν P-O-C), 964 cm^{-1} ms (ν C-C of POEt, *trans* =C-H wag), ca 920 cm^{-1} sh ? (ω $=CH_2$), 803 and 778 cm^{-1} m (POC), 730 cm^{-1} w (ν P-C), 625 cm^{-1} m (*cis* =C-H wag), 499 cm^{-1} w (P=O deformation).

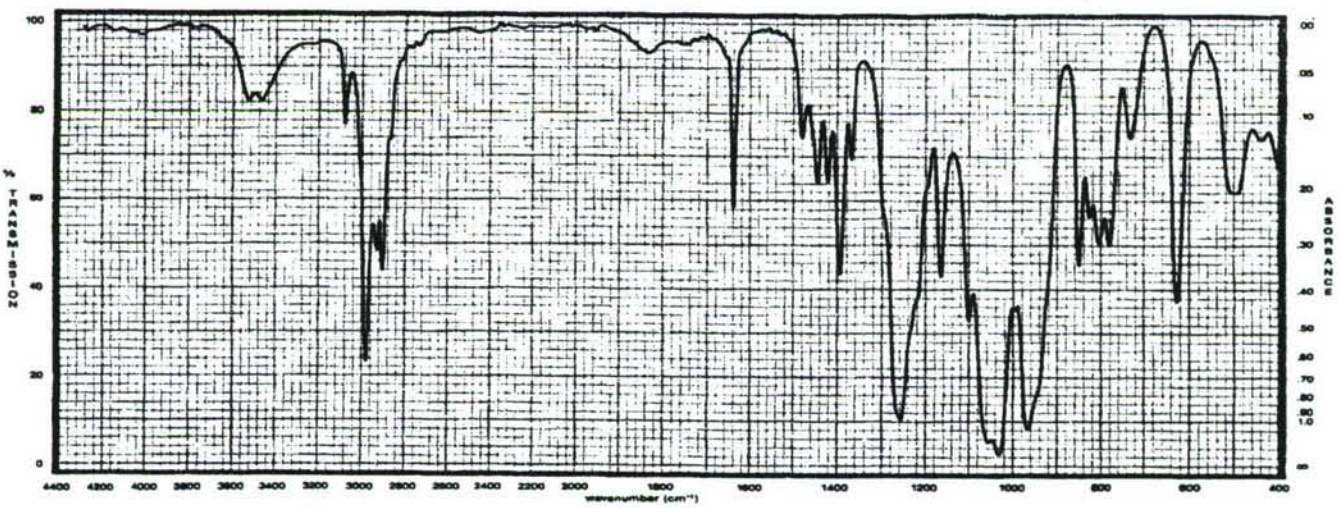


Figure 248 DIETHYL ALLYLPHOSPHONATE, 95%, LIQUID, CF/KBr

3.5.8.48 Di-*n*-butyl Allylphosphonate $H_2C=CH-CH_2-P=O(n-C_4H_9)_2$

The infrared spectrum of a liquid film of di-*n*-butyl allylphosphonate between KBr windows is given in ***Figure 249***. The band assignments are as follows: 3528 and 3471 cm^{-1} vw (H_2O), 3084 cm^{-1} vw (ν_{as} $=CH_2$), 3015 cm^{-1} vw (ν =C-H and ν_{sy} $=CH_2$), 2960 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), 2908 cm^{-1} w (ν_{sy} CH_3),

2875 cm^{-1} m (ν_{sy} CH_2), 1640 cm^{-1} w (ν C=C), 1466 cm^{-1} w (δ_{as} CH_3, δ OCH_2 ?), 1421 cm^{-1} vw (δ $=CH_2$), 1299 cm^{-1} vw (=C-H rock ?), 1255 cm^{-1} ms (ν P=O), 1166 cm^{-1} vvw, 1149 and 1119 cm^{-1} vw (triplet, CH_3 rock of PO-*n*-butyl, characteristic ?), 1063 cm^{-1} ms and 1024 cm^{-1} s (ν P-O-C), 980 cm^{-1} ms (ν C-C of POButyl, and *trans* =C-H wag), 912 cm^{-1} w (ω $=CH_2$?), 802 cm^{-1} vw (POC), 731 cm^{-1} vw (ν P-C), 625 cm^{-1} w (*cis* =C-H wag ?).

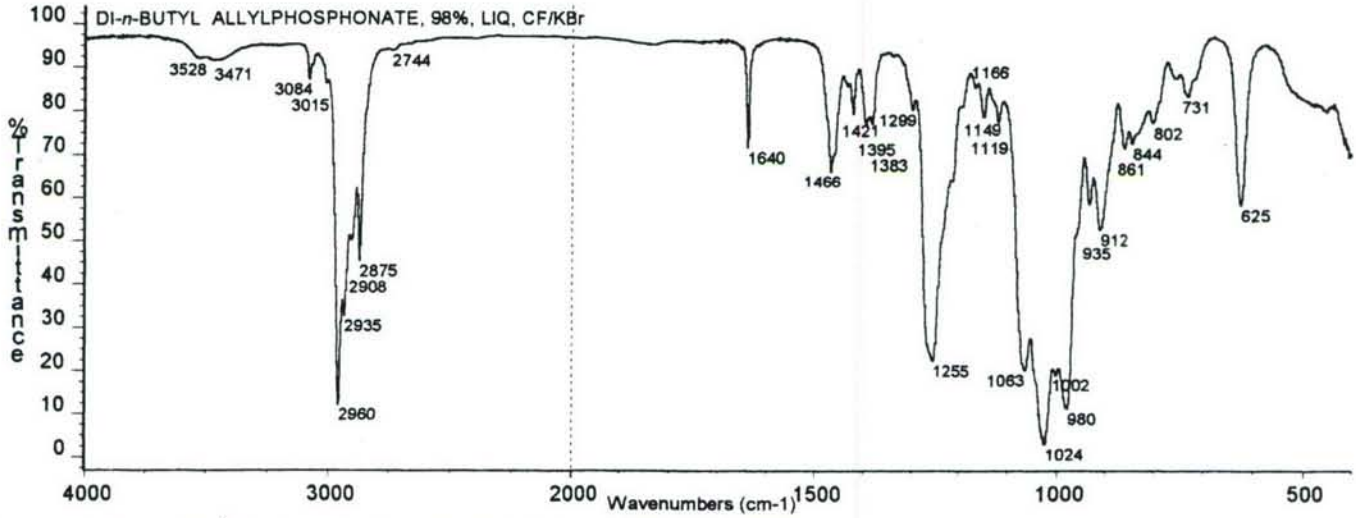


Figure 249 DI-*n*-BUTYL ALLYLPHOSPHONATE, 98%, LIQUID, CF/KBr

3.5.8.49 Dimethyl Cyclohexylphosphonate $H_{11}C_6$-P=O$(OCH_3)_2$

The infrared spectrum of dimethyl cyclohexylphosphonate as a liquid film between CsI windows is presented as ***Figure 250***. The band assignments are as follows: 3529 and 3474 cm^{-1} vvw (H_2O), 2934 cm^{-1} ms

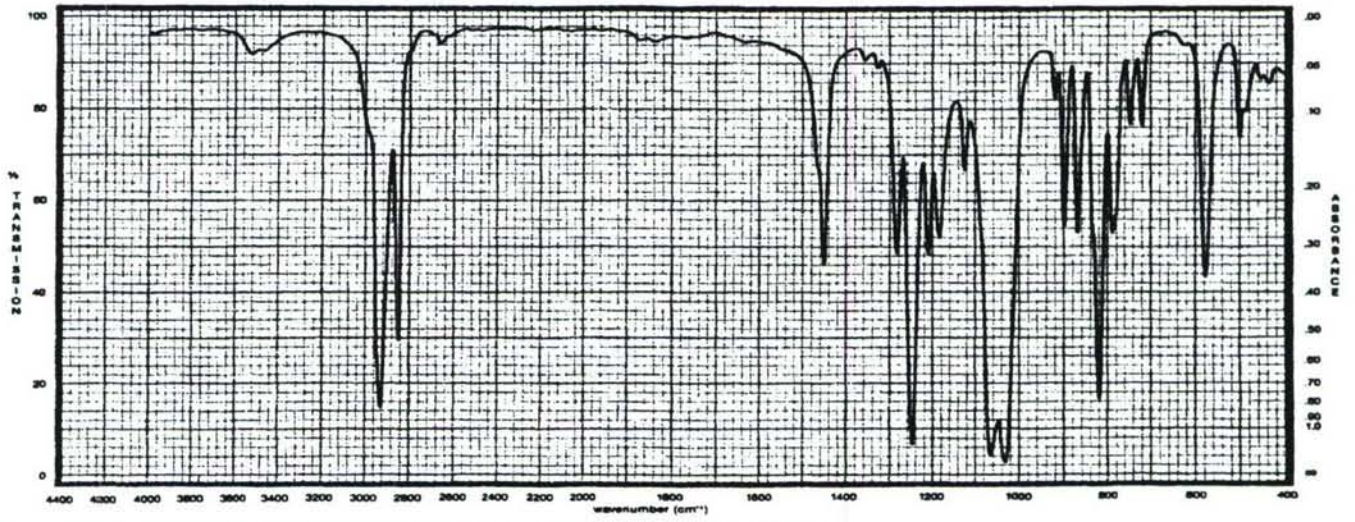


Figure 250 DIMETHYL CYCLOHEXYLPHOSPHONATE, LIQUID, CF/CsI

(ν_{as} CH_2)., 2854 cm^{-1} m (ν_{sy} CH_2), 1451 cm^{-1} m (δ CH_2 and δ CH_3), 1283 amd 1208 cm^{-1} m (ring CH_2), 1246 cm^{-1} s (ν P=O), 1182 cm^{-1} w (CH_3 rock of $POCH_3$, characteristic), 1061 and 1028 cm^{-1} s (ν P-O-C), 897 cm^{-1} m (ring), 816 cm^{-1} ms and 786 cm^{-1} m (POC), 574 cm^{-1} m (P=O deformation).

3.5.8.50 Diethyl Phenylphosphonate H_5C_6-P=O(O-CH_2-CH_3)$_2$

The infrared spectrum of diethyl phenylphosphonate as a liquid film between KBr windows is reproduced as ***Figure 251***. The band assignments are as follows: 3532 and 3478 cm^{-1} vw (H_2O), 3080 cm^{-1} sh, 3060 cm^{-1} vw (ν C-H aromatic), 2983 cm^{-1} m (ν_{as} CH_3), 2932 cm^{-1} vw (ν_{as} CH_2), 2906 cm^{-1} w (ν_{sy} CH_3), 2870 cm^{-1} vw (ν_{sy} CH_2), 1594 cm^{-1} vw, 1479 cm^{-1} vw and 1440 cm^{-1} m (aromatic ring), 1392 cm^{-1} w (ω OCH_2), 1368 cm^{-1} vw (δ_{sy} CH_3), 1251 cm^{-1} ms (ν P=O), 1164 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1132 cm^{-1} ms (phenyl-P), 1054 and 1025 cm^{-1} s (ν P-O-C), 999 cm^{-1} vvw (β C-H mono-substituted aromatic ring), 965 cm^{-1} ms (ν C-C of POEt), 798 and 768 cm^{-1} w (POC), 750 cm^{-1} m (γ C-H mono-substituted aromatic ring), 697 cm^{-1} m (δ mono-substituted aromatic ring), 562 cm^{-1} ms (out of plane ring bending ?).

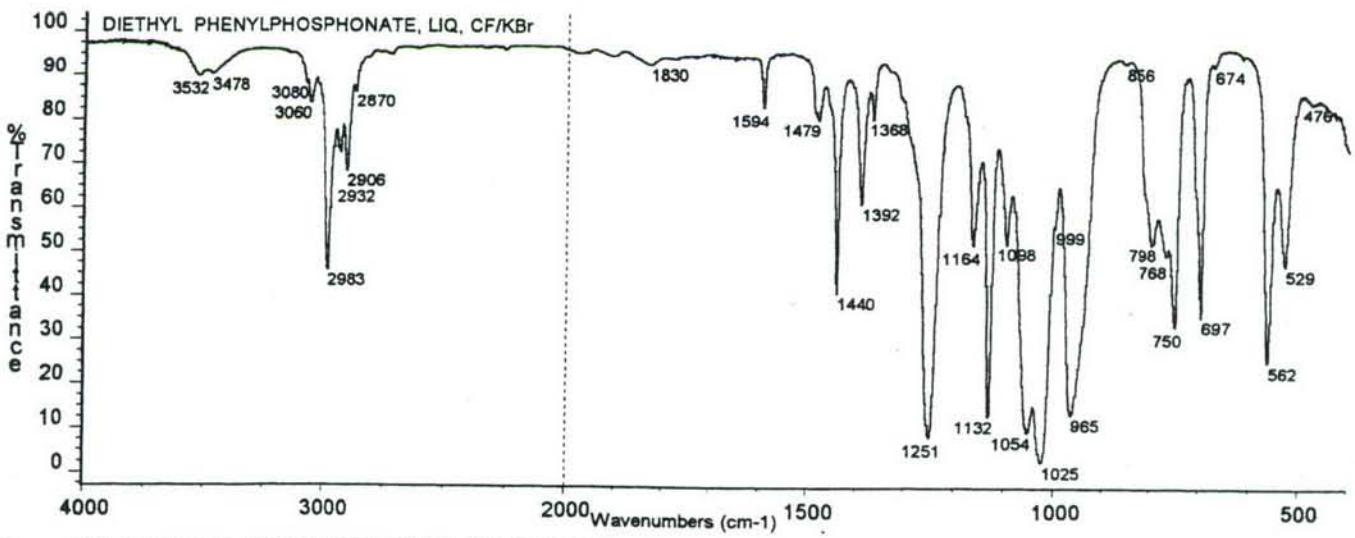


Figure 251 DIETHYL PHENYLPHOSPHONATE, LIQUID, CF/KBr

3.5.8.51 Dioctyl Phenylphosphonate H_5C_6-P=O[O-$(CH_2)_7CH_3$]$_2$

The infrared spectrum of dioctyl phenylphosphonate as a liquid film between KBr windows is given as ***Figure 252***. The band assignments are as follows: 3543 and 3465 cm^{-1} vw (H_2O), 3079 cm^{-1} sh, 3059 cm^{-1} vw

and 3015 cm^{-1} sh (ν C-H aromatic), 2955 cm^{-1} ms (ν_{as} CH_3), 2926 cm^{-1} s (ν_{as} CH_2), 2869 cm^{-1} sh (ν_{sy} CH_3), 2856 cm^{-1} s (ν_{sy} CH_2), 1594 cm^{-1} vw (aromatic ring), 1467 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1439 cm^{-1} m (aromatic ring), 1379 cm^{-1} w (δ_{sy} CH_3), 1255 cm^{-1} ms (ν P=O), 1132 cm^{-1} ms (phenyl-P), 1014 and 996 cm^{-1} ms (ν P-O-C), 798 cm^{-1} w (POC), 749 cm^{-1} m (γ C-H mono-substituted aromatic ring), 723 cm^{-1} w (CH_2 rock ?), 695 cm^{-1} m (δ mono-substituted aromatic ring), 566 cm^{-1} m (out-of-plane mono-substituted aromatic ring), 540 cm^{-1} w (O=P-O bending ?).

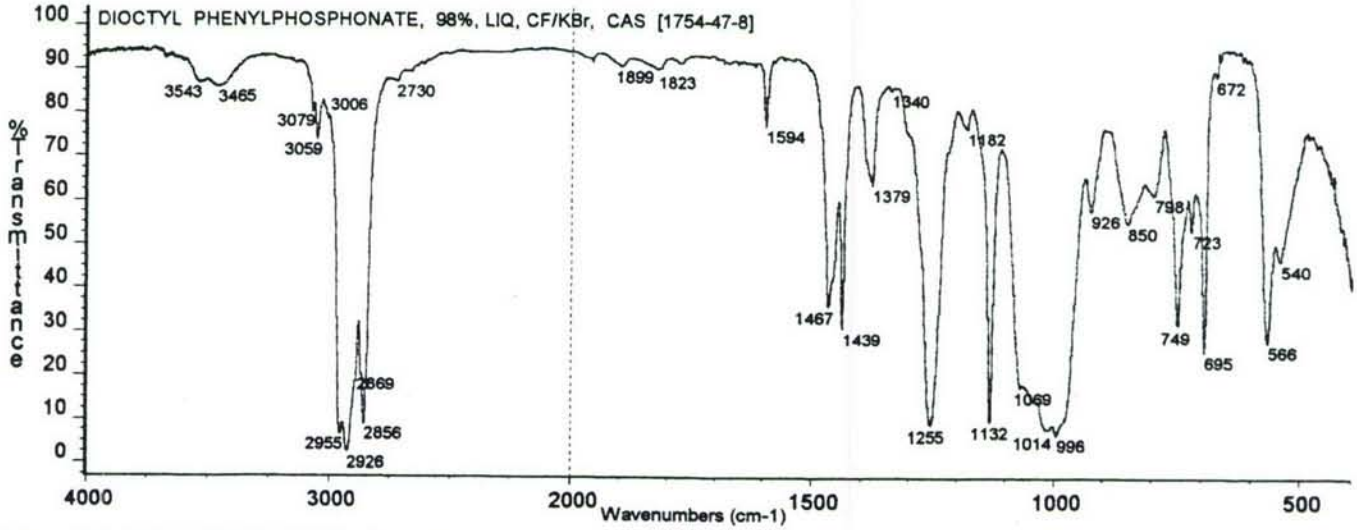


Figure 252 DIOCTYL PHENYLPHOSPHONATE, 98%, LIQUID, CF/KBr

3.5.8.52 Diethyl Benzylphosphonate H_5C_6-CH_2-P=O(O-CH_2-CH_3)$_2$

The infrared spectrum of diethyl benzylphosphonate as a liquid film between KBr windows is given as ***Figure 253***. The band assignments are as follows: 3525 and 3466 cm^{-1} vw (H_2O), 3086 cm^{-1} vvw, 3062 cm^{-1} vw, 3030 cm^{-1} w (ν C-H aromatic), 2981 cm^{-1} m (ν_{as} CH_3), 2930 cm^{-1} vw (ν_{as} CH_2), 2906 cm^{-1} w (ν_{sy} CH_3), 2868 cm^{-1} vw (ν_{sy} CH_2), 1603 cm^{-1} w, 1584 cm^{-1} vvw, 1496 cm^{-1} m and 1455 cm^{-1} m (aromatic ring), 1478 cm^{-1} vw (δ O-CH_2), 1443 cm^{-1} vw (δ_{as} CH_3), 1405 cm^{-1} sh (δ P-CH_2) , 1391 cm^{-1} m (ω OCH_2), 1367 cm^{-1} w (δ_{sy} CH_3), 1251 cm^{-1} ms (ν P=O), 1191 cm^{-1} w (ω CH_2, phenyl-CH_2-P), 1163 and 1097 cm^{-1} m (CH_3 rock of POEt, characteristic), 1055 and 1028 cm^{-1} s (ν P-O-C), 963 cm^{-1} ms (ν C-C of POEt), 801 and 772 cm^{-1} w (POC), 750 cm^{-1} w (γ C-H mono-substituted ring), 698 cm^{-1} ms (δ mono-substituted aromatic ring), 588 (mono-substituted aromatic

ring), 531 cm^{-1} m (O=P-O bending ?).

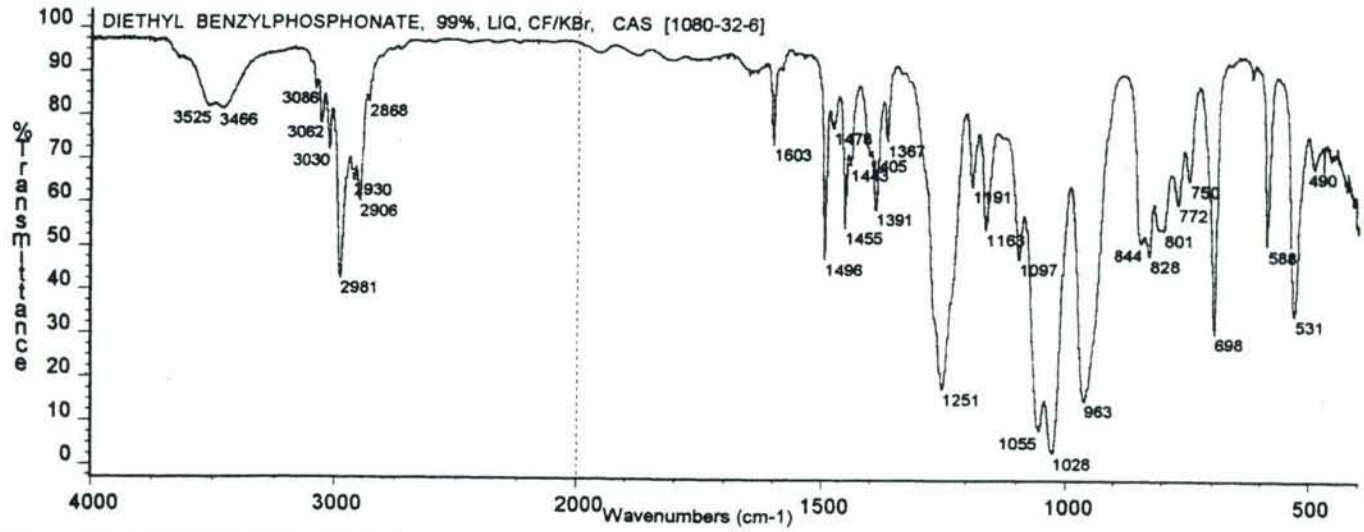


Figure 253 DIETHYL BENZYLPHOSPHONATE, 99%, LIQUID, CF/KBr

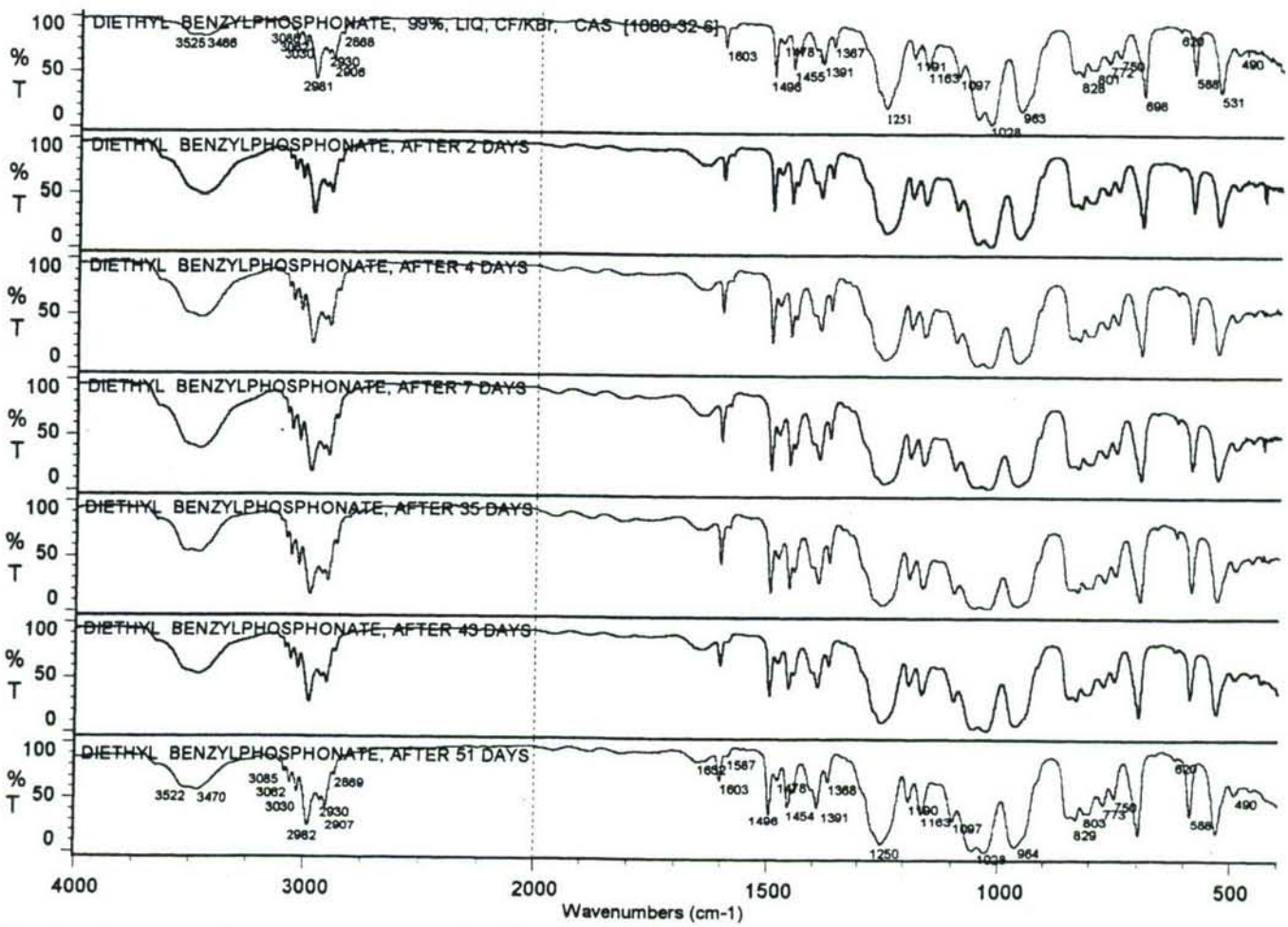


Figure 254 DIETHYL BENZYLPHOSPHONATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

Figure 254 shows the infrared spectra, for diethyl benzylphosphonate as a liquid film between KBr windows, over a period of 51 days of exposure to atmospheric moisture. No change is observed in the spectra after 51 days except for the increase in water as indicated by the bands at 3522, 3470 and 1652 cm^{-1}.

3.5.8.53 Diethyl 4-Aminobenzylphosphonate $H_2N\text{-}C_6H_4\text{-}CH_2\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl 4-aminobenzylphosphonate as a solid between CsI discs (windows) is reproduced as ***Figure 255***. The band assignments are as follows: 3429 cm^{-1} ms (ν_{as} NH_2), 3349 cm^{-1} ms (ν_{sy} NH_2), 3241 cm^{-1} w (2 x δ NH_2), 3064, 3039, 3026 cm^{-1} vw (ν C-H aromatic), 2982 cm^{-1} w (ν_{as} CH_3), 2929 cm^{-1} sh (ν_{as} CH_2), 2905 cm^{-1} w (ν_{sy} CH_3), 2869 cm^{-1} vvw (ν_{sy} CH_2), 1632 cm^{-1} m (δ NH_2), 1614 ms, 1519 cm^{-1} s (aromatic ring), 1478 cm^{-1} vw (δ OCH_2), 1441 cm^{-1} vw (δ_{as} CH_3), 1406 cm^{-1} w (δ P-CH_2; aromatic ring-para ?), 1391 cm^{-1} w (ω OCH_2), 1367 cm^{-1} vw (δ_{sy} CH_3), 1295 cm^{-1} ms (ν phenylC-N), 1224 cm^{-1} s (ν P=O), 1181 and 1129 cm^{-1} w (β C-H *para*-substituted aromatic ring), 1160 and 1101 cm^{-1} vw (CH_3 rock of POEt, characteristic), 1055 and 1028 cm^{-1} s (ν P-O-C), 967 cm^{-1} s (ν C-C of POEt), 853 and 834 cm^{-1} m (γ C-H, *para*-substituted aromatic ring, 2 adjacent H), 801 cm^{-1} m (POC), ca 700-600 cm^{-1} w, broad (ω NH_2), 567 cm^{-1} m (quadrant out-of-plane bending of *para*-substituted aromatic ring ?), 498 cm^{-1} w (P=O deformation ?).

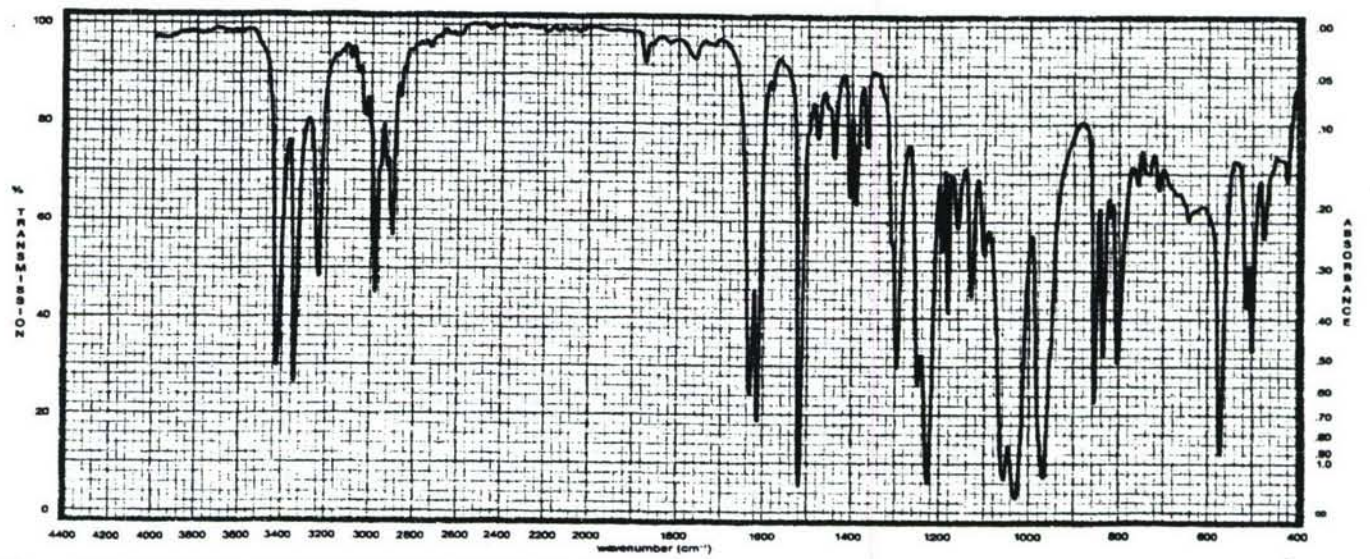


Figure 255 DIETHYL 4-AMINOBENZYLPHOSPHONATE, 99%, SOLID BETWEEN CsI DISCS (WINDOWS)

3.5.8.54 Bis(4-nitrophenyl) Phenylphosphonate H_5C_6-P=O(O-C_6H_4-NO_2)$_2$

The infrared spectrum of bis(4-nitrophenyl) phenylphosphonate both as a KBr pellet and as a solid between KBr discs (windows) is presented as ***Figure 256***. The band assignments for the KBr pellet are as follows: 3441 cm^{-1} vw (H_2O), 3202 cm^{-1} vvw (p-nitrophenol ?), 3117 and 3076 cm^{-1} vw, 3054 and 3030 cm^{-1} vvw (ν C-H aromatic), 1615 cm^{-1} m, 1590 and 1490 cm^{-1} ms and 1440 cm^{-1} m (aromatic ring), 1518 cm^{-1} s (ν_{as} NO_2), 1347 cm^{-1} s (ν_{sy} NO_2), 1272 cm^{-1} m (ν P=O), 1202 cm^{-1} s (ν C-O), 1131 cm^{-1} m (phenyl-P), 1110 cm^{-1} m β C-H *para*-disubstituted aromatic ring ?), 947 cm^{-1} s (ν P-O), 861 cm^{-1} ms (γ C-H *para*-disubstituted aromatic ring, NO_2 scissoring), 748 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 695 cm^{-1} m (δ mono-substituted aromatic ring), 555 cm^{-1} m (out-of-plane ring bending, mono-substituted and *para*-disubstituted aromatic rings ?).

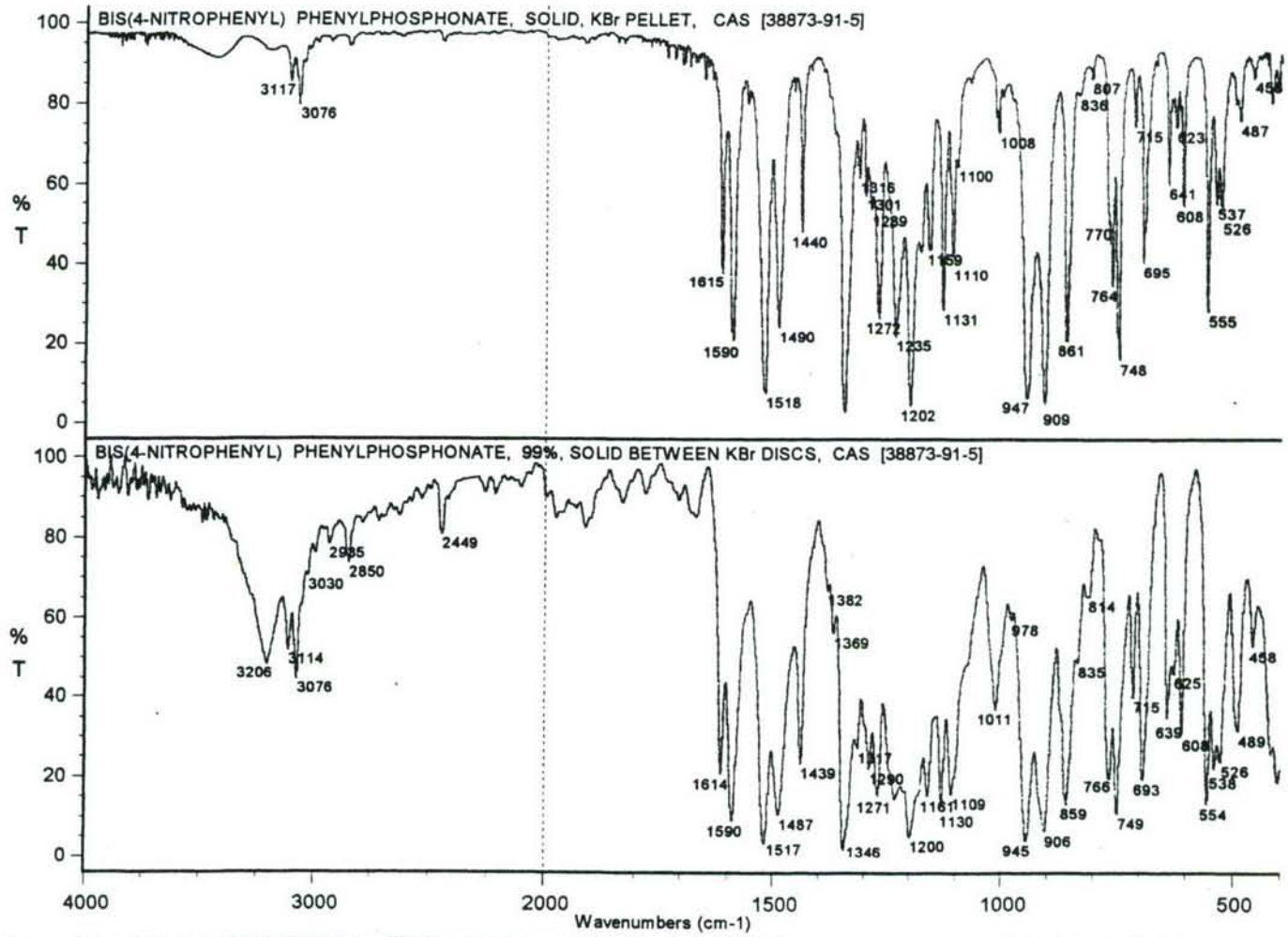


Figure 256 BIS(4-NITROPHENYL) PHENYLPHOSPHONATE, 99%, SOLID, *UPPER SPECTRUM*--AS A KBr PELLET *LOWER SPECTRUM*--AS A SOLID BETWEEN KBr DISCS (WINDOWS)

3.5.8.55 Dimethyl (2-Oxopropyl)phosphonate CH_3-C(=O)-CH_2-P=O(O-CH_3)$_2$

The infrared spectrum of a liquid film of dimethyl (2-oxopropyl)phosphonate between KBr windows is reproduced as ***Figure 257***. The band assignments are as follows: 3518 and 3469 cm^{-1} vvw (H_2O), 3411 cm^{-1} vvw [2 x 1715 (ν C=O) = 3430 cm^{-1}], 3003 cm^{-1} w, 2959 cm^{-1} w, 2922 cm^{-1} vw, 2854 cm^{-1} w (ν CH_3 and ν CH_2), 1715 cm^{-1} ms (ν C=O), 1463 cm^{-1} w (δ OCH_3), 1449 cm^{-1} vw (δ CH_3), 1425 and 1405 cm^{-1} vw (δ CH_2-C: , δ CH_3- C:), 1361 cm^{-1} w (δ_{sy} CH_3-C:), 1261 ms (ν P=O), 1186 cm^{-1} w (CH_3 rock of $POCH_3$, characteristic), 1127 cm^{-1} vs (CH_2 from -C(=O)-CH_2-P(=O)- ?), 1053 and 1030 cm^{-1} s (ν P-O-C), 830 cm^{-1} m (POC), 724 cm^{-1} vvw (CH_2 rock), 533 cm^{-1} w (O=C-X bending ?).

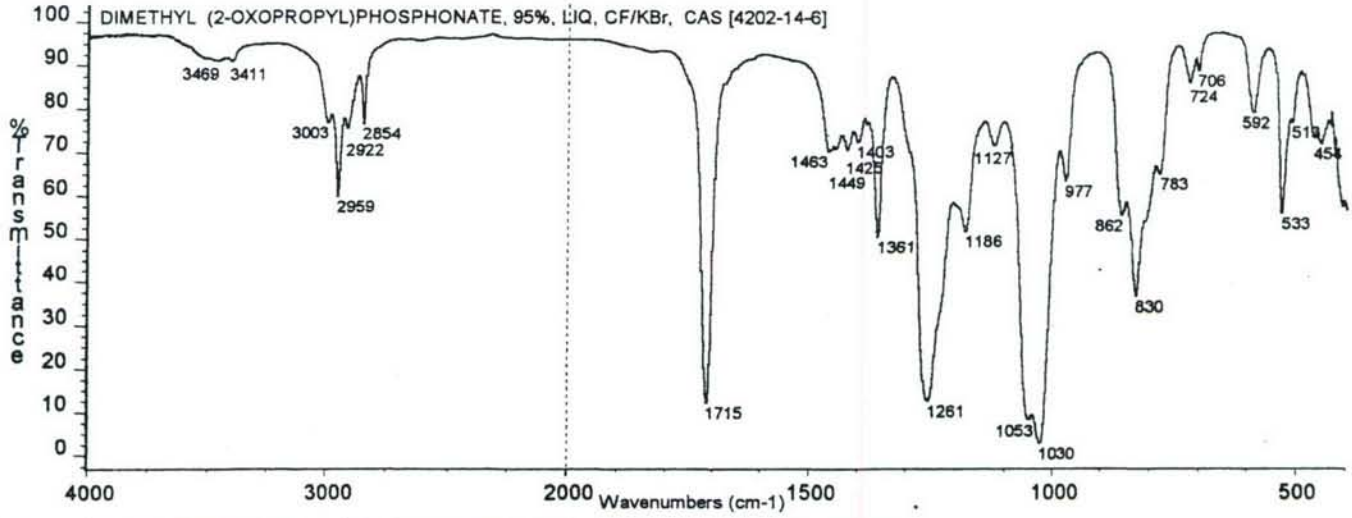


Figure 257 DIMETHYL (2-OXOPROPYL)PHOSPHONATE, 95%, LIQUID, CF/KBr

3.5.8.56 Dimethyl (2-Oxoheptyl)phosphonate CH_3-(CH_2)$_4$-C(=O)-P=O(O-CH_3)$_2$

The infrared spectrum of dimethyl (2-oxoheptyl)phosphonate as a liquid film between KBr windows is given in ***Figure 258***. The band assignments are as follows: 3534 and 3483 cm^{-1} vvw (H_2O), 3414 cm^{-1} vvw (2 x ν C=O is 3432 cm^{-1}), 2957 cm^{-1} ms (ν_{as} CH_3), 2933 cm^{-1} ms (ν_{as} CH_2), 2872 cm^{-1} m (ν_{sy} CH_3), 2858 cm^{-1} m (ν_{sy} CH_2), 1716 cm^{-1} ms (ν C=O), 1462 cm^{-1} m (δ CH_2, and δ CH_3), 1404 cm^{-1} w (δ CH_2, P-CH_2, CH_2-C=O), 1376 cm^{-1} w (δ_{sy} CH_3), 1260 cm^{-1} ms (ν P=O), 1184 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1123 cm^{-1} vw (CH_2 from -C(=O)-CH_2-P(=O)- ?), 1032 cm^{-1} s (ν P-O-C), 810 cm^{-1} m (POC), 727 cm^{-1} vw (CH_2 rock), 552 cm^{-1} w (P=O deformation).

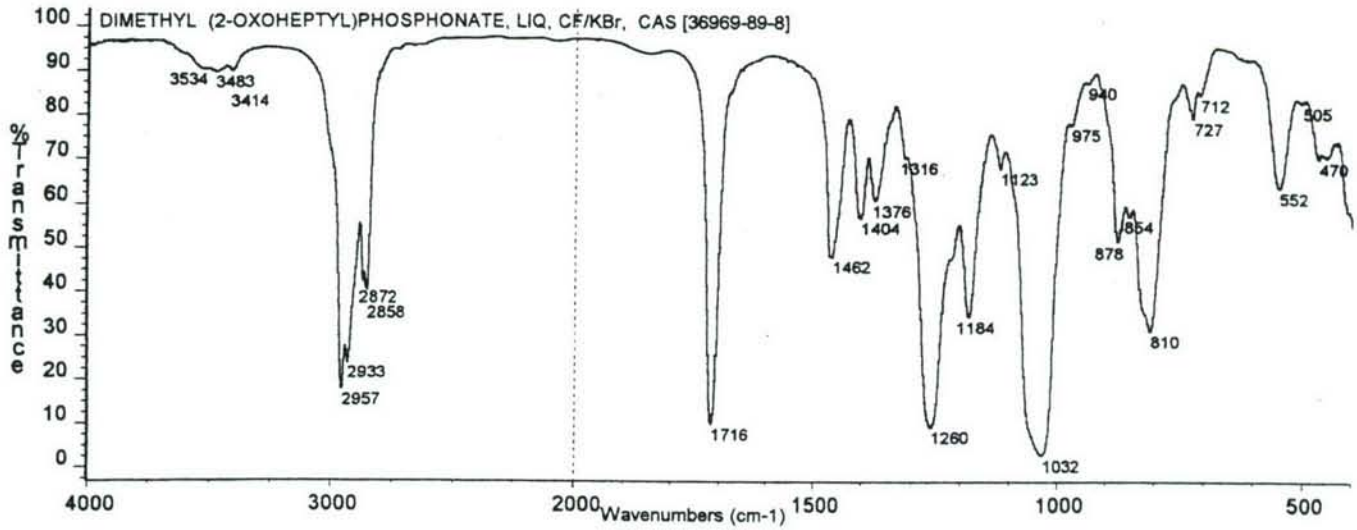


Figure 258 DIMETHYL (2-OXOHEPTYL)PHOSPHONATE, LIQUID, CF/KBr

3.5.8.57 Trimethyl Phosphonoformate CH_3-O-C(=O)-P=O(O-CH_3)$_2$

The infrared spectrum of trimethyl phosphonoformate as a liquid film between KBr windows is given in ***Figure 259***. The band assignments are as follows: 3565 and 3502 cm^{-1} w (H_2O), 3427 cm^{-1} vw (2 x 1722 = 3444 cm^{-1}), 3015 cm^{-1} w (ν_{as} CH_3, $POCH_3$), 2962 cm^{-1} m (ν_{as} CH_3, $COCH_3$), 2858 cm^{-1} w (ν CH_3), 1722 cm^{-1} s (ν C=O)m 1452 cm^{-1} m and 1434 cm^{-1} sh (δ_{as} and δ_{sy} CH_3)1384 cm^{-1} vvw (possible KNO_3 from KBr windows),

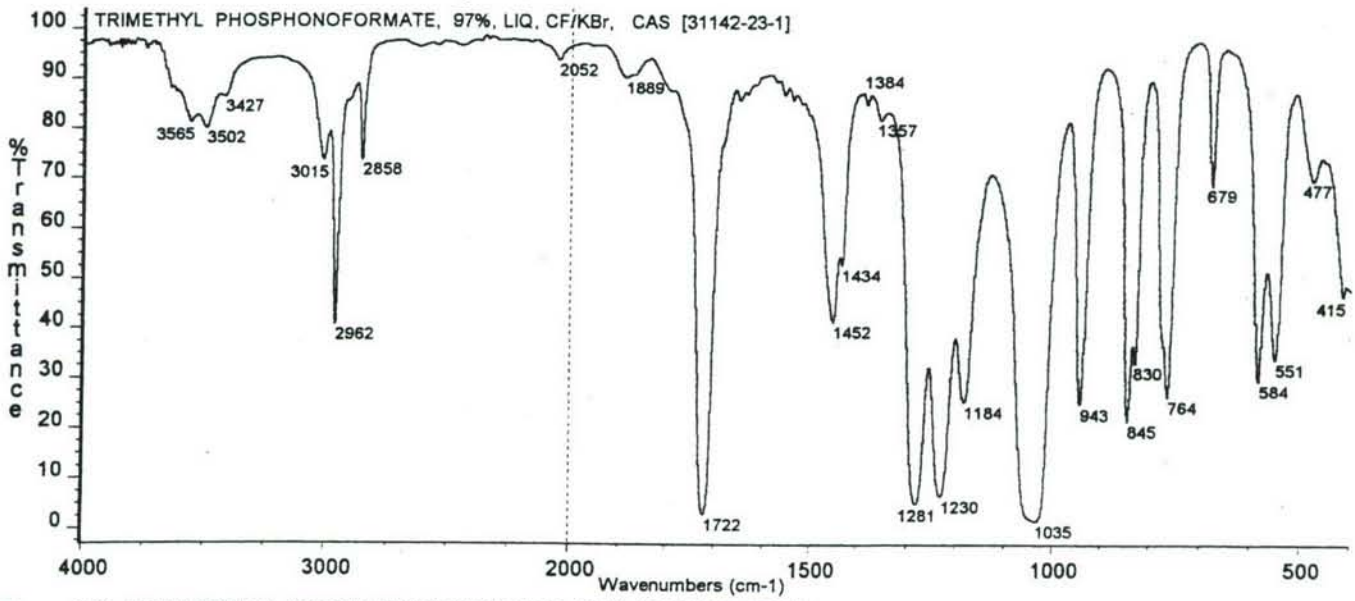


Figure 259 TRIMETHYL PHOSPHONOFORMATE, 97%, LIQUID, CF/KBr

1281 cm^{-1} s (ν P=O), 1230 cm^{-1} s (ν C-O ester), 1184 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1035 cm^{-1} s (ν P-O-C), 845 cm^{-1} ms (ester C-O), 764 cm^{-1} ms (POC), 679 cm^{-1} w (ν P-C ?), 584 cm^{-1} m (O=CX bending ?), 551 cm^{-1} m (O=PX bending ?).

3.5.8.58 Triethyl Phosphonoformate $CH_3CH_2O\text{-}C(=O)\text{-}P=O(OCH_2CH_3)_2$

The infrared spectrum of triethyl phosphonoformate (ethyl diethoxyphosphinylformate) as a liquid film between KBr windows is reproduced as ***Figure 260***. The band assignments are as follows: 3499 cm^{-1} vvw (H_2O), 3411 cm^{-1} vvw (2 x 1715 = 3430 cm^{-1}), 2986 cm^{-1} m (ν_{as} CH_3), 2938 cm^{-1} w (ν_{as} CH_2), 2911 cm^{-1} w (ν_{sy} CH_3), 2874 cm^{-1} vw (ν_{sy} CH_2), 1844 cm^{-1} vvw (1046 + 798 = 1844 cm^{-1}), 1715 cm^{-1} ms (ν C=O), 1477 cm^{-1} w (δ OCH_2), 1446 cm^{-1} w (δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1273 cm^{-1} ms (ν P=O), 1219 cm^{-1} ms (ester ν C-O), 1164 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1046 cm^{-1} sh and 1020 cm^{-1} s (ν P-O-C), 981 cm^{-1} m (ν C-C of POEt), 860 cm^{-1} w (C-O?), 798 and 753 cm^{-1} w (POC), 679 cm^{-1} vw (ν P-C ?), 586 cm^{-1} w (O=CX bending ?), 557 cm^{-1} w (O=PX bending ?).

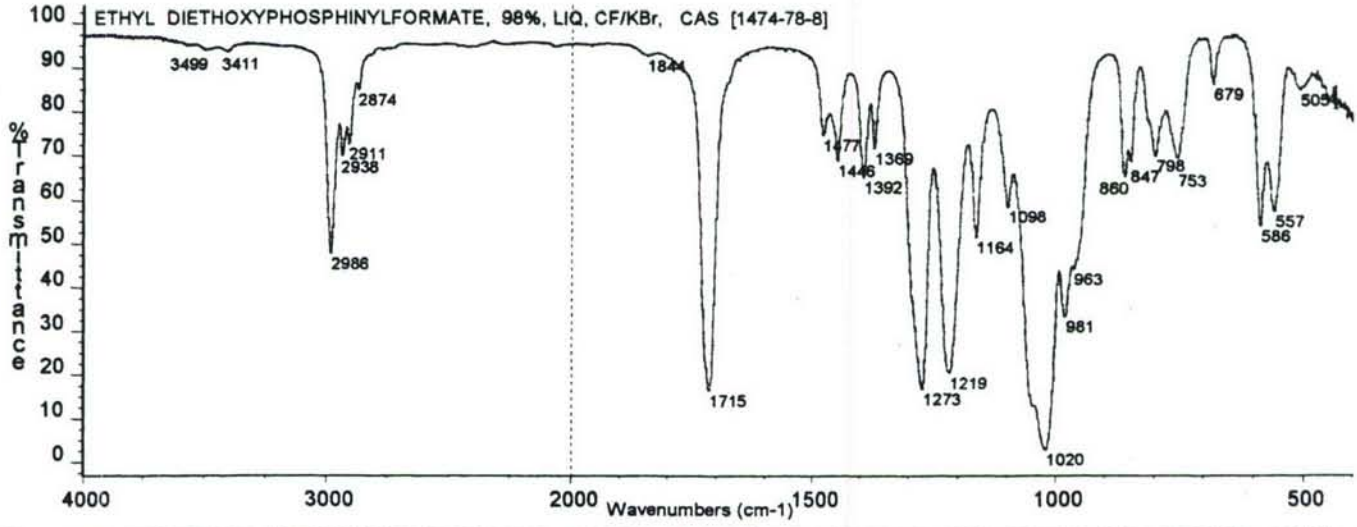


Figure 260 TRIETHYL PHOSPHONOFORMATE (ETHYL DIETHOXYPHOSPHINYLFORMATE), 98%, LIQUID, CF/KBr

3.5.8.59 Trimethyl Phosphonoacetate $CH_3O\text{-}C(=O)\text{-}CH_2\text{-}P=O(OCH_3)_2$

The infrared spectrum of a liquid film of trimethyl phosphonoaceatate (dimethyl methoxycarbonyl-methylphosphonate) between KBr windows is presented as ***Figure 261***. The band assignments are as follows:

3464 cm^{-1} vvw (2 x 1740 = 3480 cm^{-1}), 2958 cm^{-1} m (ν_{as} CH_3), 2854 cm^{-1} w (ν_{sy} CH_3), 1740 cm^{-1} s (ν C=O), 1457 cm^{-1} sh and 1438 cm^{-1} m (δ_{as} and δ_{sy} CH_3), 1402 cm^{-1} w (δ CH_2-P), 1278 cm^{-1} ms (ν P=O), 1220 cm^{-1} w (ν C-O), 1186 cm^{-1} w (CH_3 rock of $POCH_3$, characteristic), 1123 cm^{-1} m [CH_2 from -C(=O)-CH_2-P(=O)- ?], 1054 and 1030 cm^{-1} s (ν P-O-C), 808 cm^{-1} m (POC), 713 cm^{-1} vw (ν P-C ?), 614 cm^{-1} w (δ C=O ?), 503 cm^{-1} w (δ P=O).

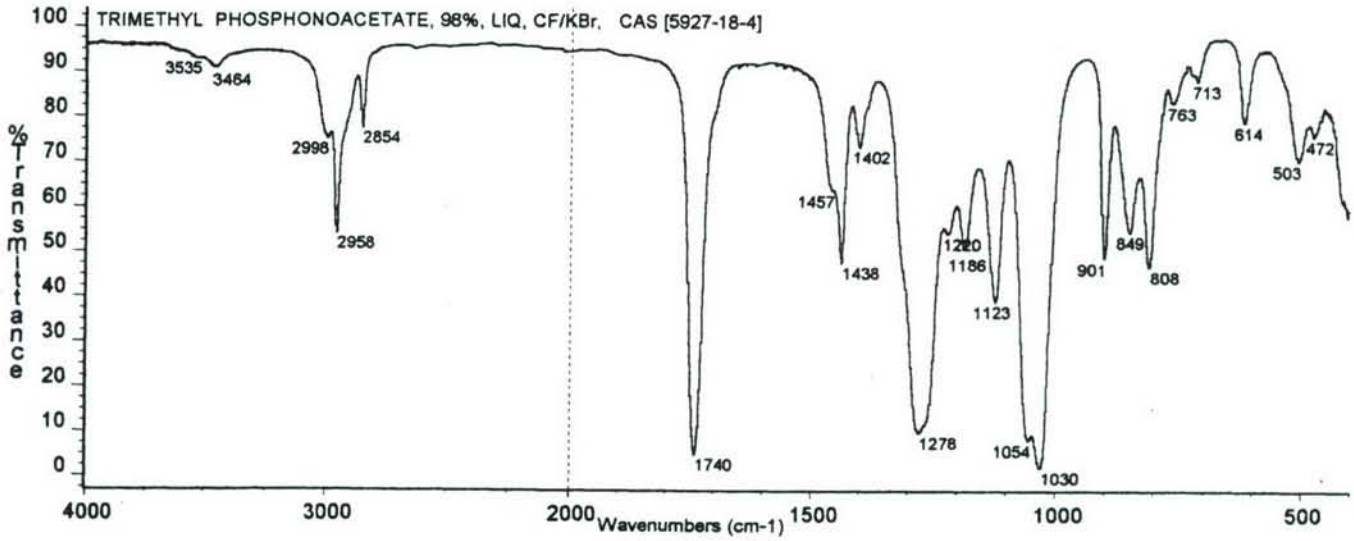


Figure 261 TRIMETHYL PHOSPHONOACETATE (DIMETHYL METHOXYCARBONYLMETHYLPHOSPHONATE), 98%, LIQUID, CF/KBr

3.5.8.60 Methyl Diethylphosphonoacetate CH_3O-C(=O)-CH_2-P=O$(OCH_2CH_3)_2$

The infrared spectrum of a liquid film of methyl diethylphosphonoacetate between KBr windows is presented as ***Figure 262***. The band assignments are as follows: 3536 cm^{-1} vvw (H_2O), 3469 cm^{-1} (2 x 1743 = 3486 cm^{-1}), 2986 cm^{-1} ms, 2956 cm^{-1} vw, 2935 cm^{-1} vw, 2911 cm^{-1} m and 2873 cm^{-1} sh (ν CH_3 and ν CH_2), 1743 cm^{-1} s (ν C=O), 1479 cm^{-1} w (δ OCH_2), 1438 cm^{-1} ms (δ_{as} CH_3), 1394 cm^{-1} m (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1275 cm^{-1} s (ν P=O), 1215 cm^{-1} w (ν C-O ester), 1164 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1121 cm^{-1} m [CH_2 from -C(=O)-CH_2-P(=O)- ?], 1053 and 1026 cm^{-1} s (ν P-O-C), 971 cm^{-1} ms (ν C-C of POEt), 841 cm^{-1} m (C-O ?), 783 cm^{-1} (POC), 715 cm^{-1} w (ν P-C), 616 cm^{-1} m (δ C=O), 501 cm^{-1} m (δ P=O).

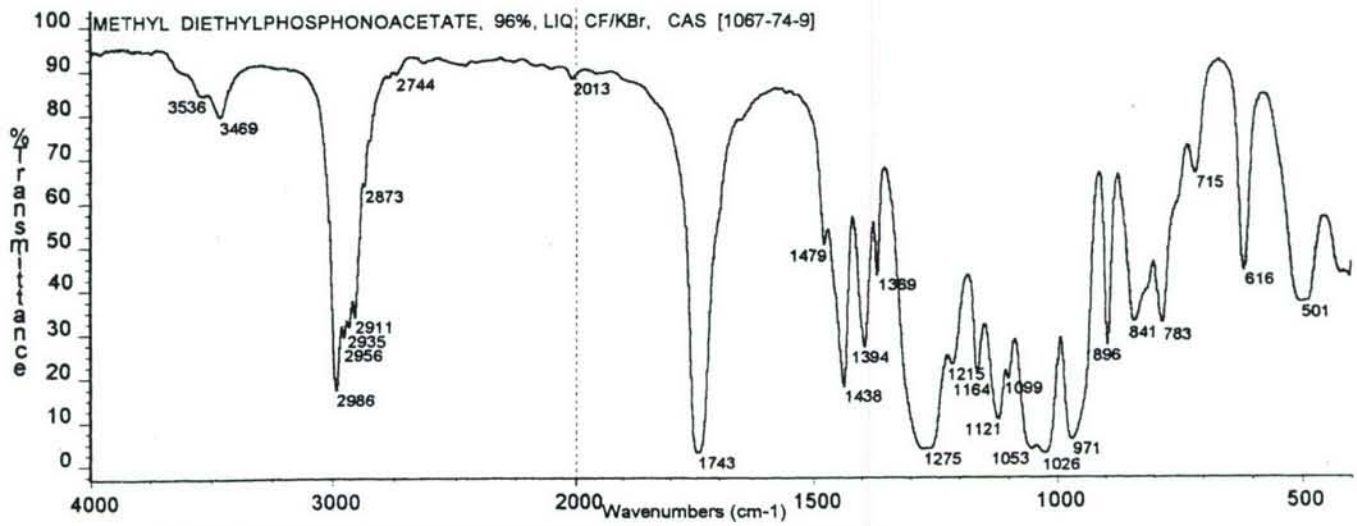


Figure 262 METHYL DIETHYLPHOSPHONOACETATE, 96%, LIQUID, CF/KBr

3.5.8.61 Triethyl Phosphonoacetate (Diethyl Ethoxycarbonylmethylphosphonate)

$CH_3CH_2O\text{-}C(=O)\text{-}CH_2\text{-}P=O(OCH_2CH_3)_2$

The infrared spectrum of triethyl phosphonoacetate (diethyl ethoxycarbonylmethylphosphonate) as a liquid film between KBr windows is given in ***Figure 263***. The band assignments are as follows: 3547 cm^{-1} vvw (H_2O), 3457 cm^{-1} vw (2 x 1739 = 3478 cm^{-1}), 2985 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), 2910 cm^{-1} m (ν_{sy} CH_3), 2874 cm^{-1} w (ν_{sy} CH_2), 1739 cm^{-1} s (ν C=O), 1479 cm^{-1} w (δ OCH_2), 1466 cm^{-1} vw and 1446 cm^{-1} m (δ_{as} CH_3), 1393 cm^{-1} m (ω OCH_2, a shoulder on this band near 1403 cm^{-1} could be the δ P-CH_2 ?), 1368 cm^{-1} m (δ_{sy} CH_3), 1272 cm^{-1} s (ν P=O), 1213 cm^{-1} w (ν C-O), 1164 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1118 cm^{-1} m [CH_2 of -C(=O)-CH_2-P(=O)- ?], 1053 and 1029 cm^{-1} s (ν P-O-C), 970 cm^{-1} ms (ν C-C of POEt), 842 cm^{-1} m (C-O ?), 785 cm^{-1} w (POC), 713 cm^{-1} vw (ν P-C), 614 cm^{-1} w (δ C=O), 504 w (δ P=O).

3.5.8.62 Triethyl 2-Phosphonopropionate $CH_3CH_2O\text{-}C(=O)\text{-}CH(CH_3)\text{-}P=O(OCH_2CH_3)_2$

The infrared spectrum of trientyl 2-phosphonopropionate as a liquid film between KBr windows is given in ***Figure 264***. The band assignments are as follows: 3448 cm^{-1} vvw (2 x 1735 = 3470 cm^{-1}), 2984 cm^{-1} m (ν_{as} CH_3), 2941 cm^{-1} w (ν_{as} CH_2), 2909 cm^{-1} w (ν_{sy} CH_3), 2886 cm^{-1} sh (ν_{sy} CH_2), 1735 cm^{-1} s (ν C=O), 1477 cm^{-1} sh (δ OCH_2), 1457 cm^{-1} w and 1448 cm^{-1} sh (δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2), 1368 cm^{-1} w (δ_{sy} CH_3),

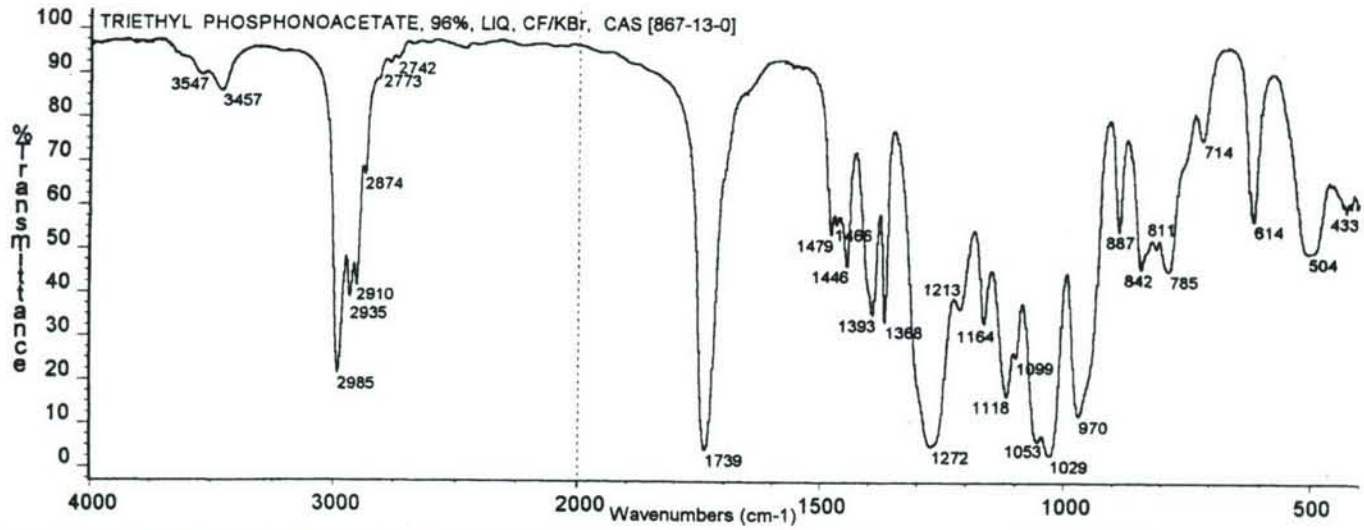


Figure 263 TRIETHYL PHOSPHONOACETATE (DIETHYL ETHOXYCARBONYLMETHYLPHOSPHONATE), 96%, LIQUID, CF/KBr

POEt, characteristic), 1052 cm^{-1} m (ν C-O ester), 1258 cm^{-1} ms (ν P=O), 1181 cm^{-1} m (CH_3 rock ?), 1164 and 1096 cm^{-1} w (CH_3 rock of and 1025 cm^{-1} s (ν P-O-C), 967 cm^{-1} m (ν C-C of POEt), 818 and 807 cm^{-1} w (POC), 627 cm^{-1} vw (O=C-X bending), 549 cm^{-1} vw (O=P-X bending).

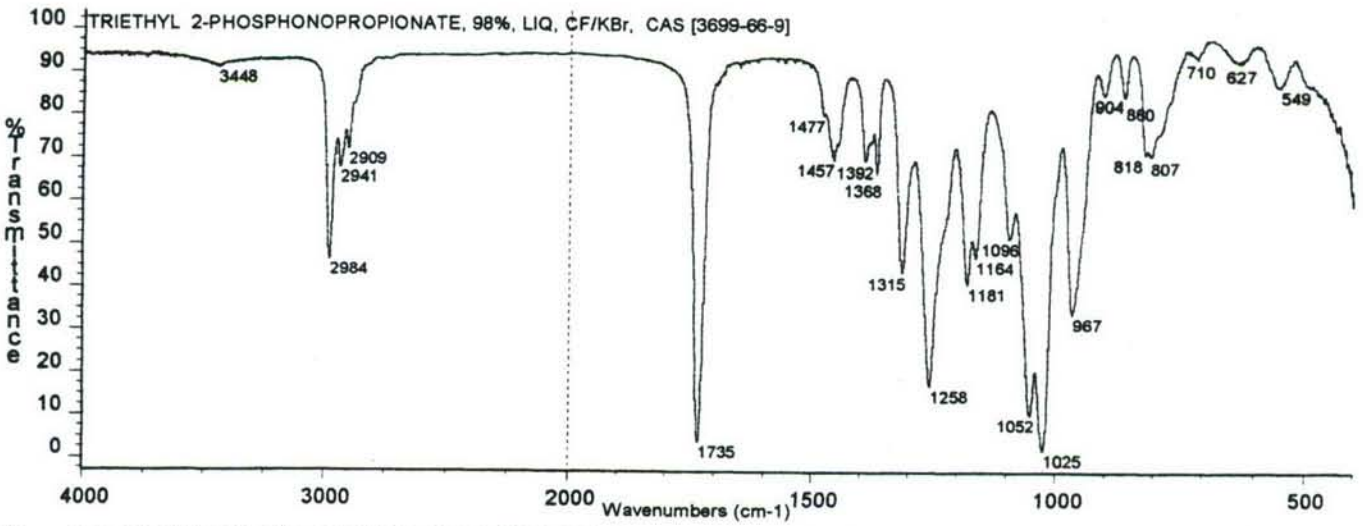


Figure 264 TRIETHYL 2-PHOSPHONOPROPIONATE, 98%, LIQUID, CF/KBr

3.5.8.63 Trimethyl 2-Phosphonoacrylate $CH_3O\text{-}C(=O)\text{-}C(=CH_2)\text{-}P=O(OCH_3)_2$

The infrared spectrum of a liquid film of trimethyl 2-phosphonoacrylate between KBr windows is given in ***Figure 265***. The band assignments are as follows: 3437 cm^{-1} vvw (2 x 1726 = 3452 cm^{-1}), 3106 cm^{-1}

vw (ν_{as} =CH_2), 3004 cm^{-1} w (ν_{sy} =CH_2), 2915 cm^{-1} sh (ν_{sy} CH_3), 2958 cm^{-1} m (ν_{as} CH_3 from $POCH_3$), 2854 cm^{-1} w (ν_{sy} CH_3 from $POCH_3$), 1726 cm^{-1} s (ν C=O), 1607 cm^{-1} w (ν C=C, lowered by conjugation with the C=O and the attached heavy P atom), 1439 cm^{-1} ms (δ CH_3), 1395 cm^{-1} m (δ CH_2, scissoring), 1303 cm^{-1} ms and ca 1275 cm^{-1} sh (CCCO), 1258 cm^{-1} s (ν P=O), 1188, 1162, 1140 cm^{-1} m (CH_3 rock of $POCH_3$ and C-C-O), 1054 and 1031 cm^{-1} s (ν P-O-C), 888 cm^{-1} ms (=CH_2 wag), 835, 803 cm^{-1} ms (=CH_2 twist and POC), 672 cm^{-1} w (C=O deformation), 556 cm^{-1} m (P=O deformation).

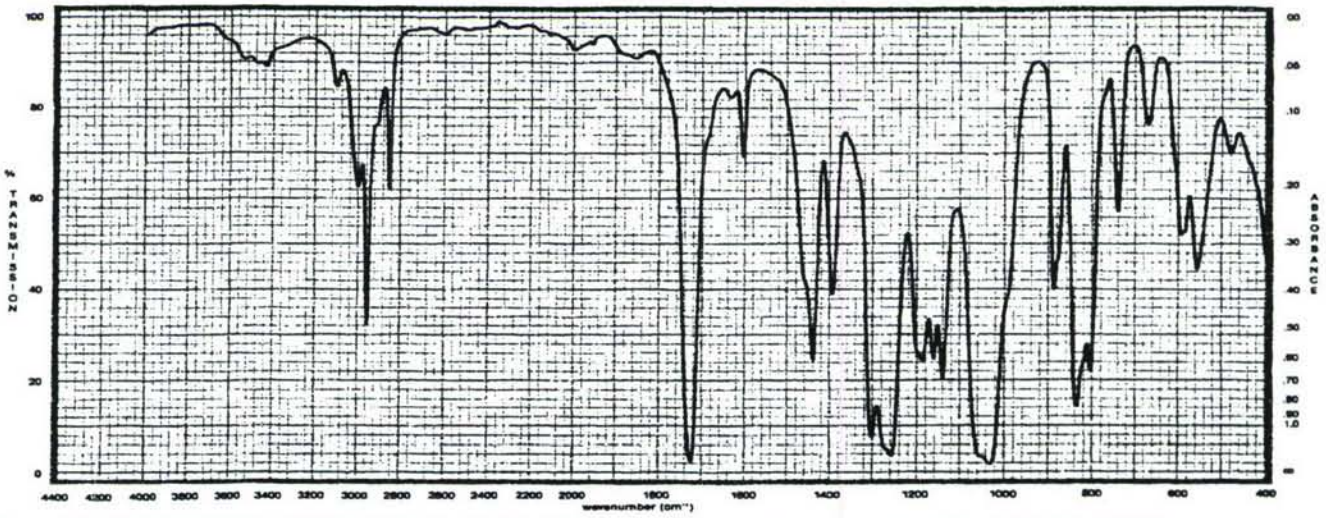


Figure 265 TRIMETHYL 2-PHOSPHONOACRYLATE (STABILIZED WITH 0.5% BHT), 95%, LIQUID, CF/KBr

3.5.8.64 Triethyl 4-Phosphonocrotonate CH_3CH_2O-C(=O)-HC=CH-CH_2-P=O(OCH_2CH_3)$_2$

The infrared spectrum of triethyl 4-phosphonocrotonate as a liquid film between KBr windows is reproduced as ***Figure 266***. The band assignments are as follows: 3422 cm^{-1} vvw (2 x 1720 = 3440 cm^{-1}), 2983 cm^{-1} m (ν_{as} CH_3), 2936 cm^{-1} w (ν_{as} CH_2), 2907 cm^{-1} w ($\nu_{sy,}$ CH_3), 2875 cm^{-1} vw (ν_{sy} CH_2), 1720 cm^{-1} ms (ν C=O), 1653 cm^{-1} m (ν C=C), 1478 cm^{-1} vw (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2), 1368 cm^{-1} w (δ_{sy} CH_3), 1322 cm^{-1} m (ν C-O, =C-H rock ?), 1260 cm^{-1} (ν P=O), 1199 cm^{-1} ms (part of ν_{as} CC-OC), 1164 and 1097 cm^{-1} w (CH_3 rock of POEt, characteristic), 1043 and 1028 cm^{-1} s (ν P-O-C), 966 cm^{-1} m (ν C-C of POEt, *trans* C-H wag ?)), 843 cm^{-1} w (ν_{sy} CCOC), 800 cm^{-1} w (POC), 738 cm^{-1} vw (*cis* C-H wag ?), 688 cm^{-1} vw (C=O wag ?), 534 cm^{-1} vw (P=O deformation).

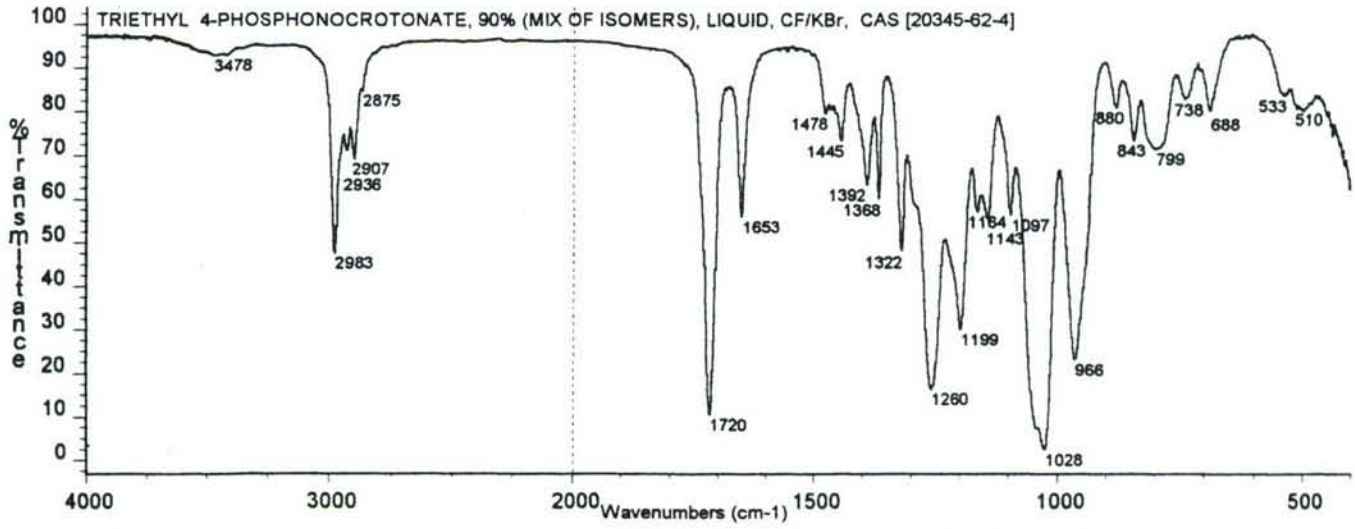


Figure 266 TRIETHYL 4-PHOSPHONOCROTONATE (90%, MIX OF ISOMERS), LIQUID, CF/KBr

3.5.8.65 Tetramethyl Methylenediphosphonate $(CH_3O)_2P(=O)\text{-}CH_2\text{-}P=O(OCH_3)_2$

The infrared spectrum of tetramethyl methylenediphosphonate as a liquid film between KBr windows is presented as ***Figure 267***. The band assignments are as follows: ca 3500 cm^{-1} vvw (H_2O), 3002 cm^{-1} sh, 2958 cm^{-1} ms, 2900 cm^{-1} w and 2854 cm^{-1} m (ν CH_3), 1875 cm^{-1} vw (1032 + 848 = 1880 cm^{-1} and 1032 + 818 = 1850 cm^{-1}), 1464 cm^{-1} m (δ_{as} and δ_{sy} CH_3), 1375 cm^{-1} w (δ CH_2, lowered by the two attached P=O groups), 1258 cm^{-1} s (ν P=O), 1189 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1032 cm^{-1} s (ν P-O-C), 848 and 818 cm^{-1} ms (POC),

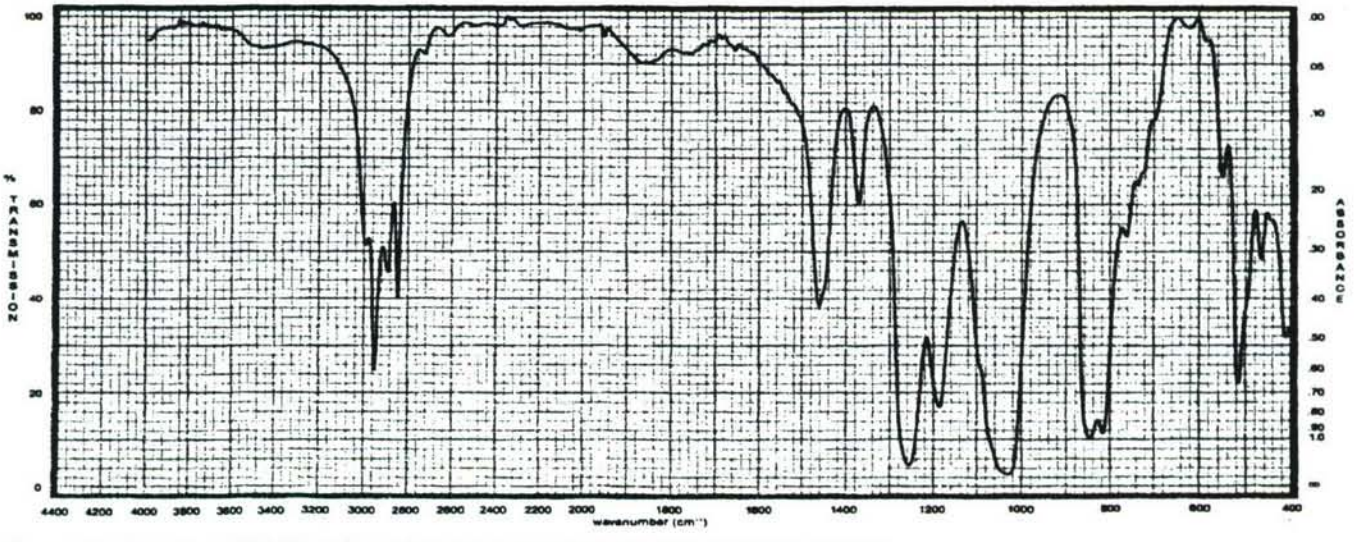


Figure 267 TETRAMETHYL METHYLENEDIPHOSPHONATE, LIQUID, CF/KBr

765 cm^{-1} vw (CH_2 rock),737 cm^{-1} vw (ν P-C), 517 m (P=O deformation).

3.5.8.66 Tetraethyl Methylenediphosphonate $(CH_3CH_2O)_2P(=O)-CH_2-P=O(OCH_2CH_3)_2$

The infrared spectrum of tetraethyl methylenediphosphonate as a liquid film between KBr windows is reproduced as ***Figure 268***. The band assignments are as follows: 3536 and 3478 cm^{-1} vvw (H_2O), 2983 cm^{-1} ms (ν_{as} CH_3), 2933 cm^{-1} m (ν_{as} CH_2), 2908 cm^{-1} m (ν_{sy} CH_2), 2874 cm^{-1} sh (ν_{sy} CH_2), 1848 cm^{-1} vvw (1028 + 830 = 1858 cm^{-1}), 1480 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1393 cm^{-1} m (ω OCH_2), 1368 cm^{-1} w (δ_{sy} CH_3), 1258 cm^{-1} s (ν P=O), 1184 cm^{-1} sh (CH_2 from P-CH_2-P ?), 1165 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1028 cm^{-1} s (ν P-O-C), 971 cm^{-1} ms (ν C-C of POEt), 830 cm^{-1} ms (POC), 724 cm^{-1} vw (ν P-C), 516 cm^{-1} m (P=O deformation).

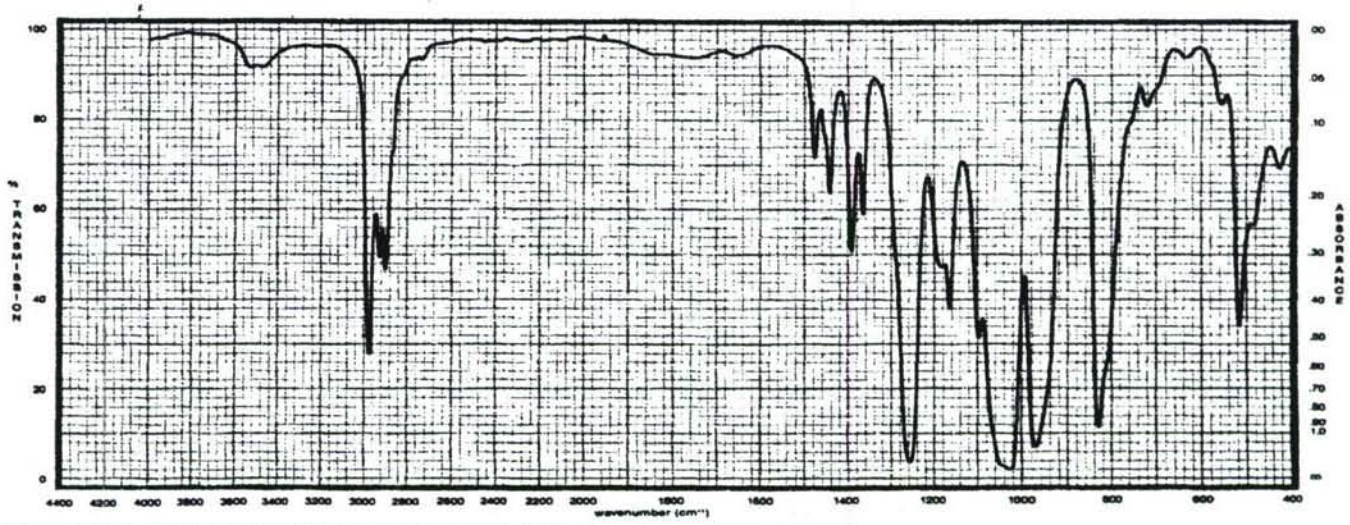


Figure 268 TETRAETHYL METHYLENEDIPHOSPHONATE, LIQUID, CF/KBr

3.5.8.67 Tetraethyl Decamethylenediphosphonate $(CH_3CH_2O)_2P(=O)-(CH_2)_{10}-P=O(OCH_2CH_3)_2$

The infrared spectrum of tetraethyl decamethylenediphosphonate as as liquid film between KBr windows is presented as ***Figure 269***. The aband assignments are as follows: 2981 cm^{-1} m (ν_{as} CH_3), 2930 cm^{-1} ms (ν_{as} CH_2), 2855 cm^{-1} m (ν_{sy} CH_2), 1959 cm^{-1} vvw (spurious band, instrumental in origin), 1465 cm^{-1} w (δ CH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2), 1368 cm^{-1} vw (δ_{sy} CH_3), 1246 cm^{-1} ms (ν P=O), 1164 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 959 cm^{-1} ms (ν C-C of POEt), 809 cm^{-1} m (POC), 788 cm^{-1} m

(POC and/or CH_2 rock ?), 726 cm^{-1} vw (ν P-C), 547 cm^{-1} w (P=O deformation).

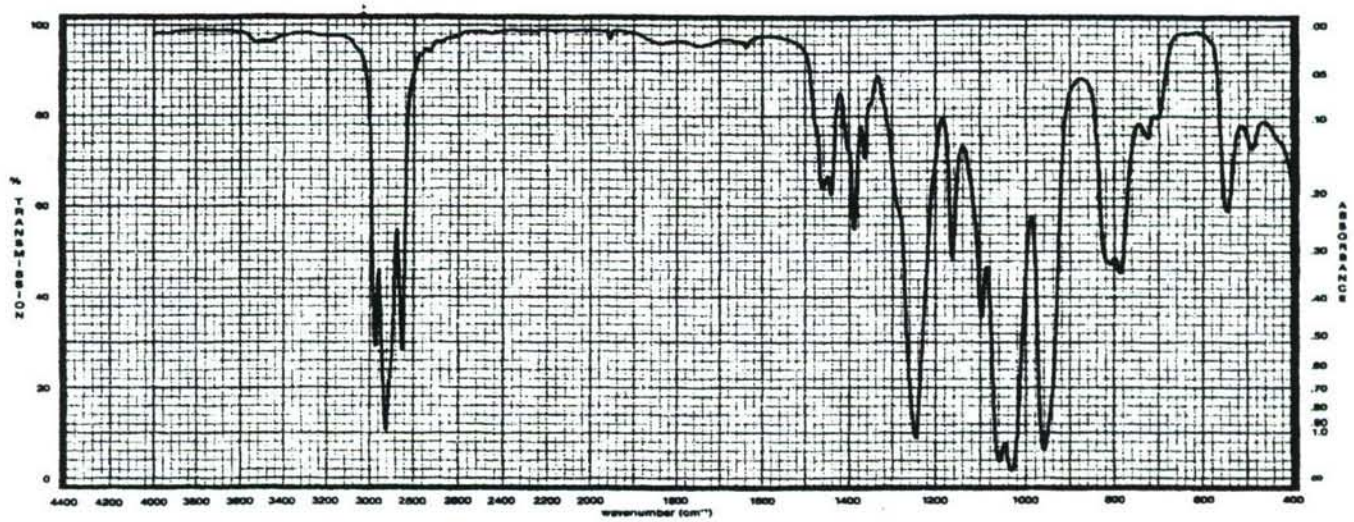


Figure 269 TETRAETHYL DECAMETHYLENEDIPHOSPHONATE, LIQUID, CF/KBr

3.5.8.68 Tetraisopropyl Methylenediphosphonate $[(CH_3)_2CH\text{-}O]_2P(=O)\text{-}CH_2\text{-}P=O[O\text{-}CH(CH_3)_2]_2$

The infrared spectrum of a thin liquid film of tetraisopropyl methylenediphosphonate between KBr windows is reproduced as ***Figure 270***. The band assignments are as follows: 3538 and 3482 cm^{-1} vw (H_2O), 2980 cm^{-1} m, 2935 cm^{-1} w and 2877 cm^{-1} vw (ν_{as} and ν_{sy} CH_3, and ν -CH), 1468 cm^{-1} w and 1454 cm^{-1} sh (δ_{as} CH_3), 1386 and 1376 cm^{-1} m (δ_{sy} CH_3), ca 1355 cm^{-1} sh (δ -C-H), 1256 cm^{-1} ms (ν P=O), 1178, 1143 and 1108 cm^{-1} w-m (triplet characteristic of P-O-isopropyl, the 1178 cm^{-1} band may also have some contribution from a

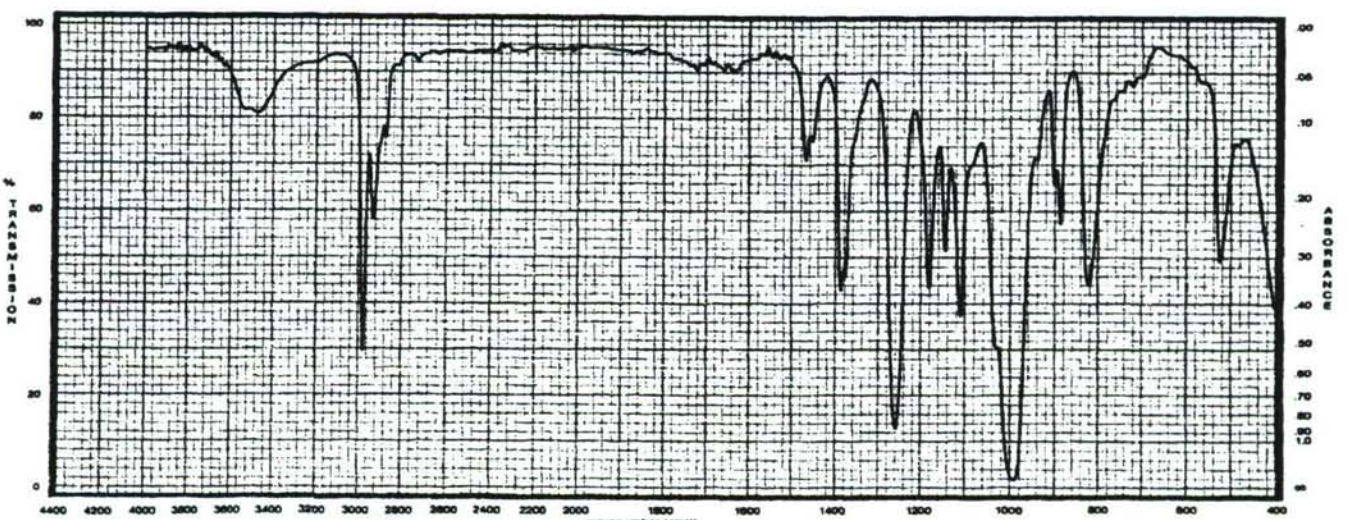


Figure 270 TETRAISOPROPYL METHYLENEDIPHOSPHONATE, LIQUID, CF/KBr

CH_2 vibration from -P-CH_2-P-), 1028 cm^{-1} sh and 988 cm^{-1} s (ν P-O-C), 899 and 885 cm^{-1} w (CH_3 rock), 819 cm^{-1} m (POC), 522 cm^{-1} w (P=O deformation).

3.5.9 **Phosphinic Halides** $(R)_2P{=}O(X)$

3.5.9.1 Methylphosphinic Fluoride CH_3-P=O(H)(F)

The infrared spectrum for a liquid film of methylphosphinic fluoride between Irtran 6 windows is presented in ***Figure 271***. The band assignments are as follows: 2998 cm^{-1} w (ν_{as} CH_3), 2924 cm^{-1} w (ν_{sy} CH_3), some broadening in the 2900 cm^{-1} region may indicate the presence of POH, 2430 cm^{-1} w (ν P-H), 1415 cm^{-1} w (δ_{as} P-CH_3), 1311 cm^{-1} ms (δ_{sy} P-CH_3), 1263 cm^{-1} s (ν P=O), 1041, 1007 cm^{-1} m and 948, 929 cm^{-1} w (possible δ and γ P-H deformations),[II] 882 cm^{-1} ms (P-CH_3 rock), 854 and 829 cm^{-1} ms (ν P-F), 733 cm^{-1} w (ν P-C), 471 cm^{-1} w and 425 cm^{-1} m (P=O and P-F deformations).

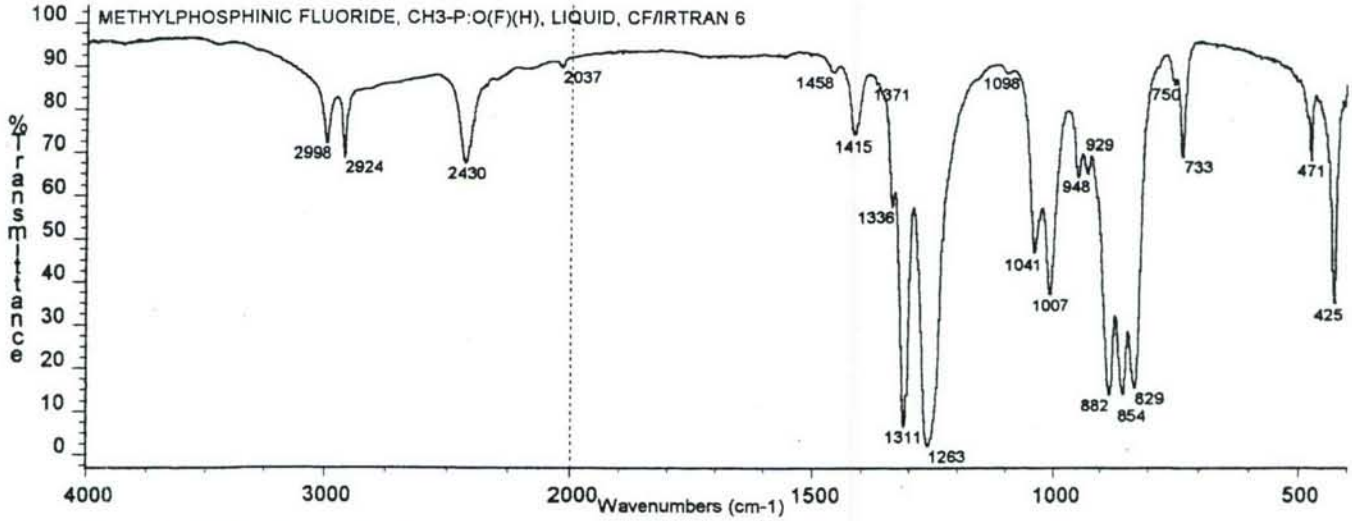


Figure 271 METHYLPHOSPHINIC FLUORIDE, LIQUID, CF/IRTRAN 6

The effect of atmospheric moisture on methylphosphinic fluoride is illustrated by the infrared spectra presented in ***Figure 272***. After 1 day of exposure to atmospheric moisture, the spectrum shows the presence of a P-acid by the formation of broad POH bands near 2788 cm^{-1}, 2403 cm^{-1} (P-H and POH) and 1650 cm^{-1}. The

[II] Thomas, L.C. in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 59, Heyden & Son Ltd, London, 1974, lists the ranges of 1015-897 cm^{-1} and 1150-1031 cm^{-1} for the P-H deformations. Thomas further states that these two bands may be the δ and γ vibrations as postulated by Schindlbauer (Schindlbauer, H. and Steininger, E., *Monatsh. Chem.*, **92**, 868 (1961).

P=O stretching vibration has fallen to 1181 cm^{-1}. By the 2nd day the P=O band has decreased to 1173 cm^{-1} while the P-H group is still evident at 2391 cm^{-1} and 1019 cm^{-1}. By the 5th day of exposure to atmospheric moisture the P=O band has decreased in value to 1165 cm^{-1} as a large amount of water is now evident in the spectrum at 3380 cm^{-1}. The hydrolysis of methylphosphinic fluoride to form methylphosphinic acid may be summarized as follows: $CH_3\text{-}P{=}O(H)(F)$ $\xrightarrow{-HOH}$ $CH_3\text{-}P{=}O(H)(OH) + HF\uparrow$.

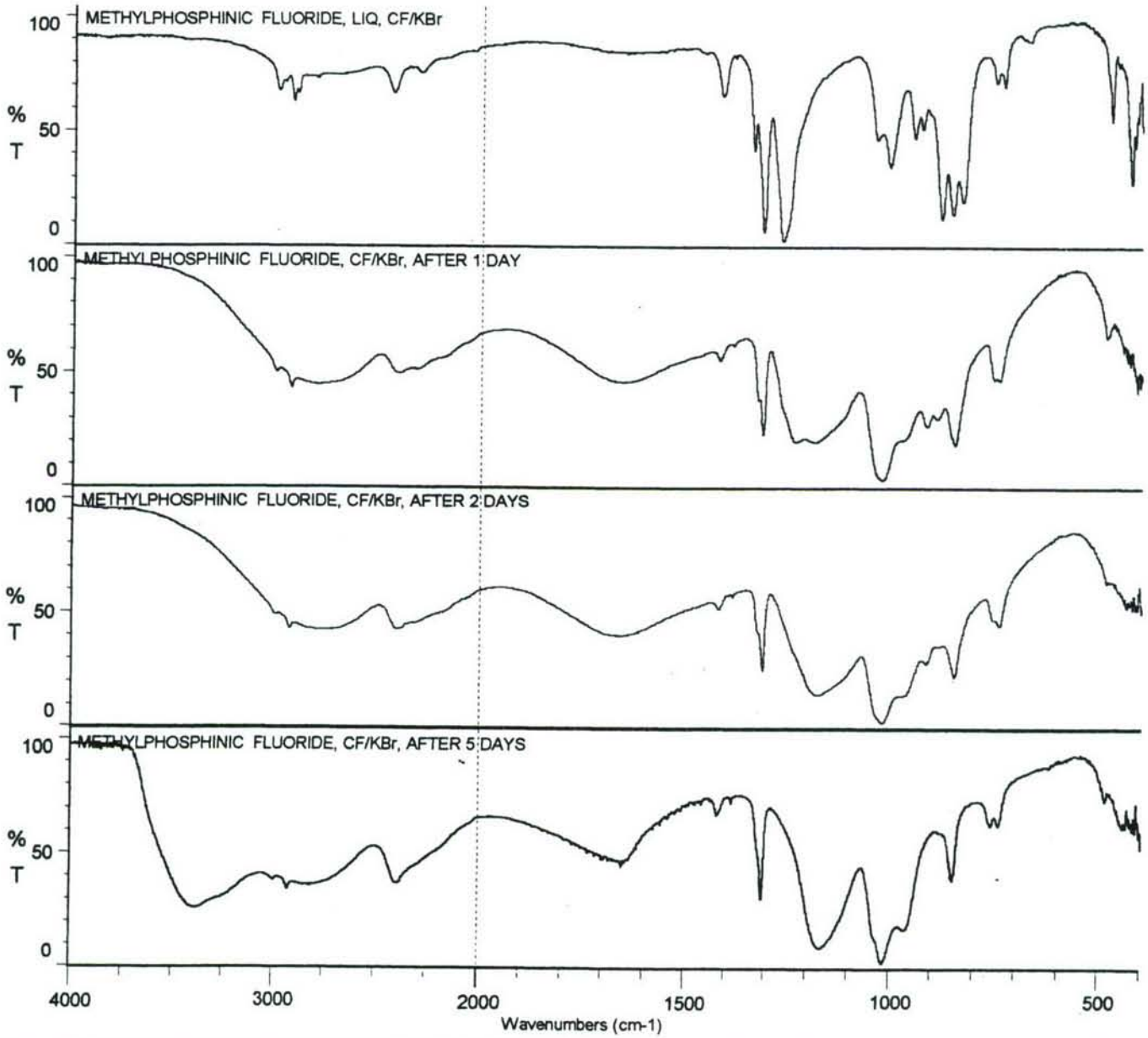


Figure 272 METHYLPHOSPHINIC FLUORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.9.2 Chloromethylmethylphosphinic Fluoride $(Cl\text{-}CH_2)CH_3P{=}O(F)$

The infrared spectrum for chloromethylmethylphosphinic fluoride as a thin liquid film between KBr windows is given in ***Figure 273***. The band assignments are as follows: 2999 cm^{-1} ms, 2943 cm^{-1} m and 2926 cm^{-1} sh (ν CH_3 and ν CH_2), ca 3000, 2300 and 1650 cm^{-1} regions (some indication of broadening in these regions due to presence of POH moiety), 1411 and 1397 cm^{-1} m (δ_{as} P-CH_3, and δ CH_2), 1310 cm^{-1} ms (δ_{sy} P-CH_3), 1271 cm^{-1} s (ν P=O), 1218 cm^{-1} ms (ω CH_2-Cl), 1129 cm^{-1} w (CH_2), ca 980 cm^{-1} sh (ν P-OH from hydrolysis), 921 cm^{-1} ms (P-CH_3 rock), 855 and 830 cm^{-1} ms (ν P-F), 769 cm^{-1} m and 741 cm^{-1} ms (ν P-C), 668 cm^{-1} m (ν C-Cl), 482 cm^{-1} w, 449 and 423 cm^{-1} ms (P=O and P-F deformations).

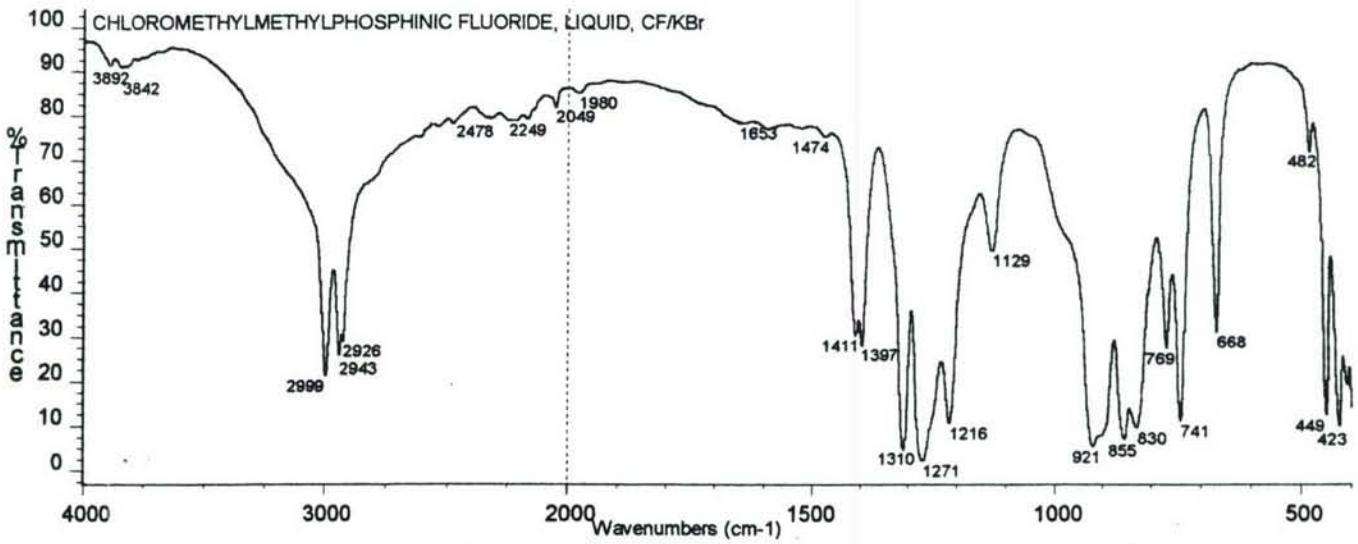


Figure 273 CHLOROMETHYLMETHYLPHOSPHINIC FLUORIDE, LIQUID, CF/KBr

3.5.9.3 Diethylphosphinic Chloride (Chlorodiethylphosphine Oxide) $(CH_3\text{-}CH_2)_2$ P=O(Cl)

The infrared spectrum of a thin liquid film of diethylphosphinic chloride (chlorodiethylphosphine oxide) between CsI windows is presented as ***Figure 274***. The band assignments are as follows: 2980 cm^{-1} ms (ν_{as} CH_3), 2944 cm^{-1} ms (ν_{as} CH_2), 2910 cm^{-1} m (ν_{sy} CH_3), 2884 cm^{-1} m (ν_{sy} CH_2), 1459 cm^{-1} ms (δ_{as} CH_3), 1405 cm^{-1} m (δ P-CH_2), 1384 cm^{-1} w (δ_{sy} CH_3), 1278 and 1252 cm^{-1} ms (ω and τ CH_2 of the P-Ethyl), 1215 cm^{-1}

s (ν P=O),[mm] 1047 and 1022 cm^{-1} m (ν C-C of P-Ethyl), 940 cm^{-1} w (may be due to the ν P-O-P of a pyro compound produced by hydrolysis), 772 cm^{-1} s (CH_2 rock), 721 and 697 cm^{-1} ms (ν P-C), 513 cm^{-1} s (ν P-Cl), 474 cm^{-1} s (O=P-C bending ?).

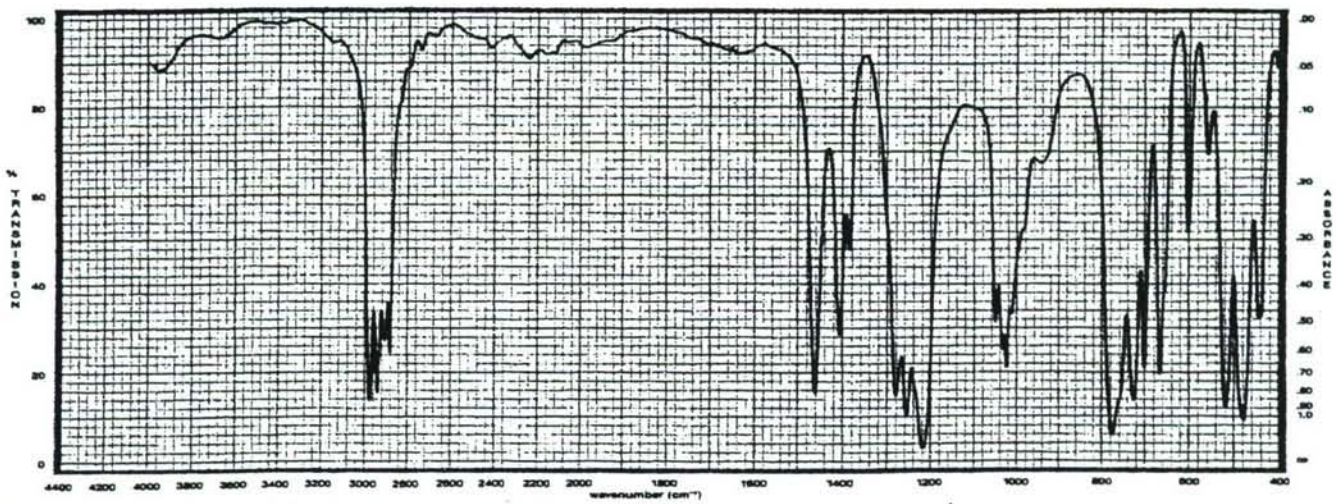


Figure 274 DIETHYLPHOSPHINIC CHLORIDE, LIQUID, CF/CsI

The effect of atmospheric moisture on diethylphosphinic chloride is illustrated by ***Figure 275***, which shows the compound after four days of exposure. The spectrum (***Figure 275***) shows the general appearance of a P-acid, with POH bands near 2800, 2240 and 1640 cm^{-1}. The P-Ethyl bands (CH_2 wag and twist) are now clearly evident at 1276 and 1239 cm^{-1}. The P=O stretch has been lowered and broadened to 1146 cm^{-1}. The bands at 1042 and 1015 cm^{-1} can be assigned to the C-C stretch, while the band at 950 cm^{-1} is assigned to the ν P-OH. The CH_2 rock is seen at 782 cm^{-1} and the ν P-C at 652 cm^{-1}. Very weak bands near 1097 and 617 cm^{-1} are indicative of cesium sulfate, Cs_2SO_4, from the cesium iodide windows used to contain the thin liquid film. The hydrolysis of diethylphosphinic chloride to diethylphosphinic acid may be summarized as follows:

$Cl\text{-}P{=}O(CH_2\text{-}CH_3)_2 \text{ -HOH} \rightarrow HO\text{-}P{=}O(CH_2\text{-}CH_3)_2 + HCl.$

[mm] The P-Ethyl group is characterized by two bands near 1250 cm^{-1}. In compounds having a P=O stretching vibration, falling in the same region as the P-Ethyl, interaction may occur. This may result in a splitting of the P=O stretching vibration band and thus may indicate the presence of the O=P-Ethyl moiety. Thomas, L.C. in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 97, Heyden and Son Ltd., London, 1974.

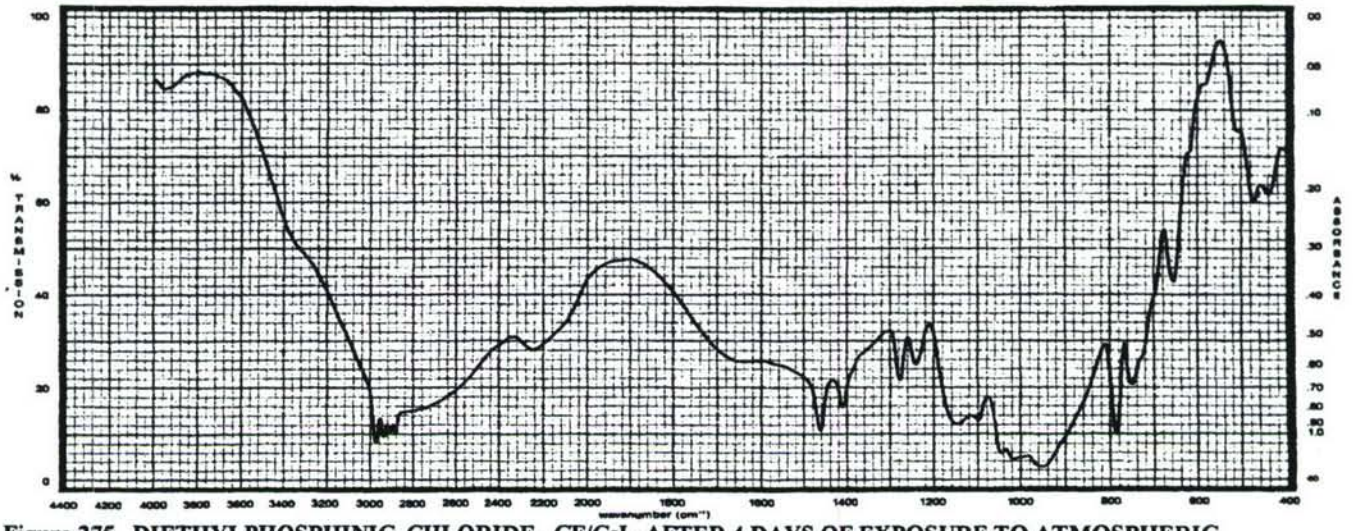


Figure 275 DIETHYLPHOSPHINIC CHLORIDE, CF/CsI, AFTER 4 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.9.4 Diphenylphosphinic Chloride (Chlorodiphenylphosphine Oxide) $(C_6H_5)_2P{=}O(Cl)$

The infrared spectrum of diphenylphosphinic chloride (chlorodiphenylphosphine oxide) as a thin liquid film between KBr discs (windows) is reproduced as ***Figure 276***. The band assignments are as follows: 3078 cm^{-1} sh, 3059 cm^{-1} w, 3026 and 2993 cm^{-1} vvw (ν C-H aromatic), 1589 cm^{-1} w, 1576 cm^{-1} vvw, 1482 cm^{-1} w and 1439 cm^{-1} ms (aromatic ring), 1234 cm^{-1} s (ν P=O), 1183, 1161, 1071, 1027 cm^{-1} all w and 997 cm^{-1} w (β C-H mono-substituted aromatic ring), 1121 cm^{-1} m (phenyl-P), 938 cm^{-1} w (somewhat broad, ν P-O-P of pyro impurity or hydrolysis product), 751 cm^{-1} m (γ C-H mono-substituted aromatic ring), 699 and 691 cm^{-1} ms

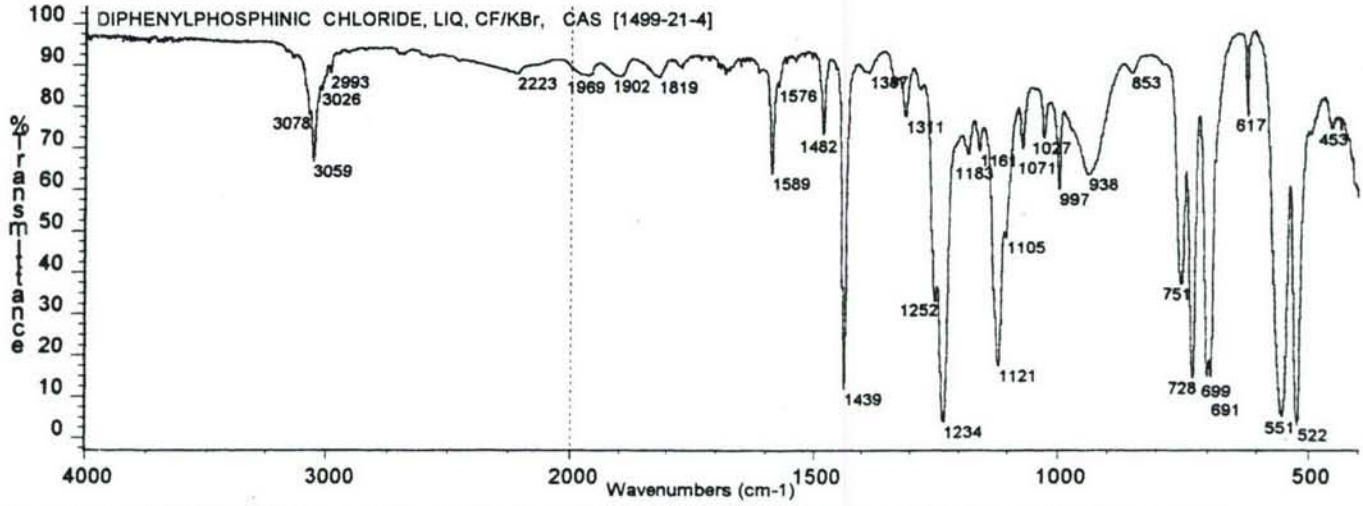


Figure 276 DIPHENYLPHOSPHINIC CHLORIDE (CHLORODIPHENYLPHOSPHINE OXIDE), LIQUID, CF/KBr

(δ mono-substituted aromatic ring), 551, 522 cm^{-1} s (ν P-Cl, mono-substituted aromatic ring quadrant out-of-plane bending mode ?).[nn]

The effect of atmospheric moisture on diphenylphosphinic chloride is illustrated by the infrared spectra presented in ***Figure 277***. The spectrum of the compound stays essentially the same over the period of 134 days. After 219 days the spectrum shows dramatic changes besides being very wet. The spectrum now resembles that given previously for diphenylphosphinic acid (***Figure 154***). Thus the hydrolysis of diphenylphosphinic chloride to diphenylphosphinic acid may be summarized as follows: $(C_6H_5)_2P{=}O(Cl)$ $\xrightarrow{-HOH}$ $(C_6H_5)_2P{=}O(OH) + HCl$

3.5.10 **Phosphinates** $(R)_2P{=}O(OR)$

3.5.10.1 Ethyl Hydrogenmethylphosphinate (YL) $CH_3\text{-}P{=}O(H)(OCH_2CH_3)$

The infrared spectrum of ethyl hydrogenmethylphosphinate (**YL**) as a liquid film between KBr windows and as a vapor is presented as ***Figure 278***. The band assignments for the liquid phase spectrum are as follows: 3519 and 3461 cm^{-1} vw (H_2O), 2984 cm^{-1} m (ν_{as} CH_3), 2934 cm^{-1} sh (ν_{as} CH_2), 2916 cm^{-1} w (ν_{sy} CH_3), 2874 cm^{-1} sh (ν_{sy} CH_2), 2356 cm^{-1} w (ν P-H), 1653 cm^{-1} vvw (H_2O), 1481 cm^{-1} vw (δ OCH_2), 1445 cm^{-1} vw (δ_{as} CH_3), 1413 cm^{-1} vw (δ_{as} P-CH_3), 1393 cm^{-1} w (ω OCH2), 1369 cm^{-1} vvw (δ_{sy} CH_3), 1303 cm^{-1} ms (δ_{sy} P-CH_3), 1227 cm^{-1} s (ν P=O, vapor is higher, 1269,1261 cm^{-1}), 1164 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1051 cm^{-1} ms (ν P-O-C), 998 cm^{-1} s (P-H deformation), 959 cm^{-1} ms (ν C-C of POEt), 848 cm^{-1} m (P-CH_3 rock),[oo] 776 cm^{-1} w (POC), 715 cm^{-1} vw (ν P-C), 465 cm^{-1} w (P=O deformation).

The effect of atmospheric moisture on ethyl hydrogenmethylphosphinate (**YL**) was discussed previously under the compound **QL** (ethyl 2-diisopropylaminoethyl methylphosphonite) ***Figures 91***, ***92*** and ***93***.

[nn] The IR-active quadrant out-of-plane bending mode of mono-substituted benzenes gives rise to a medium intensity band at 560-418 cm^{-1}. The band is somewhat substituent-sensitive and may interact with the out-of-plane bending modes of the substituent. Lin-Vien, D., Colthup, N.B., Fateley, W.G., and Grasselli, J.G. , "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules", p. 294, Academic Press, Inc., San Diego, CA, 1991.

[oo] In most P^{+5} organophosphorus compounds the P-CH_3 rock occurs with the range 935-874 cm^{-1}. However, in P^{+5} compounds containing both P-CH_3 and P-H groups the P-CH_3 rock is found within the limits of 850-842 cm^{-1}. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 95, Heyden & Son Ltd., London, 1974.

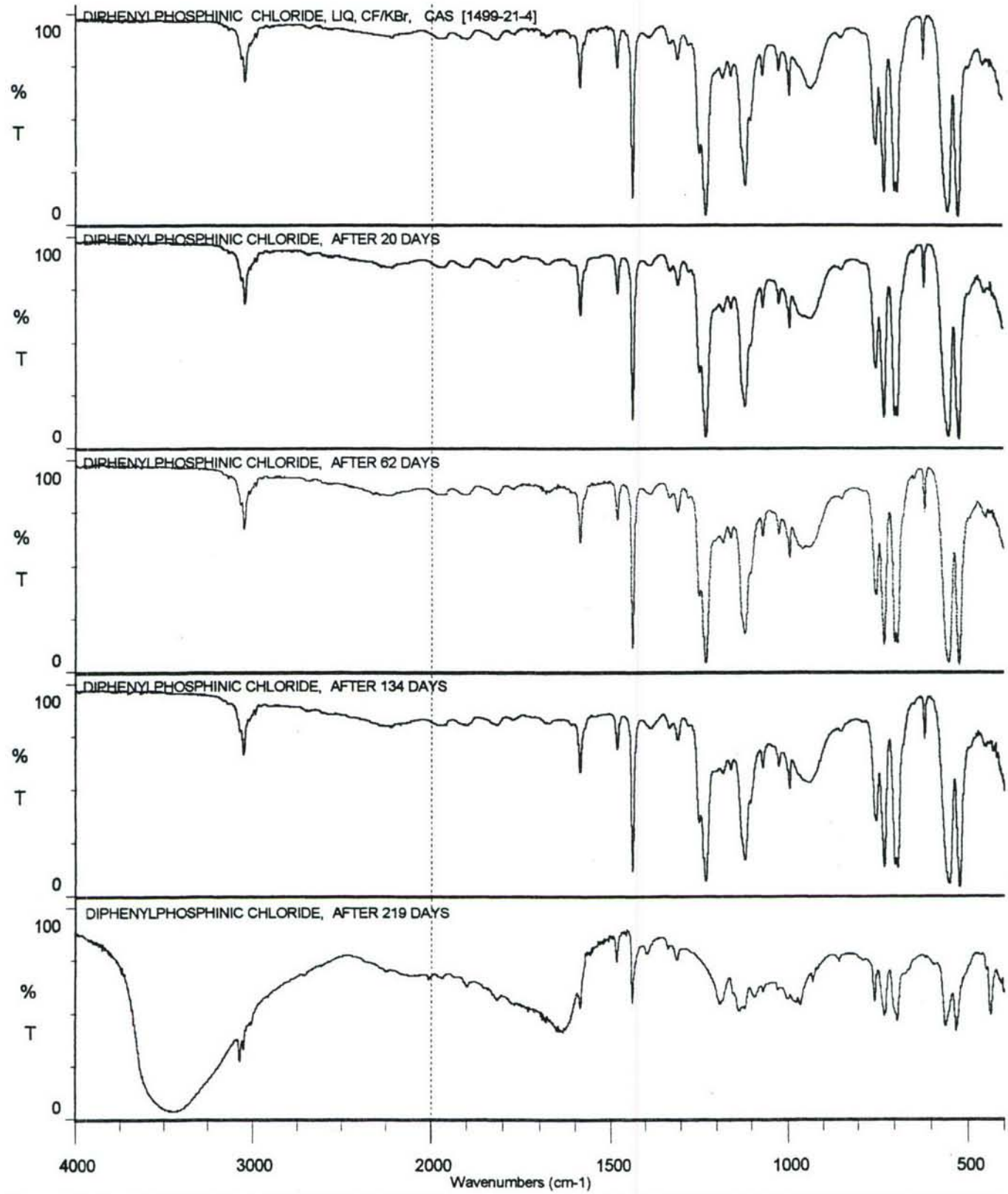


Figure 277 DIPHENYLPHOSPHINIC CHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

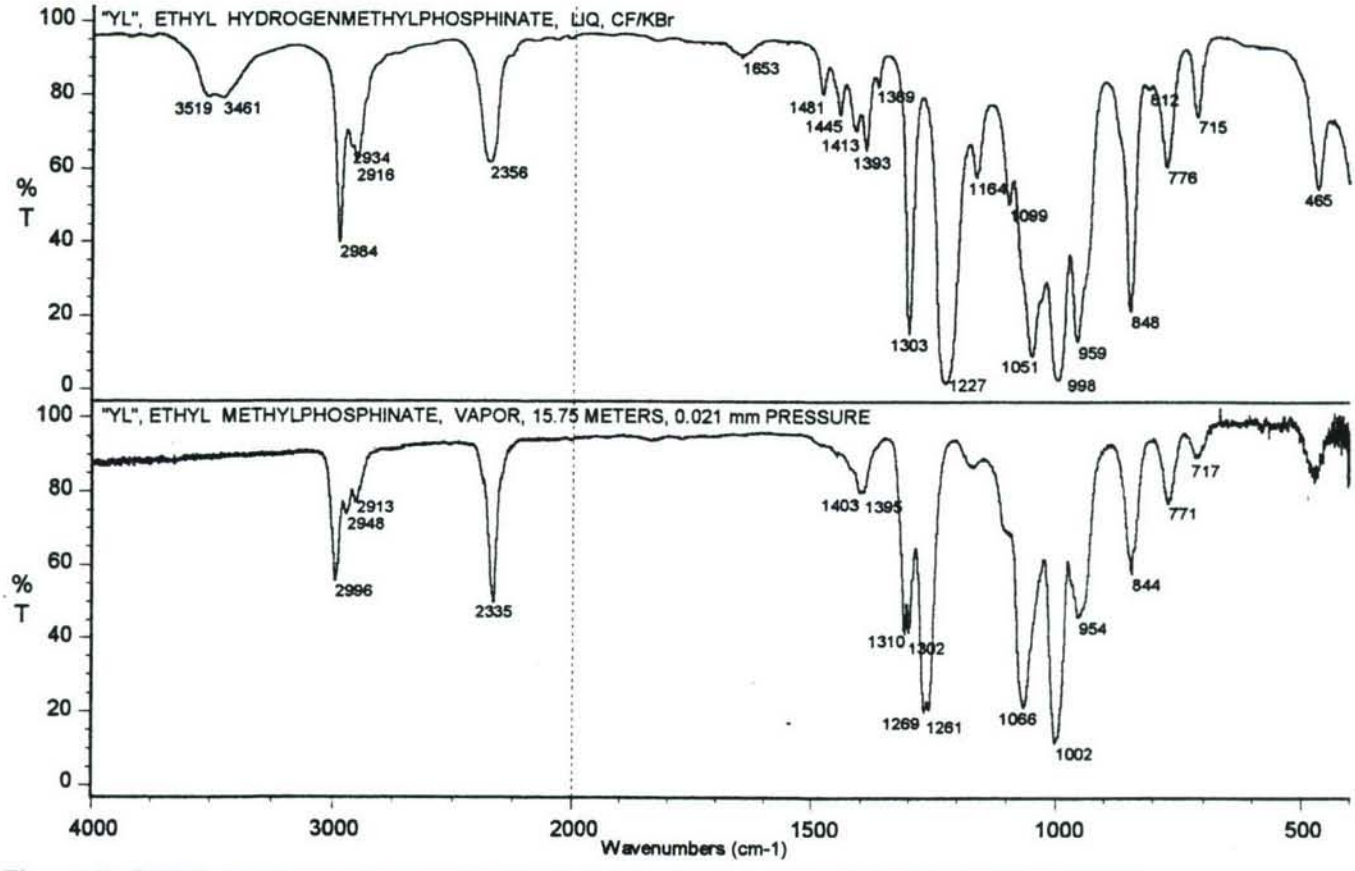


Figure 278 ETHYL HYDROGENMETHYLPHOSPHINATE (YL), UPPER SPECTRUM--LIQUID, CF/KBr, LOWER SPECTRUM--VAPOR, 15.75 Meters, 0.021 mm PRESSURE

3.5.10.2 Ethyl Ethylmethylphosphinate $CH_3\text{-}P{=}O(CH_2CH_3)(O\text{-}CH_2CH_3)$

The infrared spectrum of ethyl ethylmethylphosphinate as a thin liquid film between KBr windows is given in ***Figure 279***. The band assignments are as follows: 3505 and 3456 cm^{-1} w (H_2O), 2979 cm^{-1} ms (ν_{as} CH_3), 2941 cm^{-1} m (ν_{as} CH_2), 2914 cm^{-1} m (ν_{sy} CH_3), 2887 cm^{-1} sh (ν_{sy} CH_2), 1461 cm^{-1} m (δ OCH_2), 1446 cm^{-1} sh (δ_{as} CH_3), 1418 cm^{-1} m (δ P-CH_2, δ_{as} P-CH_3), 1392 cm^{-1} m (ω OCH_2), 1370 cm^{-1} sh (δ_{sy} CH_3), 1302 cm^{-1} ms (δ_{sy} P-CH_3), 1277 and 1242 cm^{-1} w (ω,τ CH_2 of P-Ethyl),[pp] 1211 cm^{-1} s (ν P=O, *calculated* value is 1208 cm^{-1}), 1163 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1050 cm^{-1} s (ν P-O-C), 1009 cm^{-1} w (ν C-C of P-Et), 952 cm^{-1} ms (ν C-C of POEt), 889 cm^{-1} ms (P-CH_3 rock), 797 cm^{-1} ms (POC), 753 cm^{-1} m (CH_2 rock from P-Et),

[pp] The P-Ethyl group has bands at 1290-1220 cm^{-1} w-m (doublet, ω,τ CH_2), 1050-950 cm^{-1} w-m (ν C-C), 800-700 cm^{-1} m-s (CH_2 rock) and 700-600 cm^{-1} w-m (ν P-C) according to Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S., and Mukhametov, F.S., "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)", p. 4, Nauka Publishers, Moscow, Kluwer Academic Publishers, Boston, 1990.

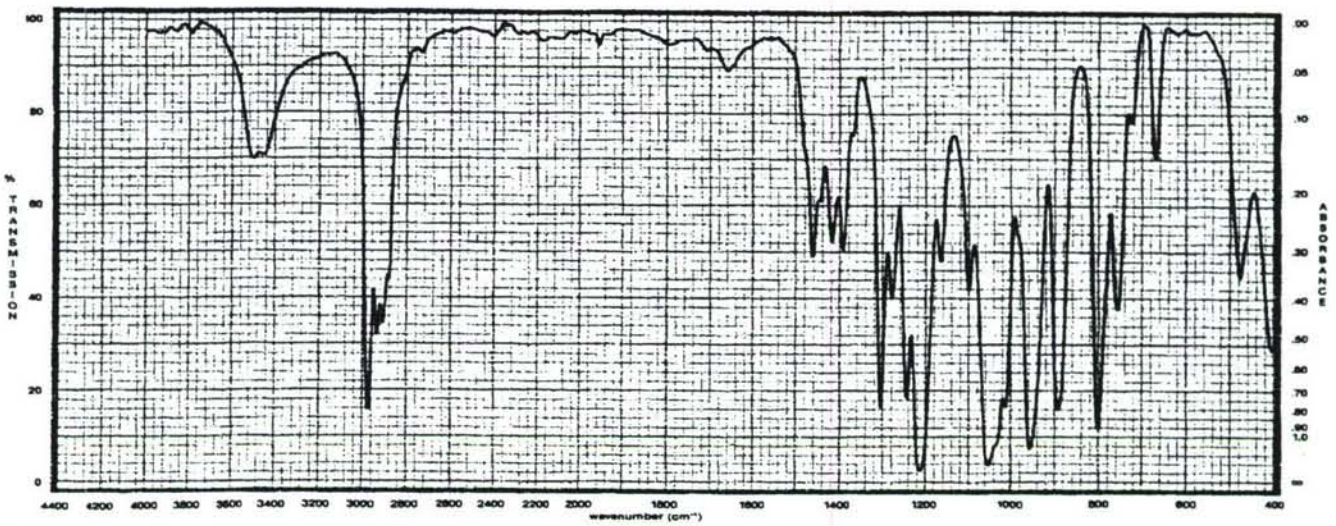


Figure 279 ETHYL ETHYLMETHYLPHOSPHINATE (TRX), LIQUID, CF/KBr

667 cm^{-1} w (ν P-C), 474 cm^{-1} w (P=O deformation).

The effect of atmospheric moisture on ethyl ethylmethylphosphinate (**TRX**) for a period of 44 hours has been previously discussed.[99] The infrared spectrum of the compound shows little change except for a decrease in the P=O stretching vibration to 1174 cm^{-1}. This decrease may be attributed to hydrogen bonding since the spectrum, after 44 hours, shows a very large increase in water content.

3.5.10.3 Ethyl Trichloromethylmethylphosphinate CH_3-P=O(CCl_3)(OCH_2CH_3)

The infrared spectrum of ethyl trichloromethylmethylphosphinate as a thin liquid film between CsI windows is presented as ***Figure 280***. The band assignments are as follows: 2987 cm^{-1} w, 2923 cm^{-1} w and 2870 cm^{-1} vvw (ν CH_3 and ν CH_2), 1745 cm^{-1} vvw (1255 + 494 = 1749 cm^{-1}), 1478 cm^{-1} vw (δ OCH_2), 1443 cm^{-1} vw (δ_{as} CH_3), 1413 cm^{-1} vw (δ_{as} P-CH_3), 1393 cm^{-1} w (ω OCH_2), 1369 cm^{-1} vw (δ_{sy} CH_3), 1305 cm^{-1} m (δ_{sy} P-CH_3), 1255 cm^{-1} s (ν P=O, *calculated* value is 1248 cm^{-1}), 1162 and 1097 cm^{-1} w (CH_3 rock of POEt, characteristic), 1034 cm^{-1} s (ν P-O-C), 972 cm^{-1} m (ν C-C of POEt), 907 cm^{-1} m (P-CH_3 rock), 763 cm^{-1} ms (ν_{as} CCl_3), 723 cm^{-1} w (ν P-C), 494 cm^{-1} m (P=O deformation).

[99] Piffath, R.J., "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part II. V-Agents and Related Compounds", 1999, U.S. Army Edgewood Research Development and Engineering Center, Aberdeen Proving Ground, Maryland, 21010, unpublished data.

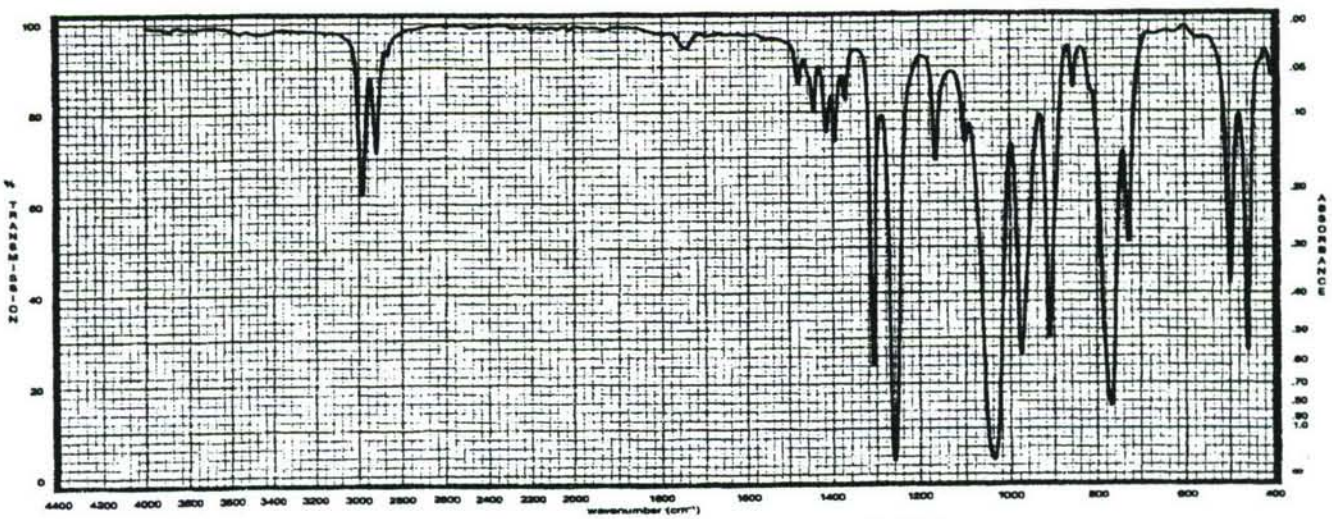


Figure 280 ETHYL TRICHLOROMETHYLMETHYLPHOSPHINATE, LIQUID, CF/CsI

3.5.10.4 Ethyl Chloromethylmethylphosphinate CH_3-P=O(CH_2Cl)(OCH_2CH_3)

The infrared spectrum of ethyl chloromethylmethylphosphinate as a thin liquid film between KBr windows is given in ***Figure 281***. The band assignments are as follows: 3463 cm^{-1} w and ca 1650 cm^{-1} vw (H_2O), 2987 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), ca 2908 cm^{-1} sh (ν_{sy} CH_3), 2872 cm^{-1} sh (ν_{sy} CH_2), 1480 cm^{-1} w (δ OCH_2), 1444 cm^{-1} w (δ_{as} CH_3), 1413 cm^{-1} sh (δ CH_2-Cl, δ_{as} P-CH_3), 1396 cm^{-1} m (ω OCH_2), 1368 vw (δ_{sy} CH_3), 1303 cm^{-1} ms (δ_{sy} P-CH_3), 1242 cm^{-1} ms (ν P=O, *calculated* value is 1236 cm^{-1}), 1202 cm^{-1} ms (ω CH_2-Cl), 1162 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1127 cm^{-1} vw (τ CH_2 ?), 1038 cm^{-1} s (ν P-O-C), 963 cm^{-1} ms (ν C-C of POEt), 907 cm^{-1} m (P-CH_3 rock), 844 cm^{-1} ms (CH_2 rock ?), 780 cm^{-1} w (POC), 728 cm^{-1} m (ν P-C), 660 cm^{-1} m (ν C-Cl), 461 cm^{-1} m (P=O deformation).

3.5.10.5 Ethyl Chloromethylphenylphosphinate C_6H_5-P=O(CH_2Cl)(OCH_2CH_3)

The infrared spectrum of ethyl chloromethylphenylphosphinate as a thin liquid film between KBr windows is reproduced as ***Figure 282***. The band assignments are as follows: 3465 cm^{-1} w and ca 1650 cm^{-1} vw (H_2O), 3078 cm^{-1} sh and 3058 cm^{-1} w (ν C-H aromatic), 2986 cm^{-1} m (ν_{as} CH_3), 2933 cm^{-1} m (ν_{as} CH_2), 2905 cm^{-1} w (ν_{sy} CH_3), 2869 cm^{-1} vw (ν_{sy} CH_2), 1971, 1908, 1830 and 1781 cm^{-1} all vw (mono-substituted aromatic ring summation band pattern), 1592 cm^{-1} w, 1483 cm^{-1} w and 1439 cm^{-1} ms (aromatic ring), 1478 cm^{-1} sh

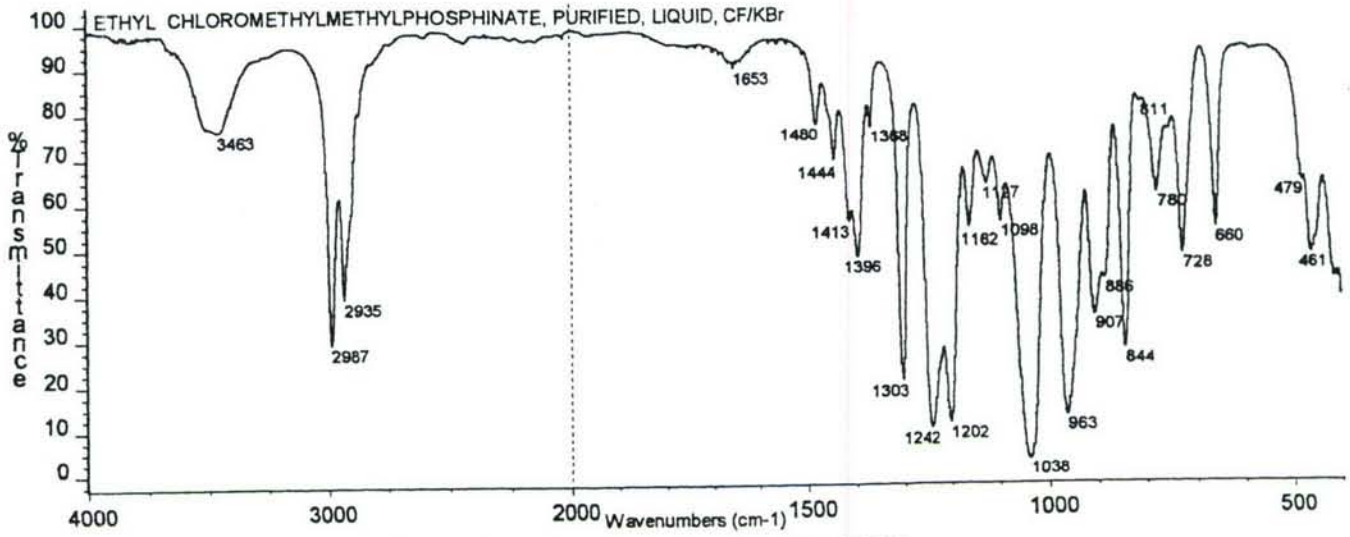


Figure 281 ETHYL CHLOROMETHYLMETHYLPHOSPHINATE, LIQUID, CF/KBr

(δ OCH_2), 1393 cm^{-1} m (ω OCH_2), 1368 cm^{-1} vw (δ_{sy} CH_3), 1243 cm^{-1} s (νP=O, the *calculated* value is 1236 cm^{-1}), 1202 cm^{-1} m (ω CH_2-Cl), 1161 and 1097 cm^{-1} w (CH_3 rock of POEt, characteristic), 1128 cm^{-1} ms (phenyl-P), 1034 cm^{-1} s (ν P-O-C), 998 cm^{-1} w (β C-H mono-substituted aromatic ring), 960 cm^{-1} ms (ν C-C of POEt), 823 cm^{-1} ms (CH_2 rock ?), 751 cm^{-1} m (γ C-H mono-substituted aromatic ring), 696 cm^{-1} ms (δ mono-substituted aromatic ring), 682 cm^{-1} w (ν C-Cl), 530 cm^{-1} ms (mono-substituted aromatic ring quadrant out-of-plane bending mode ?), 499 cm^{-1} w (P=O deformation ?).

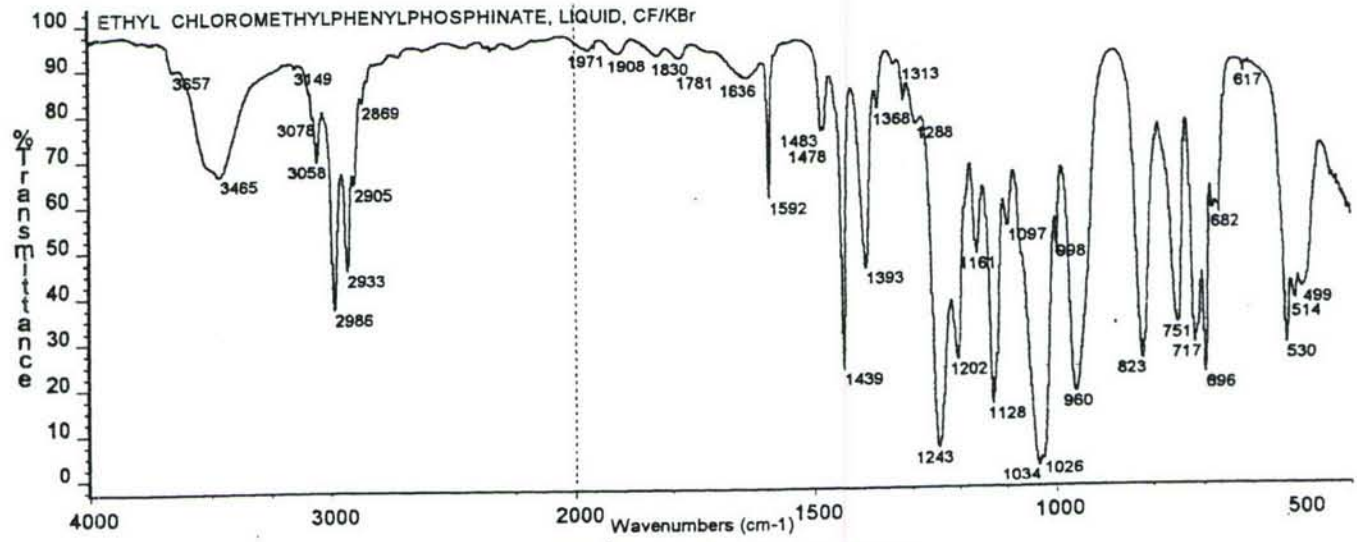


Figure 282 ETHYL CHLOROMETHYLPHENYLPHOSPHINATE, LIQUID, CF/KBr

3.5.10.6 Ethyl Trifluoromethylmethylphosphinate $CH_3\text{-}P{=}O(CF_3)(OCH_2CH_3)$

The infrared spectrum of ethyl trifluoromethylmethylphosphinate as a thin liquid film between CsI windows is presented as ***Figure 283***. The band assignments are as follows: 2990 cm^{-1} m, 2922 cm^{-1} m, 2878 cm^{-1} sh (ν CH_3 and ν CH_2), 1480 cm^{-1} w (δ OCH_2), 1446 cm^{-1} w (δ_{as} CH_3), 1415 cm^{-1} w (δ_{as} P-CH_3), 1395 cm^{-1} m (ω OCH_2), 1371 cm^{-1} w (δ_{sy} CH_3), 1312 cm^{-1} ms (δ_{sy} P-CH_3), 1274 cm^{-1} s (ν P=O, *calculated* value is 1272 cm^{-1}), 1218 and 1126 cm^{-1} s (ν_{as} and ν_{sy} CF_3), 1029 cm^{-1} s (ν P-O-C), 970 cm^{-1} ms (ν C-C of POEt), 878 cm^{-1} ms (P-CH_3 rock), 791 cm^{-1} m (POC), 746 cm^{-1} mm (δ_{sy} C-F ?), 720 cm^{-1} m (ν P-C of P-CH_3), 539 cm^{-1} w (δ_{as} C-F ?), 499 cm^{-1} ms (P=O deformation ?), 455 cm^{-1} ms (ν P-C of P-CF_3).[rr]

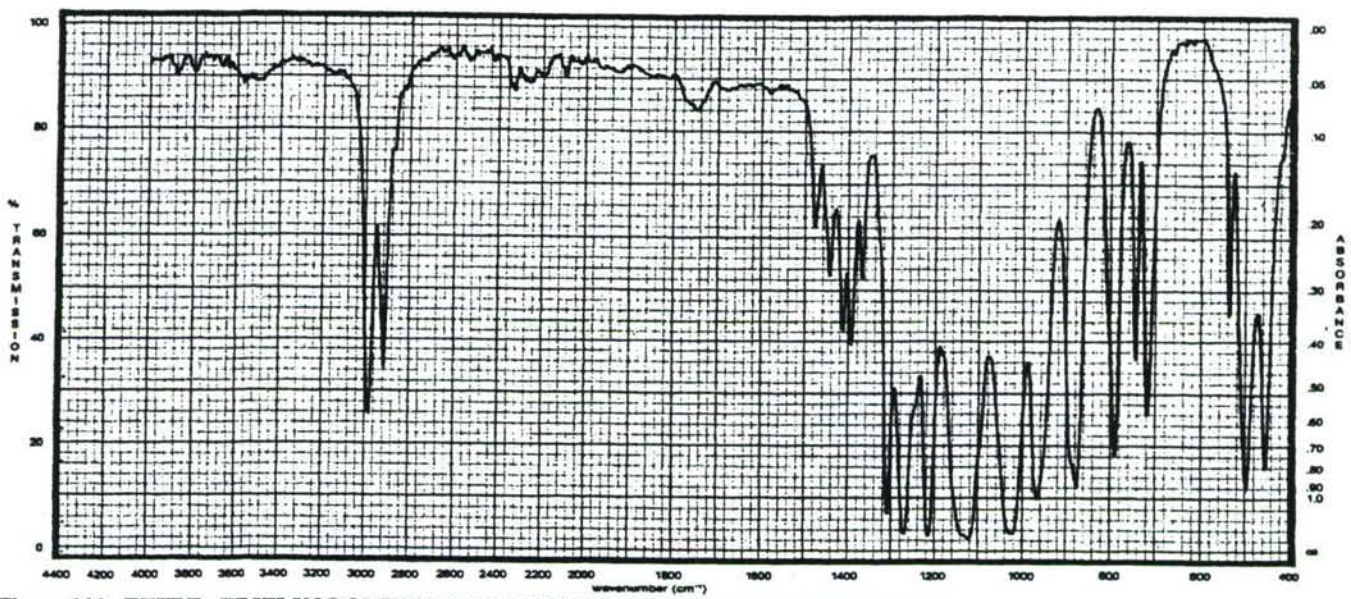


Figure 283 ETHYL TRIFLUOROMETHYLMETHYLPHOSPHINATE, LIQUID, CF/CsI

(PERKIN-ELMER MODEL 283B GRATING SPECTROPHOTOMETER)

[rr] The CF_3 deformation frequencies are assigned to the 760-520 cm^{-1} region while the P-CF_3 stretching frequencies are assigned to the region 520-409 cm^{-1} (Corbridge, D.E.C., "The Infrared Spectra of Phosphorus Compounds" in Topics in Phosphorus Chemistry, pp. 300, 346 (Table XL), Vol 6 (Eds. Grayson, M. and Griffith, E.J.), John Wiley, New York,1969. Thomas, L.C. in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 102, Heyden & Son Ltd, London, 1974, lists the range of the P-C stretch of the P-CF_3 group as 520-409 cm^{-1}.
Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S. in "Atlas of IR Spectra of Organophospho rus Compounds (Interpreted Spectrograms)", p. 4, Nauka Publishers, Moscow, Kluwer Academic Publishers, Boston, 1990, list the following bands for the P-CF_3 group: 1300-1100 cm^{-1} vs (ν C-F), 750-650 cm^{-1} s (ν P-C) and 520-409 cm^{-1} s (δ C-F).
Note, that the Russian authors differ in their assignment of the P-C stretching and C-F deformation frequencies.

3.5.10.7 2-Diisopropylaminoethyl Methylphosphinate (**QA**) CH_3-P=O(H)[O-CH_2CH_2-N(i-C_3H_7)$_2$]

The infrared spectrum of 2-diisopropylaminoethyl methylphosphinate (**QA**) is given in ***Figure 284***. The band assignments are as follows: 3409 cm^{-1} vw (H_2O), 2967 cm^{-1} s (ν_{as} CH_3), 2933 cm^{-1} sh (ν_{as} CH_2), 2873 cm^{-1} m (ν_{sy} CH_3), 2831 cm^{-1} sh (ν_{sy} CH_2), 2715 and 2607 cm^{-1} vw [these two bands appear to occur when the -N(isopropyl)$_2$ group is present], 2342 cm^{-1} w (ν P-H), 1466 cm^{-1} m (δ CH_2 and δas CH_3), ca 1410 cm^{-1} sh (δ_{as} P-CH_3), 1392 cm^{-1} sh (ω OCH_2), 1382 and 1362 cm^{-1} m (δ_{sy} CH_3 isopropyl doublet), 1300 cm^{-1} ms (δ_{sy} P-CH_3), 1232 cm^{-1} s (ν P=O, *calculated* value is 1228 cm^{-1}), 1194 cm^{-1} sh, 1149 cm^{-1} w, 1120 cm^{-1} w (isopropyl skeletal and ν C-N ?), 1047 cm^{-1} ms (ν P-O-C), 988 cm^{-1} s (P-H deformation and possibly ν C-C of $POCH_2CH_2$-), 918 cm^{-1} vw (CH_3 rock of isopropyl moiety), 846 cm^{-1} m (P-CH_3 rock),[ss] 770 cm^{-1} vw (POC), 715 cm^{-1} vw (ν P-C).

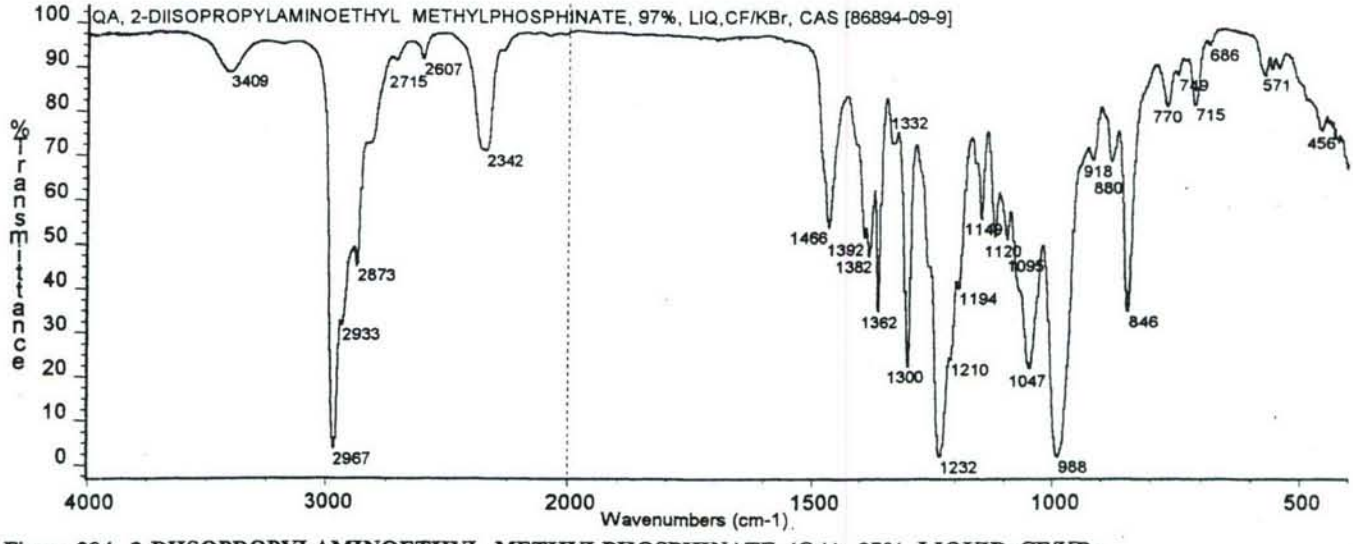


Figure 284 2-DIISOPROPYLAMINOETHYL METHYLPHOSPHINATE (QA), 97%, LIQUID, CF/KBr

The effect of atmospheric moisture on 2-diisopropylaminoethyl methylphosphinate (**QA**) has been discussed previously[tt] and will be repeated herein in an abridged version. The infrared spectra illustrating the effect of atmospheric moisture on a liquid film of **QA** between KBr windows are presented in ***Figures 285A-B***.

[ss] In most P^{+5} organophosphorus compounds the P-CH_3 rock is found within the range 935-874 cm^{-1}. However, in P^{+5} compounds containing both the P-CH_3 and P-H groups, the frequency of this vibration is lowered and found within the range 850-842 cm^{-1}. Thomas, L.C. "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 95, Heyden & Son Ltd., London, 1974.

[tt] Piffath, R.J. "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part II. V-Agents and Related Compounds", 1999, U.S. Army Edgewood Research Development and Engineering Center, Aberdeen Proving Ground, Maryland, 21010, unpublished data.

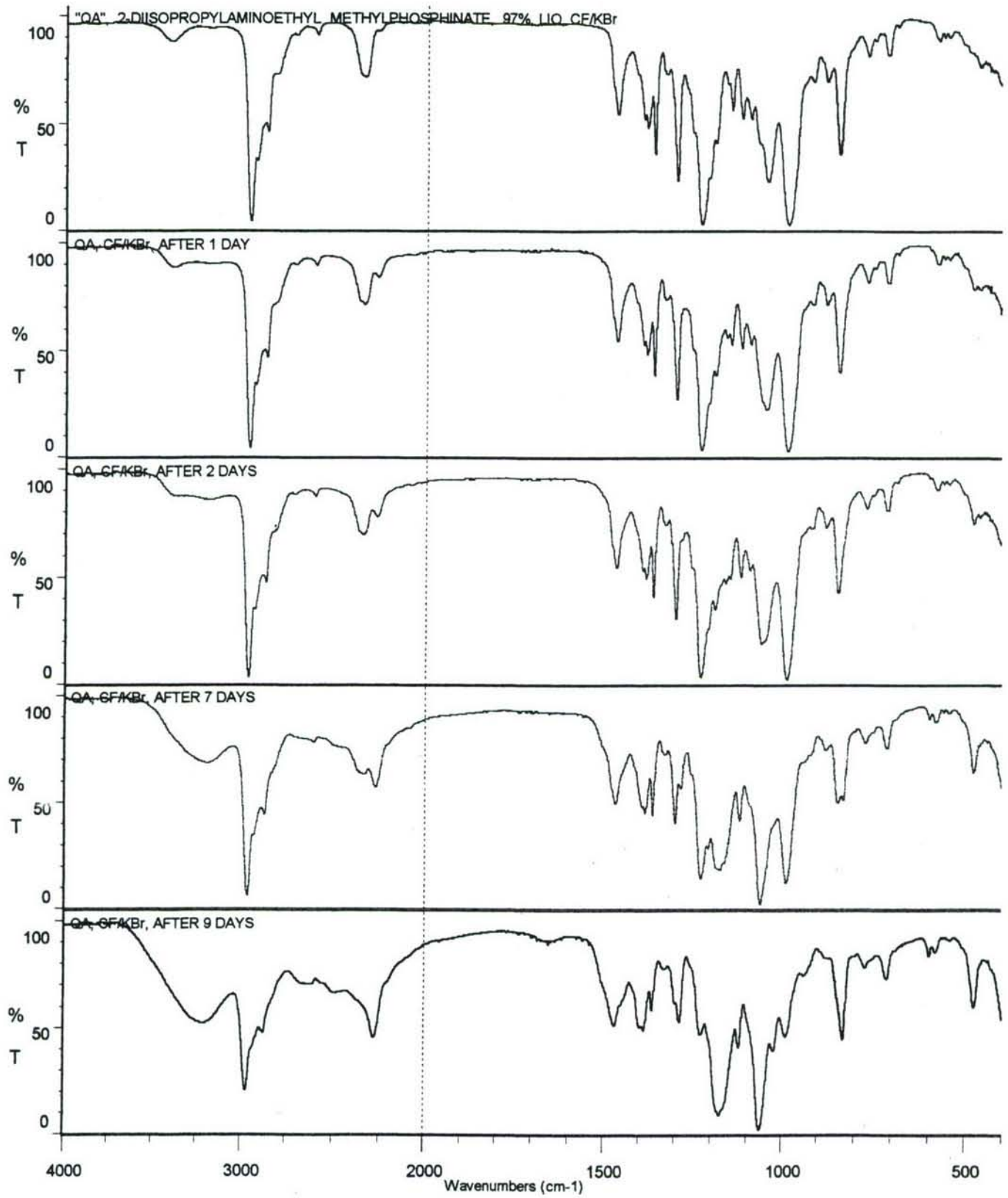


FIGURE 285A 2-DIISOPROPYLAMINOETHYL METHYLPHOSPHINATE (QA), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

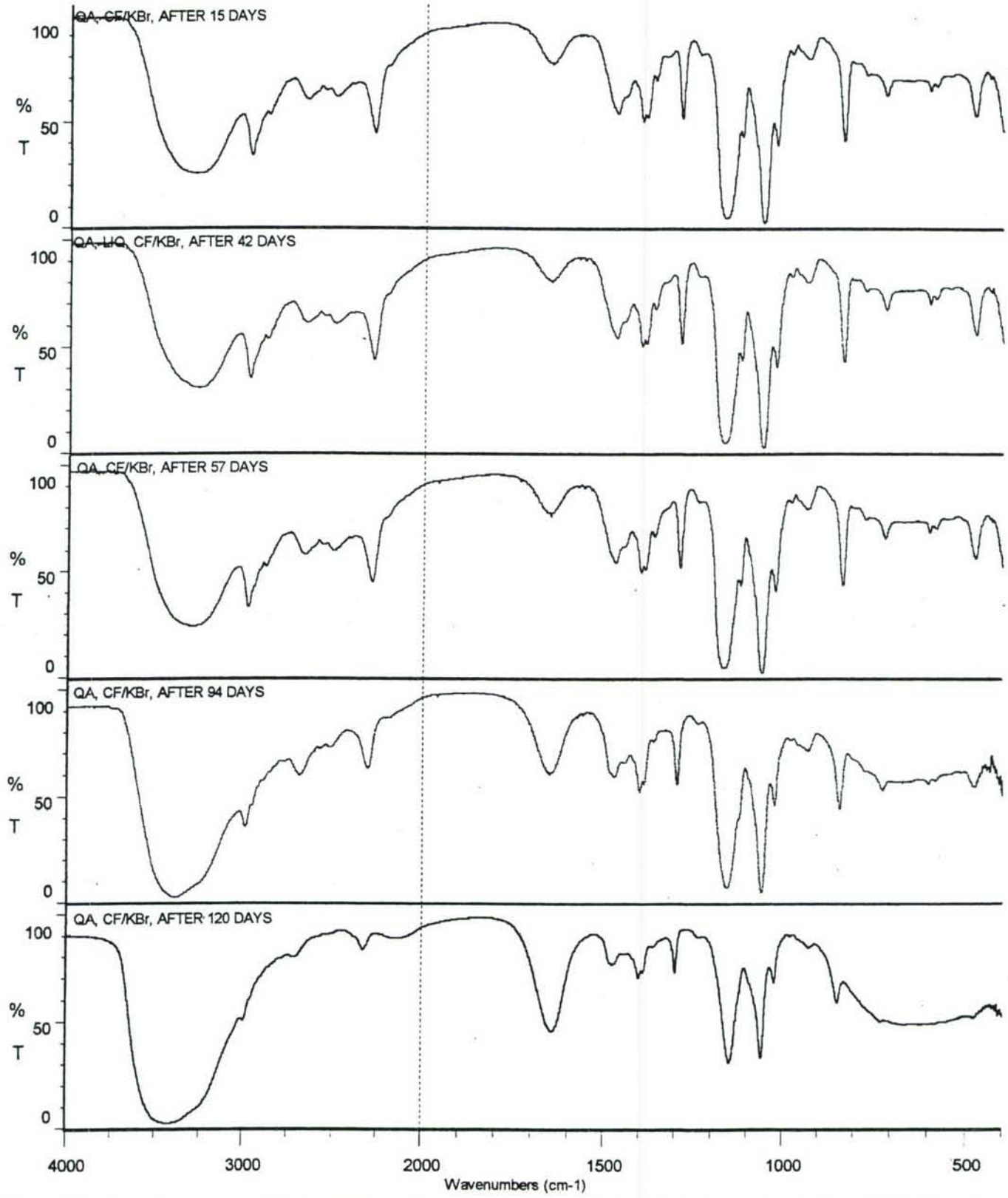


Figure 285B 2-DIISOPROPYLAMINOETHYL METHYLPHOSPHINATE (QA), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

After 1 day of exposure to atmospheric moisture (***Figure 285A***) the infrared spectrum of **QA** shows an additional band at 2271 cm^{-1} due to a new P-H stretching vibration. This P-H band grows in intensity as time progresses and becomes the predominant P-H band by 15th day of exposure, with the frequency increasing to 2287 cm^{-1} from 2271 cm^{-1} (***Figure 285B***). New bands are now visible at 1175 and 1062 cm^{-1} and are assigned to the asymmetric and symmetric stretching of the PO_2^- anion. New bands are also present near 2660 and 2500 cm^{-1} and are assigned to the NH^+ group. Other bands are assigned as follows: 3306 cm^{-1} m (ν OH alcohol, partly due to H_2O, for on the 9th day of exposure it was near 3200 cm^{-1} and gradually moves towards 3400 cm^{-1} as the amount of water increases), ca 1650 cm^{-1} (H_2O, gradually increases in intensity as time of exposure increases), 1469 cm^{-1} w (δ CH_3 and CH_2), 1399 and 1387 cm^{-1} w (δ_{sy} CH_3 isopropyl), 1361 cm^{-1} vw (δ -C-H), 1289 cm^{-1} w (δ_{sy} P-CH_3). These results are very similar to those observed for ethyl 2-diisopropylaminoethyl methylphosphonite (**QL**), and for the mix of methylphosphinic acid, $CH_3P{=}O(H)(OH)$, and 2-diisopropylaminoethanol (**KB**), $HO\text{-}CH_2CH_2N(i\text{-}C_3H_7)_2$.[uu] The hydrolysis of **QA** may be summarized as follows:

$$\underset{\textbf{(QA)}}{CH_3P{=}O(H)[OCH_2CH_2N(i\text{-}C_3H_7)_2]} \text{ -HOH} \rightarrow \underset{\textbf{(methylphosphinic acid)}}{CH_3P{=}O(H)(OH)} + \underset{\textbf{(KB)}}{HOCH_2CH_2N(i\text{-}C_3H_7)_2}$$

$$CH_3P{=}O(H)(OH) + HOCH_2CH_2N(i\text{-}C_3H_7)_2 \rightarrow [CH_3P(O_2^-)H]\ HOCH_2CH_2NH^+(i\text{-}C_3H_7)_2.$$

Thus, **QA** apparently hydrolyzes to form the P-acid, methylphosphinic acid, which then combines with the **KB**, also produced in the hydrolysis, to form the product $CH_3P(O_2^-)H]\ HOCH_2CH_2NH^+(i\text{-}C_3H_7)_2$.

3.5.10.8 2-Diisopropylaminoethyl Ethylmethylphosphinate (**QC**) $CH_3\text{-}P{=}O(CH_2CH_3)[OCH_2CH_2N(i\text{-}C_3H_7)_2$

The infrared spectrum of a liquid film of 2-diisopropylaminoethyl ethylmethylphosphinate (**QC**) between KBr windows is reproduced as ***Figure 286***. The band assignments are as follows: 3459 cm^{-1} w (H_2O), 2967 cm^{-1} s (ν_{as} CH_3), 2940 cm^{-1} sh (ν_{as} CH_2), 2882 cm^{-1} m (ν_{sy} CH_3), ca 2820 cm^{-1} (ν_{sy} CH_2), 2717 and 2607 cm^{-1} vw [these two bands seem to appear when the -N(isopropyl)$_2$ moiety is present], 1464 cm^{-1} m (δ_{as} CH_3, δ CH_2),

[uu] See the discussion in "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part II. V-Agents and Related Compounds", Piffath, R.J., 1999, U.S. Army Edgewood Research Development and Engineering Center, Aberdeen Proving Center, Maryland, 21010, unpublished data.

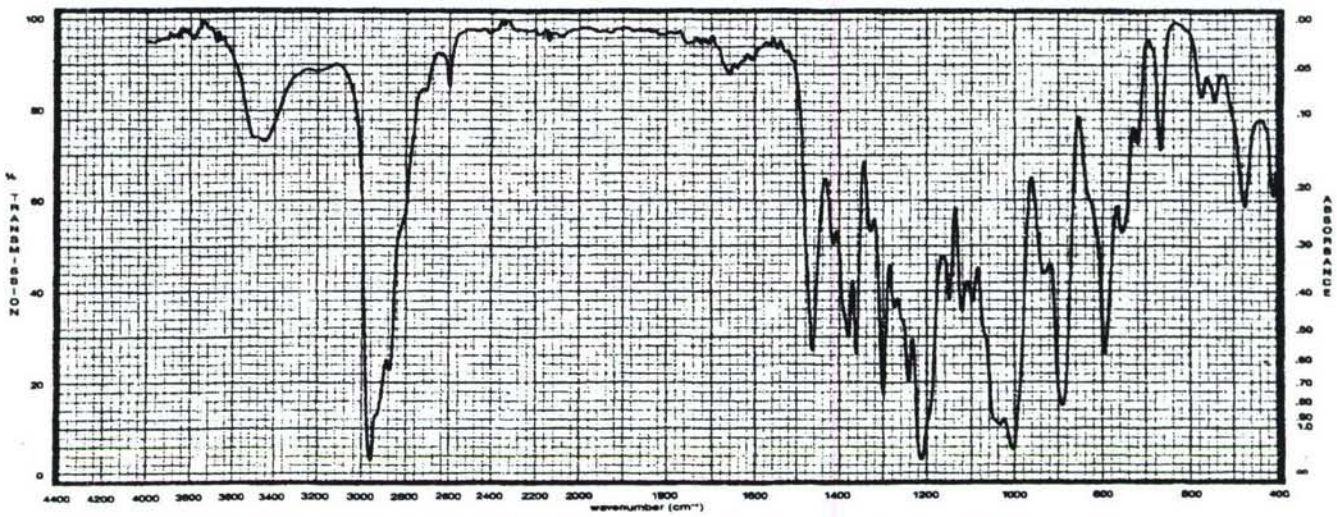


Figure 286 2-DIISOPROPYLAMINOETHYL ETHYLMETHYLPHOSPHINATE (QC), LIQUID, CF/CsI

1416 cm^{-1} w (δ_{as} P-CH_3, δ P-CH_2), 1381 and 1362 cm^{-1} m (δ_{sy} CH_3 isopropyl group), 1300 cm^{-1} m (δ_{sy} P-CH_3), 1275 and 1242 cm^{-1} w (ω, τ CH_2 of P-Ethyl), 1212 cm^{-1} s (ν P=O, *calculated* value is 1208 cm^{-1}), 1149, 1121 cm^{-1} w (isopropyl skeletal, ν C-N ?), 1034 cm^{-1} ms and 1003 cm^{-1} s (ν P-O-C and some contribution from ν C-C of P-Ethyl), 890 cm^{-1} ms (P-CH_3), 794 cm^{-1} m (POC), 754 cm^{-1} w (CH_2 rock of P-Ethyl), 720 cm^{-1} vw (ν P-C of P-CH_3), 667 cm^{-1} w (ν P-C of P-Ethyl), 474 cm^{-1} w (P=O deformation ?).

The effect of atmospheric moisture on the infrared spectra of 2-diisopropylaminoethyl ethylmethylphosphinate (**QC**), has been discussed by Piffath.[vv]

3.5.10.9 Isobutyl Hydrogenmethylphosphinate CH_3-P=O(H)[O-CH_2-$CH(CH_3)_2$]

The infrared spectrum of isobutyl hydrogenmethylphosphinate as a thin liquid film between KBr windows is reproduced in ***Figure 287***. The band assignments are as follows: 3408 cm^{-1} vw (H_2O), 2962 cm^{-1} m (ν_{as} CH_3), ca 2940 sh (ν_{as} CH_2), ca 2920 cm^{-1} sh (ν C-H), 2877 cm^{-1} w (ν_{sy} CH_3, CH_2), 2349 cm^{-1} w (ν P-H), 1472 cm^{-1} w (δ CH_2, δ_{as} CH_3, some δ OCH_2), 1414 cm^{-1} vw (δ_{as} P-CH_3), 1397 and 1369 cm^{-1} vw (δ_{sy} CH_3, some ω OCH_2 at 1397 ?), 1302 cm^{-1} m (δ_{sy} P-CH_3), 1231 cm^{-1} ms (ν P=O, *calculated* value is 1228 cm^{-1}), 1048 cm^{-1} m (ν P-O-C), 995 cm^{-1} s (P-H deformation, some contribution from ν P-O-C), 849 cm^{-1} m (P-CH_3 rock, lowered in P^{+5}

[vv] Piffath, R.J., "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part II. V-Agents and Related Compounds", 1999, U.S. Army Edgewood Research Development and Engineering Center, Aberdeen Proving Center, Maryland, 21010, unpublished data.

compounds containing both P-CH_3 and P-H groups, see footnote [ss]), 822 cm^{-1} vw (POC), 728 cm^{-1} vw (ν P-C), ca 560 cm^{-1} vvw (P=O deformation?).

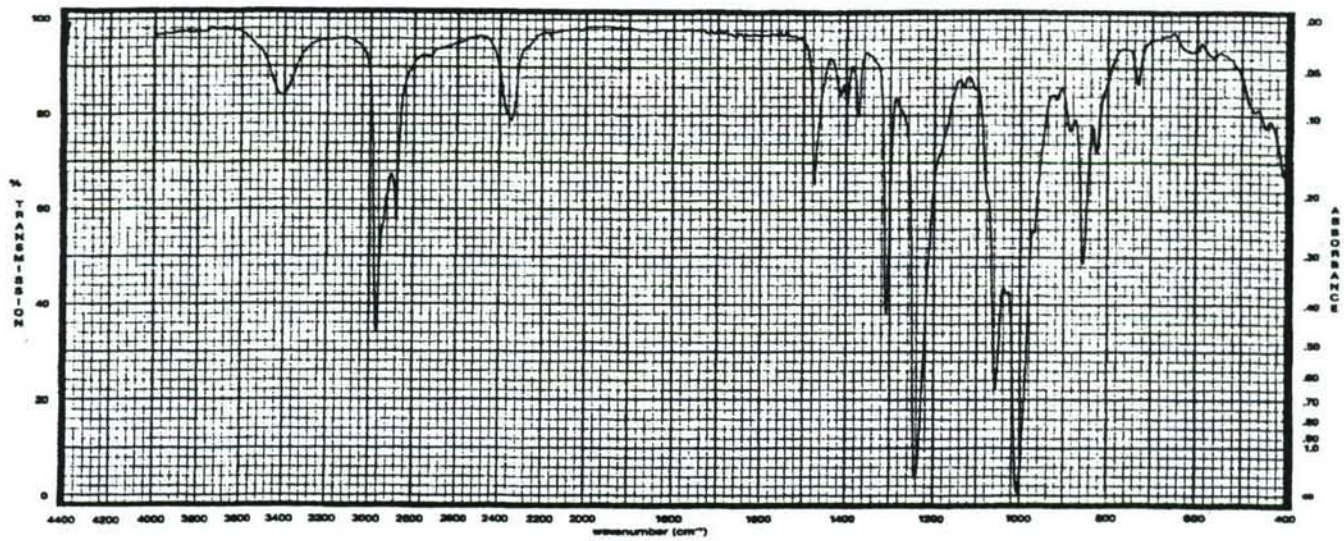


Figure 287 ISOBUTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/KBr

The effect of moisture on isobutyl hydrogenmethylphosphinate is illustrated by the infrared spectra given in ***Figures 288A-C***. After 24 hours of exposure to atmospheric moisture the spectrum (***Figure 288A***) shows the presence of weak and broad bands near 2700, 2200 and 1660 cm^{-1} assignable to the POH group. The P-H stretching vibration is visible near 2369 cm^{-1}. The P=O stretching band has decreased to 1211 cm^{-1} and has become somewhat broader. By the 12th day of exposure to atmospheric moisture (***Figure 288B***), the spectrum is that of mainly a P-acid with broad POH bands near 2700, 2200 and 1650 cm^{-1}. The bands indicative of the isobutyl ester moiety are just about absent from the spectrum. The acid P=O band, now broadened, occurs at 1175 cm^{-1}. By the 20th day of exposure (***Figure 288C***) the spectrum shows the following: 2964 and 2922 cm^{-1} vvw (ν_{as} and ν_{sy} CH_3), 2678, ca 2170 and 1670 cm^{-1} all weak and broad (POH), 2381 cm^{-1} w (ν P-H), 1416 cm^{-1} vw (δ_{as} P-CH_3), 1305 cm^{-1} m (δ_{sy} P-CH_3), 1181 cm^{-1} ms broad (ν P=O), 1017 cm^{-1} s (P-H deformation), 972 cm^{-1} w (ν P-OH), 845 cm^{-1} m (P-CH_3 rock), 736 cm^{-1} w (ν P-C), 443 cm^{-1} w (P=O deformation). Thus, the hydrolysis of isobutyl hydrogenmethylphosphinate appears to form methylphosphinic acid and isobutyl alcohol.

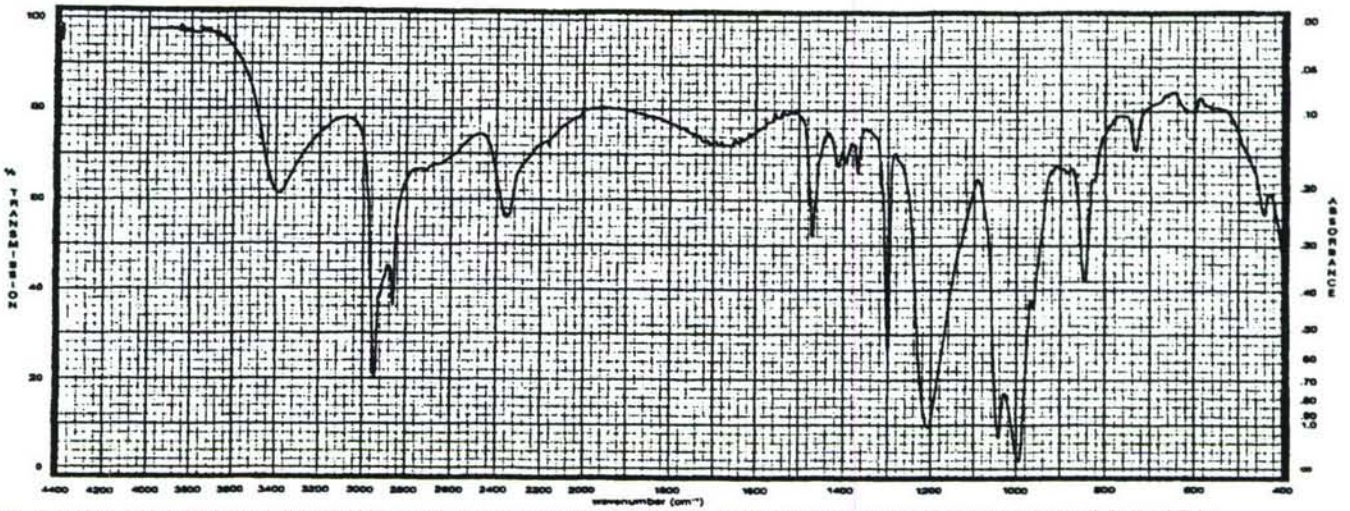


Figure 288A ISOBUTYL HYDROGENMETHYLPHOSPHINATE, CF/KBr, AFTER 24 HOURS OF EXPOSURE TO MOISTURE

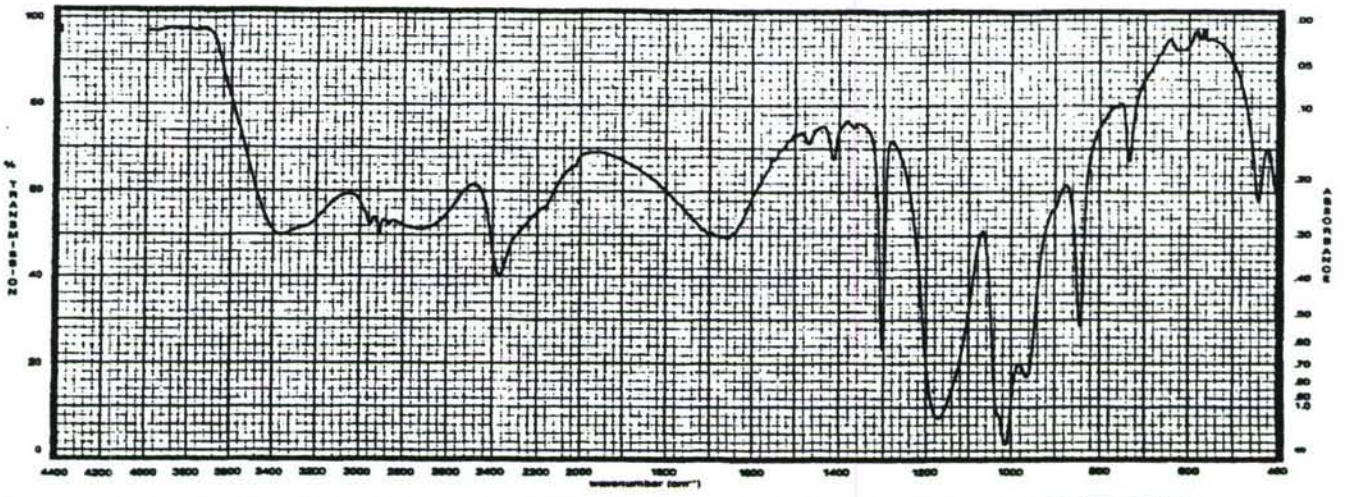


Figure 288B ISOBUTYL HYDROGENMETHYLPHOSPHINATE, CF/KBr, AFTER 12 DAYS OF EXPOSURE TO MOISTURE

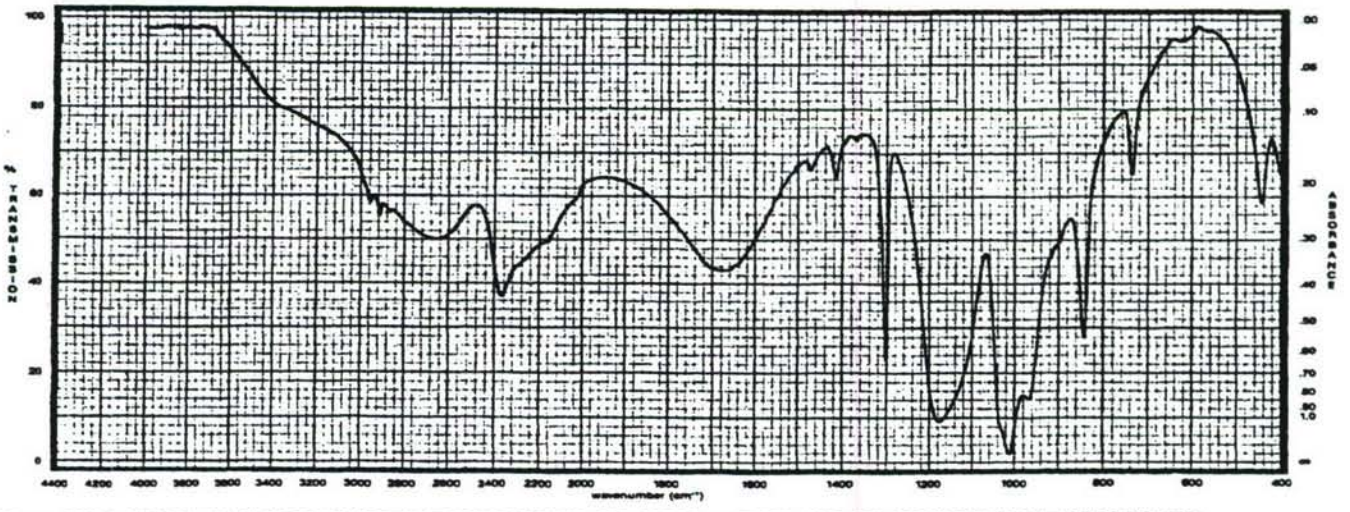


Figure 288C ISOBUTYL HYDROGENMETHYLPHOSPHINATE, CF/KBr, AFTER 20 DAYS OF EXPOSURE TO MOISTURE

3.5.10.10 Trimethylsilyl Methylphosphinate CH_3-P=O(H)[O-Si(CH_3)$_3$]

The infrared spectrum of a thin liquid film of trimethylsilyl methylphosphinate between KBr windows is reproduced as ***Figure 289***. The band assignments are as follows: 2960 cm^{-1} m (ν_{as} CH_3), 2901 cm^{-1} w (ν_{sy} CH_3), ca 2707 and ca 2200 cm^{-1} vw and broad (POH), 2359 cm^{-1} w (ν P-H), 1415 cm^{-1} w (δ_{as} CH_3 from P-CH_3 and Si-CH_3), 1301 cm^{-1} m (δ_{sy} P-CH_3), 1255 cm^{-1} ms (δ_{sy} Si-CH_3), 1235 cm^{-1} ms (ν P=O, *calculated* value is 1234 cm^{-1}), 1195 cm^{-1} w (ν P=O from acid, hydrolysis product ?), 1048 cm^{-1} ms (ν P-O-Si), 996 cm^{-1} ms (P-H deformation), 849 cm^{-1} s [P-CH_3 rock and Si(CH_3)$_3$ rock and ν Si-C], 760 cm^{-1} m [Si(CH_3)$_3$], 690 cm^{-1} vw (ν P-C).

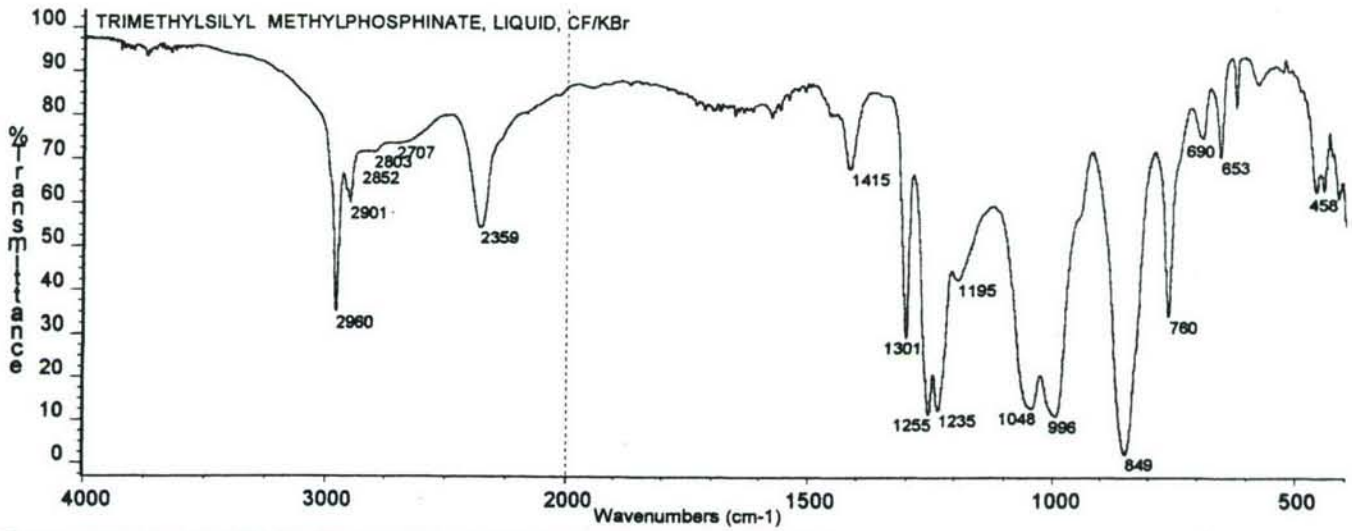


Figure 289 TRIMETHYLSILYL METHYLPHOSPHINATE, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of trimethylsilyl methylphosphinate between KBr windows is illustrated by the infrared spectra presented as ***Figure 290***. After 1 hour of exposure to atmospheric moisture, the spectrum shows an increase in the bands due to the POH moiety (2650, 2170, 1675 and 970 cm^{-1}). By the 2nd and 3rd hour of exposure, the bands of the POH moiety are even more intense. The P=O band has broadened and fallen to 1181 cm^{-1}. The P-H group is still present at 2376 and 1017 cm^{-1}. Some Si(CH_3)$_3$ bands are still evident at 1255 and 758 cm^{-1}. The 846 cm^{-1} band is now mostly due to the P-CH_3 rock with some slight residual contribution from the Si(CH_3)$_3$ moiety. Thus, trimethylsilyl methylphosphinate has apparently hydrolyzed to form the P-acid, methylphosphinic acid, CH_3-P=O(H)(OH).

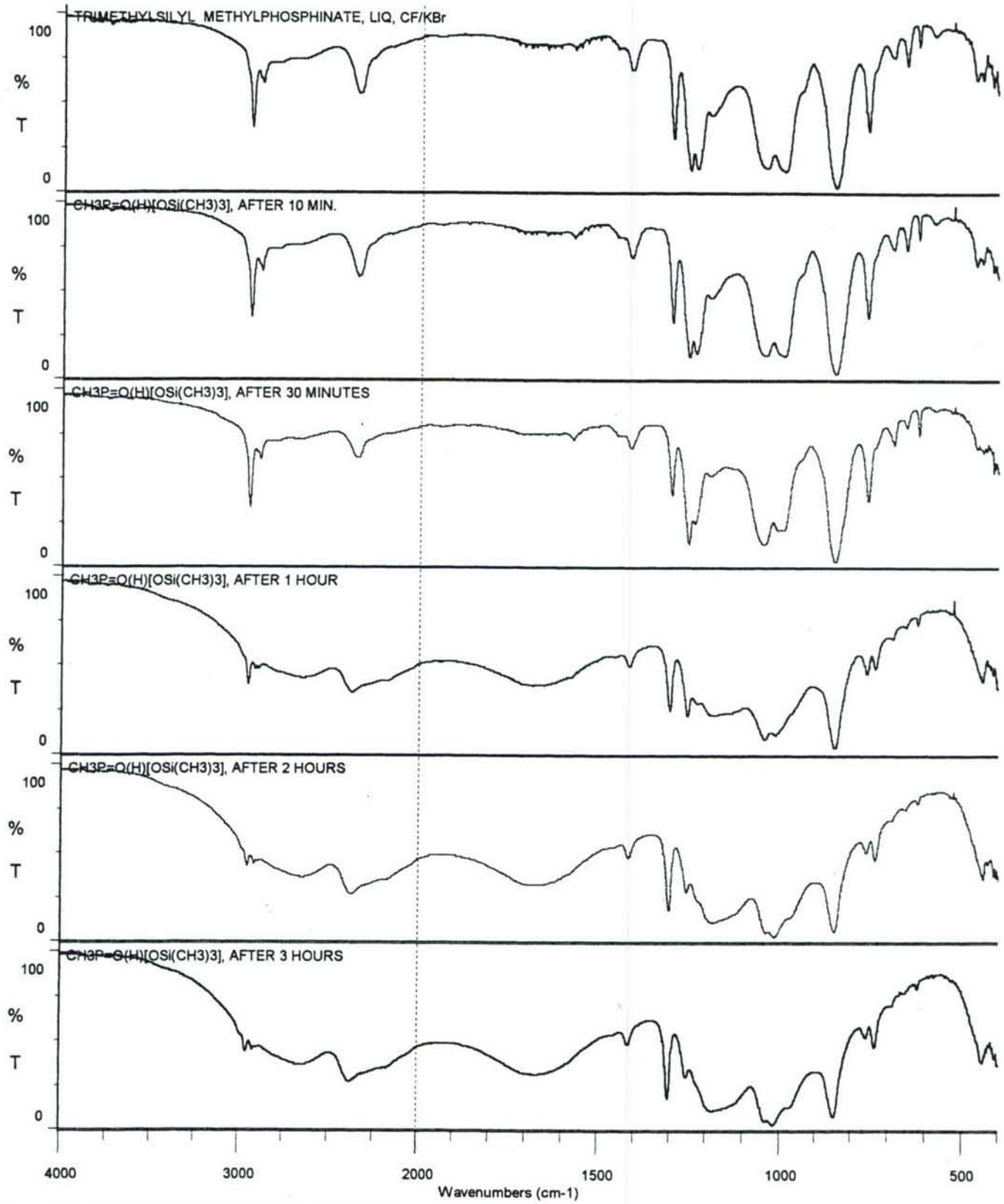


Figure 290 TRIMETHYLSILYL METHYLPHOSPHINATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.11 **Phosphates** $(RO)_3P=O$

3.5.11.1 Trimethyl Phosphate (**TMPO**) $(CH_3O)_3P=O$

The infrared spectrum of trimethyl phosphate (**TMPO**) as a liquid film between KBr discs (windows) is presented as ***Figure 291***. The band assignments are as follows: 3003 cm^{-1} w, 2960 cm^{-1} m (ν_{as} CH_3), 2919 cm^{-1} sh, 2857 cm^{-1} w (ν_{sy} CH_3), 1465 and 1451 cm^{-1} w (δ_{as} and δ_{sy} CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1283 cm^{-1} ms (ν P=O, *calculated* value is 1278 cm^{-1}), 1188 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1037 cm^{-1} s (ν P-O-C), 848 cm^{-1} ms (POC, ν P-O), 521 cm^{-1} w (P=O deformation).

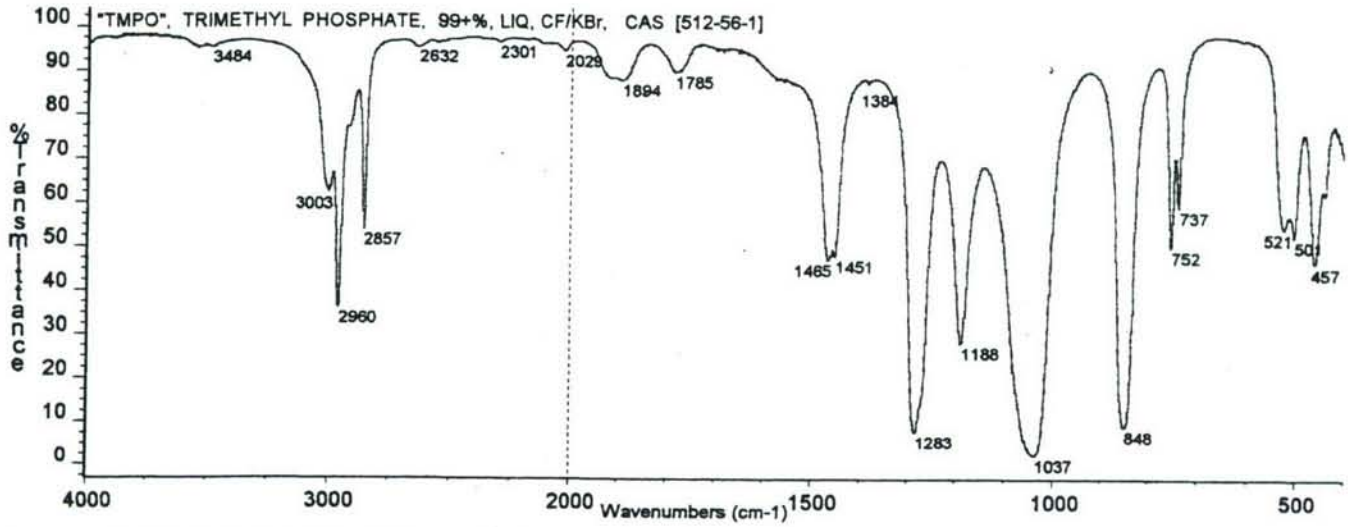


Figure 291 TRIMETHYL PHOSPHATE, 99⁺%, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin film of trimethyl phosphate between KBr windows is illustrated by the infrared spectra reproduced in ***Figures 292A*** and ***292B***. These spectra show a gradual decrease in the P=O stretching vibration from 1283 cm^{-1} to 1222 cm^{-1} (after 250 days) as the amount of water (ca 3400 and ca 1650 cm^{-1}) increases in the spectra. This is probably due to hydrogen bonding with the water.

3.5.11.2 Triethyl Phosphate (**TEPO**) $(CH_3\text{-}CH_2\text{-}O)_3P=O$

The infrared spectrum of triethyl phosphate (**TEPO**) as a liquid film between KBr windows is given in ***Figure 293***. The band assignments are as follows: 3545 and 3489 cm^{-1} vvw (H_2O), 2985 cm^{-1} m (ν_{as} CH_3), 2935 cm^{-1} w (ν_{as} CH_2), 2910 cm^{-1} w (ν_{sy} CH_3), 2873 cm^{-1} vw (ν_{sy} CH_2), 1480 cm^{-1} vw (δ OCH_2), 1445 cm^{-1} vw (δ_{as}

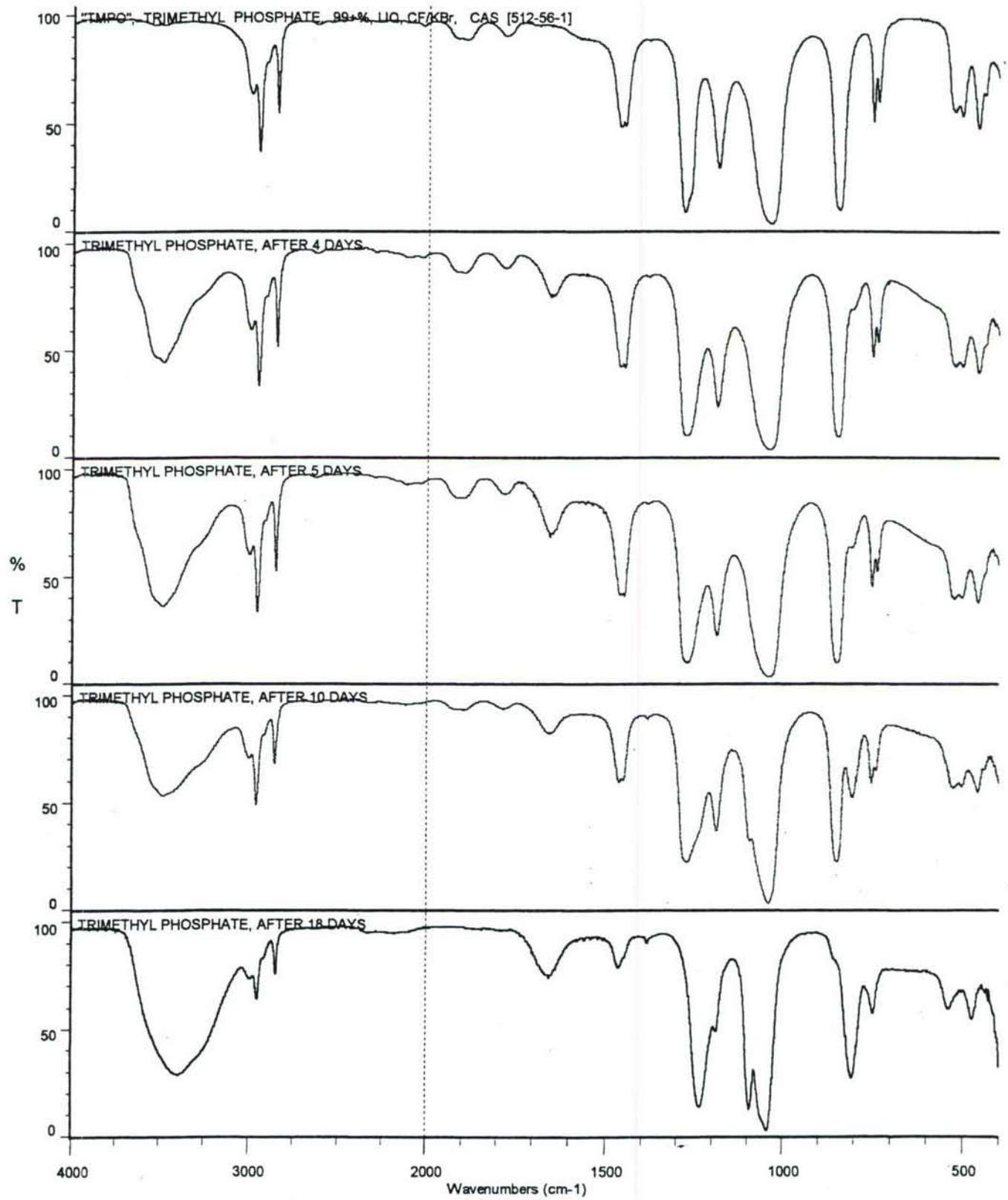


Figure 292A TRIMETHYL PHOSPHATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

(Continued)

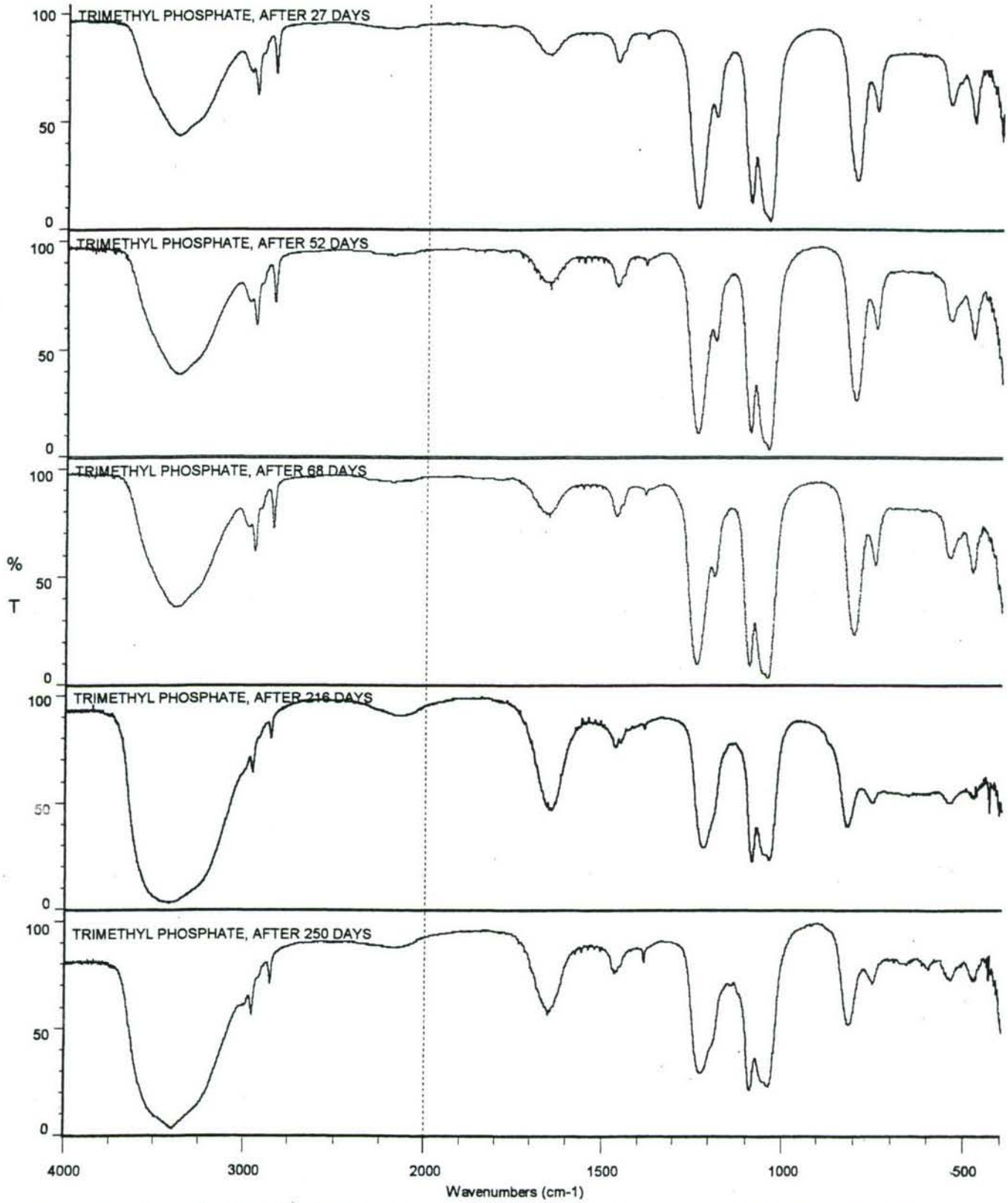


Figure 292B TRIMETHYL PHOSPHATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE
(Continued)

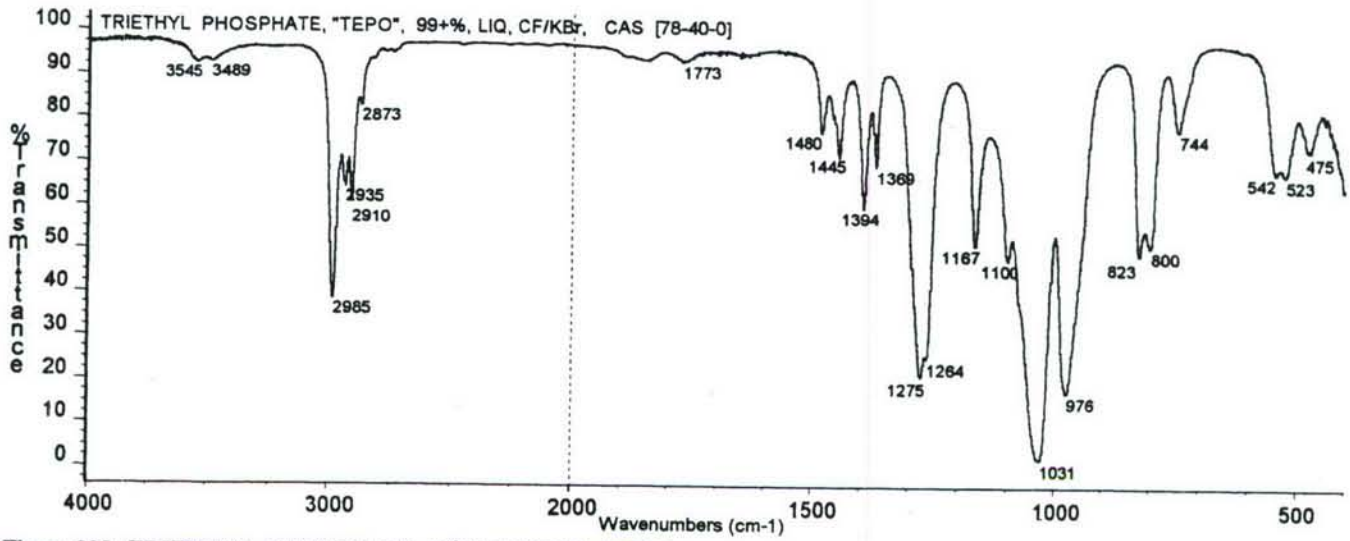


Figure 293 TRIETHYL PHOSPHATE, 99⁺%, LIQUID, CF/KBr

CH_3), 1394 cm^{-1} w (ω OCH_2), 1369 cm^{-1} vw (δ_{sy} CH_3), 1275 and 1264 cm^{-1} ms (ν P=O, isomers, *calculated* value is 1272 cm^{-1}),[ww] 1167 and 1100 cm^{-1} m (CH_3 rock of POEt, characteristic), 1031 cm^{-1} s (ν P-O-C), 976 cm^{-1} ms (ν C-C of POEt), 823 and 800 cm^{-1} m (POC),[xx] 744 cm^{-1} vw (CH_2 rock ?), 542 and 523 cm^{-1} w (P=O deformation).

The effect of atmospheric moisture on triethyl phosphate (**TEPO**) is illustrated by the infrared spectra presented in ***Figure 294***. Very little effect is observed on the compound as indicated by the spectrum given for 16 days of exposure. The main effect seems to be that the compound is beginning to evaporate from the sample-window sandwich. This is indicated by the change in relative band intensities and the appearance of the KBr rolloff (or cutoff) near 400 cm^{-1}.

3.5.11.3 Tripropyl Phosphate $(CH_3\text{-}CH_2\text{-}CH_2\text{-}O)_3P{=}O$

The infrared spectrum of tripropyl phosphate as a thin liquid film between KBr discs (windows) is

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[ww] The infrared spectra of trialkyl and triaryl phosphates show a splitting or doubling of the P=O stretching frequency. This doubling is believed to be due to rotational isomers. Mortimer, F.S., in *Spectrochim. Acta*. **9**, 270 (1957), investigated the infrared spectra of trimethyl, triethyl, and triphenyl phosphate in both the solid and liquid states and in various solvents. He found that the P=O stretching frequency for trimethyl phosphate in the solid state occurred at 1290 cm^{-1}; whereas, for the liquid and solution states, the P=O band appeared as a doublet at 1290 and 1275 cm^{-1}. The relative intensities of the absorption bands were shown to vary with the temperature and solvent used for the three phosphates studied. These doublets were taken as evidence for the presence of conformers.

[xx] Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S., and Mukhametov, F.S. in "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms), p. 262, IR No. 481, Kluwer Academic Publishers, Boston, 1990, assign the 823 and 800 cm^{-1} bands to the CH_2 rock and to the ν_{as} $P(\text{-}O)_3$. The 744 cm^{-1} band is assigned to the ν_{sy} $P(\text{-}O)_3$.

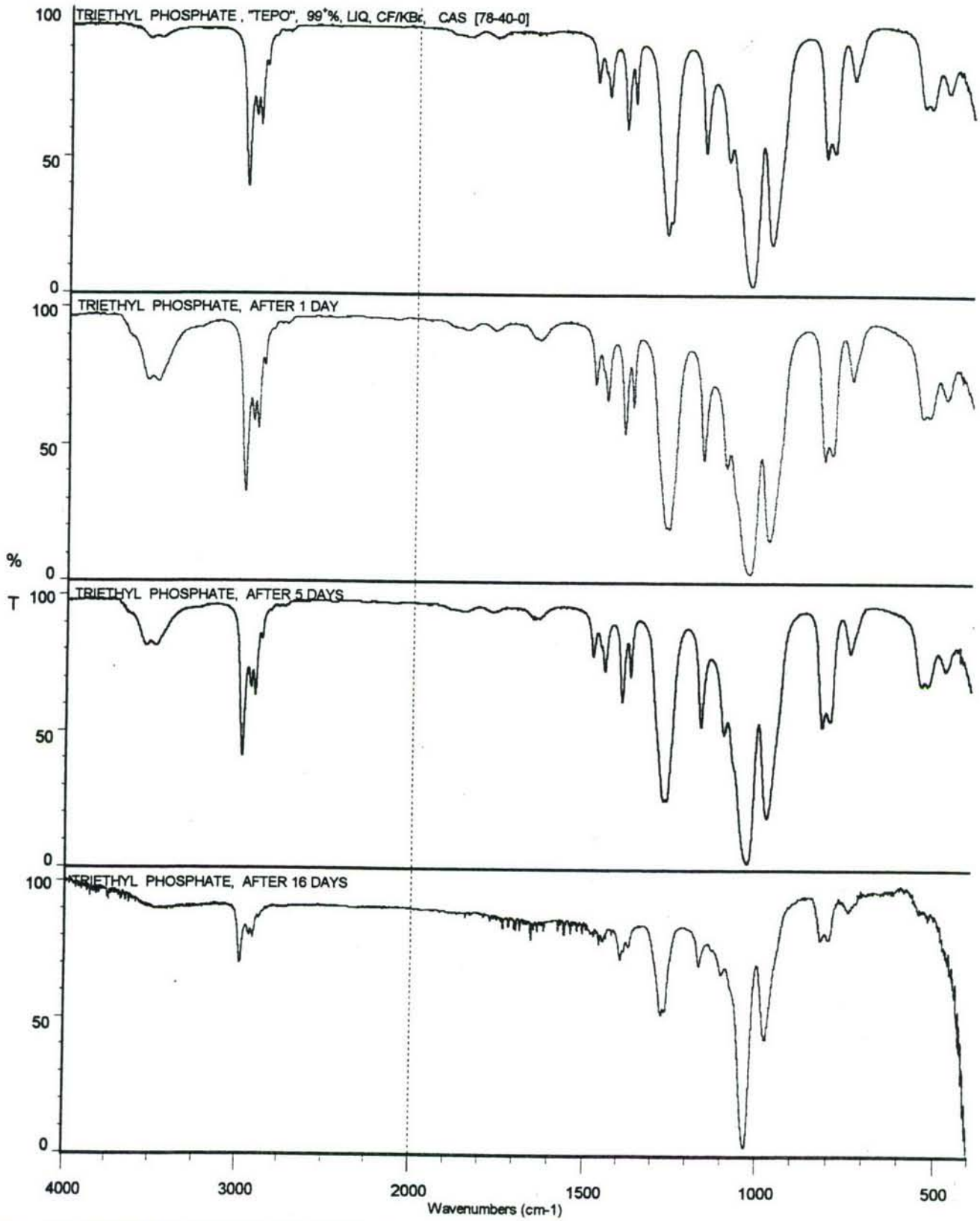

Figure 294 TRIETHYL PHOSPHATE (TEPO), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

given in ***Figure 295***. The band assignments are as follows: 3548 and 3489 cm^{-1} vw (H_2O), 2969 cm^{-1} s (ν_{as} CH_3), 2940 cm^{-1} sh (ν_{as} CH_2), 2897 and 2881 cm^{-1} ms (ν_{as} CH_3 and ν_{sy} CH_2), 1465 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2), 1379 cm^{-1} sh (δ_{sy} CH_3), 1278 cm^{-1} ms (ν P=O, *calculated* value is 1272 cm^{-1}), 1158 cm^{-1} w and 1125 cm^{-1} vw (CH_3 rock), 1058 and 1008 cm^{-1} s (ν P-O-C), 908 cm^{-1} w (ν C-C) 887 and 864 cm^{-1} m [ν_{as} $P(-O)_3$],[yy] 807 cm^{-1} w (CH_2 rock), 752 m [ν_{sy} $P(-O)_3$], 548 cm^{-1} m (P=O deformation).

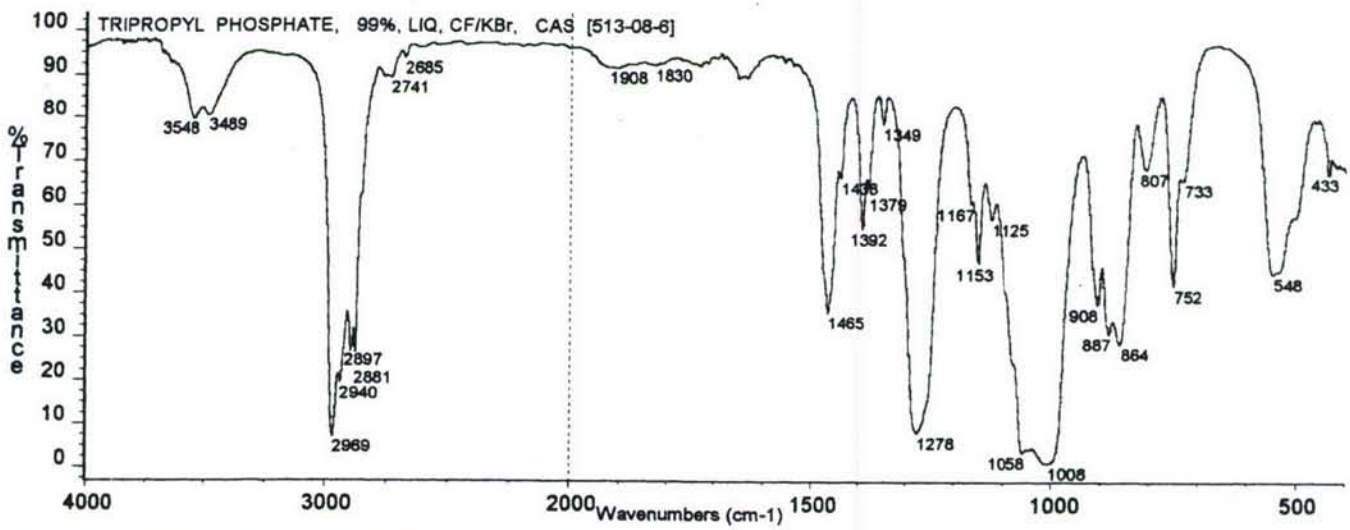

Figure 295 TRIPROPYL PHOSPHATE, 99%, LIQUID, CF/KBr

The effect of atmospheric moisture on tripropyl phosphate is illustrated by the infrared spectra given in ***Figure 296***. The infrared spectra for tripropyl phosphate remain essentially unchanged up to the 13 days of the study.

3.5.11.4 Tri-*n*-butyl Phosphate $(n\text{-}C_4H_9)_3P{=}O$

The infrared spectrum of tri-*n*-butyl phosphate as a liquid film between KBr windows is reproduced as ***Figure 297***. The band assignments are as follows: 3480 cm^{-1} vvw (H_2O), 2961 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), 2910 cm^{-1} sh (ν_{sy} CH_3), 2875 cm^{-1} w (ν_{sy} CH_2), 1466 cm^{-1} vw, 1433 cm^{-1} vvw (δ CH_2 and δ_{as} CH_3),

[yy] Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S., and Mukhametov, F.S. in "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms), p. 262, IR No. 482, Kluwer Academic Publishers, Boston, 1990, assign the 887 and 864 cm^{-1} bands to the ν_{as} $P(-O)_3$. The 807 cm^{-1} band is assigned to the CH_2 rock, while the 752 cm^{-1} band is assigned to the ν_{sy} $P(-O)_3$.

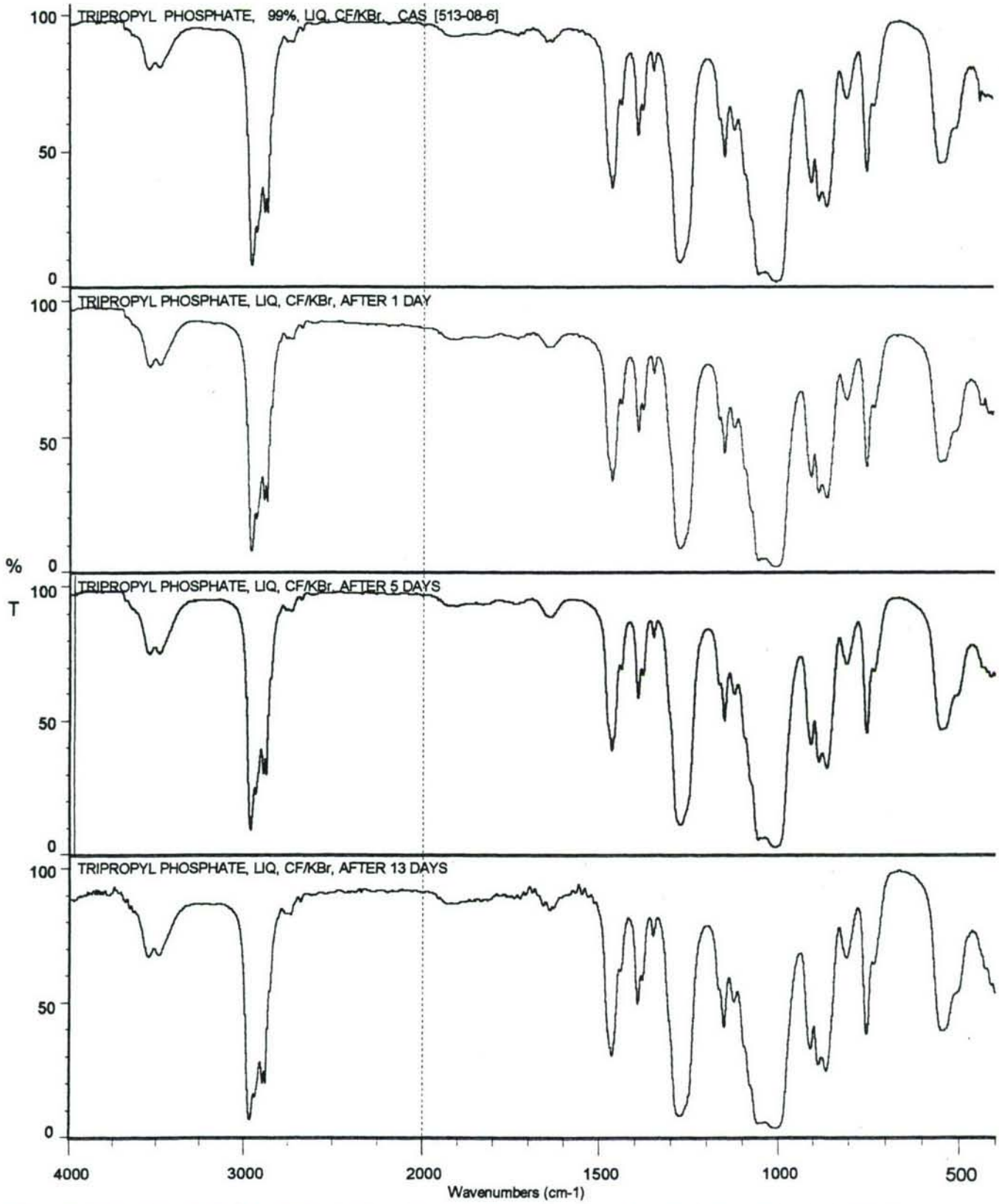

Figure 296 TRIPROPYL PHOSPHATE, LIQUID,CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

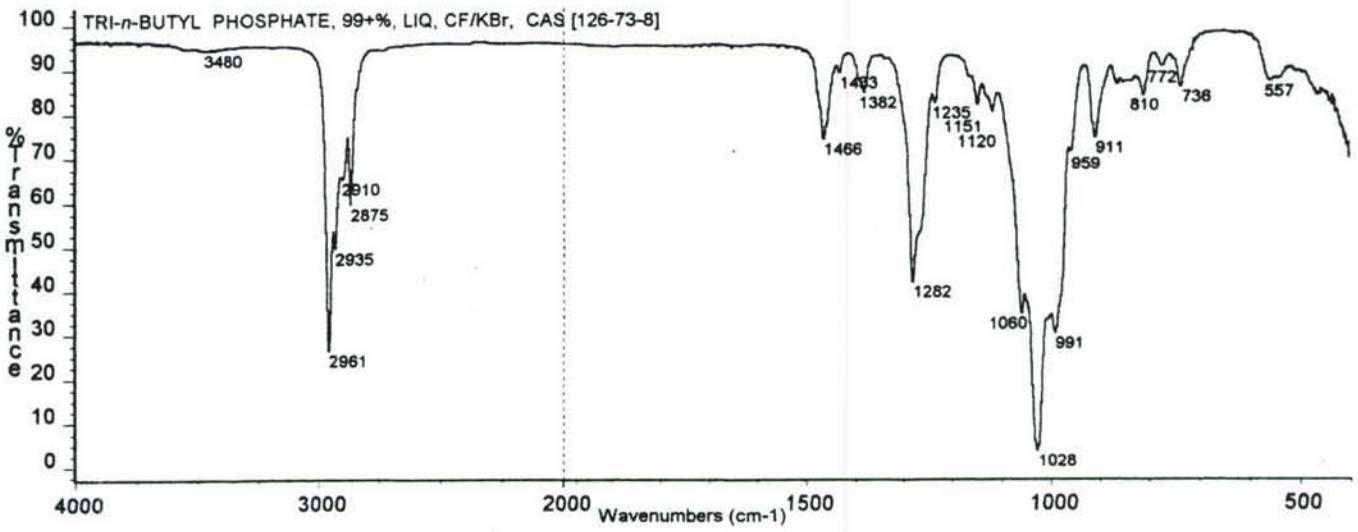

Figure 297 TRI-*n*-BUTYL PHOSPHATE, 99⁺%, LIQUID, CF/KBr

1382 cm^{-1} vw (ω QCH_2, δ_{sy} CH_3), 1282 cm^{-1} m (ν P=O, *calculated* value is 1272 cm^{-1}), 1165 cm^{-1} sh, 1151 and 1120 cm^{-1} vw (ω, τ CH_2, CH_3 rock, possibly characteristic of P-O-*n*-butyl), 1060 cm^{-1} m, 1028 cm^{-1} s and 991 cm^{-1} m (ν P-O-C), 911 cm^{-1} vw (ν C-C of PO-*n*-butyl ?), 810 cm^{-1} vvw (POC), 736 cm^{-1} vw (CH_2 rock), 557 cm^{-1} vw (P=O deformation).

3.5.11.5 Tris(2-ethylhexyl) Phosphate $[CH_3(CH_2)_3CH(C_2H_5)CH_2O]_3P=O$

The infrared spectrum of tris(2-ethylhexyl) phosphate as a thin liquid film between KBr windows is given in ***Figure 298***. The band assignments are as follows: 3552 and 3482 cm^{-1} vvw (H_2O), 2960 cm^{-1} s (ν_{as} CH_3), 2932 cm^{-1} ms (ν_{as} CH_2), 2874 cm^{-1} m (ν_{sy} CH_3), 2861 cm^{-1} m (ν_{sy} CH_2), 1464 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1380 cm^{-1} w (δ_{sy} CH_3), 1284 and 1268 cm^{-1} m (ν P=O, *calculated* value is 1272 cm^{-1}), 1151 and 1113 cm^{-1} vw (ω, τ CH_2), 885 cm^{-1} w (ν C-C ?), 822 and 772 cm^{-1} vw (POC), 727 cm^{-1} vw (CH_2 rock).

The effect of atmospheric moisture on tris(2-ethylhexyl) phosphate as a thin liquid film between KBr discs (windows) is illustrated by the infrared specta presented in ***Figure 299***. The infrared spectra show little change in the compound even after 76 days of exposure to atmospheric moisture.

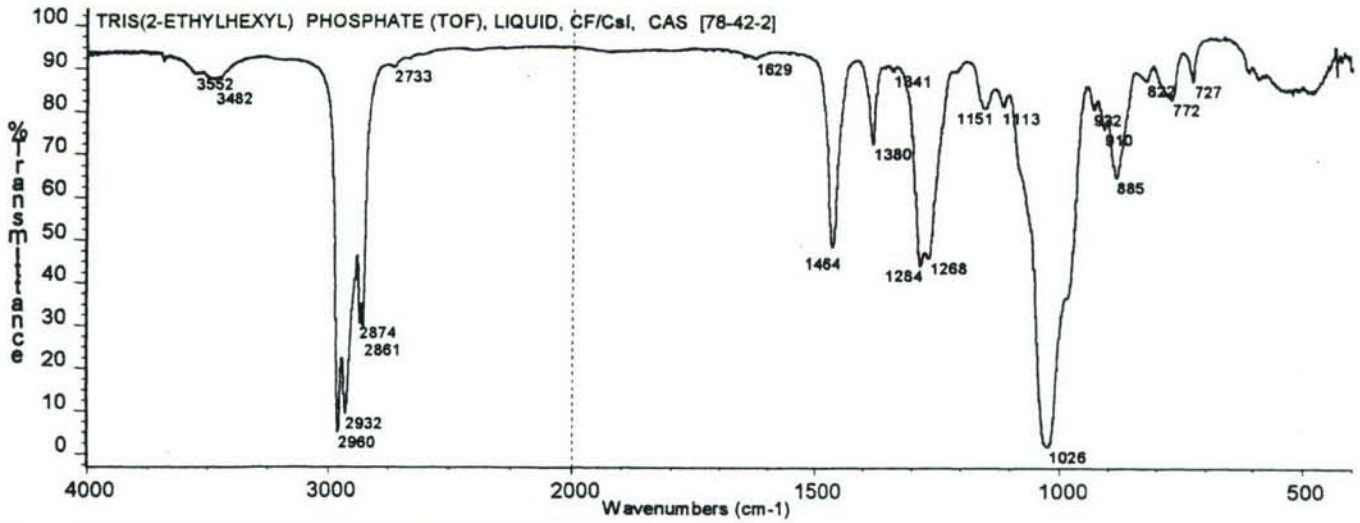

Figure 298 TRIS(2-ETHYLHEXYL) PHOSPHATE, LIQUID, CF/CsI

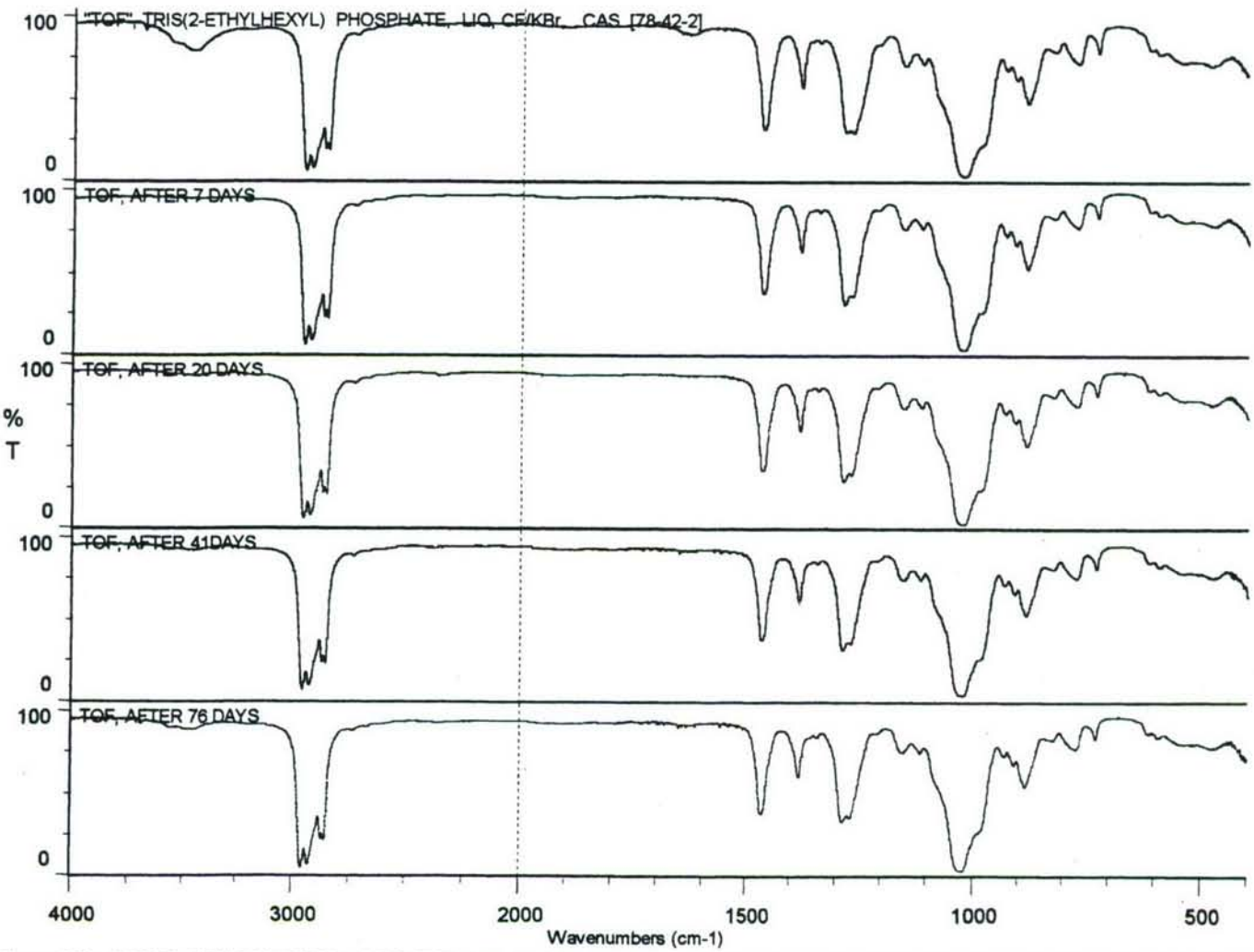

Figure 299 TRIS(2-ETHYLHEXYL) PHOSPHATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.11.6 Tris(2-butoxyethyl) Phosphate $(CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O)_3P{=}O$

The infrared spectrum of a thin liquid film of tris(2-butoxyethyl) phosphate between KBr windows is presented as ***Figure 300***. The band assignments are as follows: 3547 and 3490 vvw (H_2O), 2959 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} ms (ν_{as} CH_2), 2872 cm^{-1} ms (ν_{sy} CH_3), 2819 cm^{-1} sh (ν_{sy} CH_2), ca 1475 cm^{-1} sh (δ OCH_2), ca 1465 cm^{-1} sh and 1458 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1384 cm^{-1} w (ω OCH_2), 1364 cm^{-1} w (δ_{sy} CH_3), 1279 cm^{-1} ms (ν P=O, *calculated* value is 1272 cm^{-1}), 1134 cm^{-1} ms (ν C-O-C), 1043 cm^{-1} s (ν P-O-C), 988 cm^{-1} ms (ν C-C), 821 cm^{-1} w (POC), 739 cm^{-1} vw (CH_2 rock), 558 cm^{-1} vw (P=O deformation).

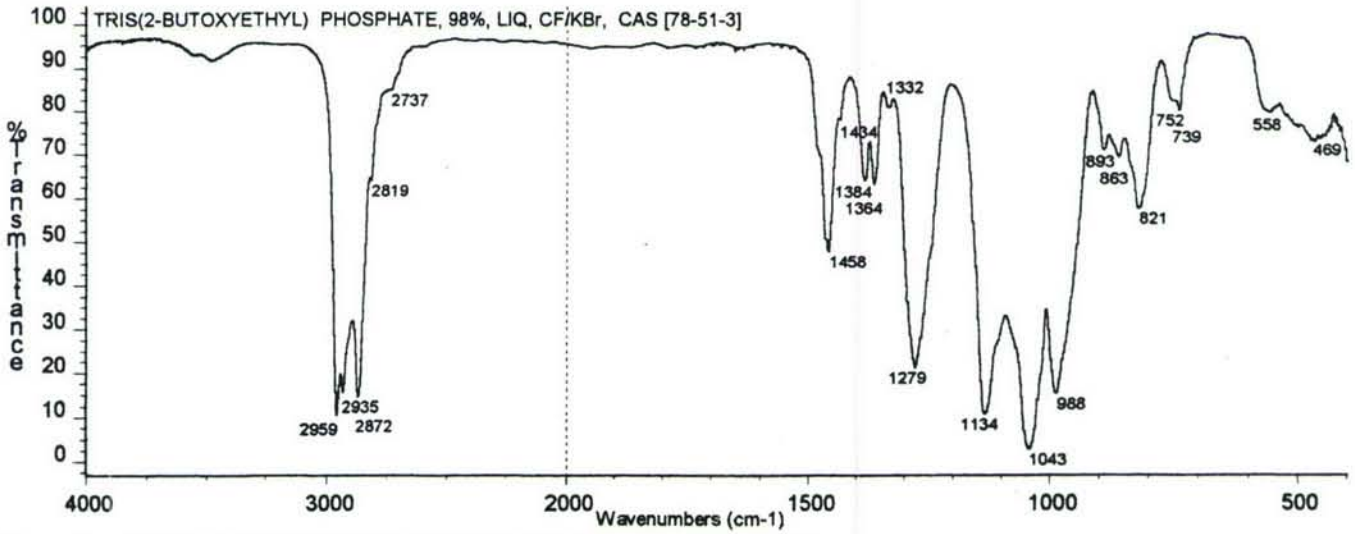

Figure 300 TRIS(2-BUTOXYETHYL) PHOSPHATE, 98%, LIQUID, CF/KBr

3.5.11.7 Tris(2-chloroethyl) Phosphate $(Cl\text{-}CH_2\text{-}CH_2\text{-}O)_3P{=}O$

The infrared spectrum of tris(2-chloroethyl) phosphate as a thin liquid film between KBr discs is reproduced as ***Figure 301***. The band assignments are as follows: 3483 cm^{-1} vvw (H_2O), 2963 cm^{-1} w (ν_{as} CH_2), 2889 cm^{-1} vw (ν_{sy} CH_2), 1457 and 1430 cm^{-1} w (δ CH_2 and δ CH_2-Cl), 1388 cm^{-1} vw (ω OCH_2), 1307 cm^{-1} m (ω CH_2-Cl), 1282 cm^{-1} ms (ν P=O, *calculated* value is 1290 cm^{-1}), 1199 cm^{-1} w (τ CH_2 ?), 1080 and 1030 cm^{-1} s (ν P-O-C), 973 cm^{-1} ms (ν C-C), 796 cm^{-1} m (POC), 669 cm^{-1} m (ν C-Cl), 532 cm^{-1} w (P=O deformation).

3.5.11.8 Tris(trimethylsilyl) Phosphate $[(CH_3)_3Si\text{-}O]_3P{=}O$

The infrared spectrum of tris(timethylsilyl) phosphate as a thin liquid film between KBr windows is

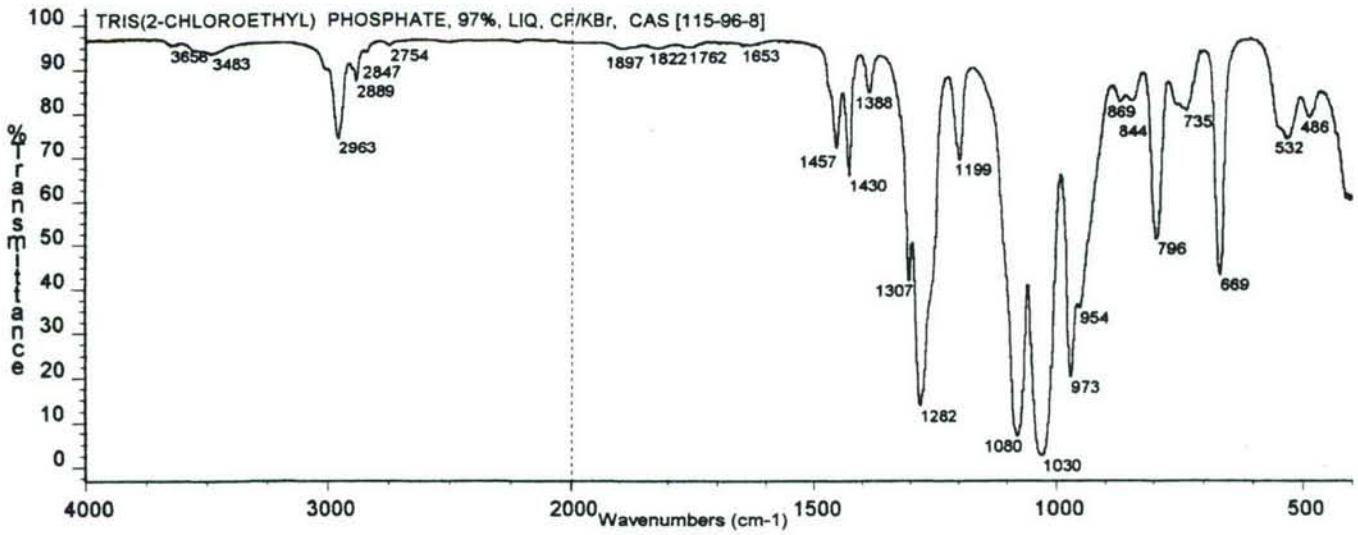

Figure 301 TRIS(2-CHLOROETHYL) PHOSPHATE, 97%, LIQUID, CF/KBr

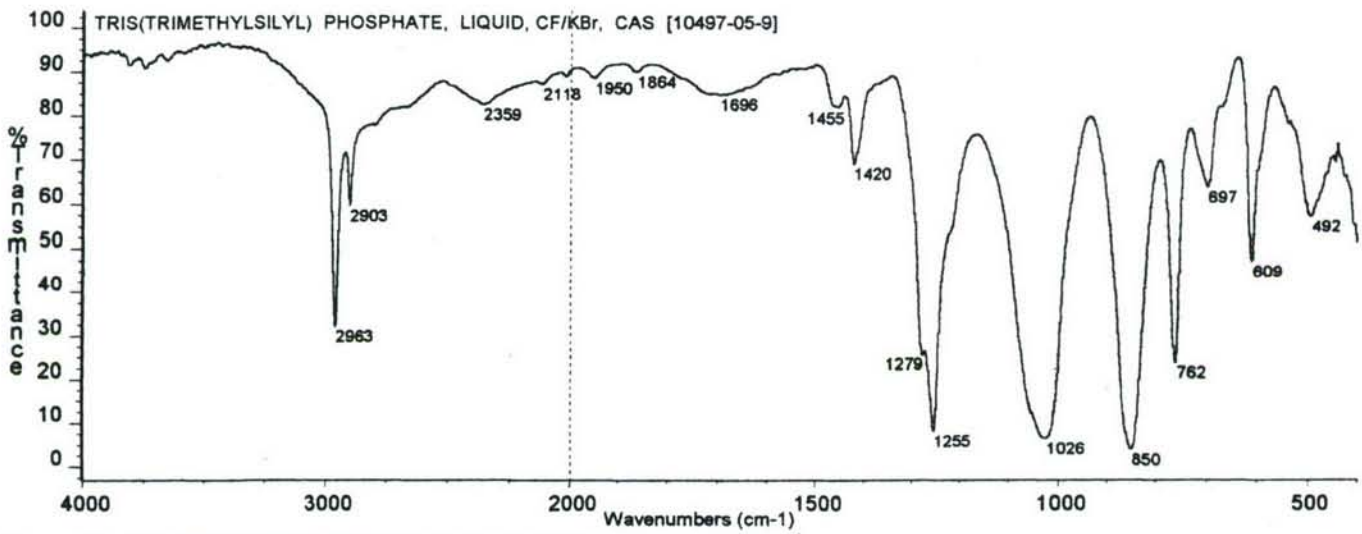

Figure 302 TRIS(TRIMETHYLSILYL) PHOSPHATE, LIQUID, CF/KBr

reproduced as ***Figure 302***. The band assignments are as follows: 2963 cm^{-1} m (ν_{as} CH_3), 2903 cm^{-1} w (ν_{sy} CH_3), ca 2700, 2359 and 1700 cm^{-1} vw and broad (POH bands due to hydrolysis), 1420 cm^{-1} w (δ_{as} CH_3), 1279 cm^{-1} m (ν P=O, *calculated* value is 1290 cm^{-1}), 1255 cm^{-1} s (δ_{sy} Si-CH_3), 1220 cm^{-1} sh (ν P=O acid, hydrolysis), 1026 cm^{-1} s (ν P-O-Si), 850 cm^{-1} s [$Si(CH_3)_3$ rock and ν Si-C), 762 cm^{-1} ms [$Si(CH_3)_3$].

The effect of atmospheric moisture on a thin liquid film of tris(trimethylsilyl) phosphate over time is illustrataed by the infrared spectra presented in ***Figure 303***. The acid POH bands near 2700, 2350 and 1700 cm^{-1}

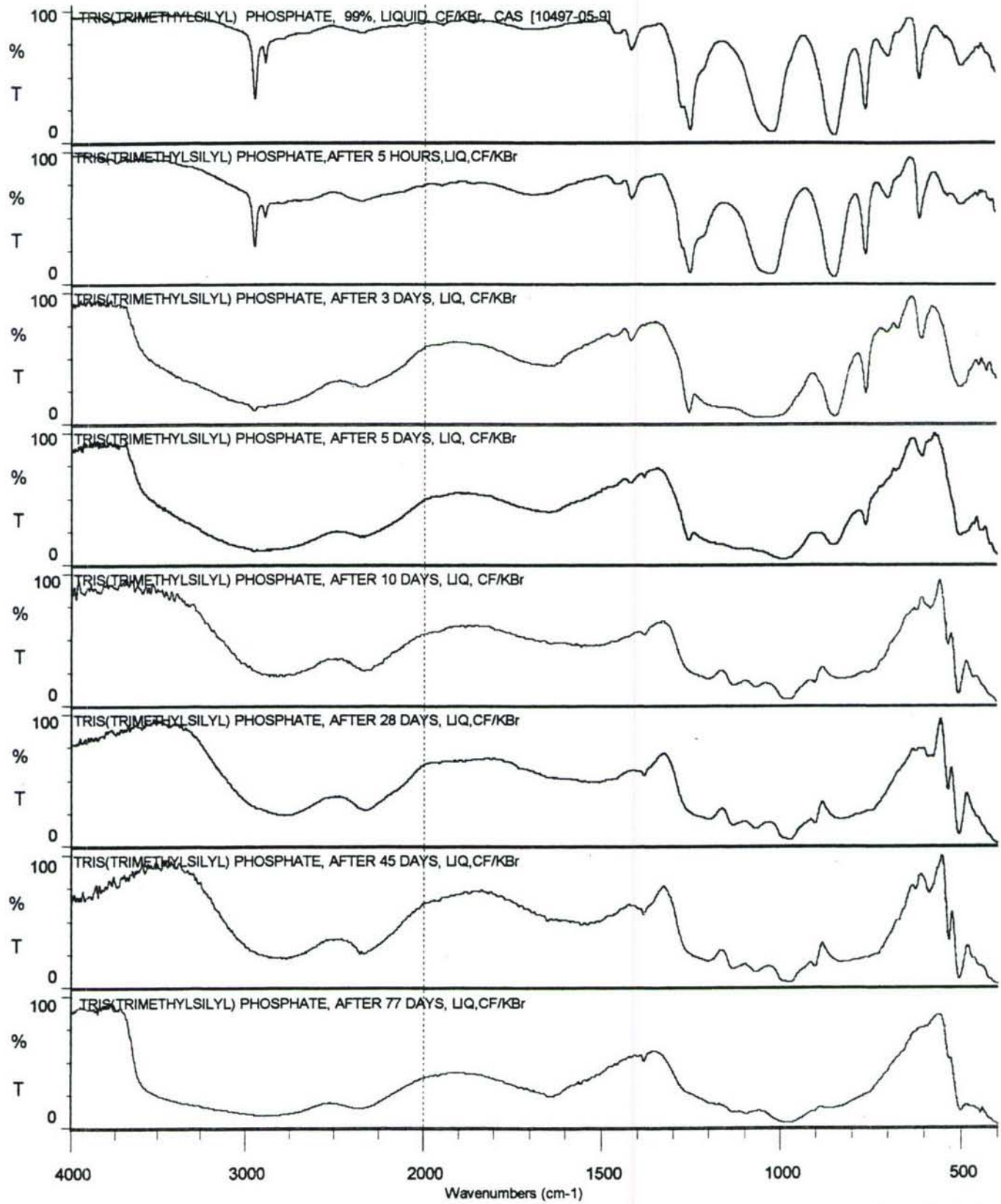

Figure 303 TRIS(TRIMETHYLSILYL) PHOSPHATE, LIQ., CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

grow in intensity with time. The original P=O stretching band at 1279 has disappeared from the spectrum by the 3rd day of exposure to atmospheric moisture, while the bands due to the $Si(CH_3)_3$ moiety are still present at 1259, ca 1000, 848 and 762 cm^{-1}. As time progresses, the acid POH moiety becomes the predominant species in the spectrum, so that by 77th day of atmospheric exposure, the hydrolysis may have produced essentially phosphoric acid, $O=P(OH)_3$.

3.5.11.9 Triallyl Phosphate $(H_2C=CH-CH_2-O)_3P=O$

The infrared spectrum (grating) of triallyl phosphate as a solid melted between CsI discs (windows) is presented as ***Figure 304***. The band assignments are as follows: 3082 cm^{-1} m (ν_{as} $=CH_2$), 3020 cm^{-1} m (ν =C-H and ν_{sy} $=CH_2$), 2944 cm^{-1} ms (ν_{as} CH_2), 2892 cm^{-1} w (ν_{sy} CH_2), 1879 cm^{-1} w (2 x ω $=CH_2$), 1647 cm^{-1} m (ν C=C), 1458 cm^{-1} ms (δ OCH_2), 1424 cm^{-1} ms (δ $=CH_2$, scissors), 1361 cm^{-1} m (ω OCH_2 ?), 1266 cm^{-1} s (ν P=O), 1012 cm^{-1} s (ν P-O-C), 986 cm^{-1} sh (ω =C-H *trans*), 922 cm^{-1} w (ω $=CH_2$), 788 cm^{-1} m (POC), 628 cm^{-1} m (ω =C-H *cis* ?), 511 cm^{-1} ms (P=O deformation).

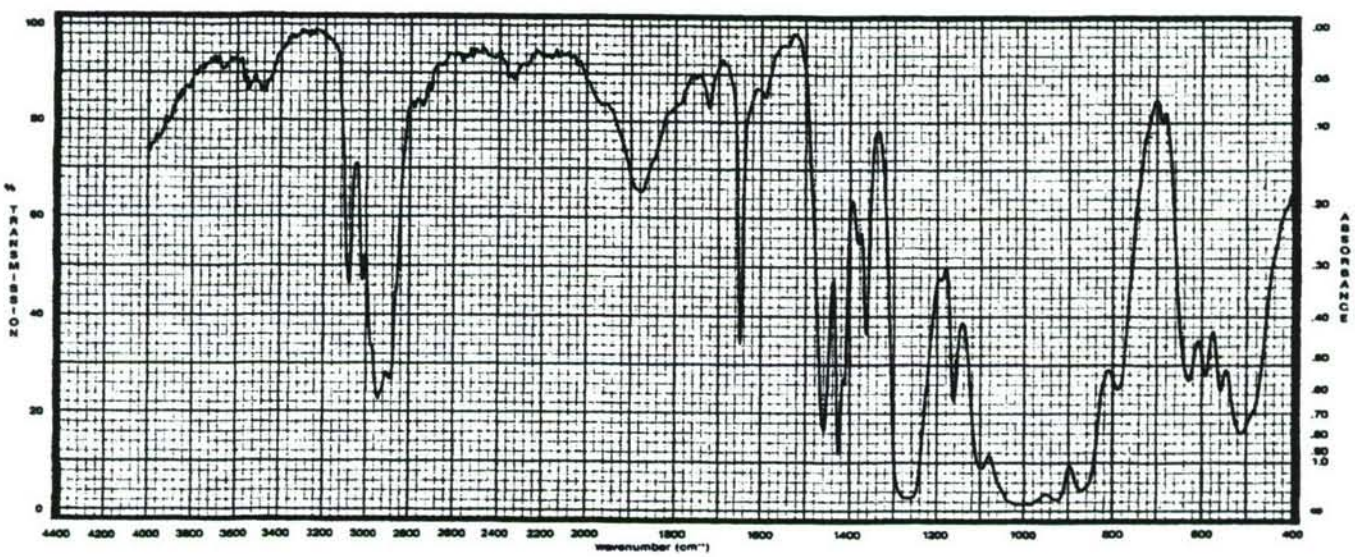

Figure 304 TRIALLYL PHOSPHATE, SOLID MELTED BETWEEN CsI WINDOWS (Perkin-Elmer Model 283B Grating Spectrophotometer)

3.5.11.10 Triphenyl Phosphate $(C_6H_5O)_3P{=}O$

The infrared spectrum of triphenyl phosphate as a KBr pellet and as a solid between KBr windows is given in ***Figure 305***. The band assignments for the compound determined as a KBr pellet are: 3437 cm^{-1} vw (H_2O), 3097 cm^{-1} vvw, 3060 cm^{-1} vw, 3044 cm^{-1} sh and 3019 cm^{-1} vvw (aromatic ν C-H), 1588 cm^{-1} w, 1489 cm^{-1} ms and 1456 cm^{-1} w (aromatic ring), 1294 cm^{-1} m (ν P=O, *calculated* value is 1290 cm^{-1}), 1193 and 1184 cm^{-1} ms (ν C-O of PO-Ph), 1163 cm^{-1} m, 1071 and 1024 cm^{-1} w and 1010 cm^{-1} m (β C-H mono-substituted aromatic ring), 956 cm^{-1} s (ν P-O of P-OPh), 783 and 772 cm^{-1} m (γ C-H mono-substituted aromatic ring), 690 cm^{-1} m (δ mono-substituted aromatic ring), 520 cm^{-1} w (out-of-plane quadrant ring bending (mono-substitution), 502 cm^{-1} vw (P=O deformation).

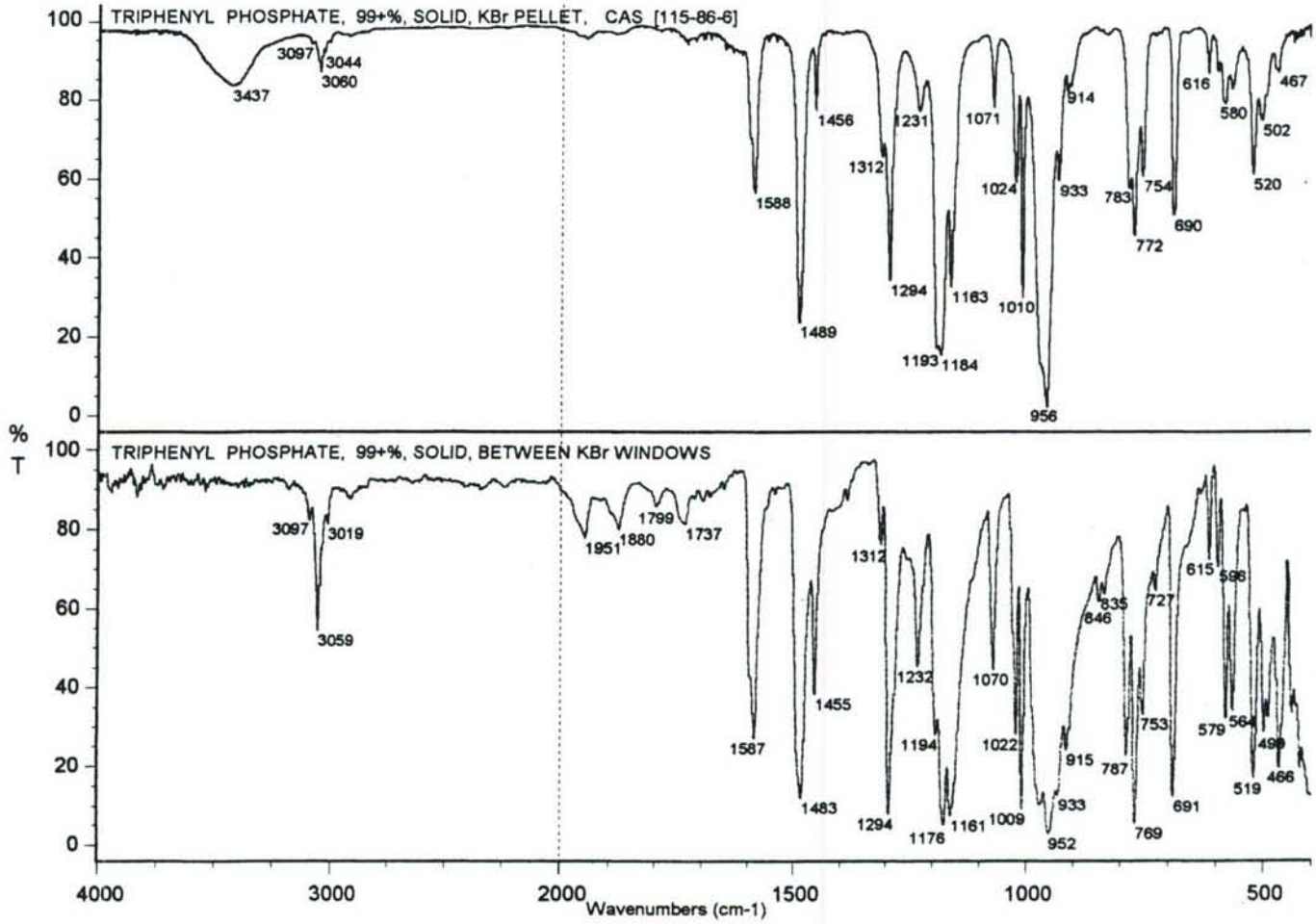

Figure 305 TRIPHENYL PHOSPHATE, 99⁺%, SOLID, UPPER SPECTUM--**AS A KBr PELLET,** LOWER SPECTRUM--**SOLID BETWEEN KBr DISCS (WINDOWS)**

3.5.11.11 Methyl Dichlorophosphate (Methyl Phosphorodichloridate) (**MDO**) $CH_3O\text{-}P{=}O(Cl)_2$

The infrared spectrum of methyl dichlorophosphate (methyl phosphorodichloridate), **MDO**, as a thin liquid film between KBr windows is given in ***Figure 306***. The band assignments are as follows: 2962 cm^{-1} w (ν_{as} CH_3), 2907 cm^{-1} vvw (2 x 1451 = 2902 cm^{-1}), 2856 cm^{-1} vw (ν_{sy} CH_3), 2600 cm^{-1} vvw (2 x 1305 = 2610 cm^{-1}), 1852 cm^{-1} vw and 1832 cm^{-1} sh (1056 + 804 = 1860 cm^{-1} and 1027 + 804 = 1831 cm^{-1}), 1451 cm^{-1} m (δ_{as} and δ_{sy} CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1305 cm^{-1} s (ν P=O, *calculated* value is 1298 cm^{-1}), 1181 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1056 and 1027 cm^{-1} s (ν POC), ca 980 cm^{-1} sh (ν P-OH, impurity from hydrolysis), 804 cm^{-1} ms (POC), 582 cm^{-1} s with shoulder near 610 cm^{-1} (ν_{as} PCl_2, doublet due to isomers), 546 cm^{-1} m and 515 cm^{-1} ms (ν_{sy} PCl_2, doublet due to isomers).[¤]

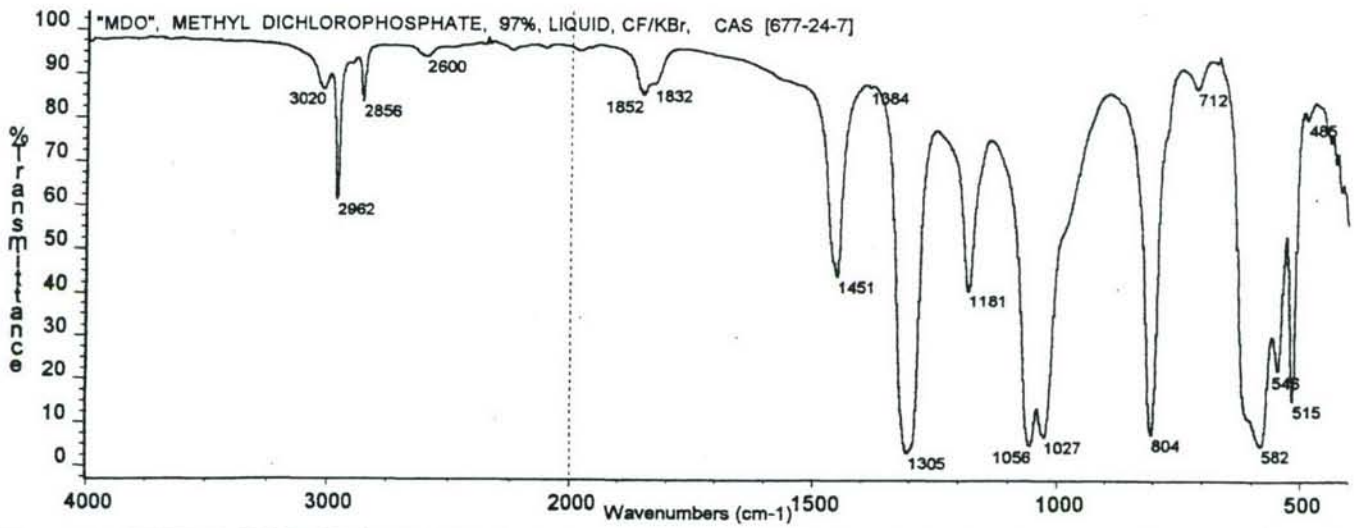

Figure 306 METHYL DICHLOROPHOSPHATE (METHYL PHOSPHORODICHLORIDATE), MDO, 97%, LIQUID, CF/KBr

The effect of atmospheric moisture on methyl dichlorophosphate (methyl phosphorodichloridate), **MDO**, is reflected by the infrared spectra reproduced in ***Figure 307***. The spectrum of **MDO** after 3 hours of exposure to atmospheric moisture shows a general broadening and decrease in the background near 2900, 2300, 1650 and 980 cm^{-1} due to the formation of the POH moiety. This becomes even more evident after 3 days of

[¤] Thomas, L.C. in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 81, Table 7.9, Heyden & Son Ltd., London, 1974, lists the ranges of the P-Cl stretching frequencies in dichloridates of the type, $RO\text{-}P{=}OCl_2$, as occurring in the range 607-576 (ν_{as} PCl_2) and 548-515 cm^{-1} (ν_{sy} PCl_2).
A detailed study of the isomers of $CH_3OP{=}OCl_2$ has been undertaken by Nyqvist. See Nyqvist, R.A., *Spectrochim. Acta*, **23A**, 845 and 1499 (1967), Nyqvist, R.A, and Muelder, W.W., *Spectrochim. Acta*, **22**,1563 (1966).

exposure to moisture as very broad and intense bands are formed in the spectrum near 2900, 2300 and 1690 cm^{-1} assignable to the POH group. The broad band near 1190 cm^{-1} is assigned to an acid P=O stretching vibration. Some residual CH_3O may be evident at 1457, 1190, 1046 and 796 cm^{-1}. By the fourth day the PCl_2 bands are gone from the spectrum. The hydrolysis of methyl dichlorophosphate may be represented as follows:

$CH_3OP{=}OCl_2$ -HOH → $CH_3OP{=}O(OH)_2$ -HOH→ $(HO)_3P{=}O$.

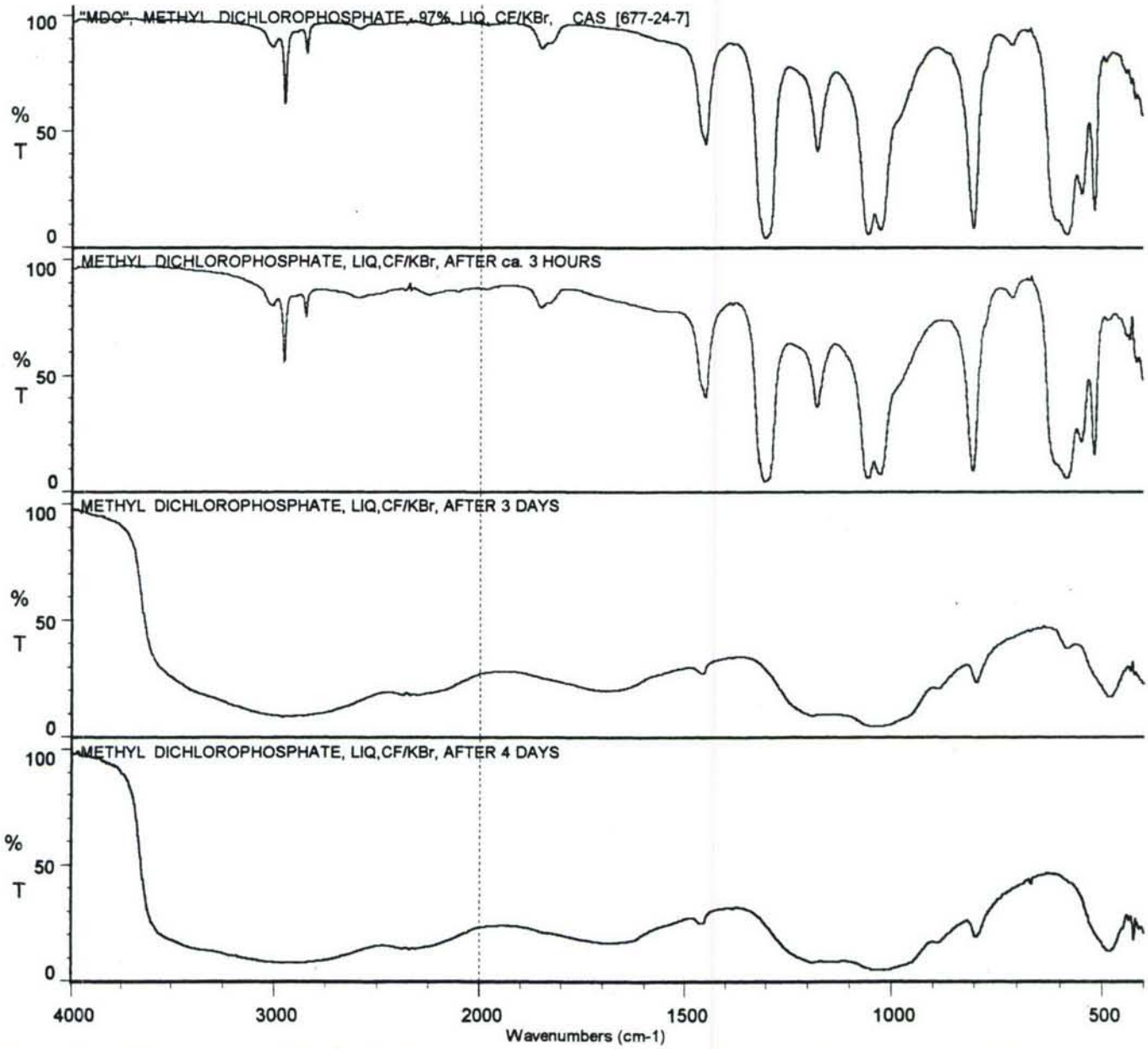

Figure 307 ETHYL DICHLOROPHOSPHATE (MDO), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.11.12 2,2-Dichlorovinyl Dimethyl Phosphate (**Dichlorvos**) $(CH_3O)_2P{=}O(O\text{-}HC{=}CCl_2)$

The infrared spectrum of 2,2-dichlorovinyl dimethyl phosphate (**Dichlorvos**) as a thin liquid film between KBr windows is given in ***Figure 308***. The band assignments are as follows: 3061 cm^{-1} vw (ν =C-H), 2961 cm^{-1} w (ν_{as} CH_3), 2859 cm^{-1} vw (ν_{sy} CH_3), 1908 cm^{-1} vvw (1051 + 857 = 1908 cm^{-1}), 1648 cm^{-1} w (ν C=C), 1460 cm^{-1} sh and 1453 cm^{-1} w (δ_{as} and δ_{sy} CH_3), 1284 cm^{-1} ms (ν P=O), 1188 cm^{-1} w (CH_3 rock of $POCH_3$, characteristic), 1152 cm^{-1} ms (ν PO-C=), 1051 cm^{-1} s (ν P-O-C), 981 cm^{-1} ms (ν P-OC=), 857 cm^{-1} ms (ν CCl_2), 774 and 765 cm^{-1} w (POC), 532 cm^{-1} m (PO=O deformation).

Figure 308 2,2-DICHLOROVINYL DIMETHYL PHOSPHATE (DICHLORVOS), LIQUID, CF/KBr

3.5.11.13 Diethyl Chlorophosphate (Diethyl Phosphorochloridate) $Cl\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl chlorophosphate (diethyl phosphorochloridate) as a thin liquid film between KBr windows is presented as ***Figure 309***. The band assignments are as follows: 2988 cm^{-1} m (ν_{as} CH_3), 2835 cm^{-1} w (ν_{as} CH_2), 2914 cm^{-1} w (ν_{sy} CH_3), 2873 cm^{-1} vw (ν_{sy} CH_2), ca 2600 and 2300 cm^{-1} vw broad (POH), ca 1837 cm^{-1} vvw (1029 + 801 = 1830 cm^{-1}), ca 1792 cm^{-1} vvw (1029 + 761 = 1790 cm^{-1}), 1479 cm^{-1} w (δ OCH_2), 1445 cm^{-1} w (δ_{as} CH_3), 1395 cm^{-1} w (ω OCH_2), 1372 cm^{-1} w (δ_{sy} CH_3), 1304 cm^{-1} ms (ν P=O, *calculated* value is 1294 cm^{-1}), ca 1245 cm^{-1} sh (broadening of the main P=O band may be due to acid P=O ?), 1165 and 1101 cm^{-1} w (CH_3 rock of POEt, characteristic), 1029 cm^{-1} s (ν P-O-C), 988 cm^{-1} sh (ν C-C of POEt), 945 cm^{-1}

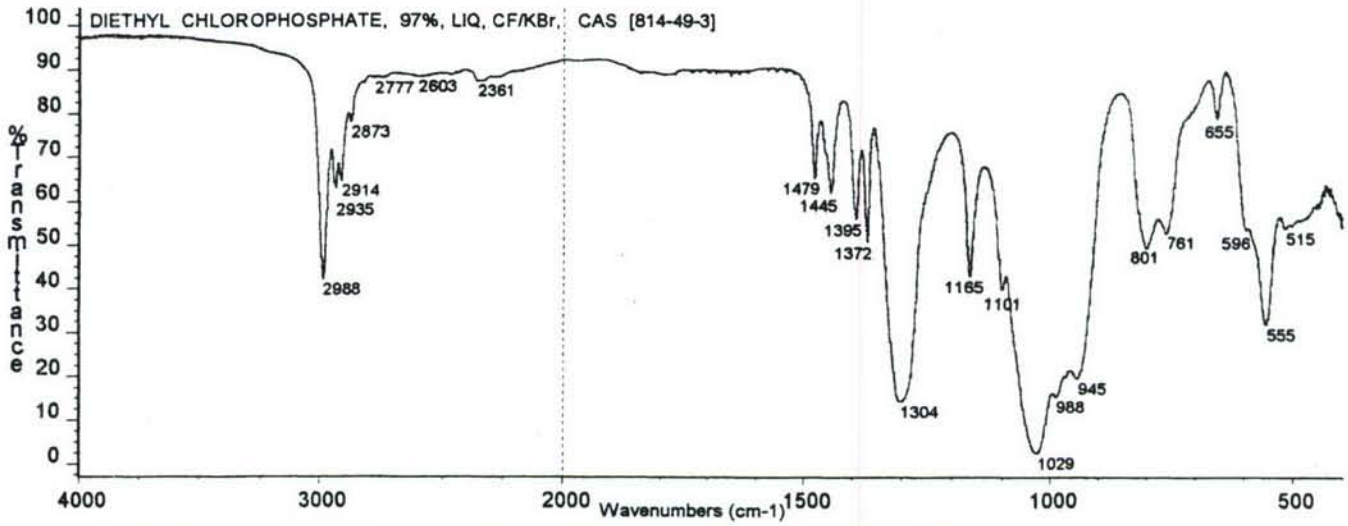

Figure 309 DIETHYL CHLOROPHOSPHATE (DIETHYL PHOSPHOROCHLORIDATE), 97%, LIQUID, CF/KBr

ms [possible ν P-O-P of pyro compound such as $EtO_2P(=O)$-O-$P(=O)OEt_2$, which would have a *calculated* P=O of 1290 cm^{-1}], 801 and 761 cm^{-1} w (POC), 555 cm^{-1} m (ν P-Cl).

The effect of atmospheric moisture on a thin film of diethyl chlorophosphate (diethyl phosphoro-chloridate) between KBr windows is illustrated by the infrared spectra reproduced in ***Figures 310A*** and ***310B***. After some 22 hours of exposure to atmospheric moisture, the infrared spectrum (***Figure 310A***), shows POH bands near 2700, 2300 and 1670 cm^{-1}. As time progresses to 6-12 days of exposure to moisture, the POH bands become more pronounced in the infrared spectrum. The P=O band has fallen to ca 1290 cm^{-1} perhaps indicative of the P=O of the pyro compound, $EtO_2P(=O)$-O-$P(=O)OEt_2$. A broad band near 1230 cm^{-1} may be assigned to the P=O stretch from a compound such as HO-$P=O(0Et)_2$. The band due to the P-Cl stretch (555 cm^{-1}) is now absent from the spectra. By the passage of 204-236 (***Figure 310B***) days the hydrolysis may have proceeded further to form $(HO)_2P=O(OEt)$. Thus, the hydrolysis of diethyl chlorophosphate may be summarized as follows:

$Cl\text{-}P=O(OEt)_2$ -HOH→ $EtO_2P(=O)$-O-$P(=O)OEt_2$ -HOH→ HO-$P=O(OEt)_2$ -HOH→ $(HO)_2P=O(OEt)$.

3.5.11.14 Ethyl Dichlorophosphate (Ethyl Phosphorodichloridate) CH_3CH_2-O-$P=O(Cl)_2$

The infrared spectrum of ethyl dichlorophosphate (ethyl phosphorodichloridate) as a liquid film

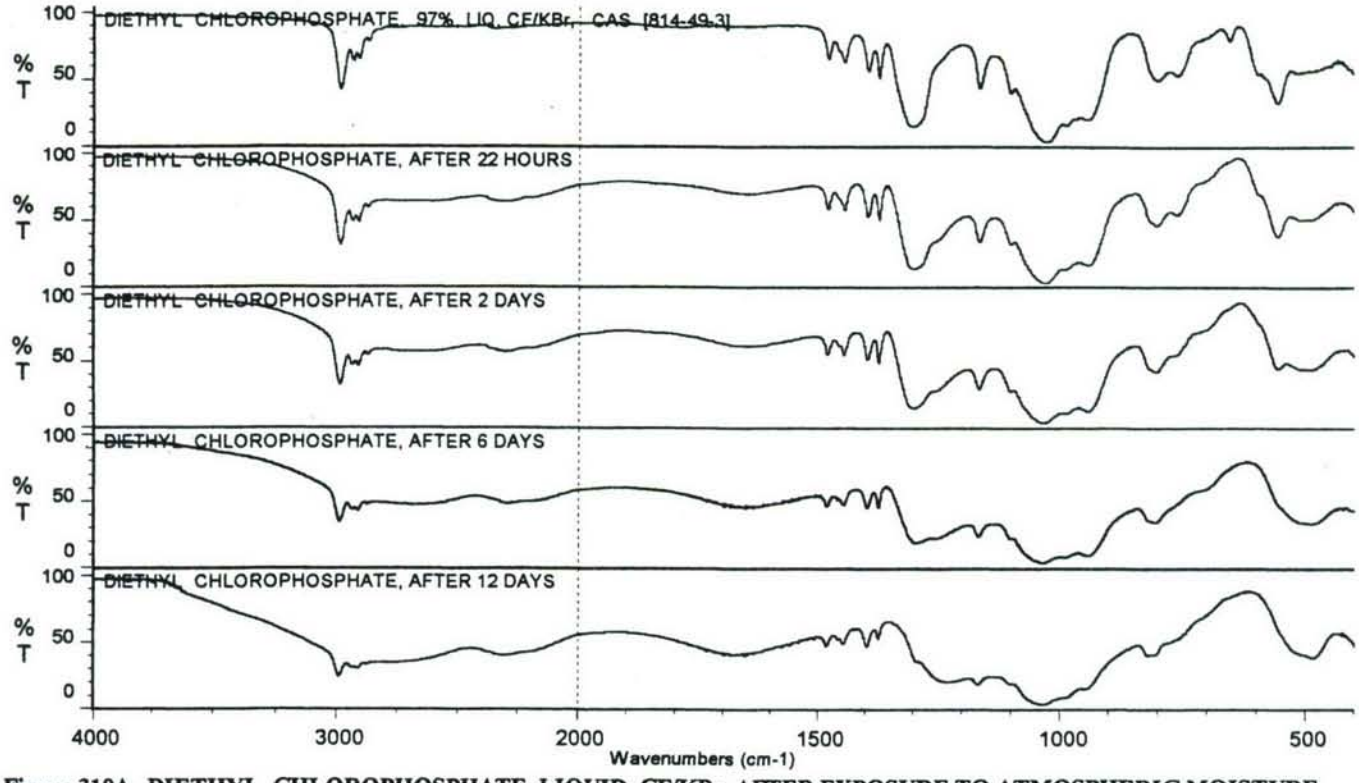

Figure 310A DIETHYL CHLOROPHOSPHATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

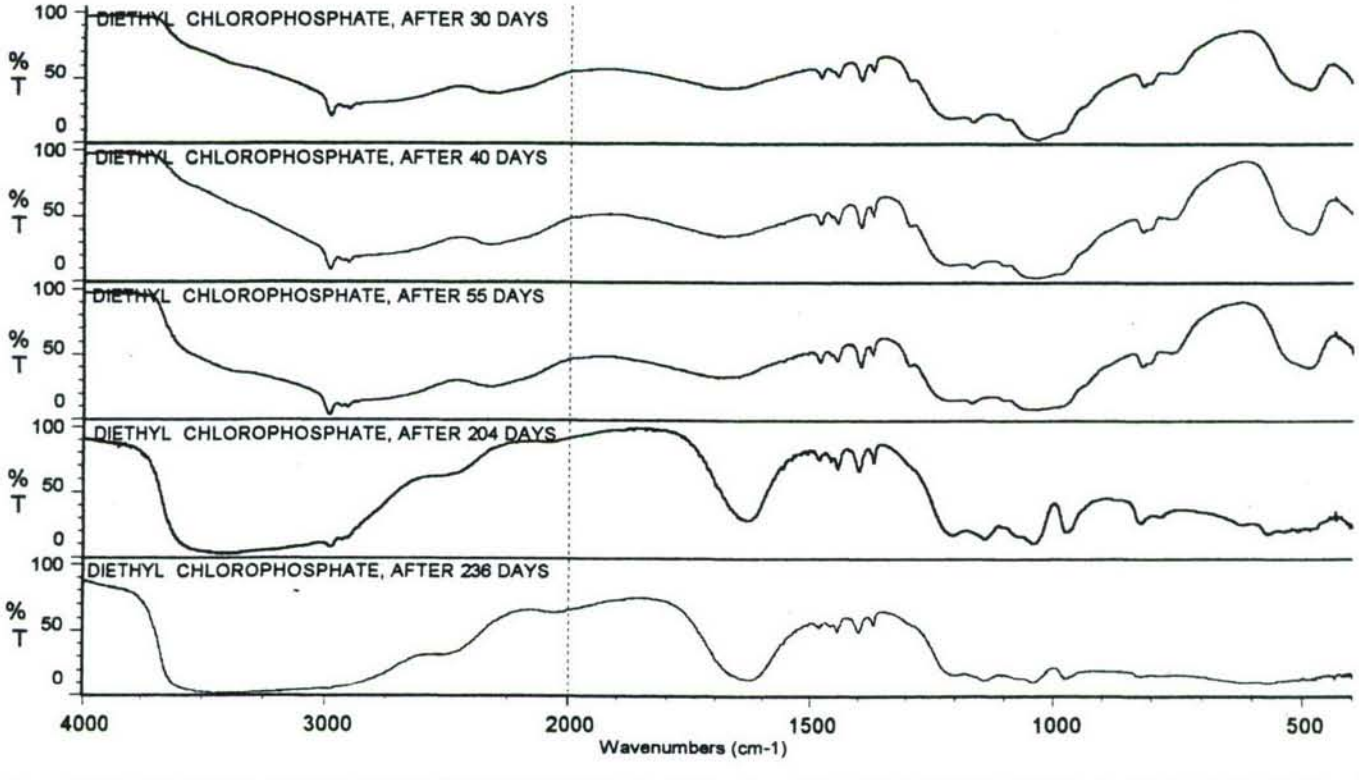

Figure 310B DIETHYL CHLOROPHOSPHATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

between KBr discs (windows) is presented as ***Figure 311***. The band assignments are as follows: 2990 cm^{-1} m (ν_{as} CH_3), 2942 cm^{-1} w (ν_{as} CH_2), 2912 cm^{-1} w (ν_{sy} CH_3), 2872 cm^{-1} vw (ν_{sy} CH_2), ca 2600 and 2265 cm^{-1} vw (POH), 1799 cm^{-1} vw and ca 1782 cm^{-1} sh (1036 + 776 = 1812 cm^{-1} , 1013 + 776 = 1789 cm^{-1}), 1476 cm^{-1} m (δ OCH_2), 1445 cm^{-1} m (δ_{as} CH_3), 1393 cm^{-1} m (ω OCH_2), 1371 cm^{-1} m (δ_{sy} CH_3), 1310 and 1295 cm^{-1} s (ν P=O, isomers), 1161 and 1101 cm^{-1} m-w (CH_3 rock of POEt, characteristic), 1036 and 1013 cm^{-1} s (ν P-O-C), 980 cm^{-1} ms (ν C-C of POEt), 776 cm^{-1} ms (POC), ca 600 cm^{-1} sh and 579 cm^{-1} s (ν_{as} PCl_2, isomers), 552 and 517 cm^{-1} ms (ν_{sy} PCl_2, isomers).

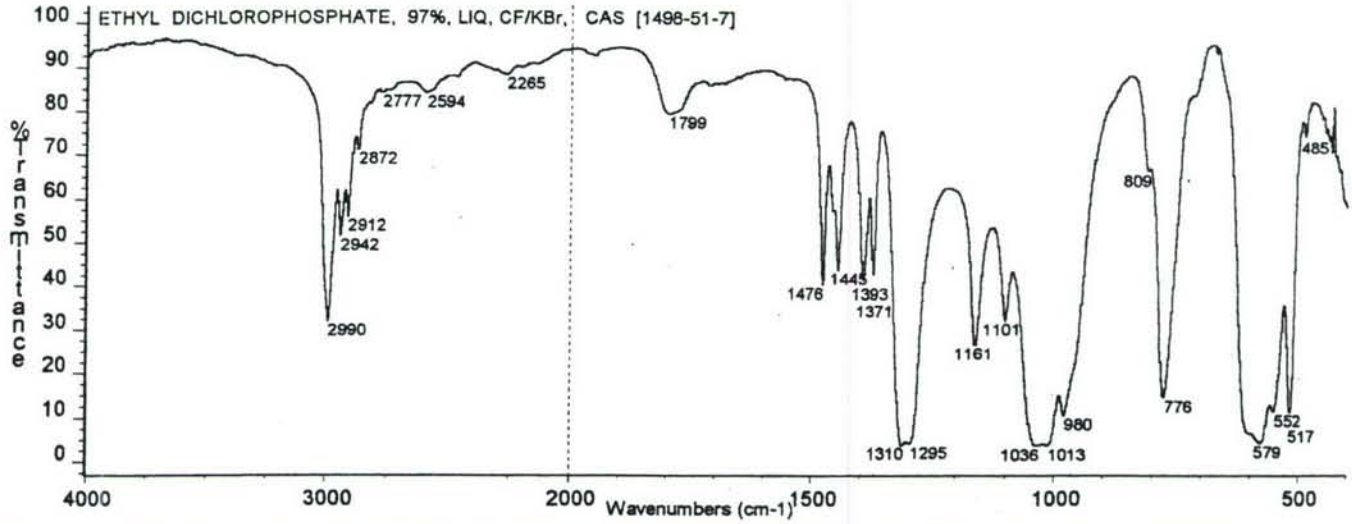

Figure 311 ETHYL DICHLOROPHOSPHATE (ETHYL PHOSPHORODICHLORIDATE), 97%, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of ethyl dichlorophosphate (ethyl phosphorodichloridate) between KBr windows is illustrated by the infrared spectra presented in ***Figure 312***. After 1 day of exposure to moisture, the spectrum is mainly that of a P-acid with broad POH bands near 2900, 2300 and 1650 cm^{-1}. Some residual P-Cl stretching is visible near 579 cm^{-1}. Bands indicative of the POEt moiety are still evident in the CH stretching region and at 1479, 1445, 1396, 1373, 1167 and 1100, and 779 cm^{-1}. The broad band near 1040 cm^{-1} is composed of the ν P-O-C, ν C-C (POEt) and ν P-OH. The P=O stretching band is broad and occurs near 1224 cm^{-1}. By the second day of exposure to atmospheric moisture, the POH bands are still in evidence, while the P=O stretch has fallen to 1205 cm^{-1}. The bands of the POEt moiety are still present. The

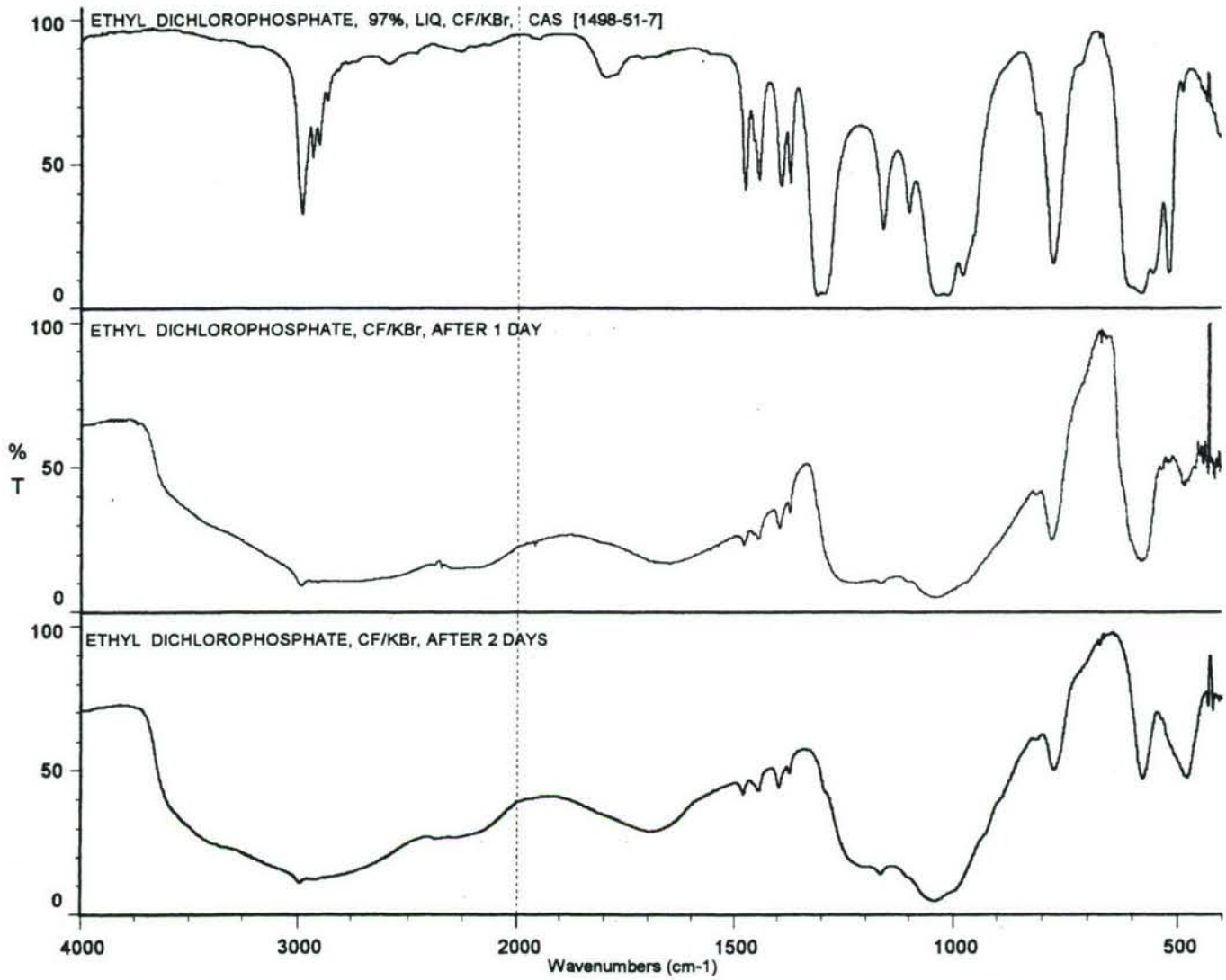

Figure 312 ETHYL DICHLOROPHOSPHATE (ETHYL PHOSPHORODICHLORIDATE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

band at 578 cm^{-1} (ν P-Cl) has become much weaker, and the band at 479 cm^{-1} may be assigned to the deformation of the P=O group. The hydrolysis of ethy dichlorophosphate may be summarized as follows:

$EtO\text{-}P{=}OCl_2$ -HOH→ $EtO\text{-}P{=}O(OH)(Cl)$ -HOH→ $EtO\text{-}P{=}O(OH)_2$

3.5.11.15 2,2,2-Trichloroethyl Dichlorophosphate $Cl_3C\text{-}CH_2\text{-}O\text{-}P{=}O(Cl)_2$

The infrared spectrum of a thin liquid film of 2,2,2-trichloroethyl dichlorophosphate between KBr windows is reproduced as ***Figure 313***. The band assignments are as follows: 3005 cm^{-1} w(ν_{as} CH_2), 2958 cm^{-1} w

(ν_{sy} CH_2), 2587 cm^{-1} vw broad (POH), 1987 cm^{-1} vvw (1098 + 887 = 1985 cm^{-1}), 1890 cm^{-1} vw (1098 + 788 = 1886 cm^{-1}), 1810 cm^{-1} vvw (1023 + 788 = 1811 cm^{-1}), 1446 cm^{-1} m (δ OCH_2), 1381 cm^{-1} w (ω OCH_2), 1297 cm^{-1} s (ν P=O), 1098 cm^{-1} s and 1023 cm^{-1} s (ν P-O-C, ν C-C), 887 cm^{-1} ms (POC), 788 cm^{-1} ms (ν CCl_3), 727 cm^{-1} s (CH_2 rock ?), ca 600 cm^{-1} sh and 591 cm^{-1} s (ν_{as} PCl_2), 533 cm^{-1} ms (ν_{sy} PCl_3).

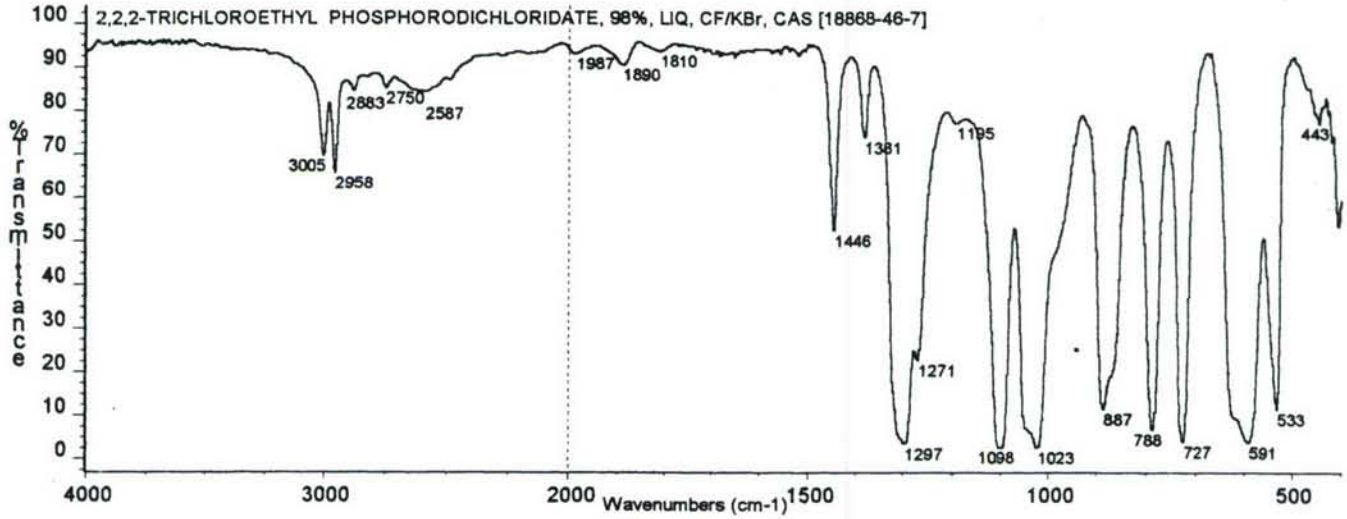

Figure 313 2,2,2-TRICHLOROETHYL DICHLOROPHOSPHATE (2,2,2-TRICHLOROETHYL PHOSPHORODICHLORIDATE), LIQUID, CF/KBr

The effect of atmospheric moisture on a thin film of 2,2,2-trichloroethyl dichlorophosphate (2,2,2-trichloroethyl phosphorodichloridate) between KBr windows is illustrated by the infrared spectra presented in ***Figures 314A*** and ***314B***. The compound shows strong POH bands near 2750, 2280 and 1685 cm^{-1} after 18 hours of exposure to atmospheric moisture (***Figure 314A***). The P=O stretching band that had occurred at 1297 cm^{-1} has fallen to 1194 cm^{-1}. The PCl_2 band near 590 cm^{-1} is almost completely gone from the spectrum, and is gone by the 42-68 hour period. The spectra now show the presence of a P-acid, probably 2,2,2-trichloroethyl phosphoric acid, Cl_3C-CH_2-O-P=O$(OH)_2$. The band assignments for this phosphoric acid are: 3003 cm^{-1} vvw (ν_{as} CH_2), 2958 cm^{-1} vvw (ν_{sy} CH_2), ca 2742, 2270 cm^{-1} m broad (POH), 1448 cm^{-1} w (δ OCH_2), 1378 cm^{-1} w (ω OCH_2), 1278 cm^{-1} m (ω CH_2-CCl_3), 1184 cm^{-1} m (ν P=O), 1041 cm^{-1} s (ν_{as} P-OH, ν P-O-C), 964 cm^{-1} s (ν_{sy} P-OH), 853 cm^{-1} s (POC), 775 cm^{-1} s (ν CCl_3).

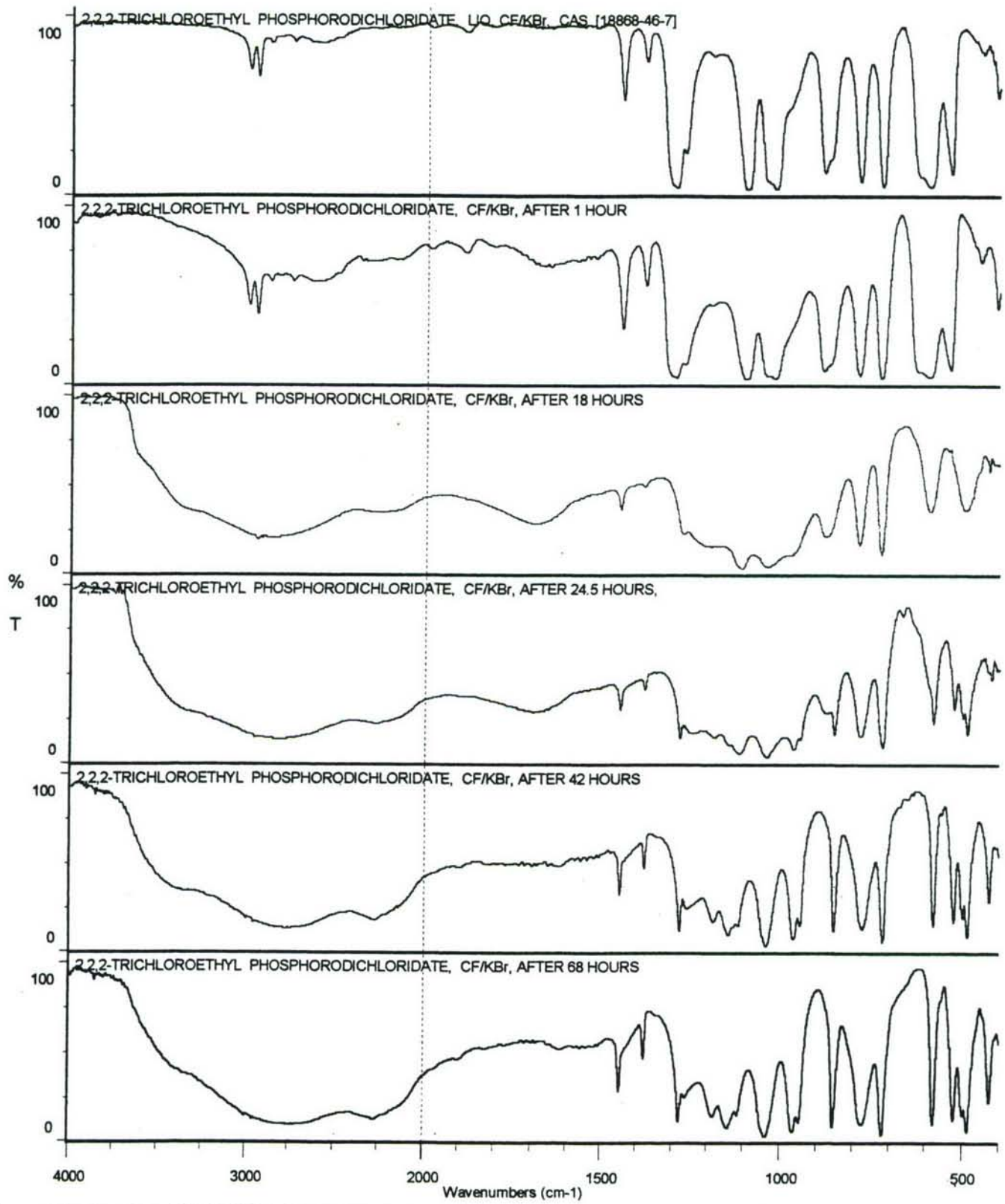

Figure 314A 2,2,2-TRICHLOROETHYL DICHLOROPHOSPHATE (2,2,2-TRICHLOROETHYL PHOSPHORODICHLORIDATE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

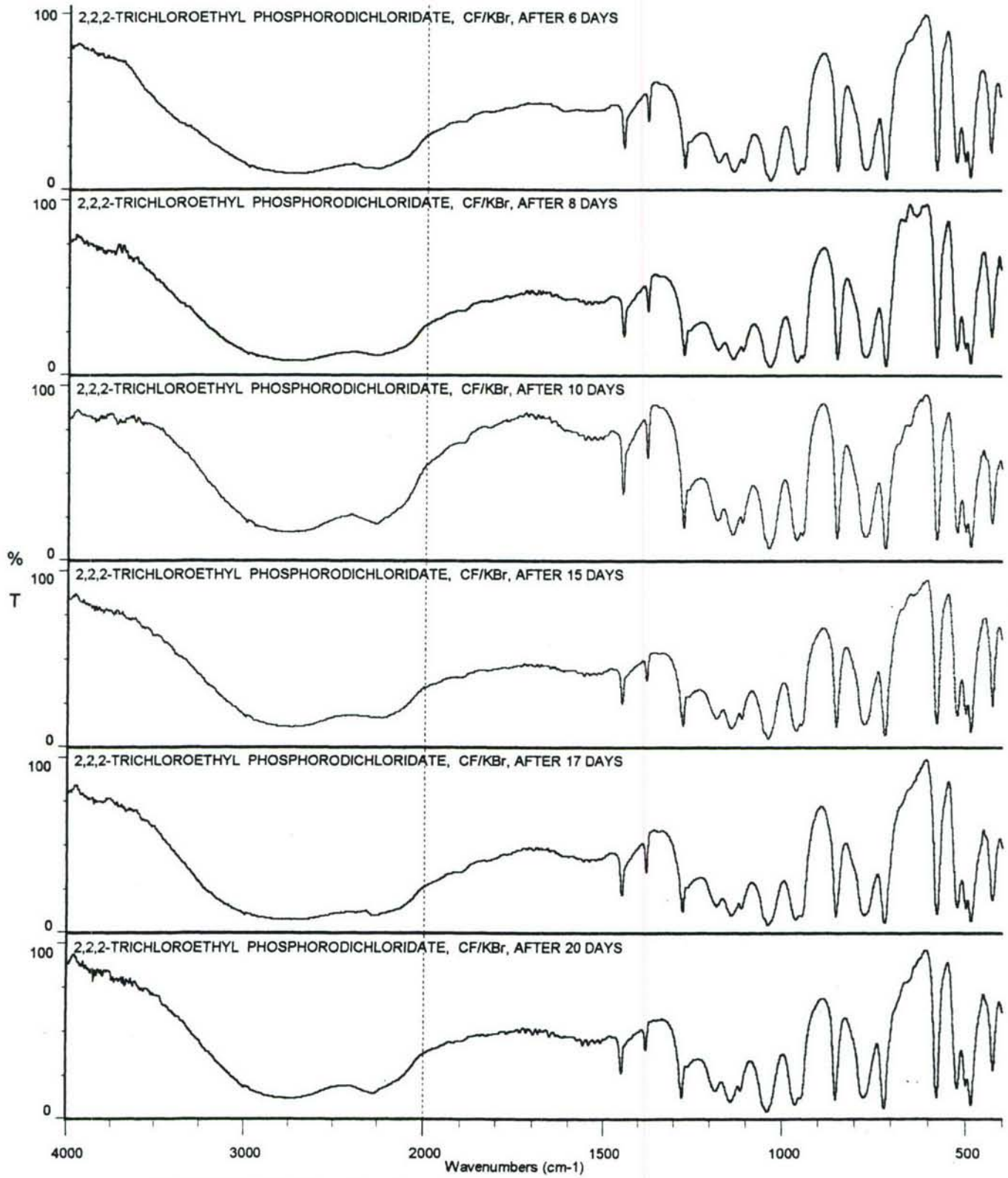

Figure 314B 2,2,2-TRICHLOROETHYL DICHLOROPHOSPHATE (2,2,2-TRICHLOROETHYL PHOSPHORODICHLORIDATE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.5.11.16 2,2,2-Tribromoethyl Dichlorophosphate $Br_3C\text{-}CH_2\text{-}O\text{-}P{=}O(Cl)_2$

The infrared spectrum of 2,2,2-tribromoethyl dichlorophosphate as a thin liquid film between KBr windows is given in ***Figure 315***. The band assignments are as follows: 2993 cm^{-1} w (ν_{as} CH_2), 2945 cm^{-1} w (ν_{sy} CH_2), 1441 cm^{-1} m (δ OCH_2), 1375 cm^{-1} w (ω OCH_2), 1299 cm^{-1} s (ν P=O, *calculated* value is 1296 cm^{-1}), 1267 cm^{-1} sh (ω CH_2-CBr_3), 1078 cm^{-1} s (ν P-O-C), 1008 cm^{-1} s (ν C-C ?), 872 cm^{-1} ms (POC), 720 cm^{-1} ms (CH_2 rock ?), 639 cm^{-1} ms (ν C-Br), ca 600 sh and 589 cm^{-1} s (ν_{as} PCl_2), 527 cm^{-1} ms (ν_{sy} PCl_2).

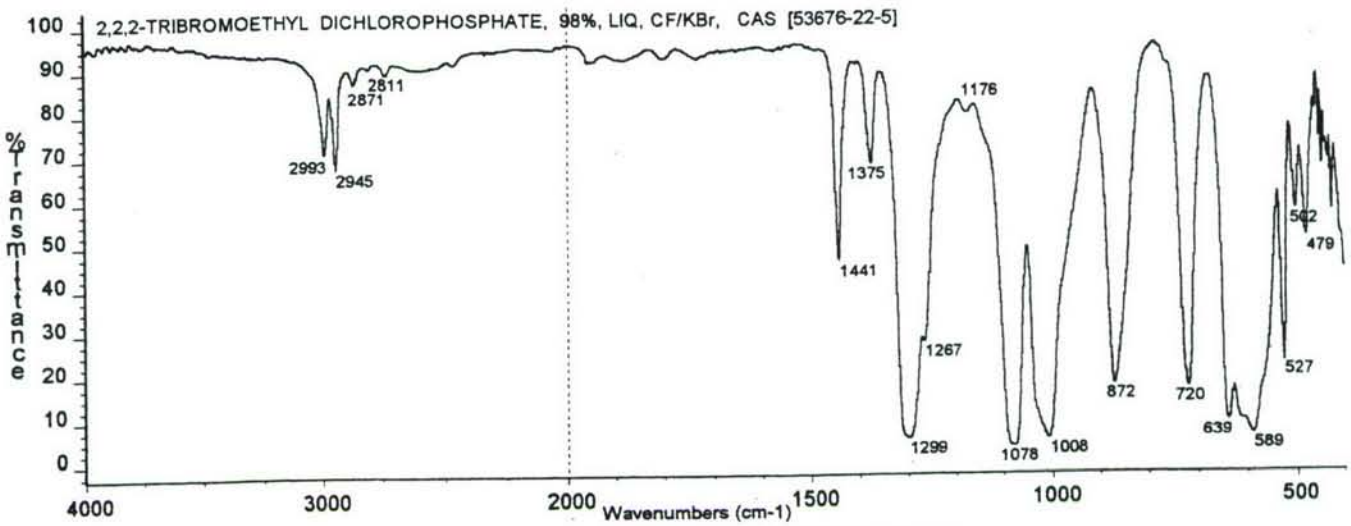

Figure 315 2,2,2-TRIBROMOETHYL DICHLOROPHOSPHATE, 98%, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of 2,2,2-tribromoethyl dichlorophosphate between KBR windows is shown by ***Figure 316***. After 20 hours of exposure to atmospheric moisture, the infrared spectrum shows some POH near 2600 cm^{-1}. After 2-3 days of exposure, the POH bands are clearly evident near 2580, 2200 and 1650 cm^{-1}. The bands due to the PCl_2 moiety are still quite evident near 590 and 527 cm^{-1} as is the C-Br band at 639 cm^{-1}. By the 7th day the compound has hydrolyzed to a P-acid and the bands due to the PCl_2 moiety (590 and 527 cm^{-1}) are now absent from the spectrum. The compound, 2,2,2-tribromoethyl phosphoric acid, $Br_3C\text{-}CH_2\text{-}O\text{-}P{=}O(OH)_2$, is believed to be the hydrolysis product. Thus, the hydrolysis of 2,2,2-tribromoethyl dichlorophosphate may be summarized as follows:

$Br_3C\text{-}CH_2\text{-}O\text{-}P{=}O(Cl)_2$ -HOH→ $Br_3C\text{-}CH_2\text{-}O\text{-}P{=}O(OH)(Cl)$ -HOH→ $Br_3C\text{-}CH_2\text{-}O\text{-}P{=}O(OH)_2$.

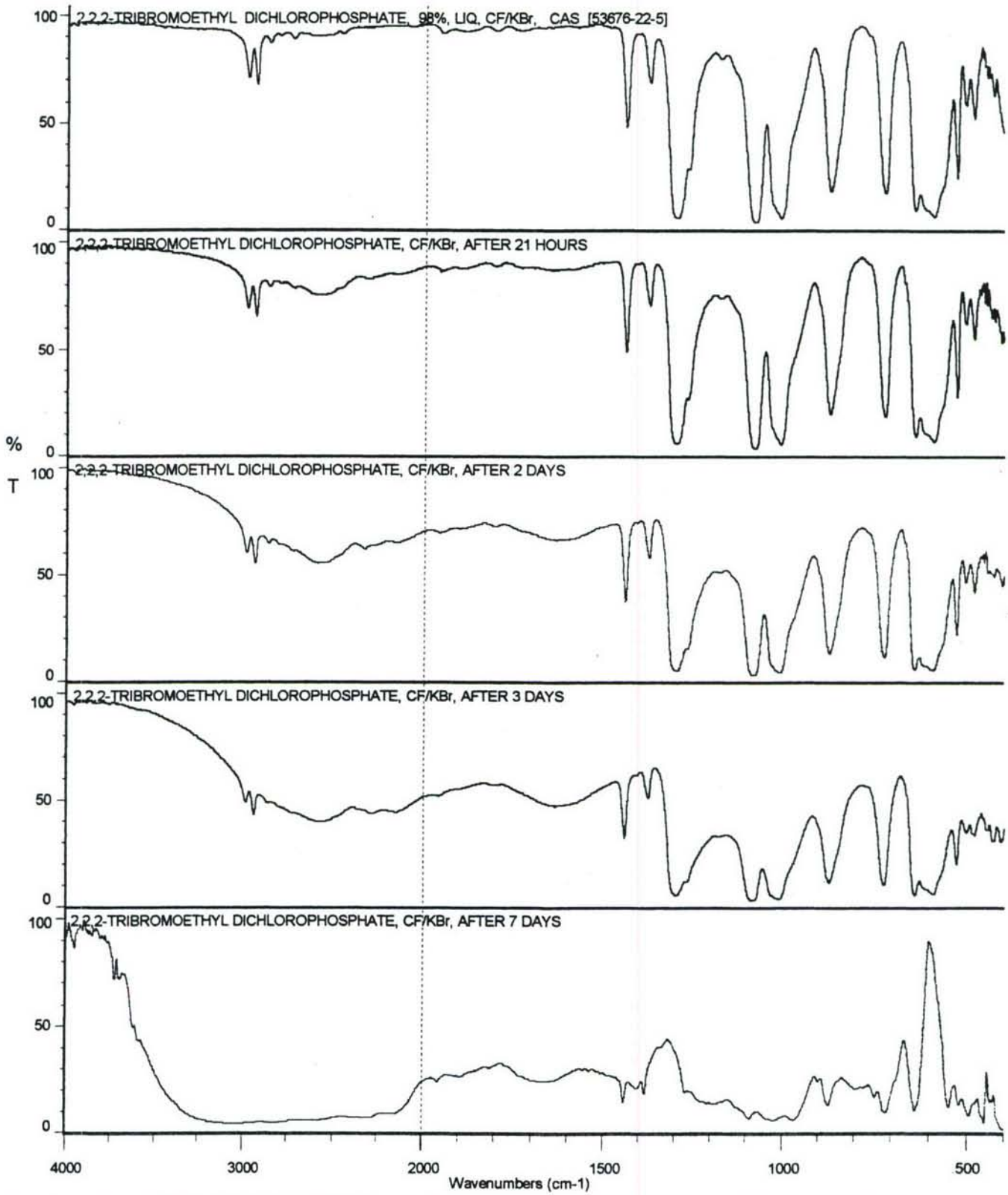

Figure 316 2,2,2-TRIBROMOETHYL DICHLOROPHOSPHATE, 98%, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.11.17 6-Amino-1-hexyl Phosphate $H_2N\text{-}CH_2CH_2CH_2CH_2CH_2CH_2O\text{-}P{=}O(OH)_2$

The infrared spectrum of 6-amino-1-hexyl phosphate as a solid between CsI discs (windows) is presented as ***Figure 317***. The band assignments are as follows: broad band 3200-2800 cm^{-1} m (ν_{as} and ν_{sy} NH_3^+), 2800-2400 cm^{-1} variable (combination bands of NH_3^+ bending vibrations), 2152 cm^{-1} w (due to a combination band of the NH_3^+ torsional oscillation and the asymmetric NH_3^+ deformation), 2940 and 2853 cm^{-1} w (ν_{as} and ν_{sy} CH_2), 1652 cm^{-1} w (δ_{as} NH_3^+), 1541 cm^{-1} m (δ_{sy} NH_3^+), 1473 cm^{-1} w (δ OCH_2), 1461 and 1444 cm^{-1} sh (δ CH_2), 1394 cm^{-1} w (ω OCH_2), 1154 cm^{-1} ms (ν_{as} PO_2^-), 1057 cm^{-1} sh and 1040 cm^{-1} s (ν P-O-C and ν_{sy} PO_2^-), 836 cm^{-1} m (POC ?), 732 cm^{-1} w (CH_2 rock), 513 cm^{-1} ms (PO_2^- deformation ?). These results show that the compound exists as the zwitterion, $H_3N^+CH_2CH_2CH_2CH_2CH_2CH_2O\text{-}PO_2^-$ (OH).

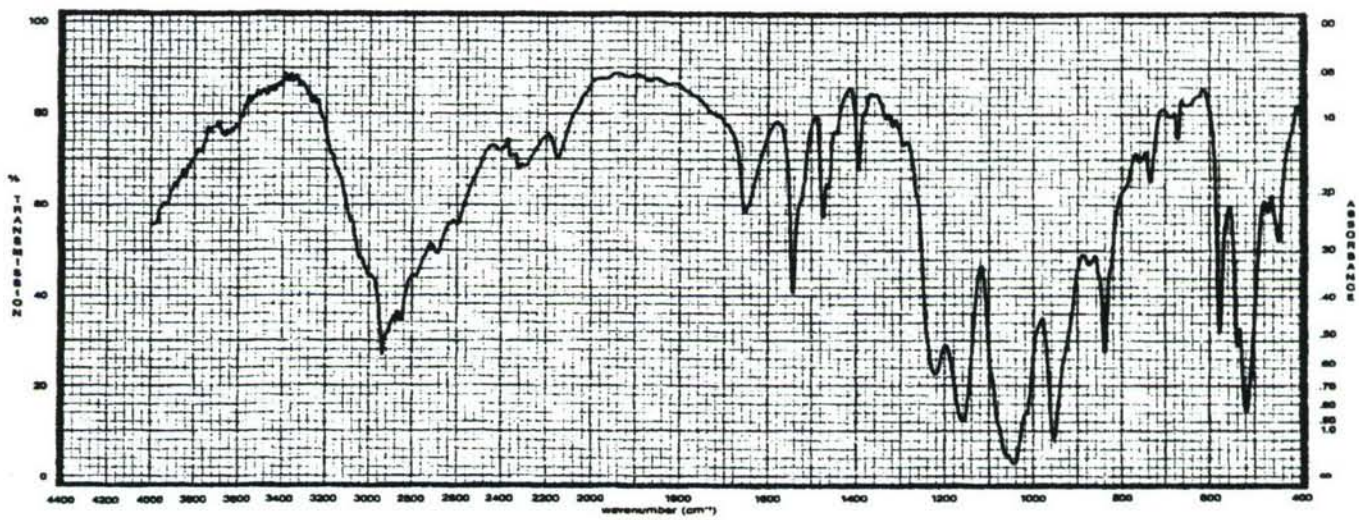

Figure 317 6-AMINO-1-HEXYL PHOSPHATE (99%), SOLID BETWEEN CsI DISCS (WINDOWS)

3.5.11.18 Diethyl *p*-Nitrophenyl Phosphate (**Paraoxon**) $(CH_3CH_2O)_2P{=}O(O\text{-}C_6H_4NO_2)$

The infrared spectrum of a thin liquid film of diethyl *p*-nitrophenyl phosphate (**Paraoxon**) between KBr windows is reproduced in ***Figure 318***. The band assignments are as follows: ca 3170 cm^{-1} w broad band (possible ν OH from *p*-nitrophenol, hydrolysis product), 3116 and 3084 cm^{-1} vw (ν C-H aromatic), 2987 cm^{-1} w (ν_{as} CH_3), 2936 cm^{-1} vw (ν_{as} CH_2), 2912 cm^{-1} vw (ν_{sy} CH_3), 2872 cm^{-1} vvw (ν_{sy} CH_2), 1614 cm^{-1} m, 1593 cm^{-1} ms, 1493 cm^{-1} ms and 1446 cm^{-1} w (aromatic ring), 1524 cm^{-1} ms (ν_{as} NO_2), 1394 cm^{-1} w (ω OCH_2), 1371 cm^{-1} w

(δ_{sy} CH_3), 1348 cm^{-1} s (ν_{sy} NO_2), 1294 cm^{-1} ms (ν P=O, *calculated* value is 1282 cm^{-1}), 1235 cm^{-1} ms (ν phenyl C-O), 1165 cm^{-1} m, 1111 cm^{-1} m (β C-H *para*-disubstituted aromatic ring), 1034 cm^{-1} s (ν P-O-C), 970 cm^{-1} m (ν C-C of POEt), 933 cm^{-1} m (ν P-O, aryl moiety), 858 cm^{-1} m (γ C-H *para*-disubstituted aromatic ring and NO_2 scissors), 820 and 803 cm^{-1} w (POC ?), 753 cm^{-1} m (C-N-O bending ?).

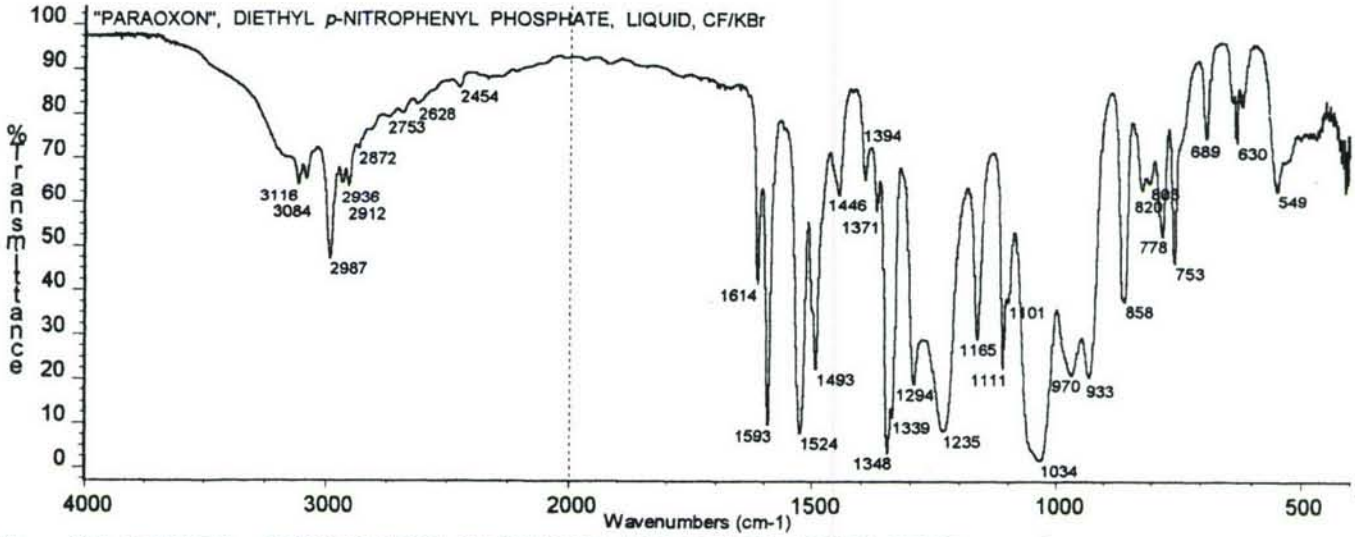

Figure 318 DIETHYL *p*-NITROPHENYL PHOSPHATE (PARAOXON), LIQUID, CF/KBr

3.5.11.19 <u>2-Chlorophenyl Dichlorophosphate (2-Chlorophenyl Phosphorodichloridate)</u> $Cl\text{-}C_6H_4O\text{-}P{=}O(Cl)_2$

The infrared spectrum of a thin liquid film of 2-chlorophenyl dichlorophosphate (2-chlorophenyl phosphorodichloridate) between KBr discs (windows) is presented in ***Figure 319***. The band assignments are as follows: 3091, 3072 and 3030 cm^{-1} vvw to vw (ν C-H aromatic), 2600 cm^{-1} vw (2 x 1304 = 2608 cm^{-1}), 1580 cm^{-1} w, 1477 cm^{-1} s and 1448 cm^{-1} m (aromatic ring), 1304 cm^{-1} s (ν P=O, *calculated* value is 1306 cm^{-1}), 1212 cm^{-1} s (ν C-O), 1160 and 1132 cm^{-1} vw and 1034 cm^{-1} w (β C-H *ortho*-disubstituted aromatic ring), 1061 cm^{-1} ms (phenyl-Cl), 952 cm^{-1} s (ν P-O), 769 and 755 cm^{-1} ms (γ C-H *ortho*-disubstituted aromatic ring), 618 and 580 cm^{-1} ms (ν_{as} PCl_2), 548 cm^{-1} ms and 538 cm^{-1} sh (ν_{sy} PCl_2), 446 cm^{-1} w (out-of-plane ring bending *ortho*-disubstituted aromatic ring ?).

The effect of atmospheric moisture on a thin liquid film of 2-chlorophenyl dichlorophosphate, while between KBr windows, is illustrated by the infrared spectra presented in ***Figure 320***. After 1 day of exposure to

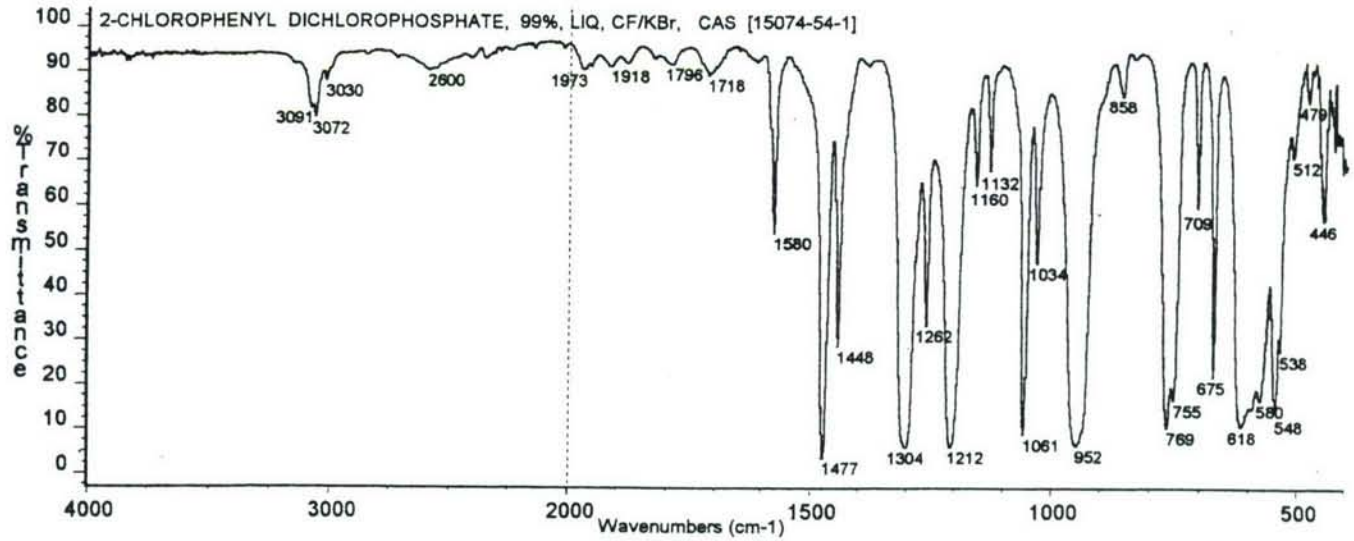

Figure 319 2-CHLOROPHENYL DICHLOROPHOSPHATE (2-CHLOROPHENYL PHOSPHORODICHLORIDATE), 99%, LIQUID, CF/KBr

atmospheric moisture, the spectrum shows the formation of bands near 2570, 2290, 2150 and 1700 cm^{-1} indicative of the POH group. After 2 days of exposure to moisture, the spectrum shows pronounced POH bands near 2860 2300 and 1700 cm^{-1}. The PCl_2 bands near 600 cm^{-1} are decreasing in intensity. The P=O band that was at 1304 cm^{-1} has fallen to 1264 cm^{-1} possibly indicative of the P-acid, 2-Cl-C_6H_4-O-P=O(OH)(Cl). As time progresses the spectra appear to become more indicative of the compound 2-chlorophenyl dihydrogen phosphate (2-chlorophenyl phosphoric acid), 2-Cl-C_6H_4-O-P=O$(OH)_2$, with the P=O band falling to about 1164 cm^{-1}. The hydrolysis of 2-chlorophenyl dichlorophosphate thus appears to occur as follows:

2-Cl-C_6H_4O-P=O$(Cl)_2$ -HOH→ 2-Cl-C_6H_4O-P=O(OH)(Cl) -HOH→ 2-Cl-C_6H_4O-P=O$(OH)_2$.

3.5.11.20 4-Chlorophenyl Dichlorophosphate (4-Chlorophenyl Phosphorodichloridate) Cl-C_6H_4OP=O$(Cl)_2$

The infrared spectrum of 4-chlorophenyl dichlorophosphate (4-chlorophenyl phosphorodichloridate) as a liquid film between KBr windows is presented in ***Figure 321***. The band assignments are as follows: 3098 cm^{-1} w and 3070 cm^{-1} vw (ν C-H aromatic), 1586 cm^{-1} w and 1485 cm^{-1} s (aromatic ring, C≈C), 1306 cm^{-1} ms (ν P=O, *calculated* value is 1306 cm^{-1}), 1189 cm^{-1} ms (ν C-O), 1162 and 1015 cm^{-1} m (β C-H *para*-disubstituted aromatic ring), 1092 cm^{-1} ms (phenyl-Cl), 951 cm^{-1} ms (ν P-O), 833 cm^{-1} ms (γ C-H *para*-disubstituted aromatic ring), 599 cm^{-1} ms (ν_{as} PCl_2), 556 cm^{-1} m (ν_{sy} PCl_2), 502 cm^{-1} m (P=O deformation ?).

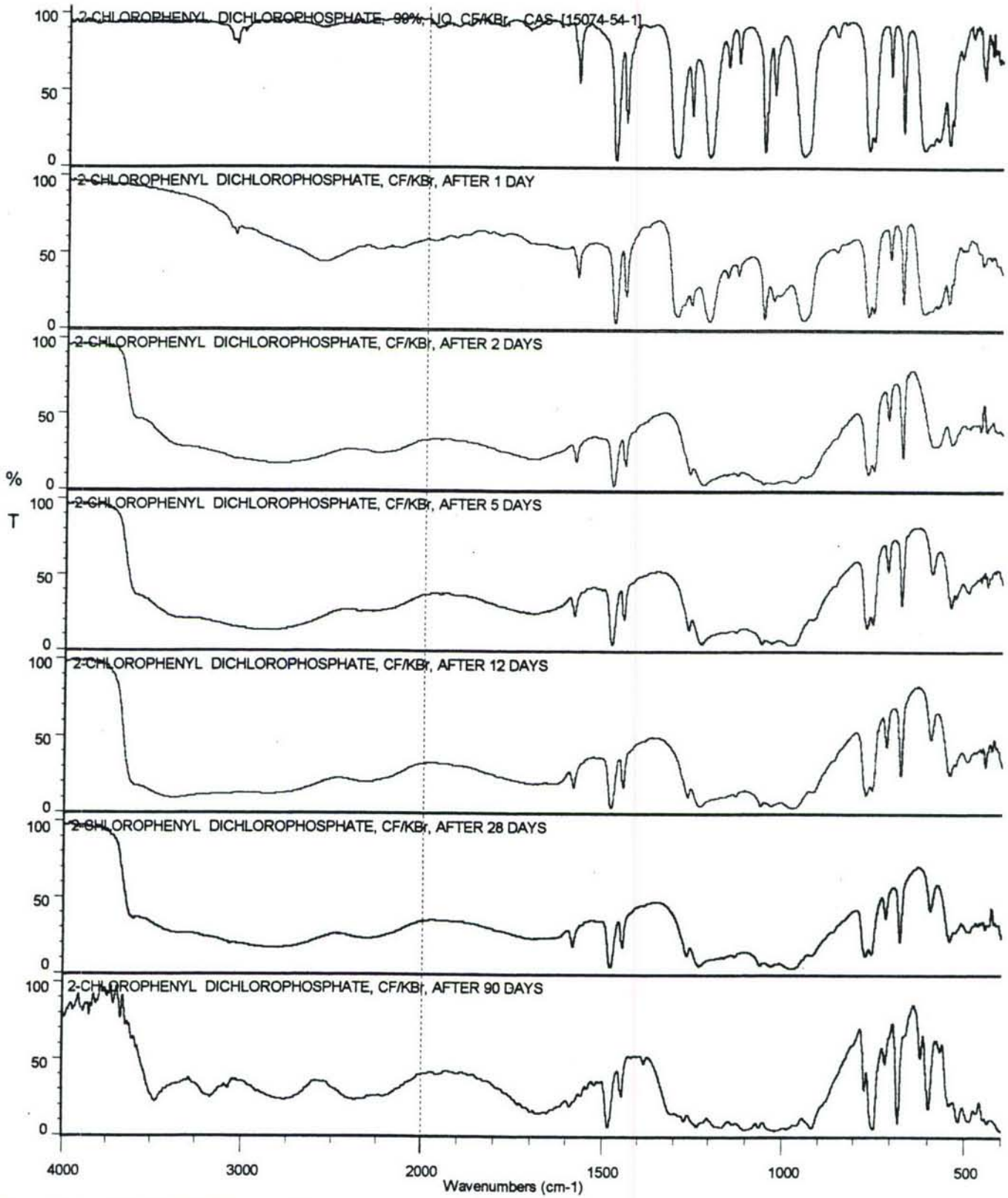

Figure 320 2-CHLOROPHENYL DICHLOROPHOSPHATE (2-CHLOROPHENYL PHOSPHORODICHLORIDATE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

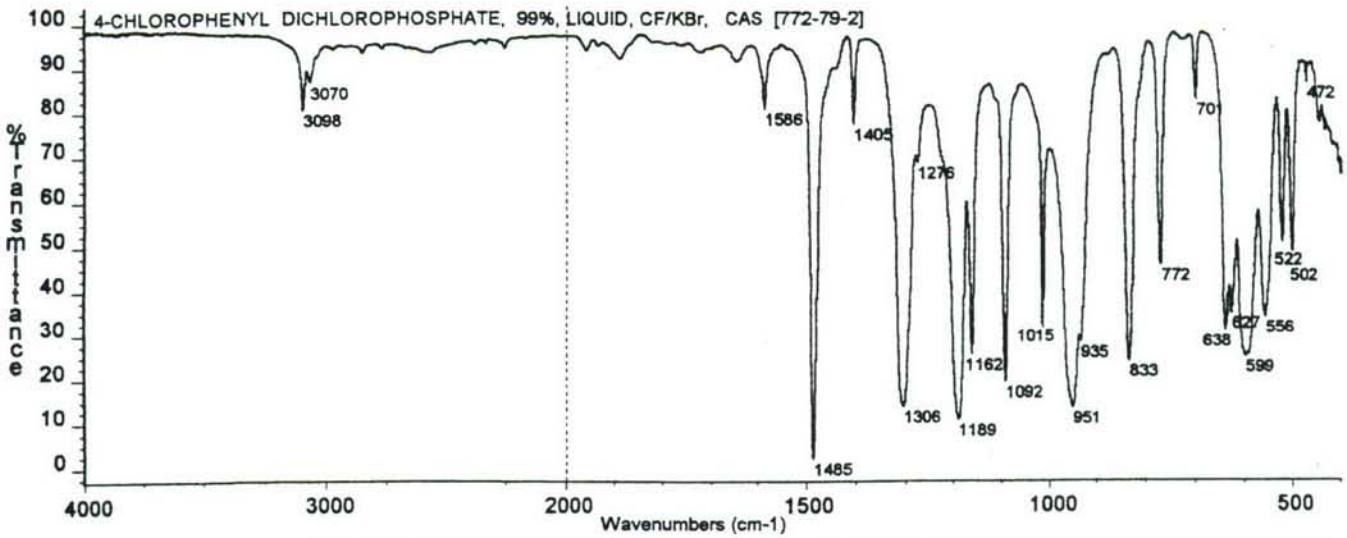

Figure 321 4-CHLOROPHENYL DICHLOROPHOSPHATE (4-CHLOROPHENYL PHOSPHORODICHLORIDATE), 99%, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of 4-chlorophenyl dichlorophosphate is illustrated by the infrared spectra depicted in ***Figure 322***. The spectrum, after 21 hours of exposure to atmospheric moisture, shows a decrease in the bands due to the PCl_2 group near 600 cm^{-1}. By the 4th day of exposure the spectrum indicates the presence of POH bands near 2700, 2200, 1700 and 1000 cm^{-1}. The sample appears to be evaporating as indicated by the increase in the instrument background noise and the appearance of interference fringes in the spectra (infrared spectra after 4 and 57 days). Nevertheless, the results should be similar to those obtained for 2-chlorophenyl dichlorophosphate as presented in ***Figure 320***. The hydrolysis of 4-chlorophenyl dichlorophosphate should produce 4-chlorophenyl dihydrogen phosphate (4-chlorophenyl phosphoric acid), $4\text{-}Cl\text{-}C_6H_4O\text{-}P{=}O(OH)_2$.

3.5.11.21 Phenyl Dichlorophosphate (Phenyl Phosphorodichloridate) $C_6H_5\text{-}O\text{-}P{=}O(Cl)_2$

The infrared spectrum of a liquid film of phenyl dichlorophosphate (phenyl phosphorodichloridate) between KBr discs (windows) is reproduced in ***Figure 323***. The band assignments are as follows: 3096 cm^{-1} sh, 3065 cm^{-1} sh (ν C-H aromatic), 1600 cm^{-1} m, 1588 cm^{-1} ms, 1488 cm^{-1} s and 1457 cm^{-1} m (aromatic ring), 1384 cm^{-1} vvw (possibly KNO_3 from the KBr windows), 1303 cm^{-1} s (ν P=O, *calculated* value is 1302 cm^{-1}), 1184 and

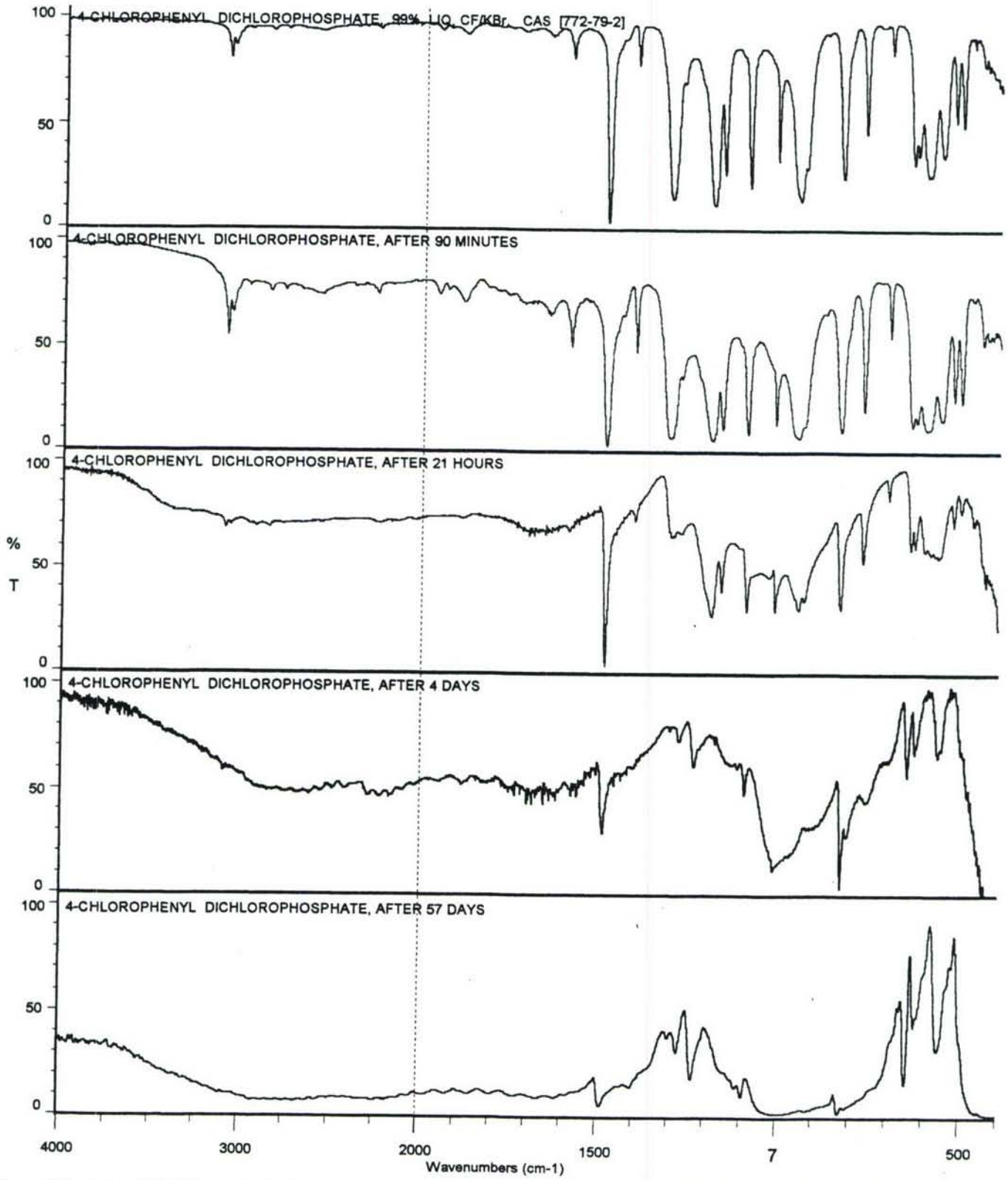

Figure 322 4-CHLOROPHENYL DICHLOROPHOSPHATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

1159 cm^{-1} s (ν C-O), 1072 cm^{-1} m, 1025 cm^{-1} ms and 1007 cm^{-1} m (β C-H monosubstituted aromatic ring), 949 cm^{-1} (ν P-O), 765 cm^{-1} s (γ C-H mono-substituted aromatic ring), 688 cm^{-1} ms (δ mono-substituted aromatic ring), 611 and 590 cm^{-1} s (ν_{as} PCl_2), 561 cm^{-1} ms (ν_{sy} PCl_2).

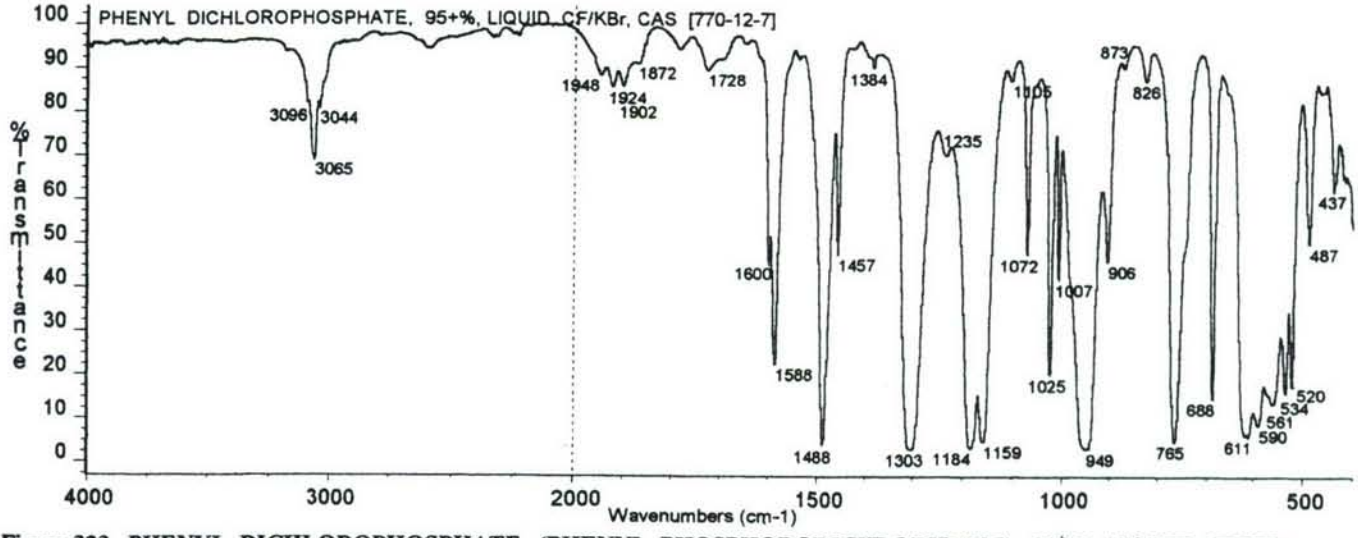

Figure 323 PHENYL DICHLOROPHOSPHATE (PHENYL PHOSPHORODICHLORIDATE), 95+%, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of phenyl dichlorophosphate (phenyl phosphorodichloridate) between KBr windows is depicted by the infrared spectra in ***Figure 324***. The spectra after 3-4 days show the formation of broad bands near 2580, 2200 and 1650 cm^{-1} indicative of the POH moiety. The P=O band falls near 1250 cm^{-1} and bands occur near 1030 cm^{-1} (ν P-OH) and 948 cm^{-1} [ν P-O(phenyl)]. The PCl_2 bands near 600 have greatly decreased in intensity. Perhaps the compound phenyl hydrogen chlorophosphate, C_6H_5O-P=O(OH)(Cl) is forming. Over the period 7 through 97 days, the spectra show a further decrease in the P=O stretching vibration to near 1188 cm^{-1} and intense and broad POH bands near 2780, 2260 and 1650 cm^{-1}. The POphenyl group is still intact as evidenced by the bands at 3064, 1593, 1490, 1457, 1164, 722 and 691 cm^{-1}. The hydrolysis has apparently now produced phenyl dihydrogen phosphate (phenyl phosphoric acid), C_6H_5O-P=O$(OH)_2$. The hydrolysis of pheny dichlorophosphate may be summarized as follows:

C_6H_5O-P=O$(Cl)_2$ -HOH→ C_6H_5O-P=O(OH)(Cl) -HOH→ C_6H_5O-P=O$(OH)_2$ + 2HCl .

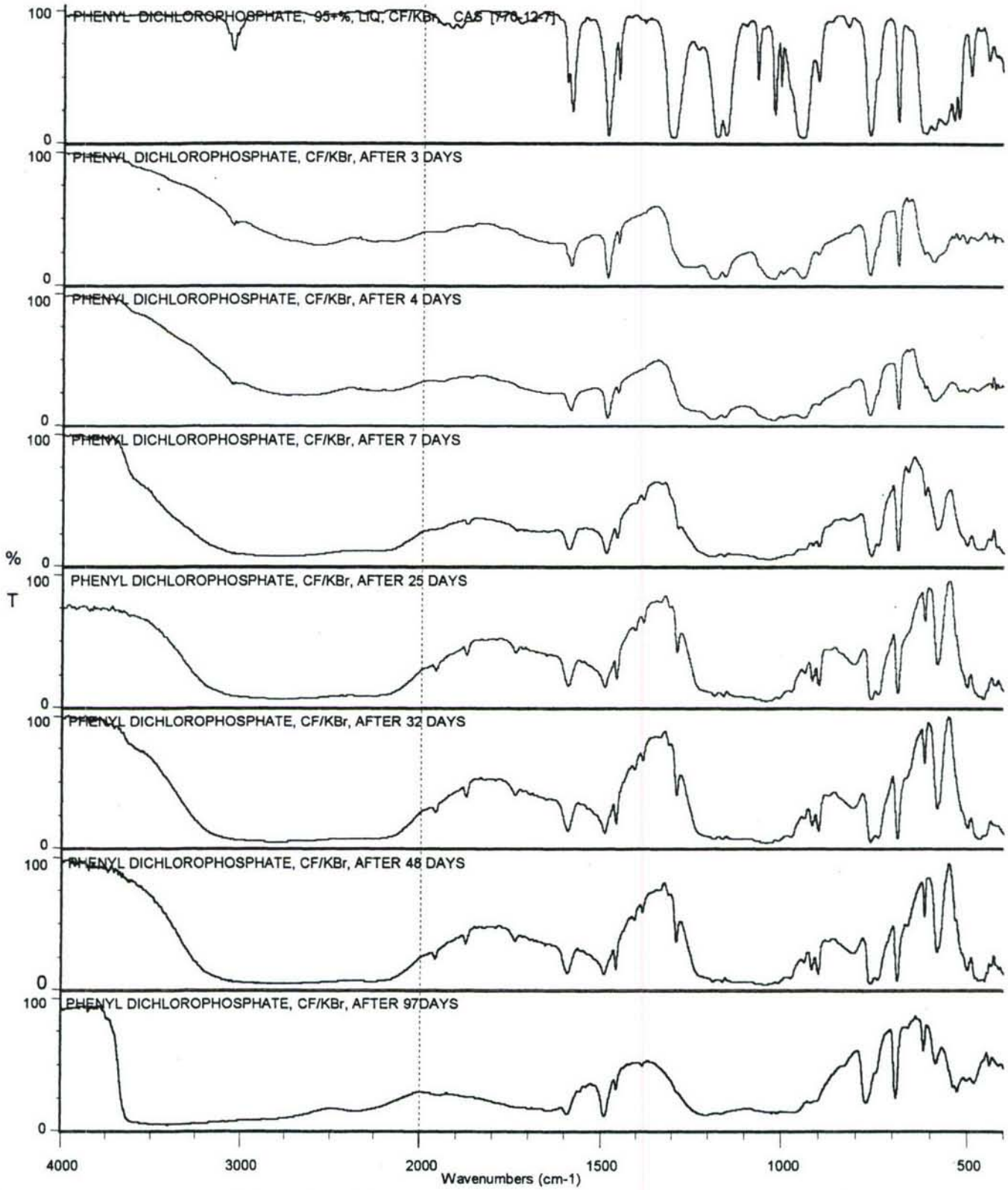

Figure 324 PHENYL DICHLOROPHOSPHATE (PHENYL PHOSPHORODICHLORIDATE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.5.11.22 Diphenyl Chlorophosphate (Diphenyl Phosphorochloridate) $(C_6H_5O)_2P{=}O(Cl)$

The infrared spectrum of diphenyl chlorophosphate (diphenyl phosphorochloridate) as a thin liquid film between KBr discs (windows) is reproduced as ***Figure 325***. The band assignments are as follows: 3097 cm^{-1} sh, 3071 cm^{-1} vw and 3044 cm^{-1} vvw (ν C-H), 1600 cm^{-1} sh, 1588 cm^{-1} m, 1489 cm^{-1} ms, 1457 cm^{-1} w (aromatic ring), 1384 cm^{-1} vvw (KNO_3 from KBr windows), 1312 and 1302 cm^{-1} ms (average is 1307 cm^{-1}, the *calculated* value is 1306 cm^{-1}), 1180 and 1160 cm^{-1} ms (ν C-O), 1071 cm^{-1} w, 1025 cm^{-1} m and 1011 cm^{-1} m (β C-H mono-substituted aromatic ring), 969 cm^{-1} s (ν P-O), 767 cm^{-1} m (γ C-H mono-substituted aromatic ring), 687 cm^{-1} m (δ mono-substituted aromatic ring), 588 and 579 cm^{-1} m (ν P-Cl), 504 cm^{-1} m (P=O deformation ?).

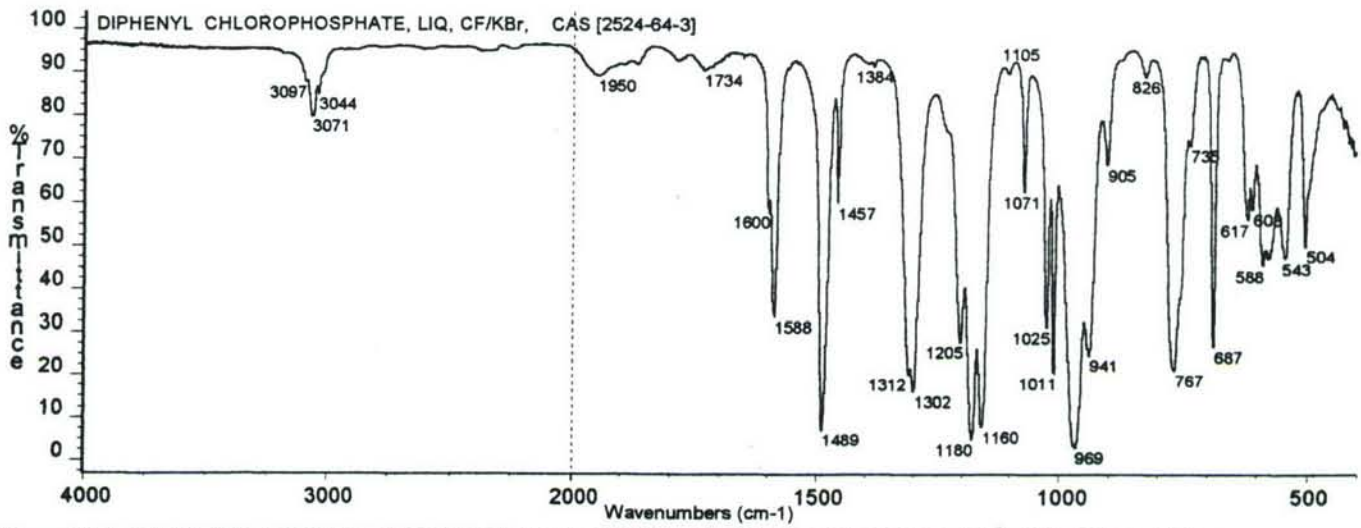

Figure 325 DIPHENYL CHLOROPHOSPHATE (DIPHENYL PHOSPHOROCHLORIDATE), LIQUID, CF/KBr

The effect of atmospheric moisture on a liquid film of diphenyl chlorophosphate (diphenyl phosphorochloridate) between KBr windows is illustrated by the infrared spectra presented in ***Figure 326***. After one day of exposure to moisture, the spectrum shows the formation of very weak and broad bands near 2577 and 2325 cm^{-1}. By the 4^{th} day, these two bands (2575 and 2324 cm^{-1}) become more predominant and are assigned to the POH group. By the 5^{th}-6^{th} days the POH bands are even more evident near 2613, 2185 and 1685 cm^{-1}. The P=O stretching region has become less distinct and the band now occurs around 1250 cm^{-1}. The POphenyl moiety is still evident by the bands near 3094, 3063 and 3042 cm^{-1} (ν C-H aromatic), 1589, 1488 and 1457 cm^{-1} (aromatic ring), 1195 and 1164 cm^{-1} (ν C-O), 960 cm^{-1} (ν P-O), ca 768 and 690 cm^{-1} (mono-substituted aromatic ring).

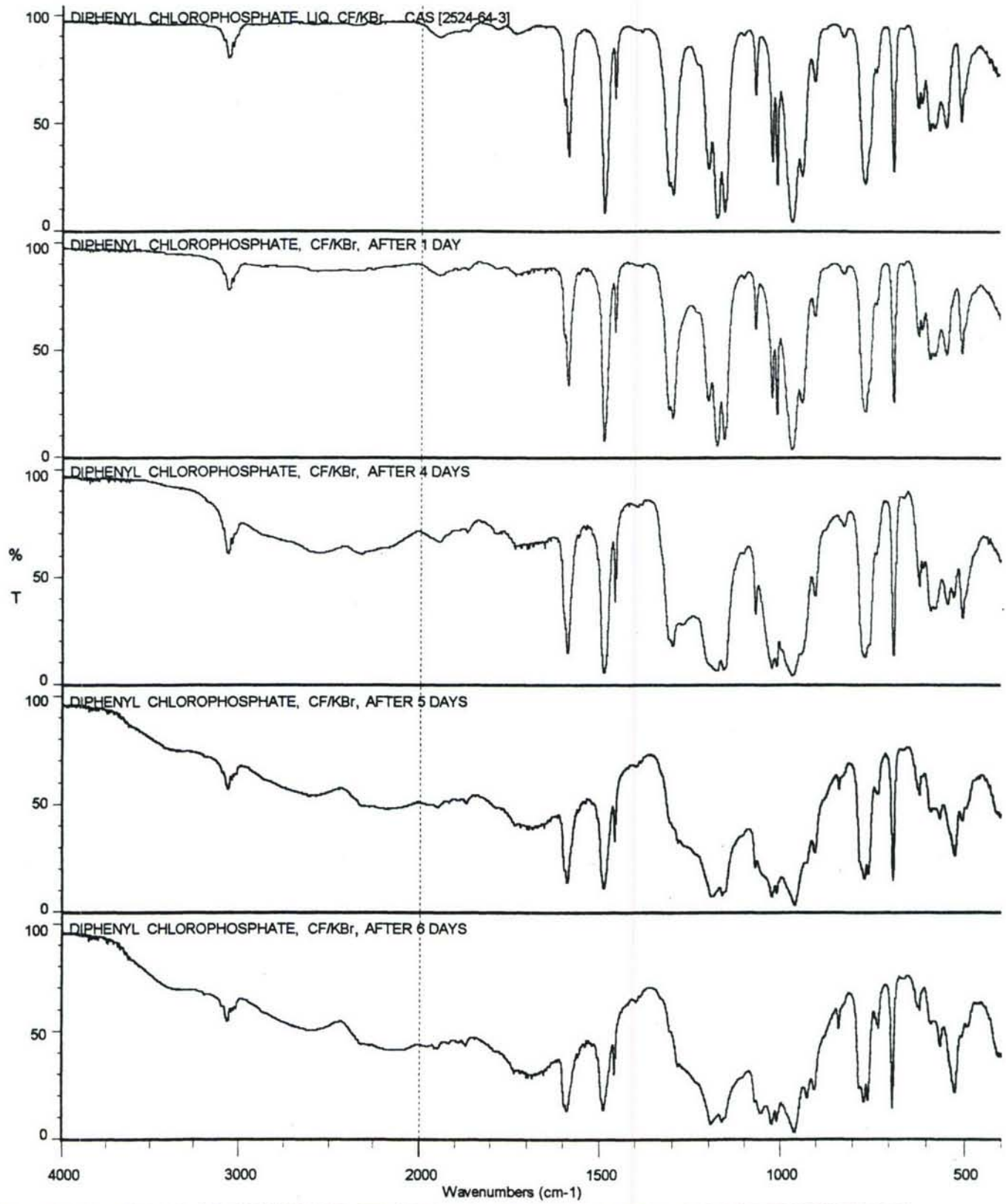

Figure 326 DIPHENYL CHLOROPHOSPHATE, CF/KBr, AFTER EXPOSURE TO ATMOSPHRERIC MOISTURE

The bands due to the ν P-Cl (588 and 575 cm^{-1}) are almost completely gone from the spectra. The compound, diphenyl chlorophosphate, has almost completely hydrolyzed to form the P-acid diphenyl hydrogen phosphate (diphenyl phosphate, diphenyl phosphoric acid), $HO\text{-}P{=}O(O\text{-}C_6H_5)_2$. The infrared spectrum of an authentic sample of diphenyl phosphate is given in the next section as ***Figure 327***.

3.5.11.23 Diphenyl Phosphate $(C_6H_5O)_2P{=}O(OH)$

The infrared spectrum of diphenyl phosphate as a solid between KBr discs (windows) is given in ***Figure 327***. The band assignments are as follows: 3096 cm^{-1} sh, 3063 cm^{-1} vw and 3041 cm^{-1} vvw (ν C-H aromatic), 2555 cm^{-1} m, 2290 and 2147 cm^{-1} w and ca 1680 cm^{-1} w all are broad (POH), 1587 cm^{-1} m, 1486 cm^{-1} s and 1457 cm^{-1} w (aromatic ring), 1270 and 1220 cm^{-1} ms (ν P=O), 1188 and 1165 cm^{-1} s (ν C-O), 1072 cm^{-1} w (β C-H mono-substituted aromatic ring), 1022 cm^{-1} s [ν P-O(H)] , 961 cm^{-1} s [ν P-O(phenyl)], 779 and 756 cm^{-1} s (γ C-H mono-substituted aromatic ring), 690 cm^{-1} s (δ mono-substituted aromatic ring), 528, 514 ms (P=O deformation ?).

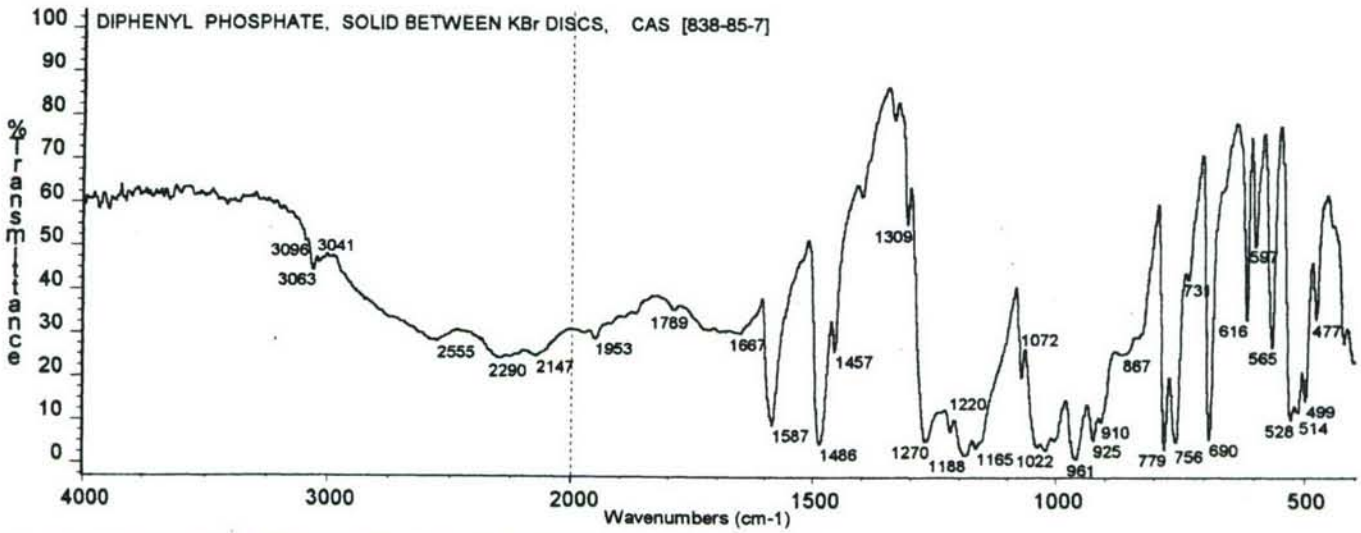

Figure 327 DIPHENYL PHOSPHATE, SOLID BETWEEN KBr DISCS (WINDOWS)

3.5.11.24 Dibenzyl Phosphate $(C_6H_5\text{-}CH_2\text{-}O)_2P{=}O(OH)$

The infrared spectrum of dibenzyl phosphate as a solid (powder) between CsI discs (windows) is presented as ***Figure 328***. The band assignments are as follows: 3091, 3064 and3034 cm^{-1} vvw (ν C-H aromatic),

2954 cm^{-1} vvw (ν_{as} CH_2), 2896 cm^{-1} vvw (ν_{sy} CH_2), ca 2643 and 2293 cm^{-1} vw broad and 1680 cm^{-1} w broad (POH), 1496 cm^{-1} vw and 1455 cm^{-1} w (aromatic ring), 1469 cm^{-1} vw ? (δ OCH_2), 1380 cm^{-1} vw (ω OCH_2), 1251, 1216, 1173 cm^{-1} w (ν P=O), 1037 cm^{-1} sh, 995, 986 cm^{-1} s [ν P-O-C and ν P-O(H)], 747 and 739 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 697 cm^{-1} s (δ mono-substituted aromatic ring), 512 and 499 cm^{-1} ms (P=O deformation).

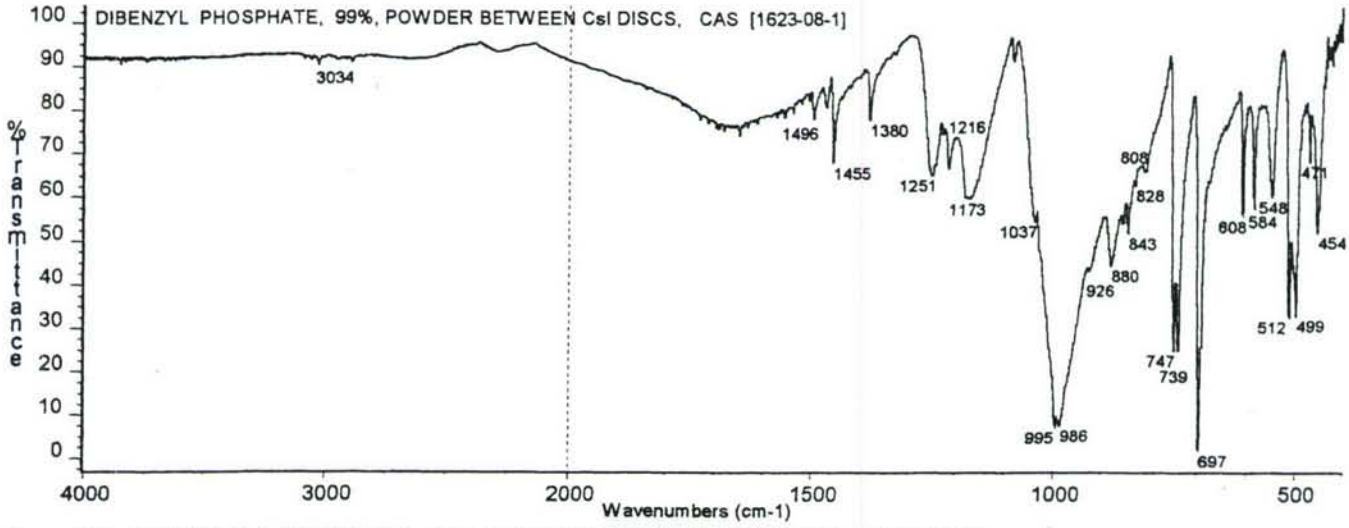

Figure 328 DIBENZYL PHOSPHATE, 99%, POWDER BETWEEN CsI DISCS (WINDOWS)

3.6 P-N Compounds

3.6.1 N,N'-Tetramethylmethylphosphonous Diamide [Bis(dimethylamino)methylphosphine]

$CH_3P[N(CH_3)_2]_2$

The infrared spectrum of N,N'-tetramethylmethylphosphonous diamide was discussed previously under bis(dimethylamino)methylphosphine (***Figure 41***) and is included here again, as a mattter of convenience, as ***Figure 329***. The band assignments are as follows: 2969 cm^{-1} m, 2907 cm^{-1} sh, 2882 cm^{-1} and 2862 cm^{-1} ms, 2832 cm^{-1} w and 2784 cm^{-1} ms [ν_{as} and ν_{sy} CH_3 , ν_{as} and ν_{sy} $N(CH_3)_2$], 1466 cm^{-1} w and 1447 cm^{-1} m (δ CH_3), 1420 cm^{-1} vw (δ_{as} P-CH_3), 1284 cm^{-1} m (δ_{sy} P-CH_3), 1259 cm^{-1} m [P-$N(CH_3)_2$][aaa], 1189 cm^{-1} ms and 1058 cm^{-1} w

[aaa] The bands assigned to the P-CH_3 and $PN(CH_3)_2$ groups occur in the 1300 cm^{-1} range. The band assigned to the $PN(CH_3)_2$ moiety is somewhat broader than that due to the P-CH_3 moiety. However, the P-CH_3 moiety has a further characteristic band near 900 cm^{-1}, which is not found in the spectra of $PN(CH_3)_2$ containing compounds. (See Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 93,95, Heyden & Son Ltd., 1974.)

[$PN(CH_3)_2$], 972 cm^{-1} ms and 953 cm^{-1} s (ν_{as} P-N-C), 875 cm^{-1} m (P-CH_3 rock), 711 cm^{-1} m (ν P-C of P-CH_3), 649 cm^{-1} ms (ν_{sy} P-N-C) [bbb].

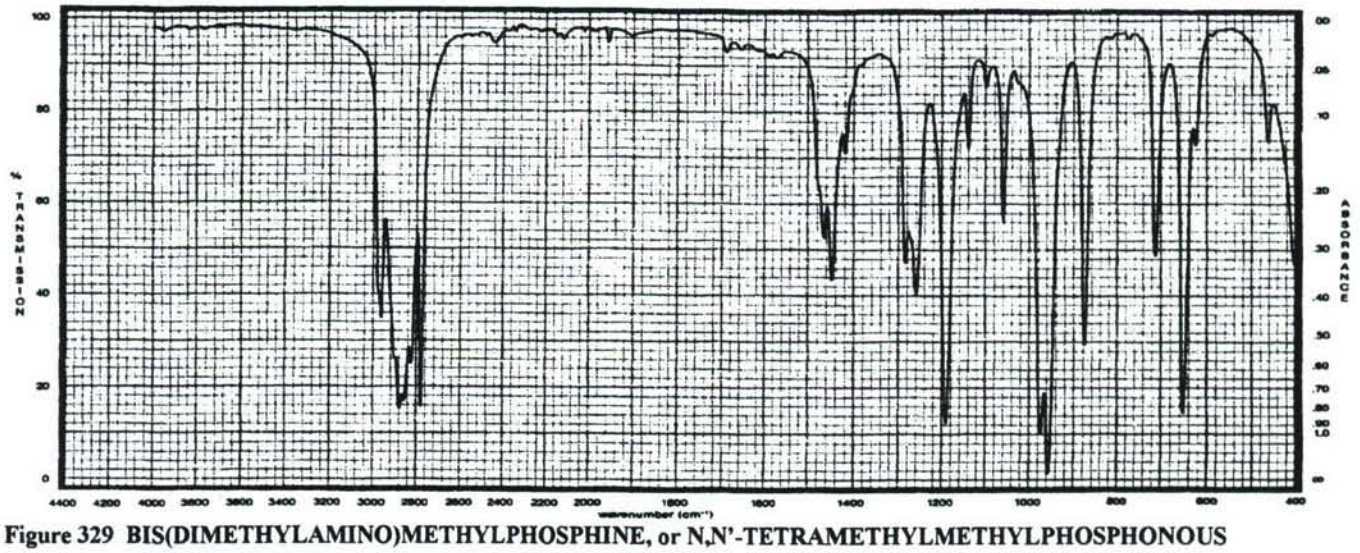

Figure 329 BIS(DIMETHYLAMINO)METHYLPHOSPHINE, or N,N'-TETRAMETHYLMETHYLPHOSPHONOUS DIAMIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on N,N'-tetramethylmethyphosphonous diamide [bis(dimethyl-amino)methylphosphine] is illustrated by the infrared spectra given previously as ***Figures 42A*** through ***42D***.

3.6.2 Hexamethylphosphorous Triamide (**HMPT**) $P[N(CH_3)_2]_3$

The infrared spectrum of hexamethylphosphorous triamide (**HMPT**) as a thin liquid film between KBr windows is reproduced as ***Figure 330***. The band assignments are as follows: 2985 and 2966 cm^{-1} w, 2924 cm^{-1} w, 2870 and 2859 cm^{-1} m (ν_{as} CH_3), 2820, 2779 cm^{-1} m (ν_{sy} CH_3), 1462 and 1452 cm^{-1} w (δ CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1268 cm^{-1} w, 1199 cm^{-1} m and 1061 cm^{-1} w [$PN(CH_3)_2$], 954 and 938 cm^{-1} s (ν_{as} P-N-C), 672 cm^{-1} m and 645 cm^{-1} w (ν_{sy} P-N-C).

The effect of atmospheric moisture on hexamethylphosphorous triamide (**HMPT**) is illustrated by the

[bbb] L.C. Thomas in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 120-123, Heyden & Son Ltd., 1974, lists the $N(CH_3)_2$ as being characterized by absorption bands in the regions of 1300 (1321-1261), 1180 (1205-1155), 1065 (1078-1050) and 975 (1008-935) cm^{-1}. Shagidullin et al ("Atlas of IR Spectra of Organophosphorus Compounds, Interpreted Spectrograms", p 5, Kluwer Academic Publishers, Boston, 1990) lists the $N(CH_3)_2$ as having bands at 1320-1260 cm^{-1} m-s (ν_{as} C-N-C), 1210-1150 cm^{-1} m-s, 1080-1050 m (CH_3 rock), 1010-970 cm^{-1} m-s (ν_{as} P-N-C), 980-940 cm^{-1} s (ν_{as} P^{+3}-N-C) and 700-650 cm^{-1} w-m (ν_{sy} P-N-C).

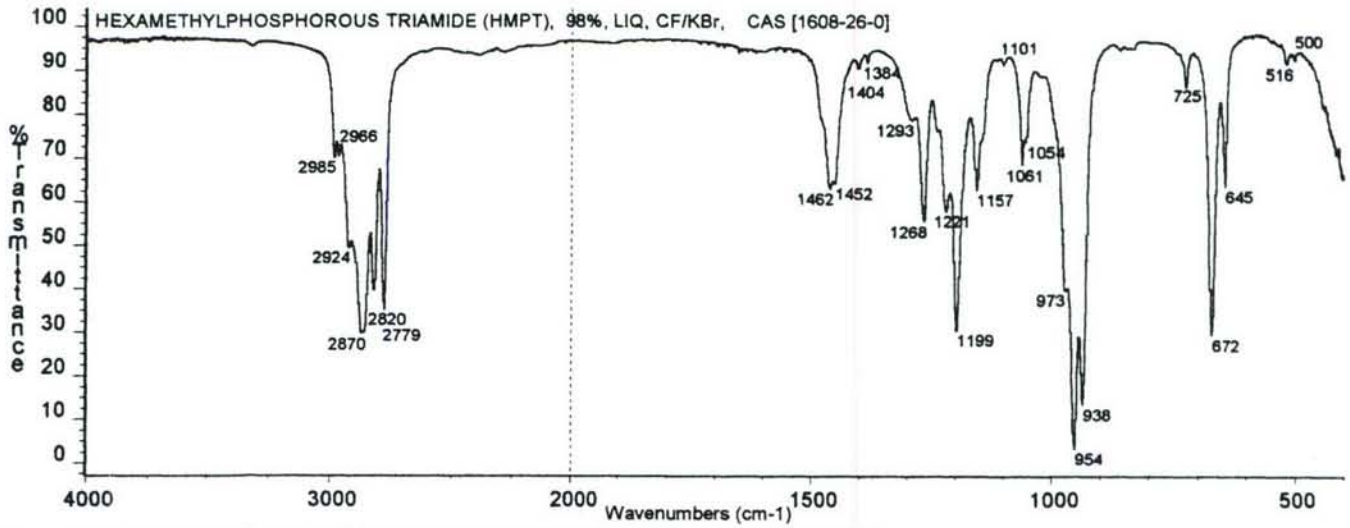

Figure 330 HEXAMETHYLPHOSPHOROUS TRIAMIDE, 85%, LIQUID, CF/KBr

infrared spectra given in ***Figures 331A*** and ***331B***. After 1-3 days of exposure to atmospheric moisture, the spectra (***Figure 331A***) show a band at 2305-2313 cm^{-1} that is assignable to a P-H stretching vibration. Bands near 2795 and 2451 cm^{-1} are assigned to a NH_2^+ moiety. Large amounts of water are visible in the spectra near 3400 and 1645 cm^{-1}. A band at 1471 cm^{-1} is assignable to a CH_3 deformation. The strong band at 1064 cm^{-1} may be due to a PO_4^{-3} group. The P-$N(CH_3)_2$ bands all seem to have disappeared from the spectra as hydrolyis occurred. By the 13th day (***Figure 331B***) bands are evident at 1159, 1067 and 914 cm^{-1} and may be due to the PO_3^{-2} and P-H groups. Perhaps two events are occurring simultaneously, namely oxidation and hydrolysis. The compound may oxidize and then hydrolze or just hydrolyze without first oxidizing. The oxidation followed by hydrolysis may be depicted as follows:

$P[N(CH_3)_2]_3$ -[O]→ $O=P[N(CH_3)_2]_3$ -3-HOH→ $O=P(OH)_3$ + 3 $(CH_3)_2NH$ → $[PO_4^{-3}]$ $3(CH_3)_2NH_2^+$.

The hydrolysis only reaction may be depicted as follows:

$P[N(CH_3)_2]_3$ -HOH→ H-O-$P[N(CH_3)_2]_2$ → H-P=$O[N(CH_3)_2]_2$ -2-HOH→ H-P=$O(OH)_2$ + 2 $(CH_3)_2NH$

→ $[H\text{-}PO_3^{-2}]$ $2(CH_3)_2NH_2^+$.

3.6.3 Methyl N,N-diethylmethylphosphonamidite CH_3-$P(OCH_3)[N(CH_2CH_3)_2]$

The infrared spectrum of methyl N,N-diethylmethylphosphonamidite as a thin liquid film between

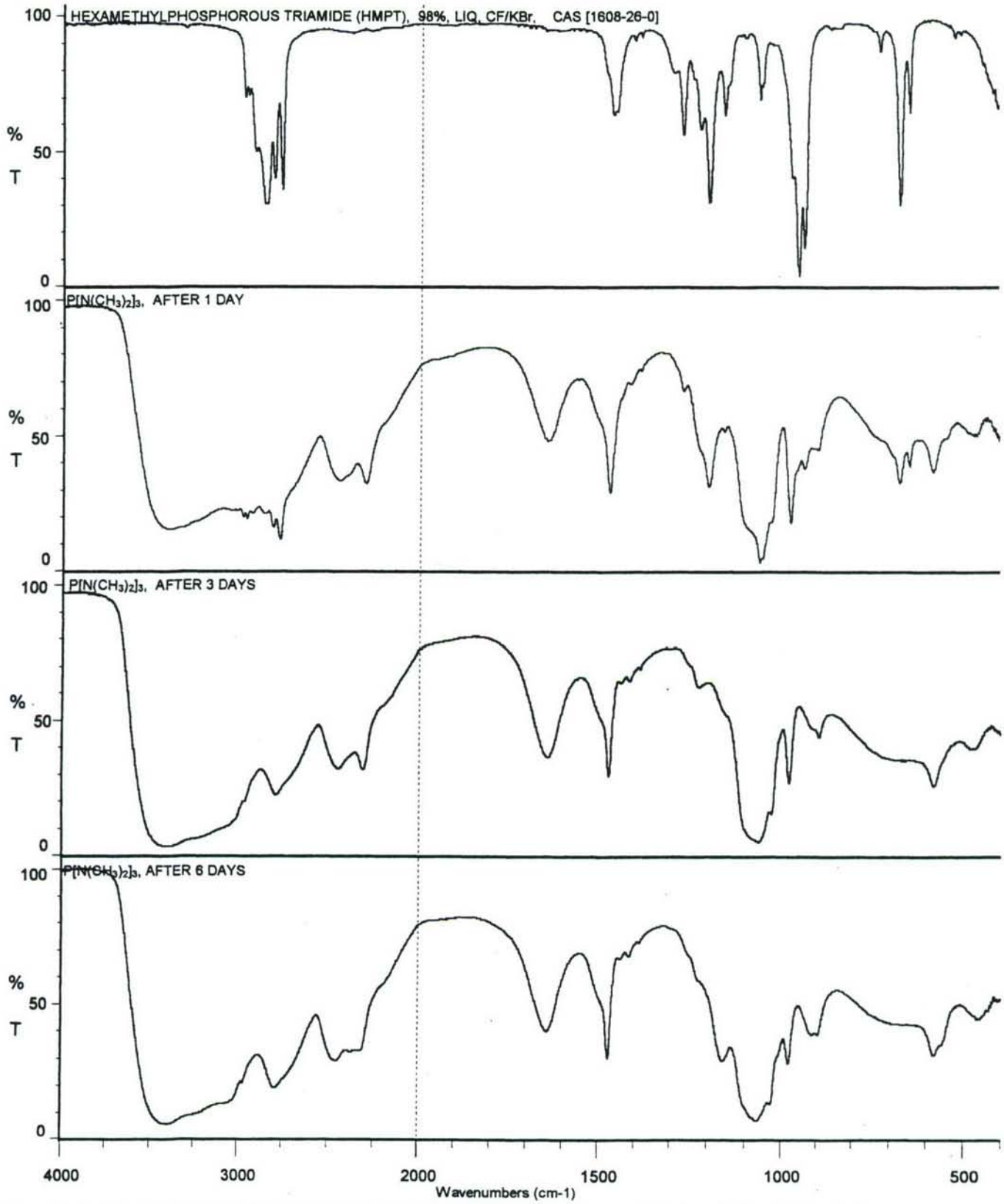

Figure 331A HEXAMETHYLPHOSPHOROUS TRIAMIDE (HMPT), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

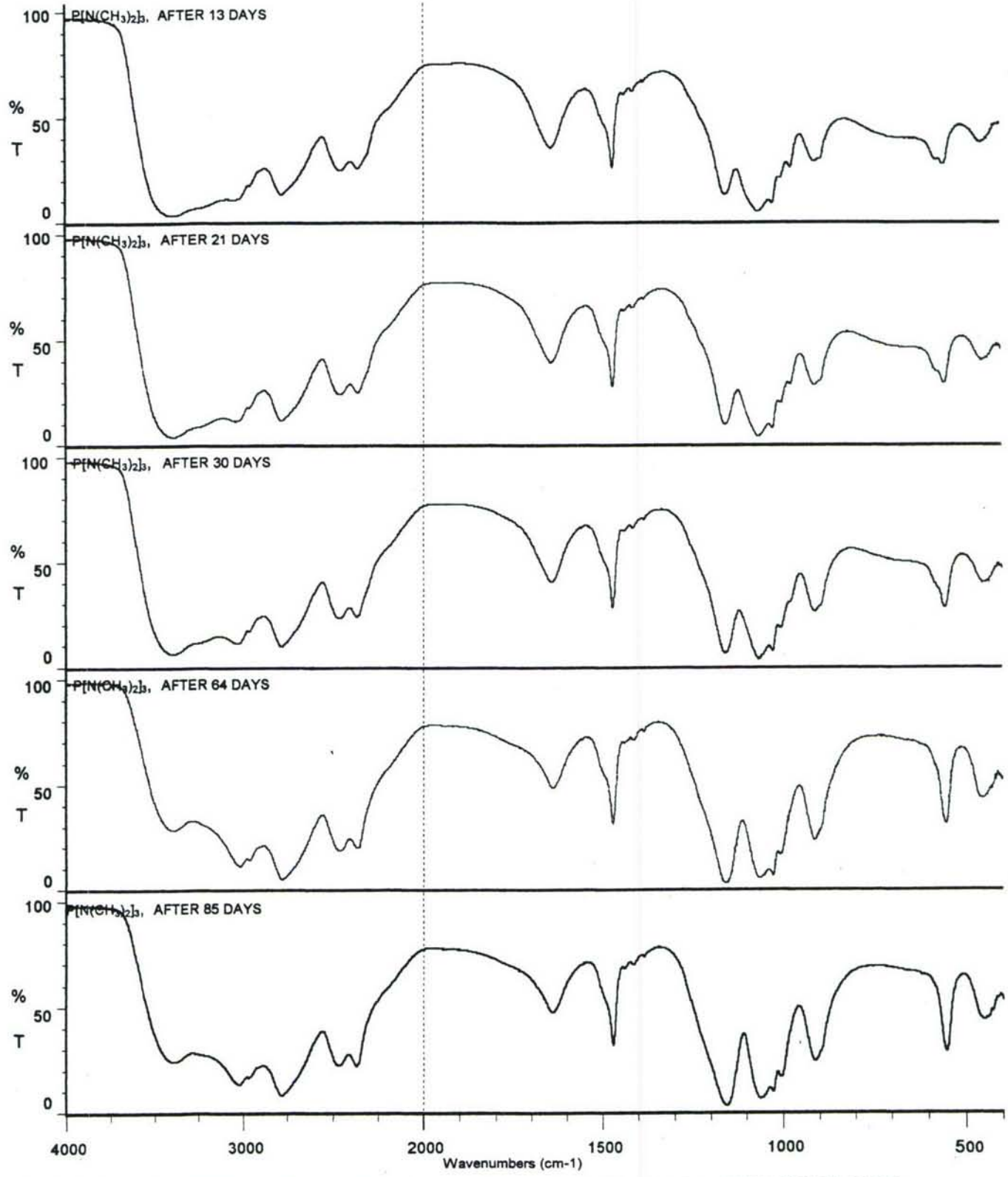

Figure 331B HEXAMETHYLPHOSPHOROUS TRIAMIDE (HMPT), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

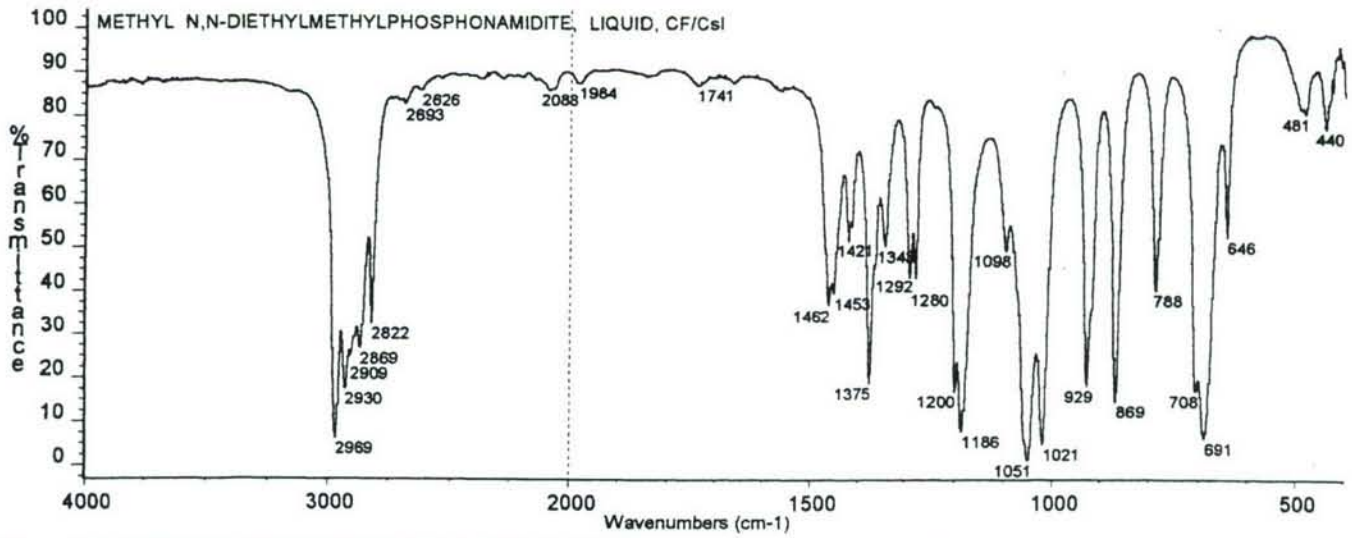

Figure 332 METHYL N,N-DIETHYLMETHYLPHOSPHONAMIDITE, LIQUID, CF/CsI

CsI windows is presented as ***Figure 332***. The band assignments are as follows: 2969 cm^{-1} s (ν_{as} CH_3), 2930 cm^{-1} ms (ν_{as} CH_2), 2869 cm^{-1} m (ν_{sy} CH_3), 2822 cm^{-1} m (ν_{sy} CH_2), 1462 and 1453 cm^{-1} m (δ CH_2 and $\delta_{as}CH_3$), 1421 cm^{-1} w (δ_{as} P-CH_3), 1375 cm^{-1} ms (δ_{sy} CH_3), 1292, 1280 cm^{-1} m (δ_{sy} P-CH_3), 1200 and 1186 cm^{-1} ms ($PNEt_2$,[ccc] some contribution from the CH_3 rock of the $POCH_3$), 1098 cm^{-1} w ($PNEt_2$), 1051 cm^{-1} s (ν P-O-C), 1021 cm^{-1} (ν_{as} P-N-C), 929 cm^{-1} ms ($PNEt_2$), 869 cm^{-1} ms (P-CH_3 rock), 788 cm^{-1} m (POC), 708 cm^{-1} sh and 691 ms (ν_{sy} P-N-C).

The effect of atmospheric moisture on methyl N,N-diethylmethylphosphonamidite is depicted by the infrared spectra reproduced in ***Figures 333A*** and ***333B***. After one day of exposure to atmospheric moisture, the spectrum of the compound (***Figure 333A***) shows a band at 2286 due to P-H stretching and bands at ca 3000, 2730 and 2501 cm^{-1} due to the NH_2^+ group. Water bands are predominant at 3370 and 1636 cm^{-1}. The P-CH_3 group is

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[ccc] Thomas, L.C. in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p.123-125, Heyden & Son Ltd., 1974, gives the following bands as being characteristic of the $PNEt_2$ group, 1200, 1170, 1100, 1060, 1025 and 950 cm^{-1}.
Colthup, N.B., Daly, L.H., and Wiberley, S.E., in Introduction to Infrared and Raman Spectroscopy", p. 350, Academic Press, New York, 1975 assigns the bands of the $PNEt_2$ as occurring at 1110-930 cm^{-1} (ν_{as} P-N-C), 770-680 cm^{-1} (ν_{sy} P-N-C), near 1210 cm^{-1} and near 1175 cm^{-1}.
Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S., and Mukhametov, F.S. in "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)", p. 5, Kluwer Academic Publishers, Boston, 1990, lists the following bands as being characteristic of the $PNEt_2$ group: 1230-1170 cm^{-1} m (ν_{as} C-N-C), 1190-1150 cm^{-1} m (ω, τ CH_2), 1110-1080 cm^{-1} w, 1080-1050 w-m (CH_3 rock), 1050-1010 cm^{-1} s (ν_{as} P-N-C), 980-930 cm^{-1} s (ν NC-C), 800-750 cm^{-1} m-s (CH_2 rock), 700-650 cm^{-1} w-m (ν_{sy} P-N-C).

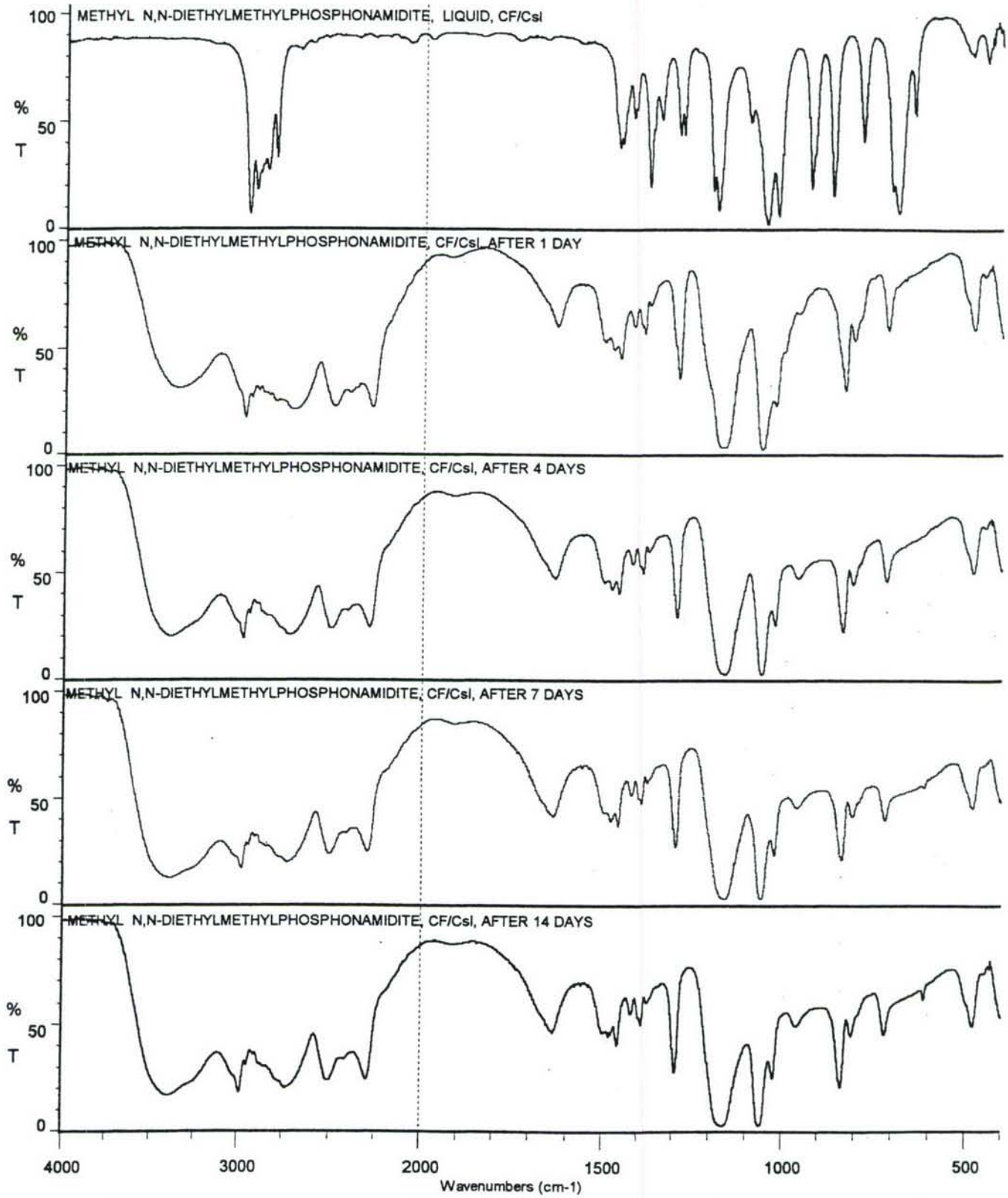

Figure 333A METHYL N,N-DIETHYLMETHYLPHOSPHONAMIDITE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

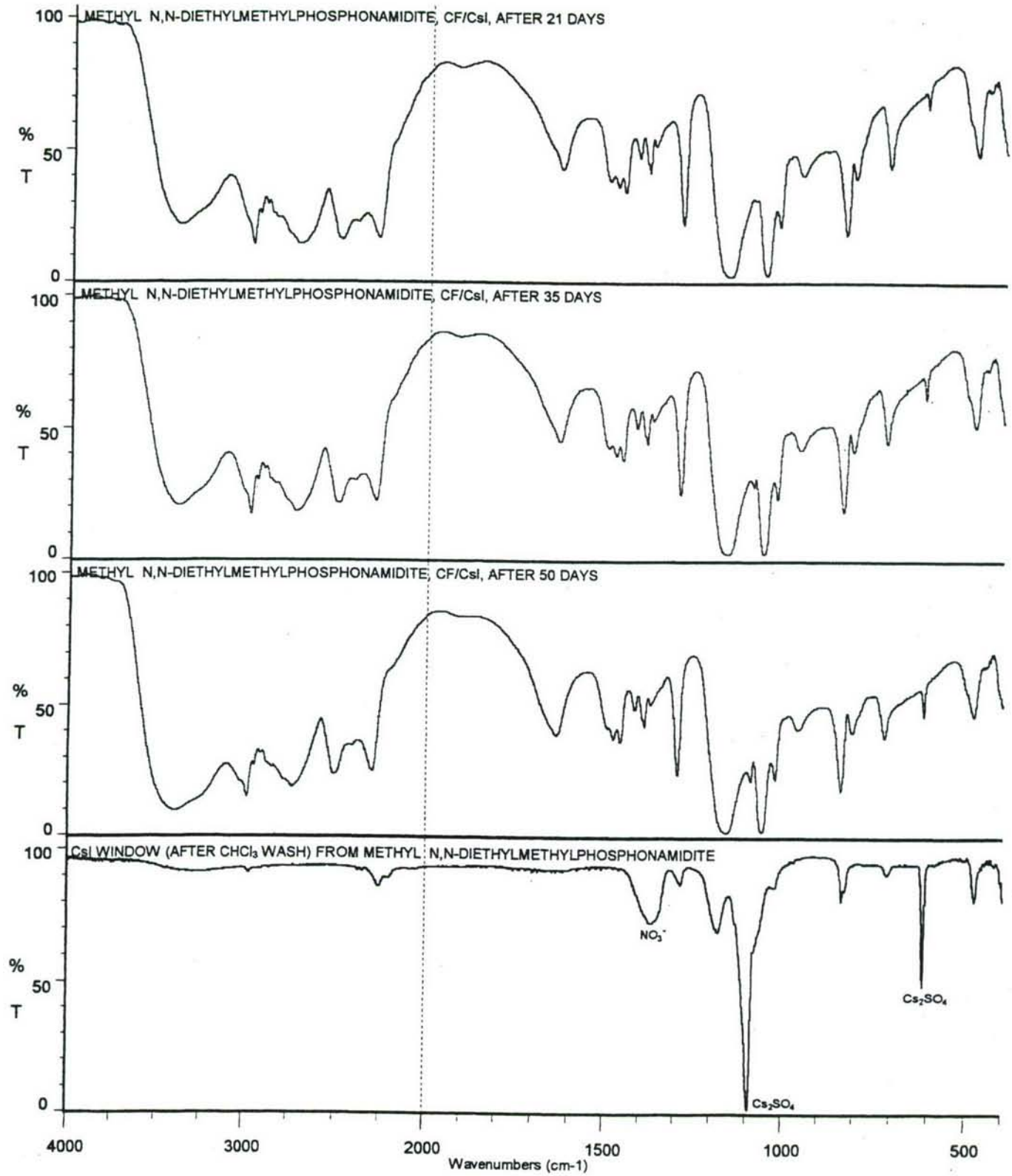

Figure 333B METHYL N,N-DIETHYLMETHYLPHOSPHONAMIDITE, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED). BOTTOM SPECTRUM SHOWS THE MATERIAL LEFT ON THE CsI WINDOWS AFTER A CHLOROFORM RINSE.

indicated at 1290 and 833 cm^{-1}. The bands at 1170 and 1062 are assigned to the asymmetric and symmetric stretching of the PO_2^- anion. Little change is apparent through the rest of the 50 days that constituted the study. The end product of the hydrolysis may be best represented as $[CH_3\text{-}PO_2^-(OCH_3)]Et_2NH_2^+$. After the 50th day of the study, the CsI windows were separated (with the aid of a razor blade) and rinsed off with chloroform. An infrared spectrum of the chloroform rinsed windows were then determined as given in the bottom spectrum in ***Figure 333B***. Bands due to cesium sulfate (Cs_2SO_4), 612 and 1092 cm^{-1}, and nitrate (NO_3^-), 1368 cm^{-1}, are visible in the spectrum. Cesium sulfate can be seen in the spectra after 7 days by a very weak band near 613 cm^{-1}. Both of the bands of cesium sulfate (1092 and 612 cm^{-1}) are present after 35 days have passed.

3.6.4 Methyl N,N-diethylethylphosphonamidite $CH_3\text{-}CH_2\text{-}P(OCH_3)[N(CH_2CH_3)_2]$

The infrared spectrum of methyl N,N-diethylethylphosphonamidite as a liquid film between CsI discs (windows) is reproduced in Figure ***334***. The band assignments are as follows: 2966 cm^{-1} s (ν_{as} CH_3), 2931 cm^{-1} ms (ν_{as} CH_2), 2874 cm^{-1} m (ν_{sy} CH_3), 2821 cm^{-1} m (ν_{sy} CH_2), 1460 cm^{-1} m (δ CH_2, CH_3), 1424 cm^{-1} vvw (δ P-CH_2), 1375 cm^{-1} m (δ_{sy} CH_3), 1222 cm^{-1} vw (P-Ethyl), 1200 and 1184 cm^{-1} ms ($PNEt_2$, some contribution from the CH_3 rock of $POCH_3$ near 1180 cm^{-1}), 1098 cm^{-1} w ($PNEt_2$), 1057 cm^{-1} s (ν P-O-C), 1016 cm^{-1} s (ν_{as} P-N-C), 924 cm^{-1} ms ($PNEt_2$), 788 cm^{-1} m (POC, $PNEt_2$), 759 cm^{-1} m (CH_2 rock of PEt ?), 714, 681 cm^{-1} ms (ν_{sy} P-N-C).

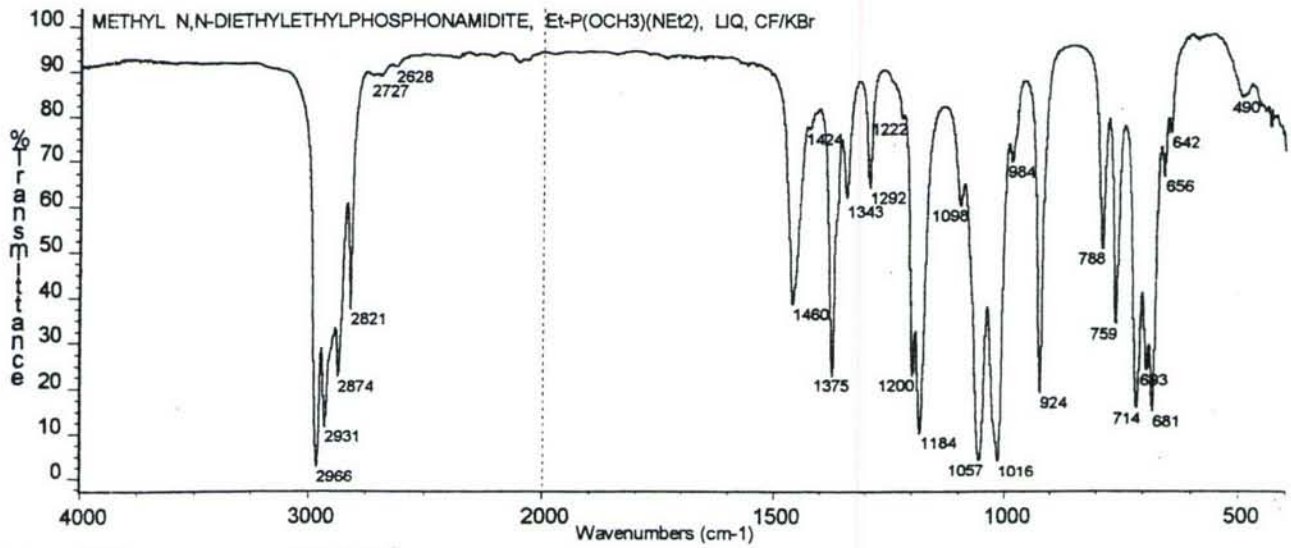

Figure 334 **METHYL N,N-DIETHYLETHYLPHOSPHONAMIDITE, LIQUID, CF/KBr**

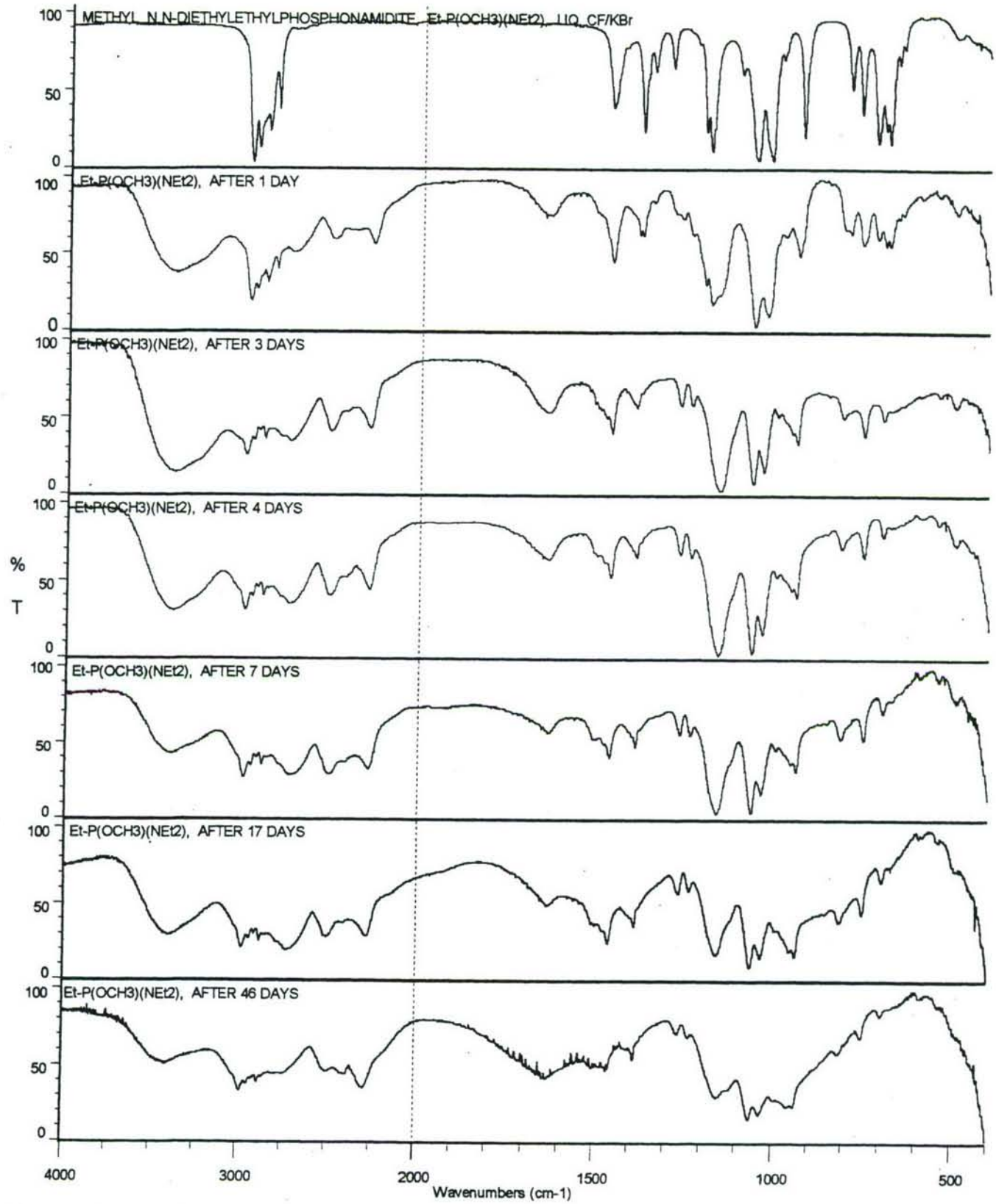

FIGURE 335 METHYL N,N-DIETHYLETHYLPHOSPHONAMIDITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

The effect of atmospheric moisture on a thin liquid film of methyl N,N-diethylethylphosphonamidite is illustrated by the infrared spectra presented in ***Figure 335***. The spectrum after 1 day of exposure shows the formation of bands near 3000, 2732 and 2498 cm^{-1} due to the asymmetric and symmetric stretching of the NH_2^+ group. The band near 2275 cm^{-1} may be assigned to a P-H stretching vibration. By the 3rd day of exposure to moisture, these bands have become more defined. The appearance of intense bands at 1154 and 1062 cm^{-1} may be assigned to the formation of the PO_2^- anion, with the bands being due to the asymmetric and symmetric stretching vibrations respectively. Two bands appear near 1263 and 1233 cm^{-1} which are assigned to the P-ethyl group. This picture of the hydrolysis appears to hold steady through the 46 days of the observations. The hydrolysis of methyl N,N-diethylethylphosphonamidite may be depicted as the following:

$Et\text{-}P(NEt_2)(OCH_3)$ -HOH→ $Et\text{-}P{=}O(H)(OCH_3)$ -HOH→ $Et\text{-}P{=}O(H)(OH)$ + $HNEt_2$ → $[Et\text{-}P(O_2^-)H]Et_2NH_2^+$.

3.6.5 <u>N,N,N',N'-tetraethylethylphosphonodiamidite</u> $CH_3CH_2\text{-}P[N(CH_2CH_3)_2]_2$

The infrared spectrum of N,N,N',N'-tetraethylethylphosphonodiamidite as a liquid film between CsI windows is reproduced as ***Figure 336***. The band assignments are as follows: 2963 cm^{-1} s (ν_{as} CH_3), 2929 cm^{-1} ms (ν_{as} CH_2), 2868 and 2857 cm^{-1} ms (ν_{sy} CH_3 and CH_2), 1460 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1424 cm^{-1} sh (δ P-CH_2), 1373 cm^{-1} ms (δ_{sy} CH_3), 1342 and 1290 cm^{-1} m (ω, τ CH_2), 1231 cm^{-1} w (P-Et), 1187 cm^{-1} s ($PNEt_2$), 1097

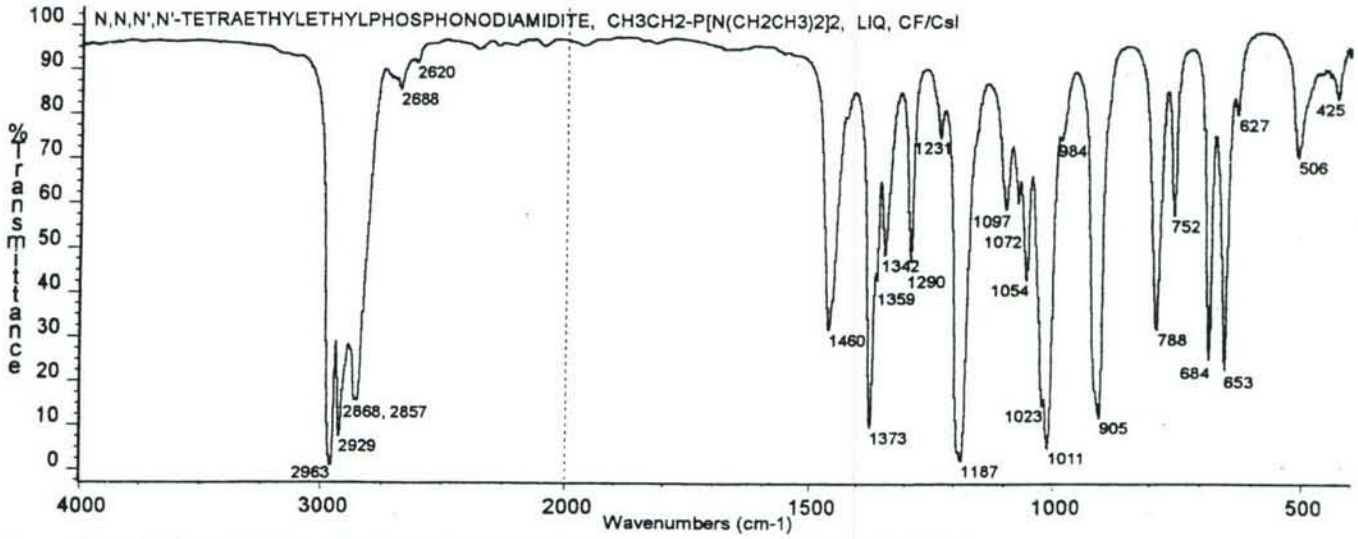

Figure 336 N,N,N',N'-TETRAETHYLETHYLPHOSPHONODIAMIDITE, LIQUID, CF/CsI

and 1054 cm^{-1} w ($PNEt_2$), 1011 cm^{-1} ms (ν_{as} P-N-C), 905 cm^{-1} ms ($PNEt_2$), 788 cm^{-1} m ($PNEt_2$, CH_2 rock), 752 cm^{-1} w (CH_2 rock, PEt), 684 and 653 cm^{-1} m (ν_{sy} P-N-C), 627 cm^{-1} vw (ν P-C of PEt ?).

The effect of atmospheric moisture on a thin liquid film of N,N,N',N'-tetraethylethylphosphonodiamidite is depicted by the infrared spectra reproduced in ***Figure 337***. After 3 days of exposure to atmospheric moisture, the infrared spectrum showed NH_2^+ bands near 2700 and 2500 cm^{-1}. A band near 2270 cm^{-1} can be assigned to a P-H stretching vibration. The bands due to the $PNEt_2$ moiety are gone from the spectra. New bands near 1160 and and 1063 cm^{-1} can be assigned to the asymmetric and symmetric stretching of the PO_2^- group. Bands near 1034 cm^{-1} and 936 may be P-H deformations. Two bands become visible near 1260 and 1233 cm^{-1} and may be due to the P-Et group. By the 19th through the 52nd days two bands are visible near 1091 and 613 cm^{-1} and are assigned to cesium sulfate (Cs_2SO_4) from the cesium iodide windows. The hydrolysis of N,N,N',N'-tetraethylethylphosphonodiamidite is believed to produce the following compound $[Et\text{-}P(O_2^-)H]Et_2NH_2^+$. A comparison of the hydrolysis of N,N,N',N'-tetraethylethylphosphonodiamidite (***Figure 337***) with the hydrolysis of methyl N,N-diethylethylphosphonamidite (***Figure 335***)show that the compounds yield the same end product.

3.6.6 Hexaethylphosphorous Triamide [Tris(N,N-diethylamino)phosphine] $P[N(CH_2CH_3)_2]_3$

The infrared spectrum of hexaethylphosphorous triamide or (tris(N,N-diethylamino)phosphine, has been discussed previously as ***Figure 43*** and will be repeated here as ***Figure 338***. The band assignments are as follows: 2966 cm^{-1} s (ν_{as} CH_3), 2930 cm^{-1} ms (ν_{as} CH_2), 2865 cm^{-1} and 2852 cm^{-1} ms (ν_{sy} CH_3 and ν_{sy} CH_2), 1461 cm^{-1} m (δ_{as} CH_3 and δ CH_2), 1374 cm^{-1} ms (δ_{sy} CH_3), 1292 and 1231 cm^{-1} w (ω, τ CH_2 ?), 1194 s, 1156 m, 1102 w, 1053 w, 1009 s and 908 m cm^{-1} (characteristic of the $PNEt_2$ group). The strong band at 1009 cm^{-1} can be assigned to the asymmetric P-N-C stretch. The symmetric P-N-C stretch absorbs at 664 cm^{-1}. Shagidullin et al.[ddd] list the following bands as being characteristic of the $PNEt_2$ group: 1230-1170 cm^{-1} m (ν_{as} C-N-C), 1190-1150 cm^{-1} m (ω, τ CH_2), 1110-1080 cm^{-1} w, 1080-1050 cm^{-1} w-m (CH_3 rock), 1050-1010 cm^{-1} s (ν_{as} P-N-C),

[ddd] Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S. in "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)", p. 5, Kluwer Academic Publishers, Boston, 1990.

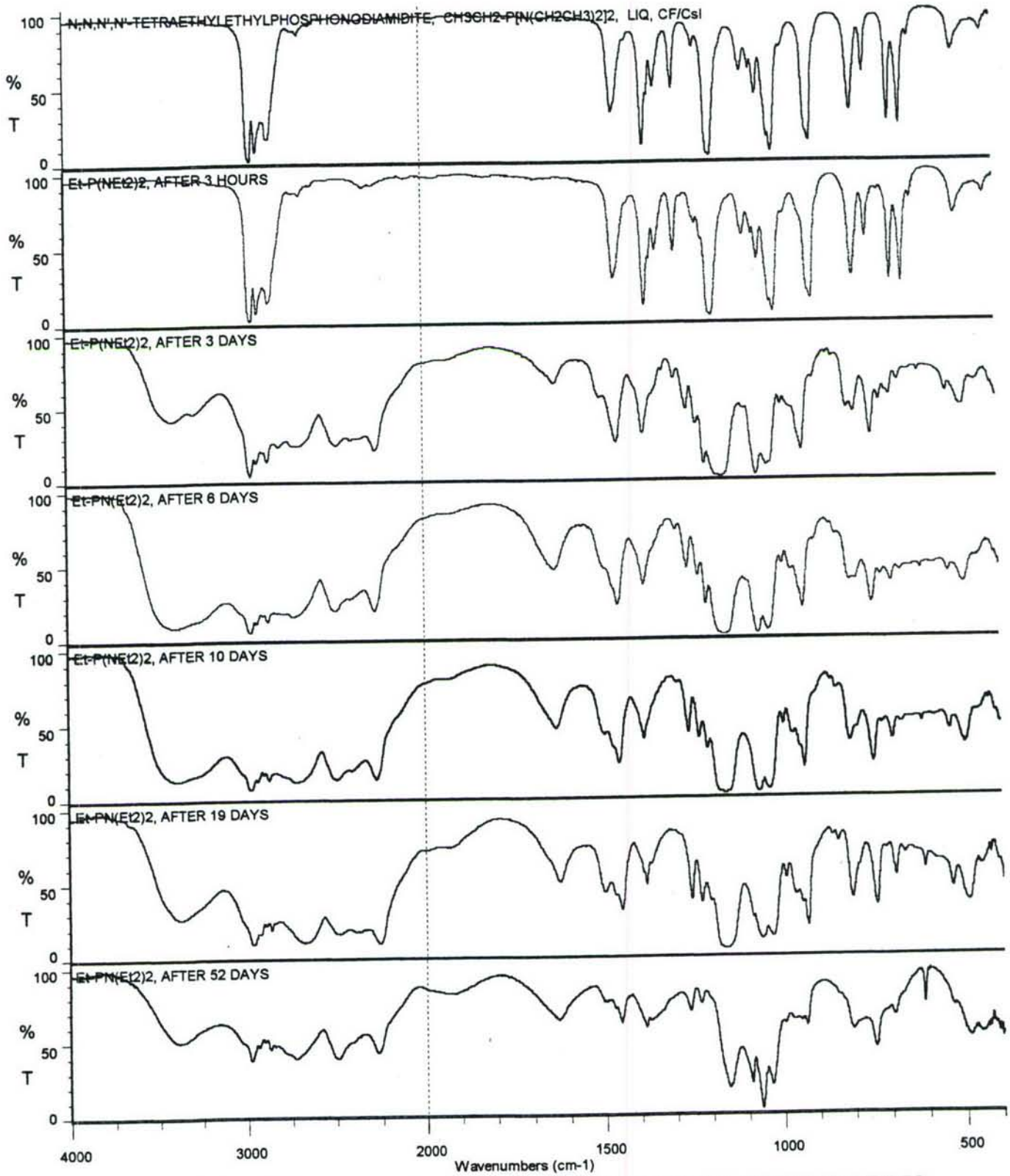

Figure 337 N,N,N',N'-TETRAETHYLETHYLPHOSPHONODIAMIDITE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

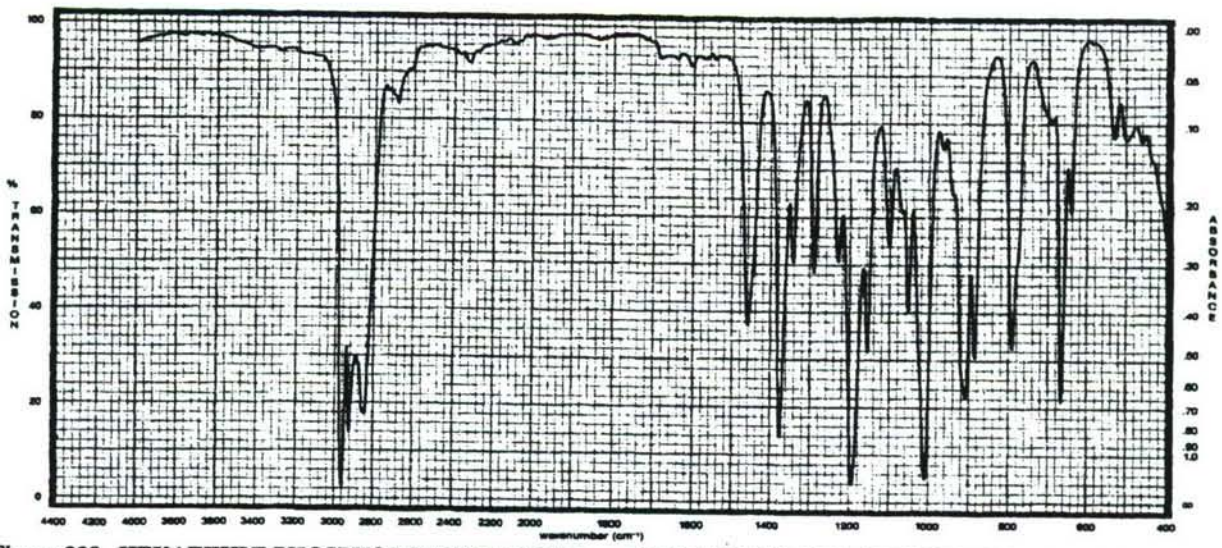

Figure 338 HEXAETHYLPHOSPHOROUS TRIAMIDE or TRIS (N,N-DIETHYLAMINO)PHOSPHINE, LIQUID, CF/KBr

980-930 cm^{-1} s (ν NC-C), 800-750 cm^{-1} m-s (CH_2 rock), 700-650 cm^{-1} w-m (ν_{sy} P-N-C). ***Figure 43*** shows bands for the compound at 1194, 1156, 1102, 1053, 1009 , 966 (very weak, with much stronger bands at 908 and 886 cm^{-1}), 791 and 664 cm^{-1}.

The infrared spectra illustrating the effect of atmospheric moisture on hexaethylphosphorous triamide [tris(N,N-diethylamino)phosphine] are given in ***Figures 44A*** through ***44C***.

3.6.7 N,N-diethylphosphoramidous Dichloride $(CH_3CH_2)_2N\text{-}PCl_2$

The infrared spectrum of N,N-diethylphosphoramidous dichloride as a thin liquid film between CsI discs (windows) is given in ***Figure 339***. The band assignments are as follows: 2976 cm^{-1} s (ν_{as} CH_3), 2937 cm^{-1} ms (ν_{as} CH_2), 2874 cm^{-1} m (ν_{sy} CH_3), 2822 cm^{-1} vw (ν_{sy} CH_2), 2482 cm^{-1} vw (ν P-H ?), 1691 cm^{-1} vw (1022 + 672 = 1694 cm^{-1}), 1617 cm^{-1} vvw (948 + 672 = 1620 cm^{-1}), 1463 and 1445 cm^{-1} ms-m (δ CH_2, δ_{as} CH_3), 1204 and 1165 cm^{-1} s, 1102 and 1061 cm^{-1} m ($PNEt_2$), 1022 cm^{-1} s (ν_{as} P-N-C), 948 cm^{-1} ms ($PNEt_2$), 791 cm^{-1} ms (CH_2 rock), 672 cm^{-1} ms (ν_{sy} P-N-C), 515, 484 cm^{-1} ms and 419 cm^{-1} s (ν_{as} and ν_{sy} PCl_2).[eee]

[eee] For P^{+3} organophosphorus compounds, the ν_{sy} PCl_2 is listed as occurring higher than the ν_{as} PCl_2. See Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S., and Mukhametov, F.S., "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms), p. 4, Kluwer Academic Publishers, Boston, 1990.

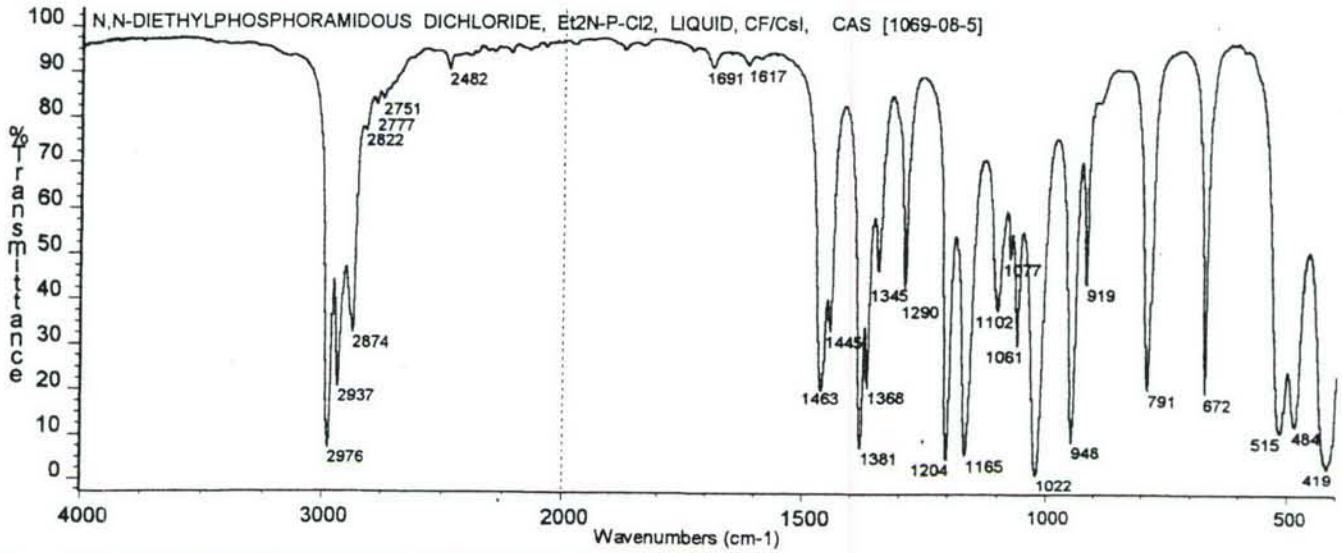

Figure 339 N,N-DIETHYLPHOSPHORAMIDOUS DICHLORIDE, LIQUID, CF/CsI

The effect of atmospheric moisture on a thin liquid film of N,N-diethylphosphoramidous chloride between CsI windows is illustrated by the infrared spectra presented in ***Figures 340A*** and ***340B***. The picture is somewhat unclear as to whether hydrolysis proceeds alone or if oxidation occurs first followed by hydrolysis. Even after some 31 days of exposure to atmospheric moisture bands are still evident for the $PNEt_2$ group (1204, 1166, 1022, 946, 791 and 671 cm^{-1}). Bands are still present from the PCl_2 moiety (487, 421 cm^{-1}). By the 35th day of exposure, the spectrum takes on the general appearance of a P-acid with bands near 2807and 2481 cm^{-1} (POH), 2390 cm^{-1} (POH, P-H ?), 1650 cm^{-1} (POH), 1200 cm^{-1} (P=O) and ca 1000 cm^{-1} (P-OH). Bands also appear at 1090 and 612 cm^{-1} assignable to cesium sulfate, Cs_2SO_4 (from the CsI windows). As the time of exposure to atmospheric moisture increases from 35 to 75 days, bands occur at 1163 and 1070 cm^{-1} which may be assigned to the asymmetric and symmetric stretching of the PO_2^- anion. The band near 1007 cm^{-1} may be a P-OH stretching vibration. However, bands are still present near 1477, 1457 and 1394 cm^{-1} and may be due to the NEt_2 moiety. The broad bands near 3000, 2850 and 2500 cm^{-1} may be due in part to POH and NH_2^+ vibrations, while the 2384 cm^{-1} band may be due to P-H and or POH. The picture is confusing and perhaps the oxidation/hydrolysis and hydrolysis reactions are both occurring. This picture may be best described as follows:

Oxidation/Hydrolysis Et_2NPCl_2 -[O]→ $Et_2NP{=}O(Cl)_2$ -HOH→ $HOP{=}O(Cl)_2$ -HOH→ $HOP{=}O(OH)(Cl)$

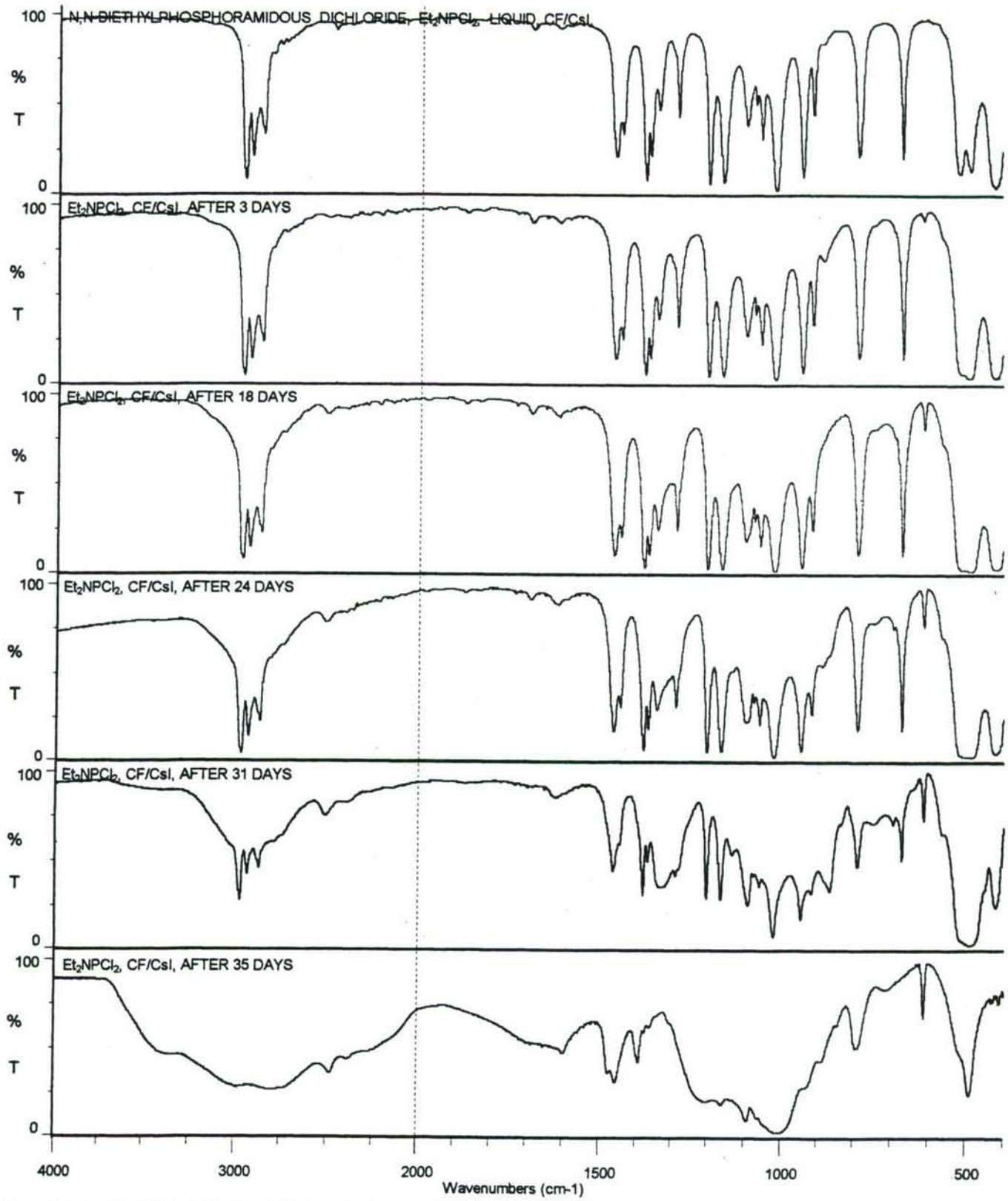

Figure 340 A N,N-DIETHYLPHOSPHORAMIDOUS DICHLORIDE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

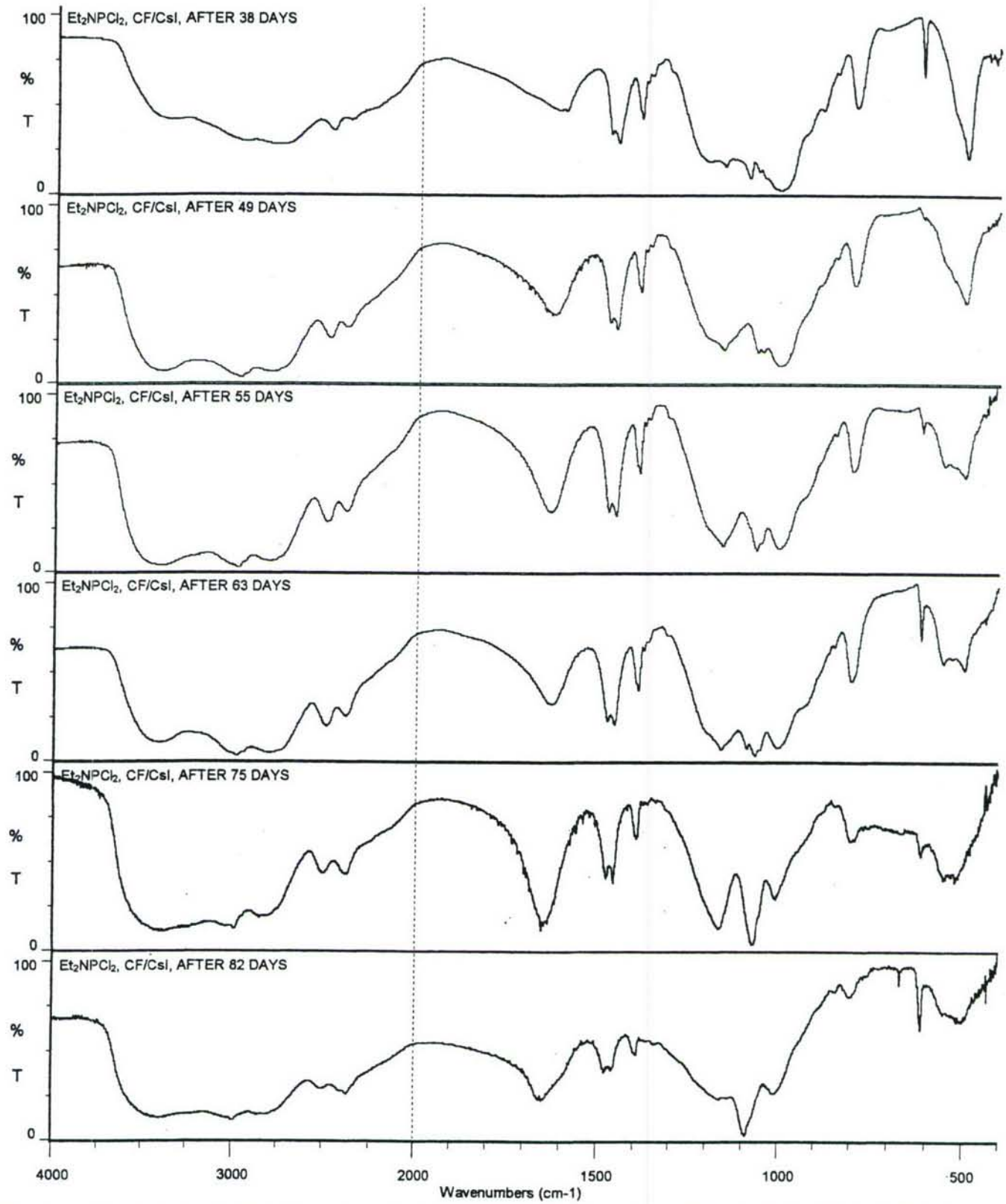

Figure 340B **N,N-DIETHYLPHOSPHORAMIDOUS DICHLORIDE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE** (CONTINUED)

$$-HOH\rightarrow (HO)_3P{=}O + HNEt_2 \rightarrow [(HO)_2PO_2^-]Et_2NH_2^+.$$

Hydrolysis Et_2NPCl_2 $-HOH\rightarrow$ H-O-PCl_2 $\rightarrow$ H-P=OCl_2 $-HOH\rightarrow$ H-P=O(OH)(Cl) $-HOH\rightarrow$ H-P=$O(OH)_2$

$$H\text{-}P{=}O(OH)_2 + Et_2NH \rightarrow [H\text{-}PO_2^-(OH)]Et_2NH_2^+ .$$

3.6.8 N,N-diethylphosphoramidous Difluoride $(CH_3CH_2)_2N\text{-}PF_2$

The infrared spectrum of a thin liquid film of N,N-diethylphosphoramidous difluoride between CsI windows is presented as ***Figure 341***. The band assignments are as follows: 2977 cm^{-1} ms (ν_{as} CH_3), 2940 cm^{-1} m (ν_{as} CH_2), 2879 cm^{-1} w (ν_{sy} CH_3), 2822 cm^{-1} vw (ν_{sy} CH_2), 2483 cm^{-1} vvw (ν P-H ?), 1465 cm^{-1} w and 1449 cm^{-1} vw (δ CH_2 and δ_{as} CH_3) 1384 cm^{-1} m (δ_{sy} CH_3), 1211 and 1181 cm^{-1} m, 1106 and 1066 cm^{-1} w ($PNEt_2$), 1030 cm^{-1} ms (ν_{as} P-N-C), 950 cm^{-1} m ($PNEt_2$), 800 and 793 cm^{-1} s (ν_{as} PF_2), 740 cm^{-1} s (ν_{sy} PF_2), 682 cm^{-1} m (ν_{sy} P-N-C), 515, 481 and 408 cm^{-1} vw (possible ν_{sy} and ν_{as} PCl_2, impurity).

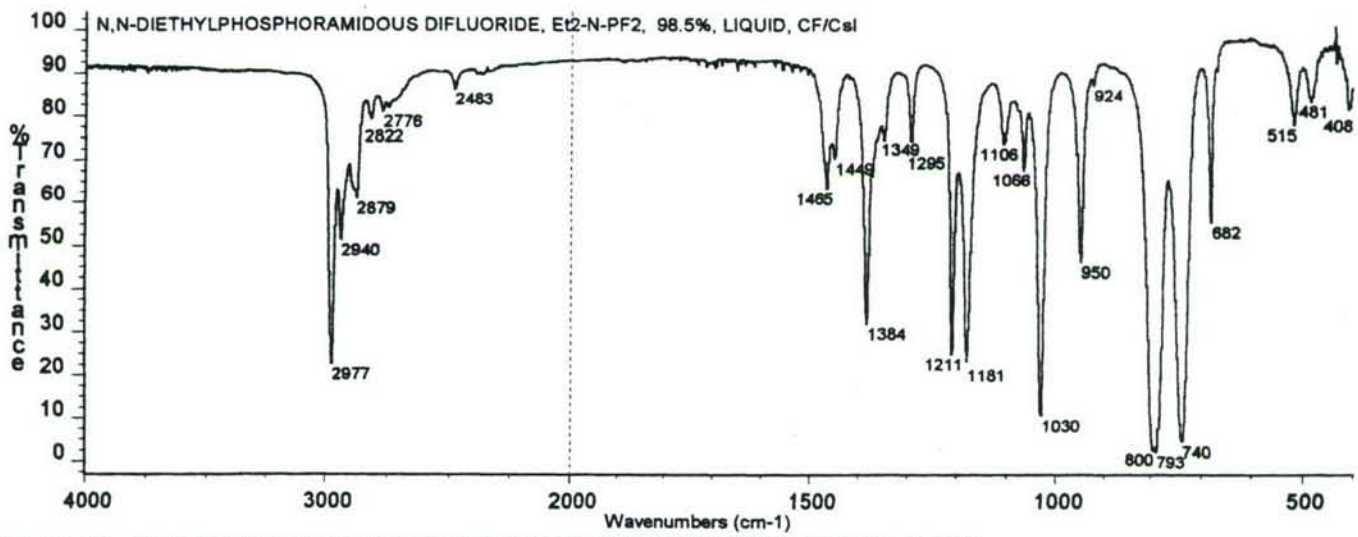

Figure 341 N,N-DIETHYLPHOSPHORAMIDOUS DIFLUORIDE, 98.5%, LIQUID, CF/CsI

3.6.9 N,N-diethylethylmethylphosphinamidate $CH_3\text{-}P{=}O(CH_2CH_3)[N(CH_2CH_3)_2]$

The infrared spectrum of N,N-diethylethylmethylphosphinamidate as a liquid film between KBr windows is given in ***Figure 342***. The band assignments are as follows: 2970 cm^{-1} ms (ν_{as} CH_3), 2935 cm^{-1} m (ν_{as} CH_2), ca 2916 cm^{-1} sh (ν_{sy} CH_3), 2877 cm^{-1} m (ν_{sy} CH_2), 1461 cm^{-1} w (δ CH_2 and δ_{as} CH_3), 1418 cm^{-1} vw (δ P-CH_2, δ_{as} P-CH_3), 1380 cm^{-1} m (δ_{sy} CH_3), 1298 cm^{-1} m (δ_{sy} P-CH_3), 1268 vvw (PEt), 1211 cm^{-1} s ($PNEt_2$), 1192

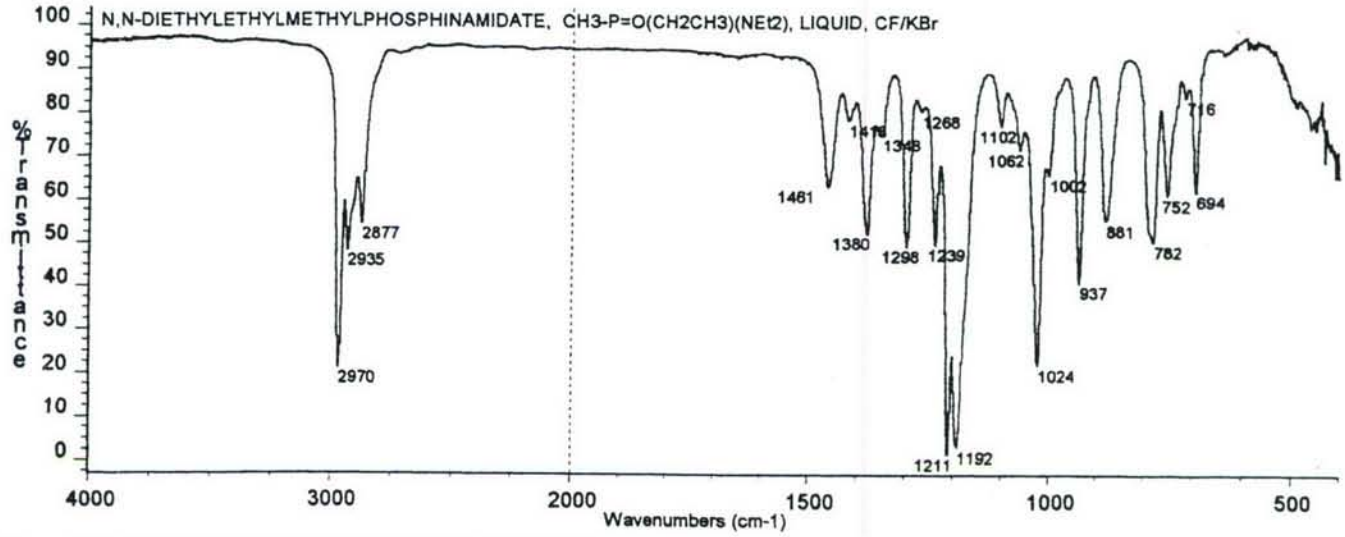

Figure 342 N,N-DIETHYLETHYLMETHYLPHOSPHINAMIDATE, LIQUID, CF/KBr

cm^{-1} s ($PNEt_2$ and ν P=O, *calculated* value for ν P=O is 1190 cm^{-1}), 1102 and 1062 cm^{-1} vw ($PNEt_2$), 1024 cm^{-1} ms (ν_{as} P-N-C), 1002 cm^{-1} vw (ν C-C of PEt ?), 937 cm^{-1} m ($PNEt_2$, ν NC-C), 881 cm^{-1} m (P-CH_3 rock), 782 cm^{-1} m (CH_2 rock of $PNEt_2$), 752 cm^{-1} w (CH_2 rock of P-Et), 716 cm^{-1} vw (ν P-C ?), 694 cm^{-1} w (ν_{sy} P-N-C).

The effect of atmospheric moisture on a thin liquid film of N,N-diethylethylmethylphosphinamidate between KBr windows is illustrated by the infrared spectrum presented in ***Figure 343***. After 7 days of exposure to atmospheric moisture, the spectrum shows new bands near 2724, 2483 and 2406 cm^{-1} (NH_2^+) , 1157 cm^{-1} and 1041 cm^{-1} (ν_{as} PO_2^- and ν_{sy} PO_2^-). By 13 days of exposure, the bands near 1147 and 1043 cm^{-1} (PO_2^- anion) have become predominant. After 40 days of exposure to atmospheric moisture the P-Et bands at 1265 and 1237 cm^{-1} have become quite evident. The P-CH_3 group is still present as indicated by the bands at 1293 and 874 cm^{-1}. The hydrolysis of N,N-diethylethylmethylphosphinamidate may be summarized as follows:

$$CH_3\text{-}P{=}O(CH_2CH_3)(NEt_2) \xrightarrow{-HOH} CH_3\text{-}P{=}O(OH)(CH_2CH_3) + HNEt_2 \rightarrow [CH_3\text{-}PO_2^-(CH_2CH_3)]Et_2NH_2^+ .$$

3.6.10 N,N-Diethyldimethylphosphinamidate $(CH_3)_2P{=}O[N(CH_2CH_3)_2$

The infrared spectrum of N,N-diethyldimethylphosphinamidate as a liquid film between CsI discs (windows) is presented as ***Figure 344***. The band assignments are as follows: 2970 cm^{-1} ms, 2932 cm^{-1} m, ca 2912 cm^{-1} sh and 2874 cm^{-1} m (ν_{as} and ν_{sy} CH_3 and CH_2), 1465 and 1454 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1421 cm^{-1}

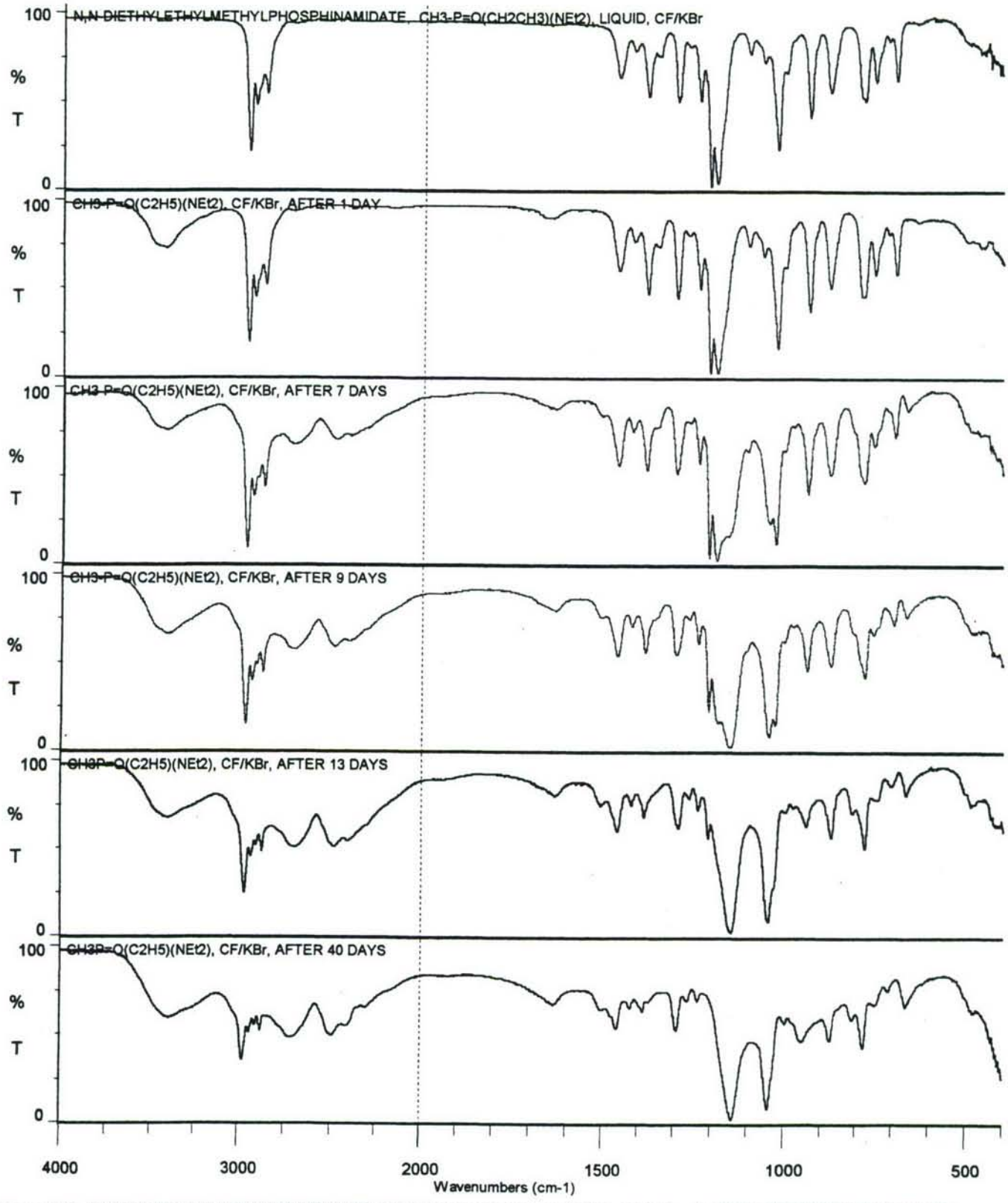

Figure 343 N,N-DIETHYLETHYLMETHYLPHOSPHINAMIDATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

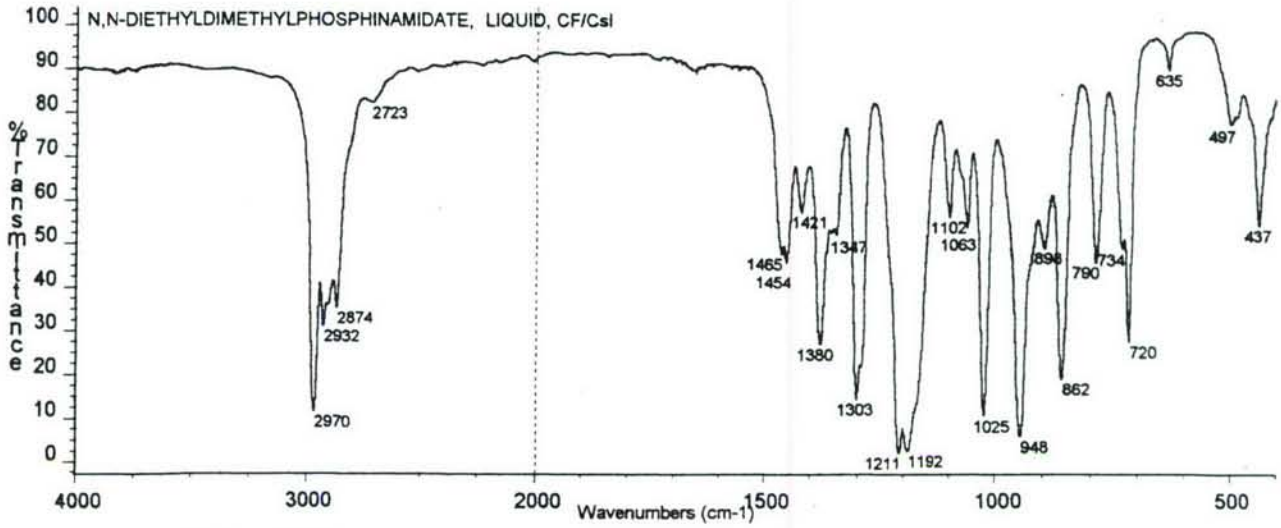

Figure 344 N,N-DIETHYLDIMETHYLPHOSPHINAMIDATE, LIQUID, CF/CsI

w (δ_{as} P-CH_3), 1380 cm^{-1} m (δ_{sy} CH_3), 1303 cm^{-1} ms and 1298 cm^{-1} sh (δ_{sy} P-CH_3), 1211, 1192 cm^{-1} s and ca 1174 cm^{-1} sh ($PNEt_2$ and ν P=O, the *calculated* value of the ν P=O is 1194 cm^{-1} and the actual value may be the shoulder near 1174 cm^{-1}), 1102 and 1063 cm^{-1} w ($PNEt_2$), 1025 cm^{-1} ms (ν P-N-C), 948 cm^{-1} ms (ν C-C), 862 cm^{-1} m (P-CH_3 rock), 790 cm^{-1} w (CH_2 rock from $PNEt_2$), 734 cm^{-1} sh (ν P-C ?), 720 cm^{-1} m (ν_{sy} P-N-C).

The effect of atmospheric moisture on a liquid film of N,N-diethyldimethylphosphinamidate between CsI windows is illustrated by the infrared spectra reproduced in ***Figures 345A*** and ***345B***. By the 4th day of exposure to atmospheric moisture, bands appear in the spectrum near 2700, 2480 cm^{-1} (POH) and 1160 cm^{-1} (P=O). After 8 days have passed, the bands occur near 3000, 2729, 2493 and 2414 cm^{-1} (now possibly POH and NH_2^+). Bands at 1137 and 1039 cm^{-1} may be assigned to a PO_2^- moiety. The P-CH_3 group is still indicated by bands at 1295 and 860 cm^{-1}. As time progresses, bands appear near 613 and 1098 cm^{-1} and are believed to be due to the formation of cesium sulfate, Cs_2SO_4, from the cesium iodide windows used to contain the sample. After 55 days had elapsed, the cesium iodide windows were separated, with the aide of a razor blade, and the windows rinsed off with chloroform. The bottom spectrum in ***Figure 345B*** shows a CsI window (from the hydrolysis) after a chloroform rinse. The spectrum shows the presence of cesium nitrate ($CsNO_3$) at 1349 and 834 cm^{-1} and cesium sulfate (Cs_2SO_4) at 1097 and 613 cm^{-1}. The hydrolysis of N,N-diethyldimethylphosphinamidate as a liquid film between cesium iodide windows may be summarized as follows:

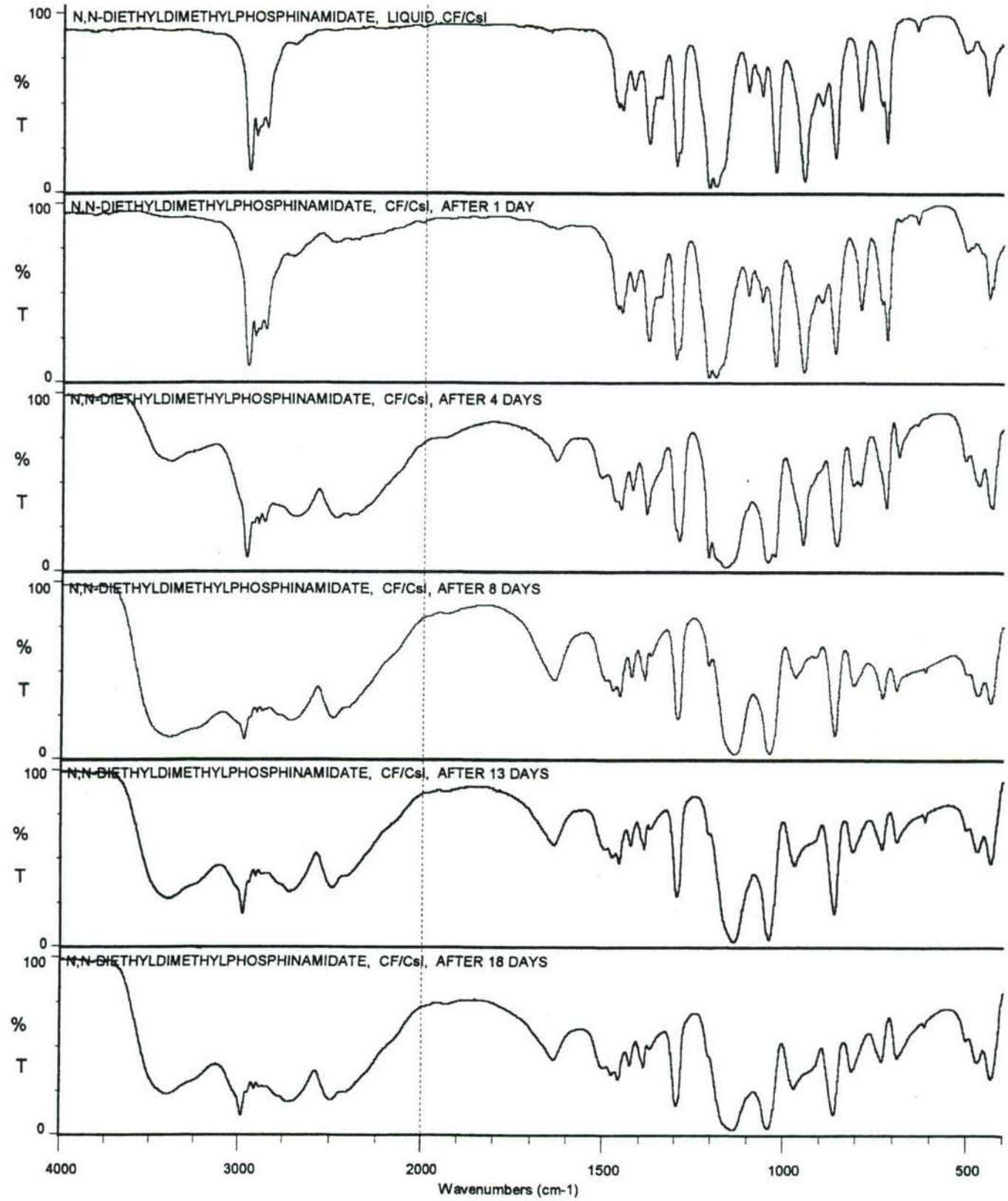

Figure 345A N,N-DIETHYLDIMETHYLPHOSPHINAMIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

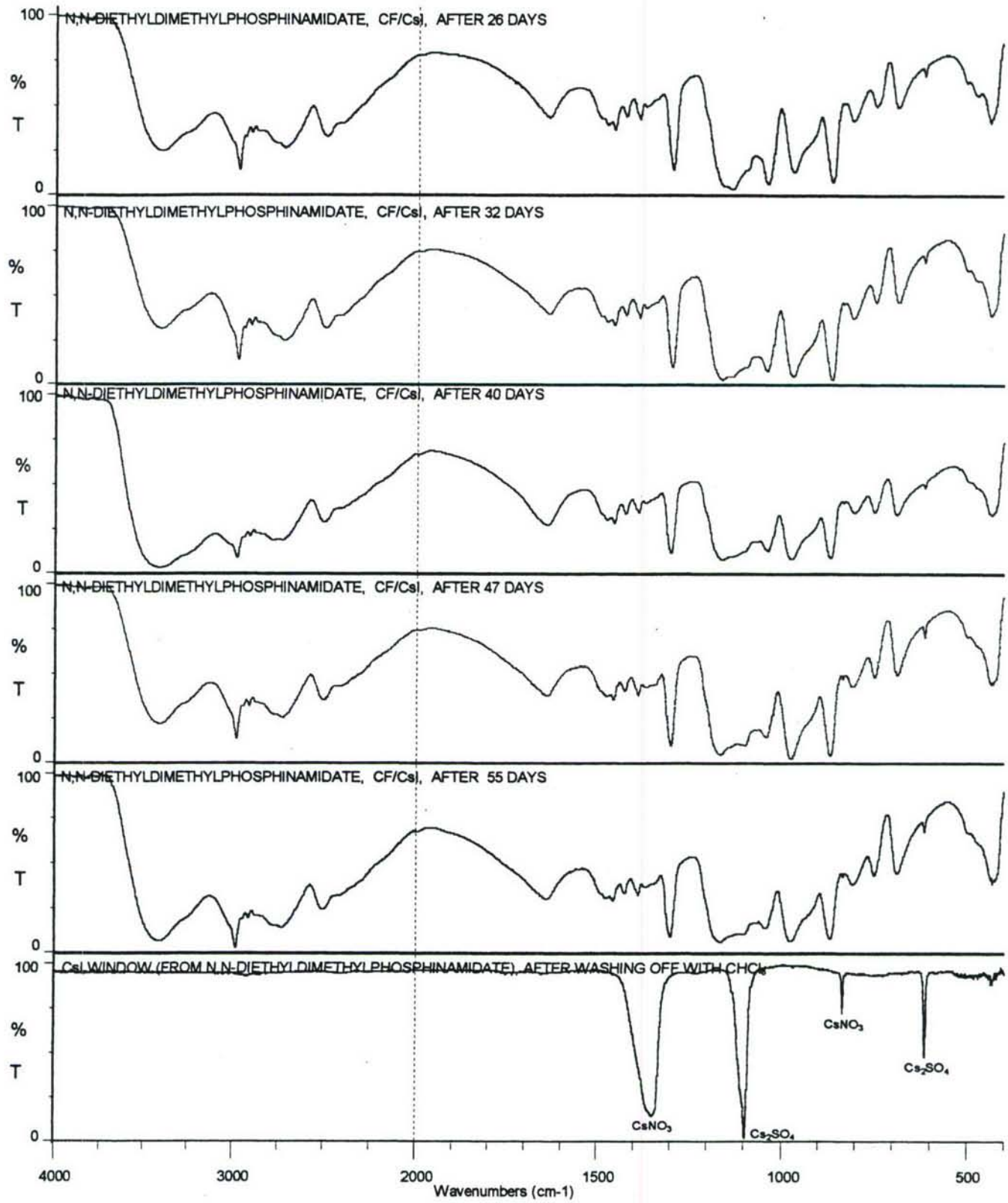

Figure 345B N,N-DIETHYLDIMETHYLPHOSPHINAMIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

$(CH_3)_2P{=}O(NEt_2)$ $\xrightarrow{-HOH}$ $(CH_3)_2P{=}O(OH)$ + $HNEt_2$. The acid and the amine then react to produce the following salt: $(CH_3)_2P{=}O(OH) + HNEt_2 \rightarrow [(CH_3)_2PO_2^-]Et_2NH_2^+$. The spectra of the hydrolysis product could thus be a mixture of the acid, amine and acid/amine salt.

(DIMETHYLPHOSPHINIC ACID)

3.6.11 N,N-Diethylethylphosphinamidate $CH_3\text{-}CH_2\text{-}P{=}O(H)[N(CH_2CH_3)_2]$

The infrared spectrum of a liquid film of N,N-diethylethylphosphinamidate between CsI windows is given in ***Figure 346***. The band assignments are as follows: 2970 cm^{-1} ms, 2934 and 2876 cm^{-1} m (ν CH_3 and ν CH_2), 2730 and 2472 cm^{-1} vw (POH), 2325 cm^{-1} w (ν P-H), 1459 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1407 cm^{-1} sh (δ P-CH_2), 1381 cm^{-1} m (δ_{sy} CH_3), 1267 and 1238 cm^{-1} w (ω, τ CH_2 of P-Et), 1213 and 1182 cm^{-1} s ($PNEt_2$, a shoulder occurs ca 1192 cm^{-1} which is assigned to the ν P=O, *calculated* value is 1206 cm^{-1}), 1103 and 1064 cm^{-1} w ($PNEt_2$), 1022 cm^{-1} ms [ν_{as} P-N-C, the P-H deformation may also occur near here (1150-965 cm^{-1})[fff] as may the ν C-C of the P-Et moiety (1050-950 cm^{-1})[ggg]], 940 cm^{-1} m ($PNEt_2$, ν C-C), 791 cm^{-1} m ($PNEt_2$, CH_2 rock), 744 cm^{-1} m (PEt, CH_2 rock), 720 and 702 cm^{-1} w (ν P-C of PEt and ν_{sy} P-N-C), 514 cm^{-1} w (P=O, CNC deformations ?).

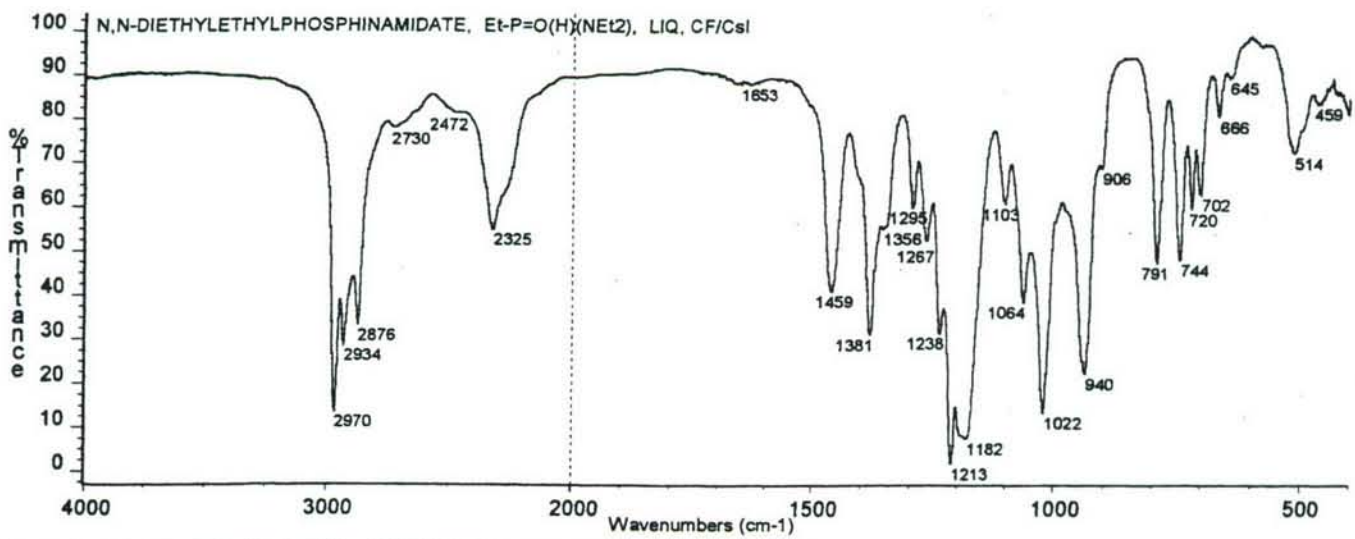

Figure 346 N,N-DIETHYLETHYLPHOSPHINAMIDATE, LIQUID, CF/CsI

[fff] Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 59, Heyden & Son Ltd., London, 1974.

[ggg] Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S., and Mukhametov, F.S., "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)",p. 4, Kluwer Academic Publishers, Boston, 1990.

The effect of atmospheric moisture on a liquid film of N,N-diethylethylphosphinamidate between CsI windows is illustrated by the infrared spectra presented in ***Figure 347***. The first spectrum shows some weak bands near 2730 and 2472 which may be due to the POH group present as a result of hydrolysis. After 3 days of exposure to moisture, the spectrum shows strong bands near 3000, 2705, 2491 and 2412 cm^{-1} assignable to the NH_2^+ group. Bands at 1160 and 1063 cm^{-1} are assigned to the asymmetric and symmetric stretching of the PO_2^- anion respectively. Bands at 1090 and 613 cm^{-1} are due to the formation of cesium sulfate, Cs_2SO_4, from the cesium iodide windows used to contain the original sample. Bands at 1262, 1232, 745 and 694 cm^{-1} are due to the P-Et group. Tbe bands near 1034 and 936 cm^{-1} may be due to deformations of the P-H group. The P-H stretching vibration occurs over the range 2293-2271 cm^{-1} for the interval of the hydrolysis observations (up to 61 days). The hydrolysis of N,N-diethylethylphosphinamidate may be summarized as follows:

$$Et\text{-}P{=}O(H)(NEt_2) \xrightarrow{-HOH} Et\text{-}P{=}O(H)(OH) + Et_2NH \rightarrow [Et\text{-}PO_2^-(H)]Et_2NH_2^+ .$$

3.6.12 Methylphosphonic Bis(dimethylamide) $CH_3\text{-}P{=}O[N(CH_3)_2]_2$

The infrared spectrum of methylphosphonic bis(dimethylamide), N,N,N',N'-tetramethylmethylphosphonic diamide, as a thin liquid film between KBr discs (windows) is given in ***Figure 348***. The band assignments are as follows: 2986 cm^{-1} m , 2918 cm^{-1} sh, 2886 cm^{-1} ms, 2848 cm^{-1} sh and 2802 cm^{-1} m (ν_{as} and ν_{sy} CH_3), 1481 cm^{-1} sh and 1461 cm^{-1} m (δ_{as} and δ_{sy} CH_3), 1420 cm^{-1} w (δ_{as} P-CH_3), 1302 cm^{-1} ms [$PN(CH_3)_2$, and δ_{sy} P-CH_3],

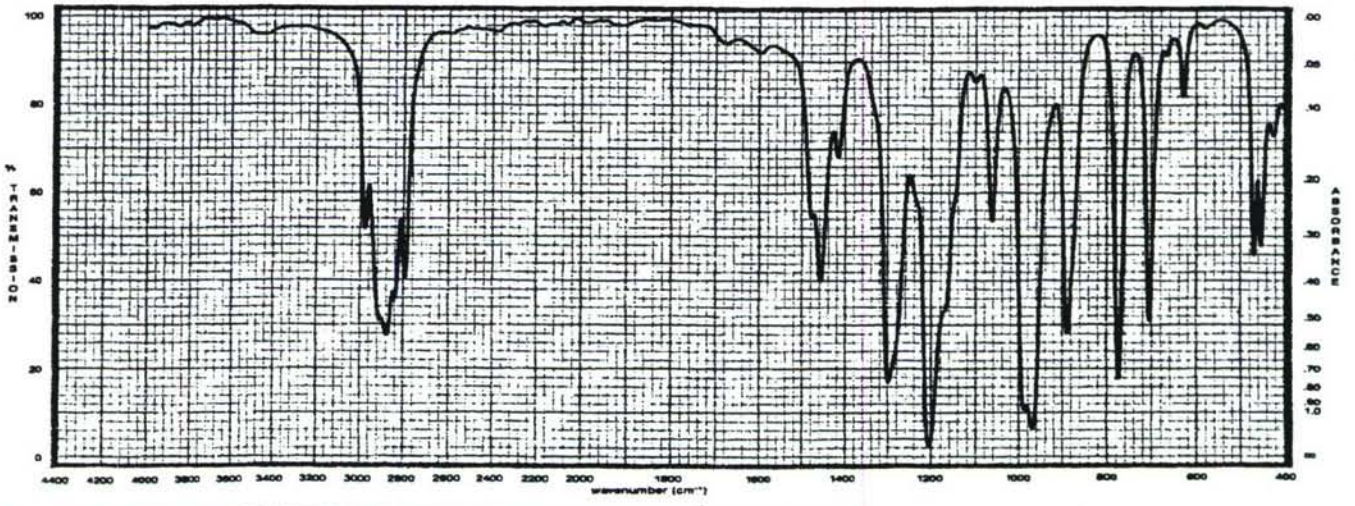

Figure 348 METHYLPHOSPHONIC BIS(DIMETHYLAMIDE), LIQUID, CF/KBr

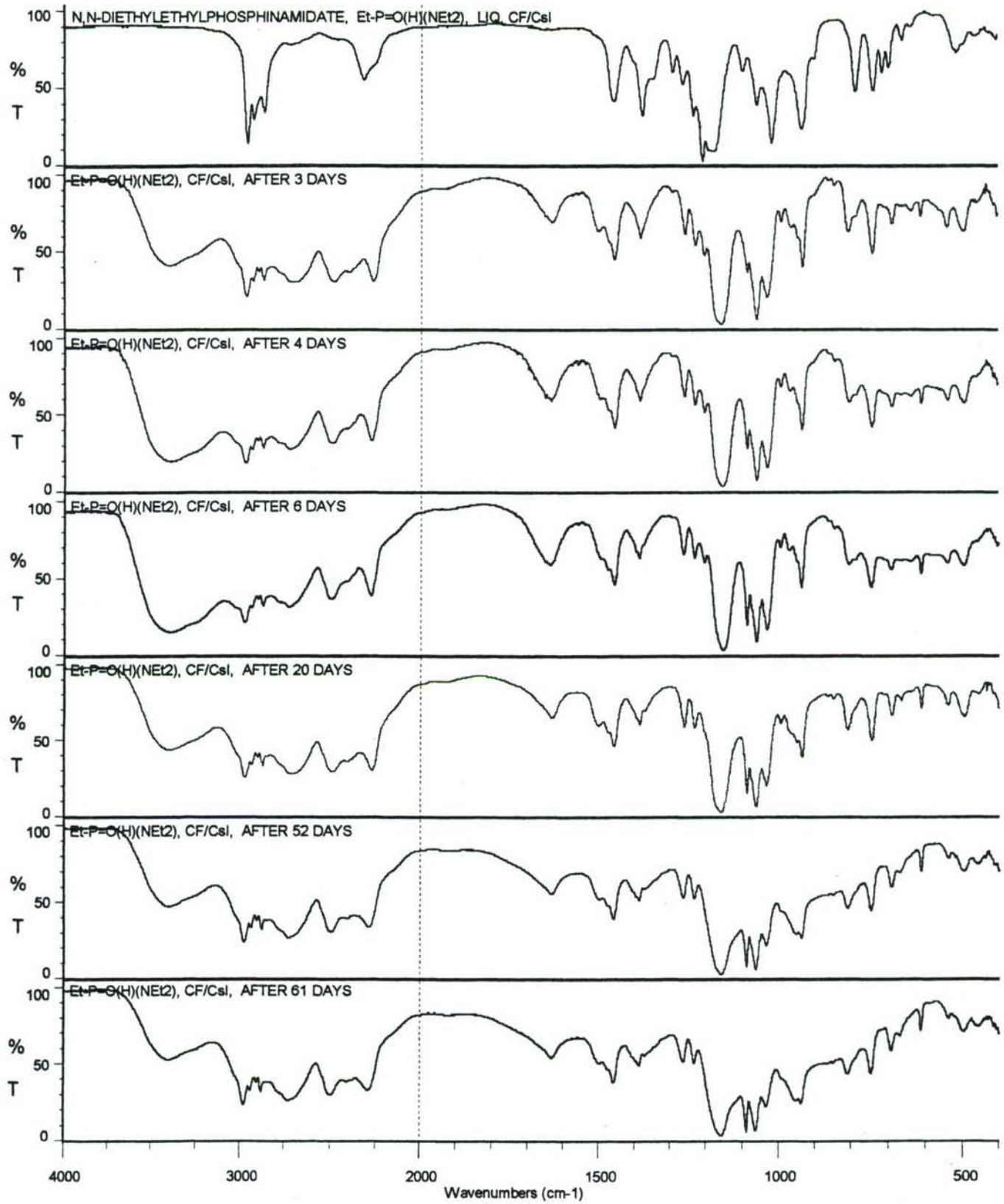

Figure 347 N,N-DIETHYLETHYLPHOSPHINAMIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

1207 cm^{-1} s (ν P=O, calculated value is 1206 cm^{-1}), ca 1170 cm^{-1} sh and 1066 cm^{-1} w [$PN(CH_3)_2$], 991 cm^{-1} sh and 971 cm^{-1} ms (ν_{as} P-N-C), 890 cm^{-1} m (P-CH_3 rock), 775 cm^{-1} ms (ν_{sy} P-N-C), 707 cm^{-1} m (ν P-C ?).

The effect of atmospheric moisture on a liquid film of methylphosphonic bis(dimethylamide) between KBr windows is illustrated by the infrared spectra presented in ***Figures 349A*** through ***349F***. After 7

Figure 349A METHYLPHOSPHONIC BIS(DIMETHYLAMIDE), LIQUID, CF/KBr, AFTER 7 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

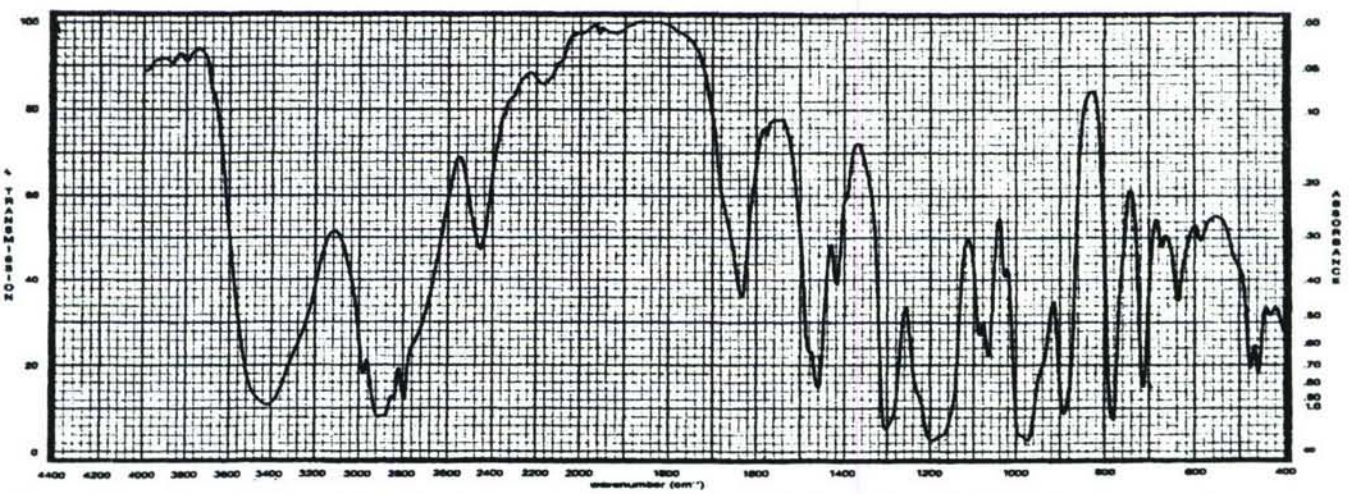

Figure 349B METHYLPHOSPHONIC BIS(DIMETHYLAMIDE), CF/KBr, AFTER 17 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

days of exposure to moisture, the spectrum (***Figure 349A***) shows the formation of a very weak band near 2465 cm^{-1} and much stronger bands due to water near 3400 and 1640 cm^{-1}. After 17 days of exposure, the spectrum (***Figure 349B***) shows broadening of the band near 3000-2800 cm^{-1} and an increase in the intensity of the 2465 cm^{-1} band. The water bands near 3400, ca 2170 and 1635 cm^{-1} have increased in intensity. The band near 1200

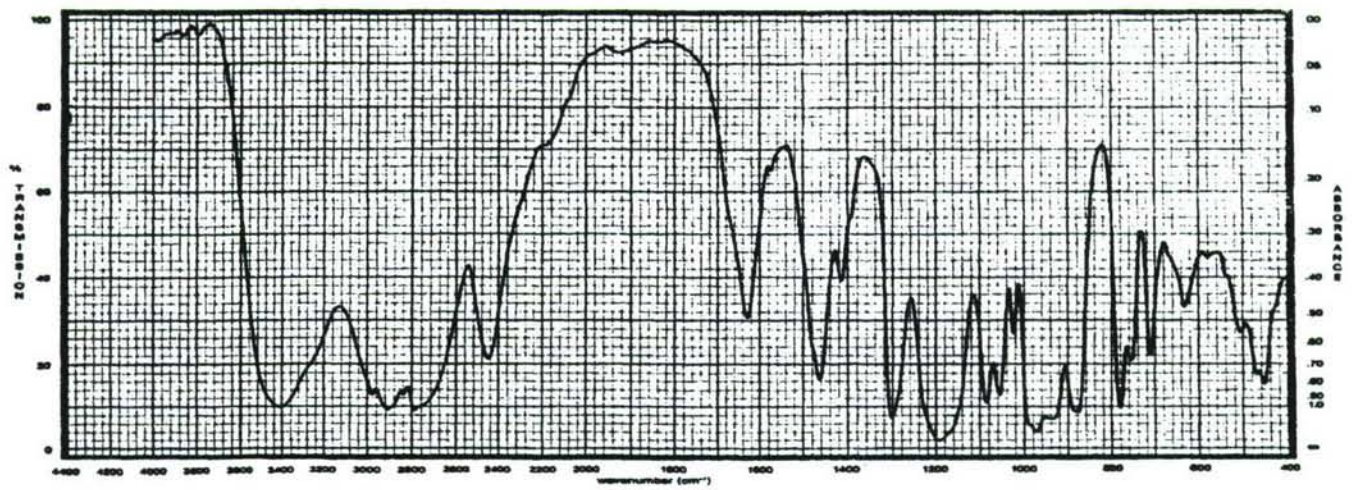

Figure 349C METHYLPHOSPHONIC BIS(DIMETHYLAMIDE), CF/KBr, AFTER 24 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

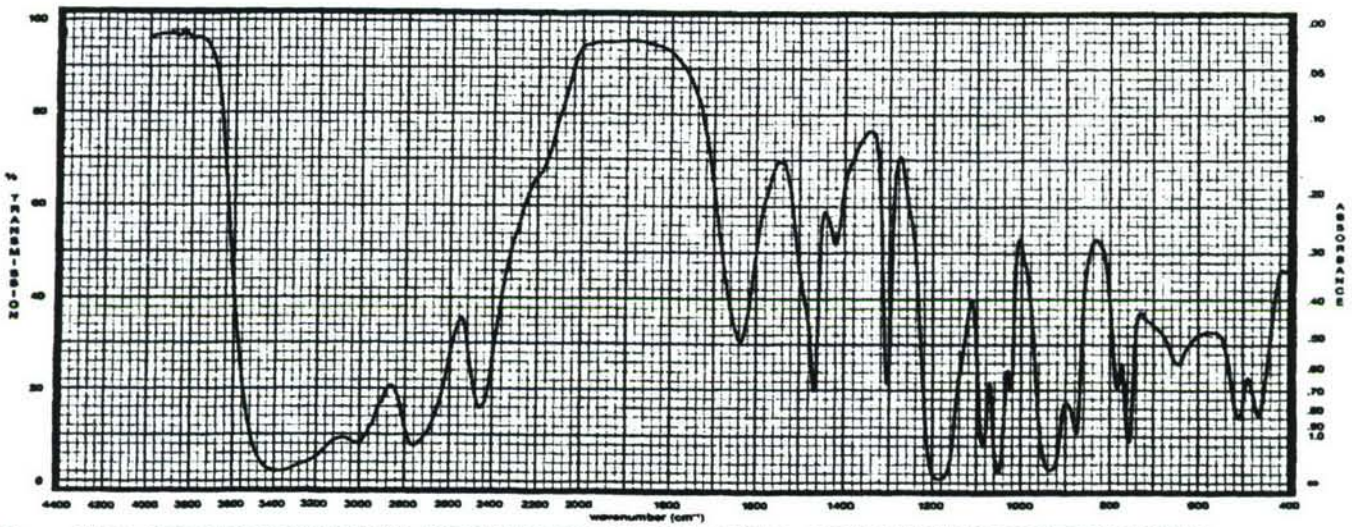

Figure 349D METHYLPHOSPHONIC BIS(DIMETHYLAMIDE), CF/KBr, AFTER 47 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

cm^{-1} has become somewhat broader. By the 24th day of exposure to atmospheric moisture, the infrared spectrum (***Figure 349C***) shows intense water bands near 3400 and 1633 cm^{-1}. The band near 3000-2800 cm^{-1} has resolved into two bands, with a third band occurring near 2460 cm^{-1}. These three bands may be due to the NH_2^+ group. By the 47th day of exposure to atmospheric moisture, the spectrum (***Figure 349D***) shows intense water bands near 3400 and 1640 cm^{-1}. The three bands believed to be due to the NH_2^+ group are now resolved and occur at 3026, 2783 and 2479 cm^{-1}. The band near 1300 cm^{-1}, originally assigned to both the P-CH_3 and $PN(CH_3)_2$ groups, has

become much sharper and is now assigned to just the P-CH_3 symmetric deformation (δ_{sy}). The bands due to the $PN(CH_3)_2$ group (1305, 991and 711 cm^{-1}) are gone from the spectrum. The strong bands at 1192 and 1057 cm^{-1} are assigned to the asymmetric and symmetric stretching of the PO_2^- group. The strong band near 940 cm^{-1} is believed to be due to a P-O(H) stretch. The band at 881 cm^{-1} is assigned to the P-CH_3 rock.

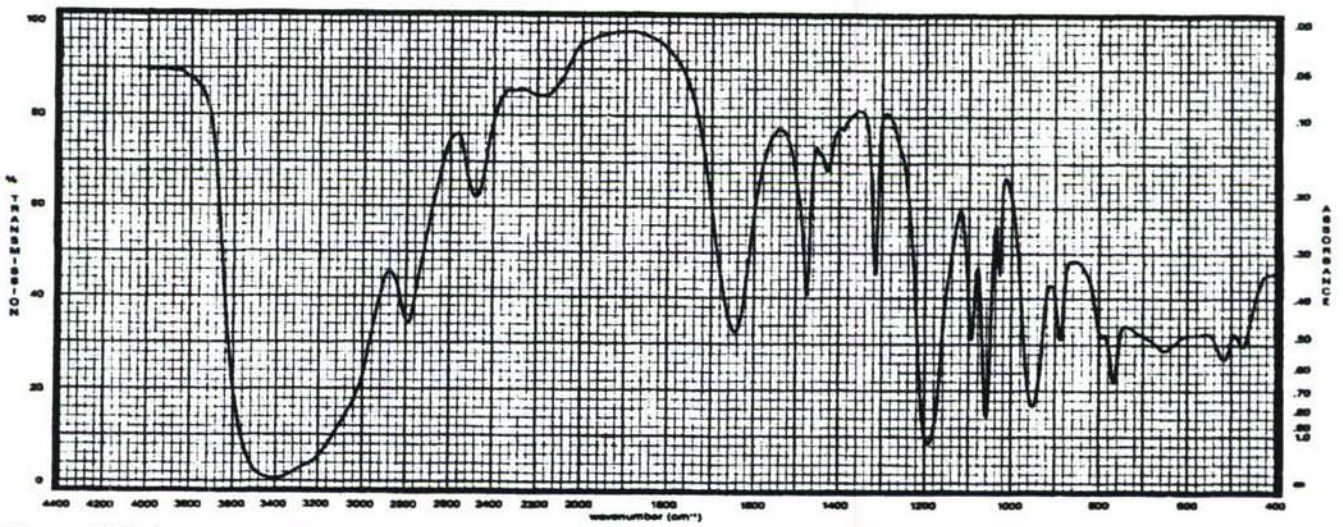

Figure 349E METHYLPHOSPHONIC BIS(DIMETHYLAMIDE), CF/KBr, AFTER 80 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE

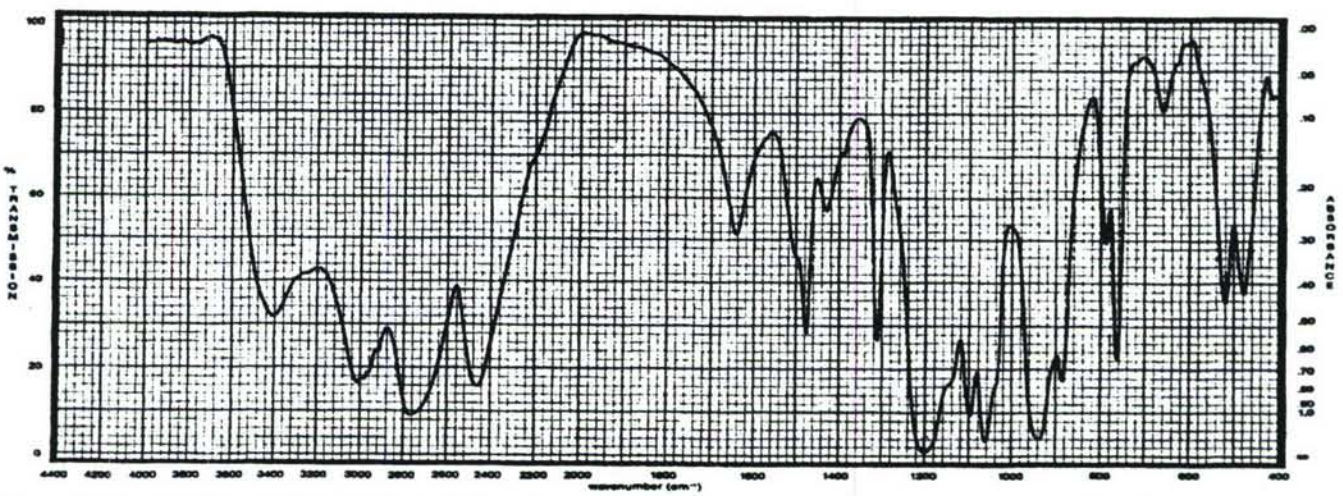

Figure 349F METHYLPHOSPHONIC BIS(DIMETHYLAMIDE), CF/KBr, AFTER 144 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE (SAMPLE DRIED FOR 26 DAYS OVER SILICA GEL IN A PLASTIC BAG)

The spectrum after 80 days of exposure to atmospheric moisture (***Figure 349E***) is similar to the spectrum for the 47 day period except for the increase in the water content. The infrared spectrum given in ***Figure 349F*** is for the sample after 144 days, but dried in a plastic bag containing silica gel for 26 days. The

sample holder containing the salt window/sample sandwich was placed in the plastic bag containing silica gel for the specified time. The spectrum represented as ***Figure 349F*** shows a great decrease in the water content of the sample, thus allowing better visualization of the NH_2^+ bands at 3017, 2772 and 2460 cm^{-1}. The spectrum again shows bands due to the P-CH_3 group (1425, 1307 and 879 cm^{-1}). Bands at 1195 and 1057 cm^{-1} are assigned to the asymmetric and symmetric stretching of the PO_2^- group respectively. The band at 932 cm^{-1} is believed to be due to the P-O stretching of P-OH group. The band at 1472 cm^{-1} is assigned to the N(CH_3) group. The hydrolysis of the methylphosphonic bis(dimethylamide) is believed to occur as follows:

$CH_3\text{-}P{=}O[N(CH_3)_2]_2$ -HOH→ $CH_3\text{-}P{=}O(OH)[N(CH_3)_2]$ + $HN(CH_3)_2\uparrow$ -HOH→

$CH_3\text{-}P{=}O(OH)_2$ + $HN(CH_3)_2$ → $[CH_3\text{-}PO_2^-(OH)]\,(CH_3)_2NH_2^+$

3.6.13 N,N-Dimethylphosphoramidic Dichloride $(CH_3)_2N\text{-}P{=}O(Cl)_2$

The infrared spectrum of a liquid film of N,N-dimethylphosphoramidic dichloride between KBr discs (windows) is presented as ***Figure 350***. The band assignments are as follows: 3007 cm^{-1} vw, 2938 cm^{-1} w, 2860 cm^{-1} vw and 2825 cm^{-1} vw (ν_{as} and ν_{sy} CH_3), 1715 cm^{-1} vvw (992 + 724 = 1716 cm^{-1}), 1480 and 1457 cm^{-1} m (δ CH_3), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1309 cm^{-1} ms [$PN(CH_3)_2$], 1267 cm^{-1} s (ν P=O, *calculated* value is 1278 cm^{-1}), 1171 and 1066 cm^{-1} m [$PN(CH_3)_2$], 992 cm^{-1} s (ν_{as} P-N-C), 724 cm^{-1} ms (ν_{sy} P-N-C), 561 cm^{-1} s (ν_{as} PCl_2), 518 cm^{-1} ms (ν_{sy} PCl_2).

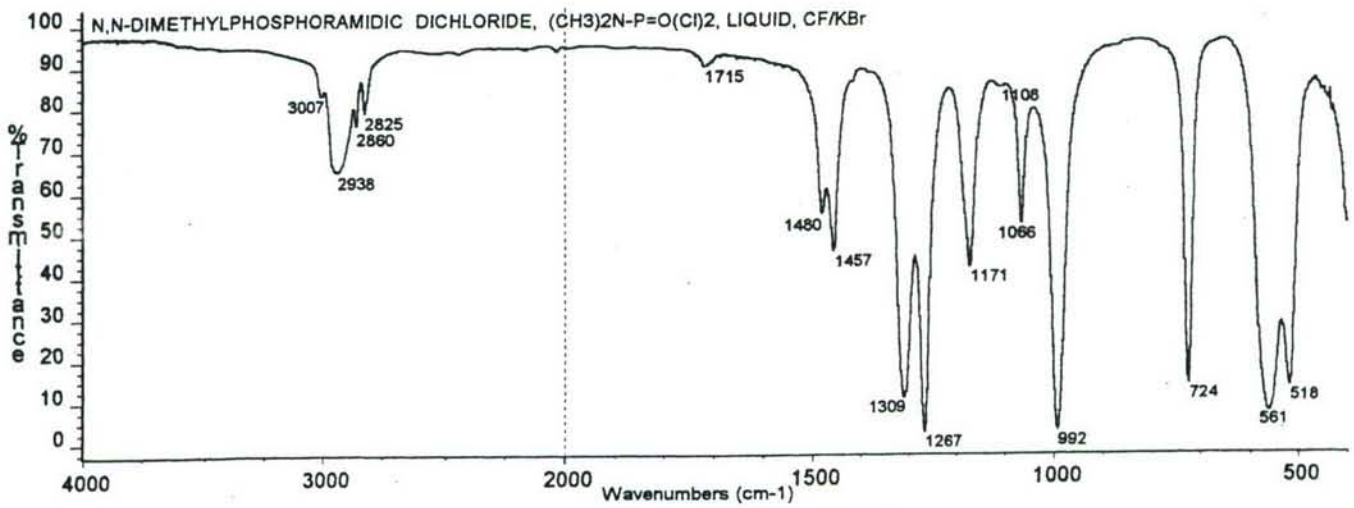

Figure 350 N,N-DIMETHYLPHOSPHORAMIDIC DICHLORIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on a liquid film of N,N-dimethylphosphoramidic dichloride between KBr windows is demonstrated by the infrared spectra given in ***Figure 351***. The compound appears to hydrolyze somewhere between the 5 and 23 hours of exposure to atmospheric moisture. The bands near 3020, 2780 and 2439 cm^{-1} may be assigned to the NH_2^+ group. The bands due to the PCl_2 group at 561 and 518 cm^{-1} are almost gone from the spectrum (after 23 hours) as are the bands due to the $PN(CH_3)_2$ group (1480, 1457, 1309, 1171, 1066, 992 and 724 cm^{-1}). By the second day of exposure to atmospheric moisture the remaining material may be a mix of $HO\text{-}P{=}O(OH)_2$ and $(CH_3)_2NH$, perhaps best represented as $[(HO)_2PO_2^-](CH_3)_2NH_2^+$.

3.6.14 N,N-Dimethyl phosphoramidic Difluoride $(CH_3)_2N\text{-}P{=}OF_2$

The infrared spectrum of N,N-dimethylphosphoramidic Difluoride as a liquid film between KBr windows is reproduced as ***Figure 352***. The band assignments are as follows: 3006 cm^{-1} sh, 2951 cm^{-1} m, 2927 cm^{-1} sh, 2878 and 2839 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1730 cm^{-1} vvw (1022 + 711 = 1733 cm^{-1}), 1491 and 1458 cm^{-1} m (δ CH_3), 1345 cm^{-1} s (ν P=O, *calculated* value is 1346 cm^{-1}), 1307 cm^{-1} ms, 1183 cm^{-1} m and 1078 cm^{-1} m [$PN(CH_3)_2$], 1022 cm^{-1} ms (ν_{as} P-N-C), 884 cm^{-1} s (ν PF_2), 711 cm^{-1} m (ν_{sy} P-N-C), 490 cm^{-1} m, 476 and 455 cm^{-1} ms (P=O, PF_2 deformations). The very weak bands at 575 and 520 cm^{-1} may be due to a PCl_2 impurity.

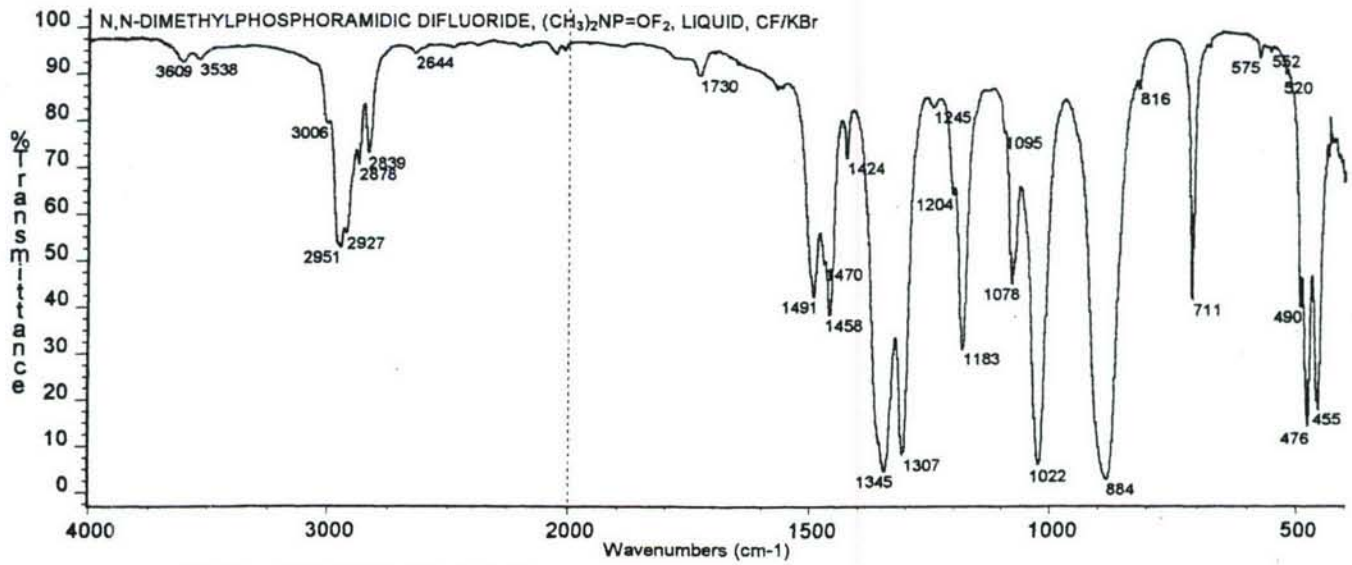

Figure 352 N,N-DIMETHYLPHOSPHORAMIDIC DIFLUORIDE, LIQUID, CF/KBr

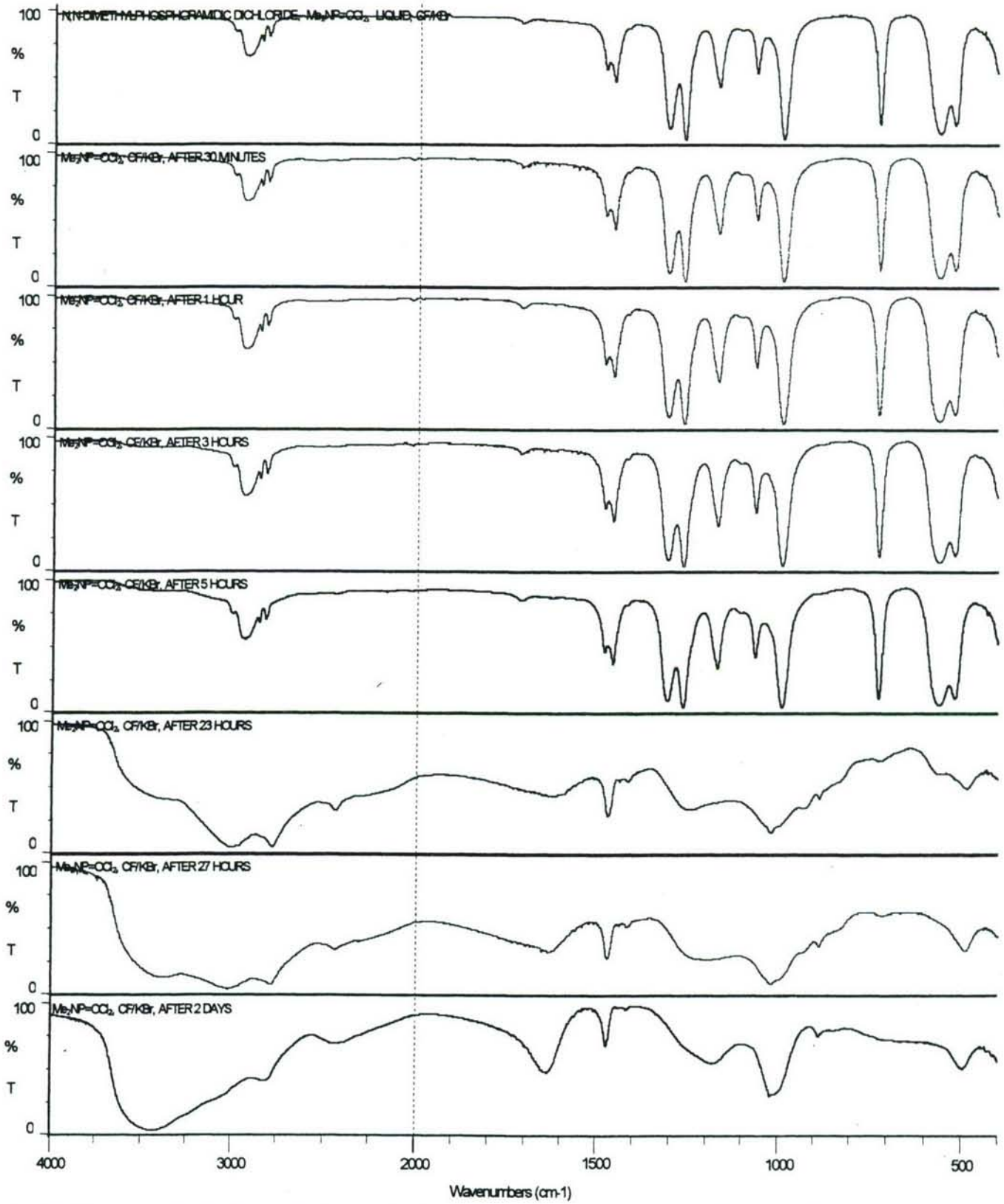

Figure 351 N,N-DIMETHYLPHOSPHORAMIDIC DICHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

The effect of atmospheric moisture of N,N-dimethylphosphoramidic difluoride as a liquid film between KBr windows is depicted by the infrared spectra presented in ***Figures 353A*** and ***353B***. After 1 day of exposure to atmospheric moisture, the spectrum (***Figure 353A***) shows bands at 3089, 2808 and 2487 cm^{-1} assignable to the NH_2^+ group. The bands at 3346, 2137 and 1636 cm^{-1} are due to water. The bands due to the $PN(CH_3)_2$ moiety (1307, 1183, 1078 and 711cm^{-1}) have disappeared from the spectrum. The 1022 cm^{-1} band is greatly reduced in intensity and is no longed related to the $PN(CH_3)_2$ moiety as the other bands assignable to this group are no longer present in the spectrum. The PF_2 is apparently still present in the spectrum as bands are evident at 870 and 842 cm^{-1} (ν_{as} and ν_{sy} PF_2). The P=O stretch at 1345 cm^{-1} is gone from the spectrum and has been replaced by the two bands at 1298 and 1140 cm^{-1}, which are assigned to the asymmetric and symmetric stretching of the PO_2^- anion. Thomas[hhh] lists compounds of the type $F_2PO_2^-$ as absorbing over the ranges 1323-1273 cm^{-1} (ν_{as} PO_2^-) and 1164-1137 cm^{-1} (ν_{sy} PO_2^-). So, after one day of exposure to atmospheric moisture the compound seems to have hydrolyzed to $[F_2PO_2^-](CH_3)_2NH_2^+$. As the time of exposure continues the bands at 870 and 842 cm^{-1} (PF_2) diminish in intensity as the P-F bonds are broken by hydrolysis. New bands are appearing near 1225 and 1108 cm^{-1} (a new ν_{as} and ν_{sy} PO_2^-) and near 948 cm^{-1} (ν P-OH). The NH_2^+ group is still indicated by the bands near 2808 and 2468 cm^{-1}. The hydrolysis may be summarized as follows:

$(CH_3)_2N\text{-}P{=}OF_2$ -HOH→ $HO\text{-}P{=}OF_2$ + $(CH_3)_2NH$ → $[F_2PO_2^-](CH_3)_2NH_2^+$ -HOH→ $[(OH)(F)PO_2^-](CH_3)_2NH_2^+$ -HOH→ $[(HO)_2PO_2^-](CH_3)_2NH_2^+$.

3.6.15 N,N-dimethylmethylphosphonamidic Cyanide $CH_3\text{-}P{=}O(C{\equiv}N)[N(CH_3)_2]$

The infrared spectrum of N,N-dimethylmethylphosphonamidic cyanide as a liquid film between **NaCl** windows is given in ***Figure 354***. The band assignments are as follows: 2989 cm^{-1} m, 2955 cm^{-1} sh, 2918 cm^{-1} ms, 2861 and 2823 cm^{-1} m (ν_{as} and ν_{sy} CH_3), 2188 cm^{-1} ms (ν C≡N), 1664 cm^{-1} vw (990 + 678 = 1668 cm^{-1}), 1483 and 1460 cm^{-1} m-ms [δ CH_3 of $N(CH_3)_2$], 1410 cm^{-1} w (δ_{as} P-CH_3), 1310 cm^{-1} s [δ_{sy} P-CH_3 and $PN(CH_3)_2$],

[hhh] Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 160, Heyden & Son Ltd., London, 1974.

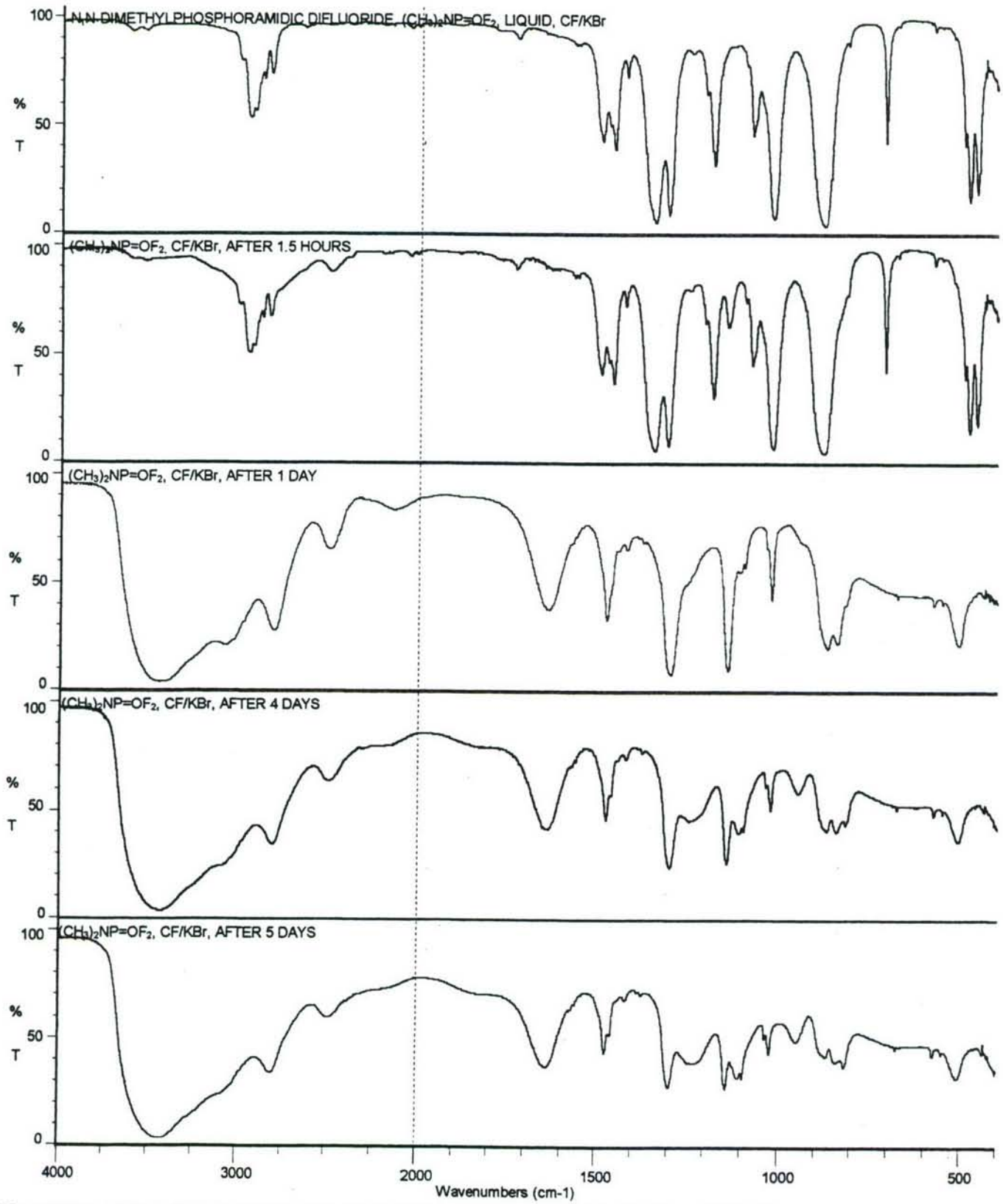

Figure 353 A N,N-DIMETHYLPHOSPHORAMIDIC DIFLUORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

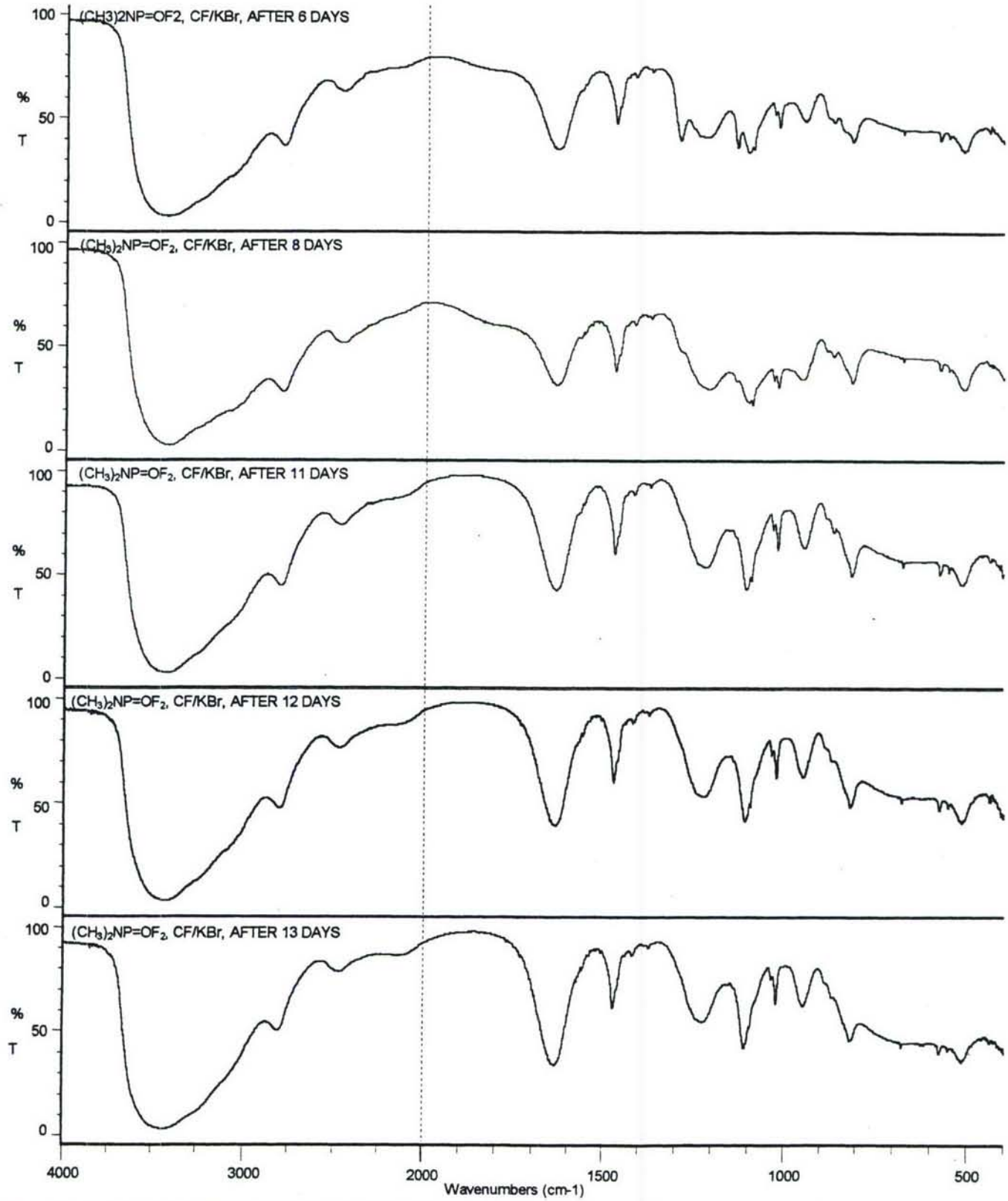

Figure 353B N,N-DIMETHYLPHOSPHORAMIDIC DIFLUORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

1237 cm^{-1} s (ν P=O, *calculated* value is 1250 cm^{-1}), 1174 and 1066 cm^{-1} m [$PN(CH_3)_2$], 990 cm^{-1} s (ν_{as} P-N-C), 894 cm^{-1} ms (P-CH_3 rock), 793 cm^{-1} ms (ν P-C), 678 cm^{-1} ms (ν_{sy} P-N-C).

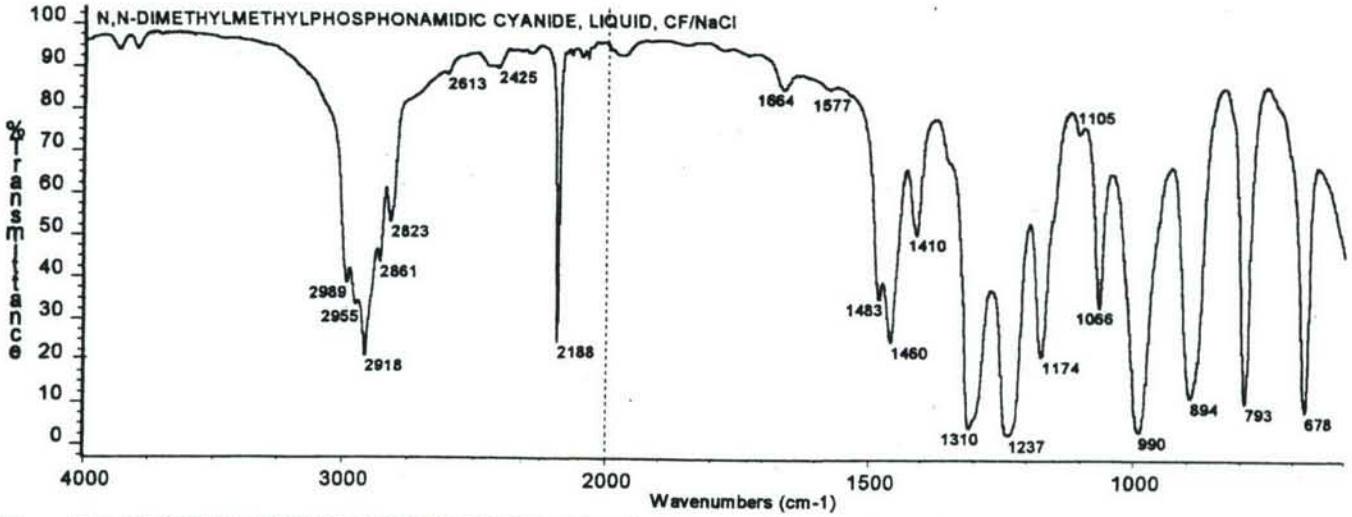

Figure 354 N,N-DIMETHYLMETHYLPHOSPHONAMIDIC CYANIDE, LIQUID, CF/NaCl

3.6.16 Tetramethylphosphorodiamidic Chloride $Cl\text{-}P{=}O[N(CH_3)_2]_2$

The infrared spectrum of tetramethylphosphorodiamidic chloride as a liquid film between KBr windows is reproduced as ***Figure 355***. The band assignments are as follows: 3002 cm^{-1} w, 2936 and 2899 cm^{-1} m, 2854 and 2814 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1741 cm^{-1} vvw (993 + 755 = 1748 cm^{-1}), 1480 and 1459 cm^{-1} m (δ CH_3), 1303 cm^{-1} ms [$PN(CH_3)_2$], 1240 cm^{-1} s (ν P=O, *calculated* value is 1258 cm^{-1}), 1171 and 1066 cm^{-1} m [$PN(CH_3)_2$], 993 cm^{-1} s (ν_{as} P-N-C), 755, 672 cm^{-1} ms (ν_{sy} P-N-C), 537 cm^{-1} ms (ν P-Cl).

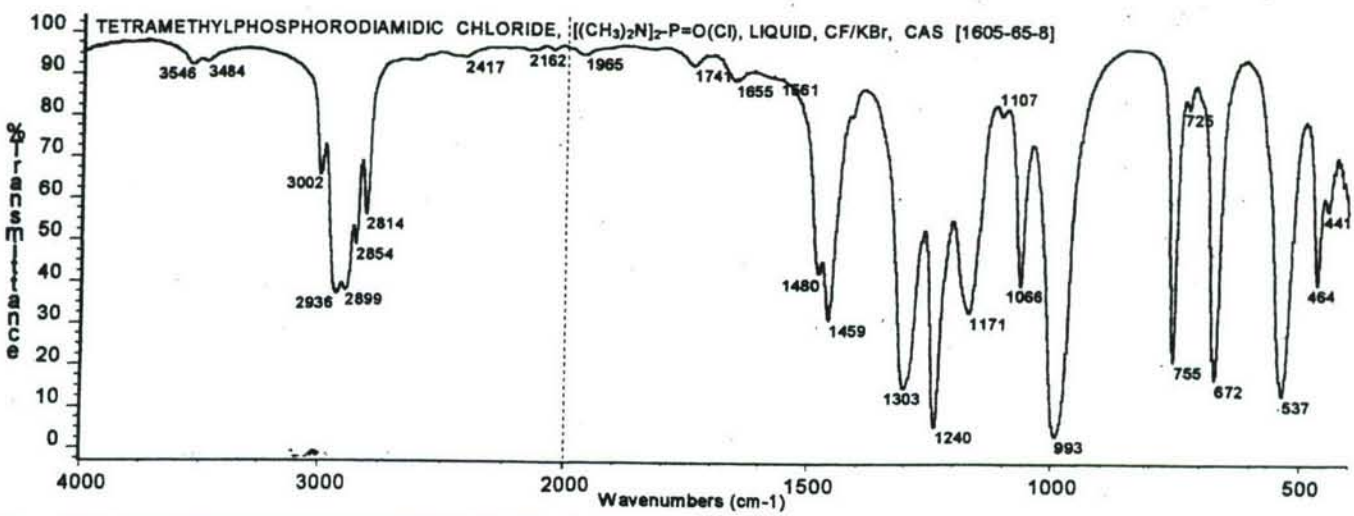

Figure 355 TETRAMETHYLPHOSPHORODIAMIDIC CHLORIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on tetramethylphosphorodiamidic chloride, as a liquid film between KBr windows, is illustrated by the infrared spectra given in ***Figures 356A***, ***356B*** and ***356C***. By 18 hours of exposure to atmospheric moisture, the spectrum (***Figure 356A***) shows a new weak band at 2459 cm^{-1}, with some broadening of the CH band in the vicinity of 3000-2800 cm^{-1}. Some change is also occurring near 930 cm^{-1}. By the 11th day (***Figure 356B***) these effects have become quite evident with new bands near 3000, 2780 and 2440 cm^{-1} which can be attributed to the NH_2^+ group. A weak band near 1590 cm^{-1} may be due to the NH_2^+ deformation.[iii] The bands indicative of the $PN(CH_3)_2$ moiety have been just about eliminated from the spectrum as has the P-Cl band at 537 cm^{-1}. The P=O band at 1240 cm^{-1} has been replaced by two bands near 1260 and 1086 cm^{-1}, which can be assigned to the PO_2^- moiety. Bands near 1035 and 950 cm^{-1} may be due to P-OH stretching vibrations (***Figure 356C***). The final product may best be represented as $[(HO)_2PO_2^-](CH_3)_2NH_2^+$.

3.6.17 Hexamethylphosphoramide (**HMPA**) $[(CH_3)_2N]_3P=O$

The infrared spectrum of hexamethylphosphoramide (**HMPA**) as a liquid film between KBr discs (windows) is reproduced as ***Figure 357***. The band assignments are as follows: 3498 cm^{-1} vw (H_2O), 2995 cm^{-1} m, 2880 cm^{-1} ms, 2842 and 2801 cm^{-1} ms (ν_{as} and ν_{sy} CH_3), 1483 cm^{-1} sh and 1460 cm^{-1} m (δ CH_3), 1296 cm^{-1} s [$(PN(CH_3)_2]$, 1211 cm^{-1} s (ν P=O, *calculated* value is 1218 cm^{-1}), 1170 and 1067 cm^{-1} m [$(PN(CH_3)_2]$, 984 cm^{-1} s (ν_{as} P-N-C), 745 cm^{-1} s (ν_{sy} P-N-C), 482 cm^{-1} ms (CNC, P=O deformations ?).

3.6.18 Trimethylsilyl N,N-dimethylphosphoramidofluoridate $(CH_3)_2N$-P=O(F)[O-Si$(CH_3)_3$]

The infrared spectrum of a liquid film of trimethylsilyl N,N-dimethylphosphoramidofluoridate between CsI windows is reproduced in ***Figure 358***. The band assignments are as follows: 2998 cm^{-1} sh, 2963 cm^{-1} ms, 2905 cm^{-1} ms, 2862 and 2824 cm^{-1} m (ν_{as} and ν_{sy} CH_3), 1689 cm^{-1} w (the band at 855 is probably composed of the Si$(CH_3)_3$ and ν P-F, so the 1689 band is possibly a combination of these two vibrations), 1487

[iii] Secondary amine salts such as hydrochlorides have strong multiple bands between 3000 and 2700 cm^{-1} (ν_{as} and ν_{sy} NH_2^+), weaker bands at 2700-2300 cm^{-1} (combination bands) and a medium band at 1620-1560 cm^{-1} due to the NH_2^+ deformation. Cothup, N.B., Daly, L.H., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", p. 325, second edition, Academic Press, New York, 1975.

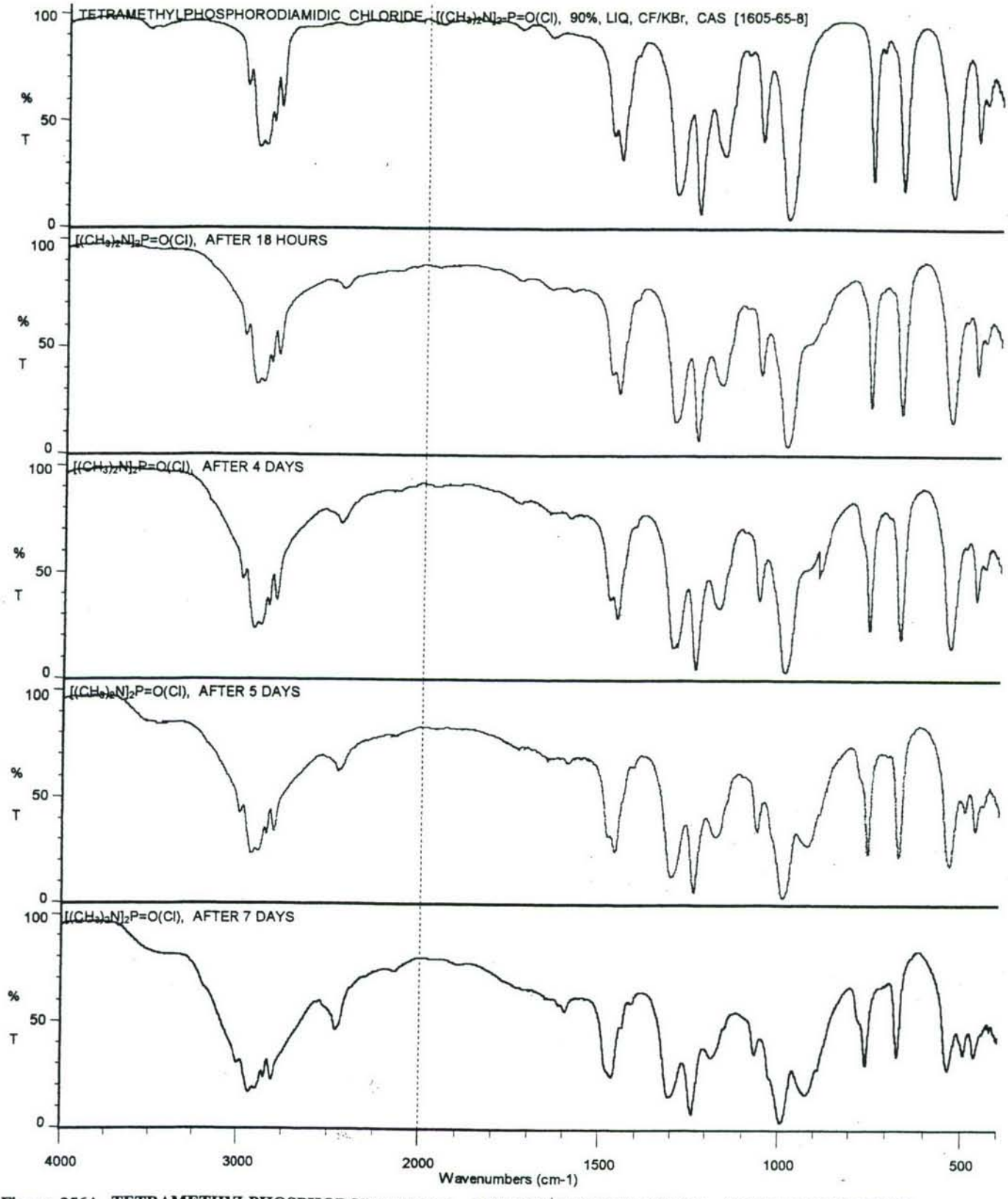

Figure 356A TETRAMETHYLPHOSPHORODIAMIDIC CHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

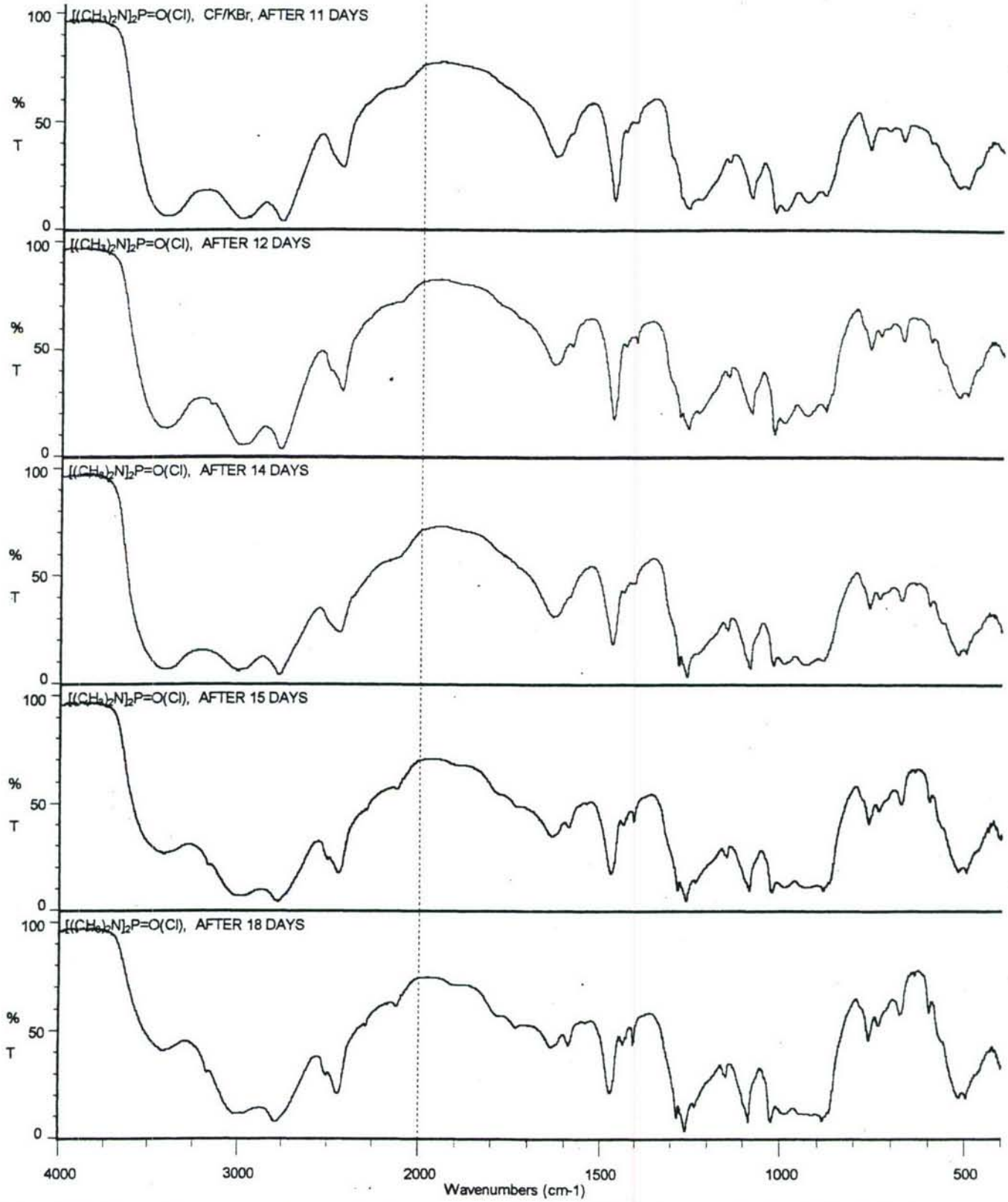

Figure 356B TETRAMETHYLPHOSPHORODIAMIDIC CHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

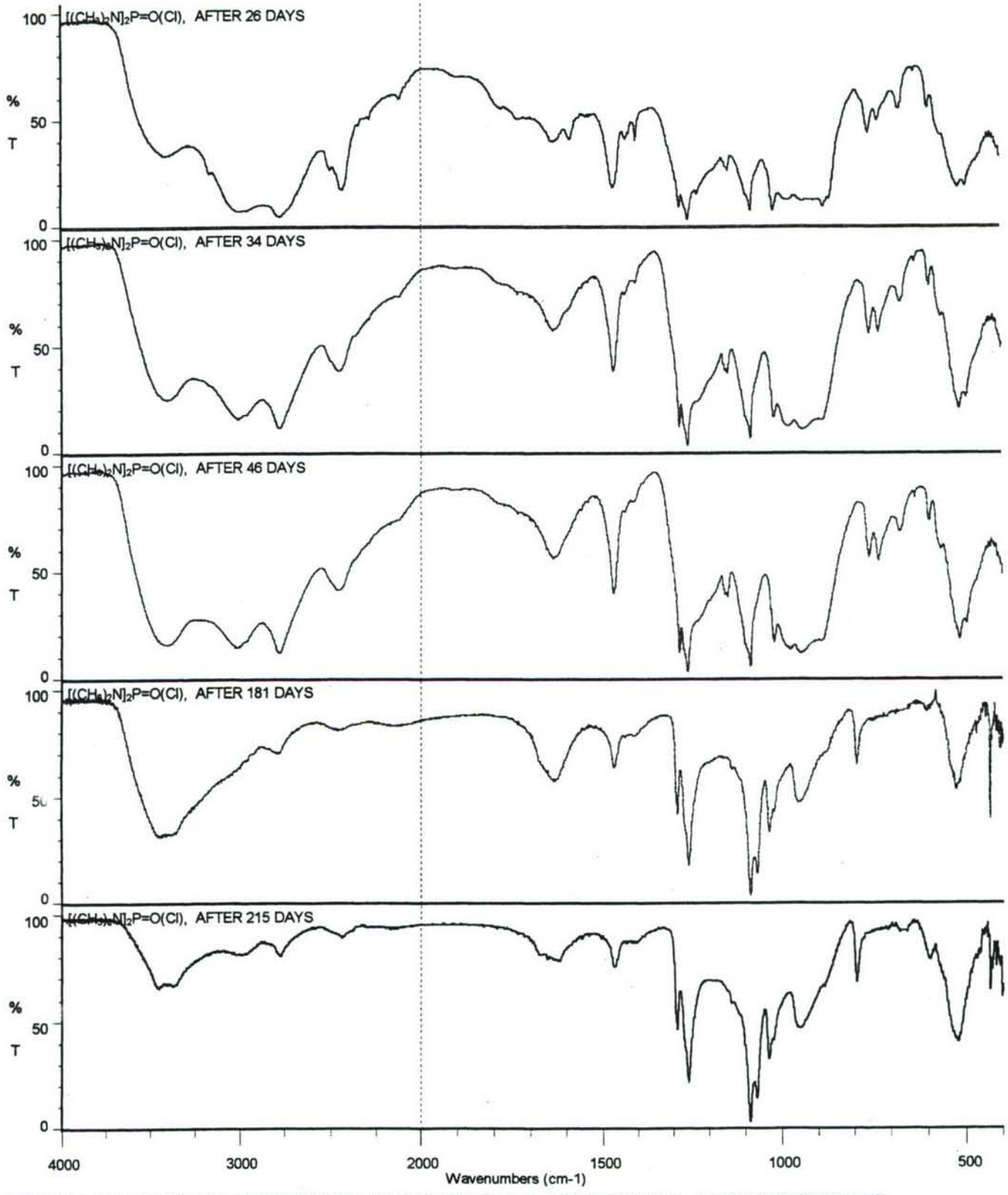

FIG 356C TETRAMETHYLPHOSPHORODIAMIDIC CHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

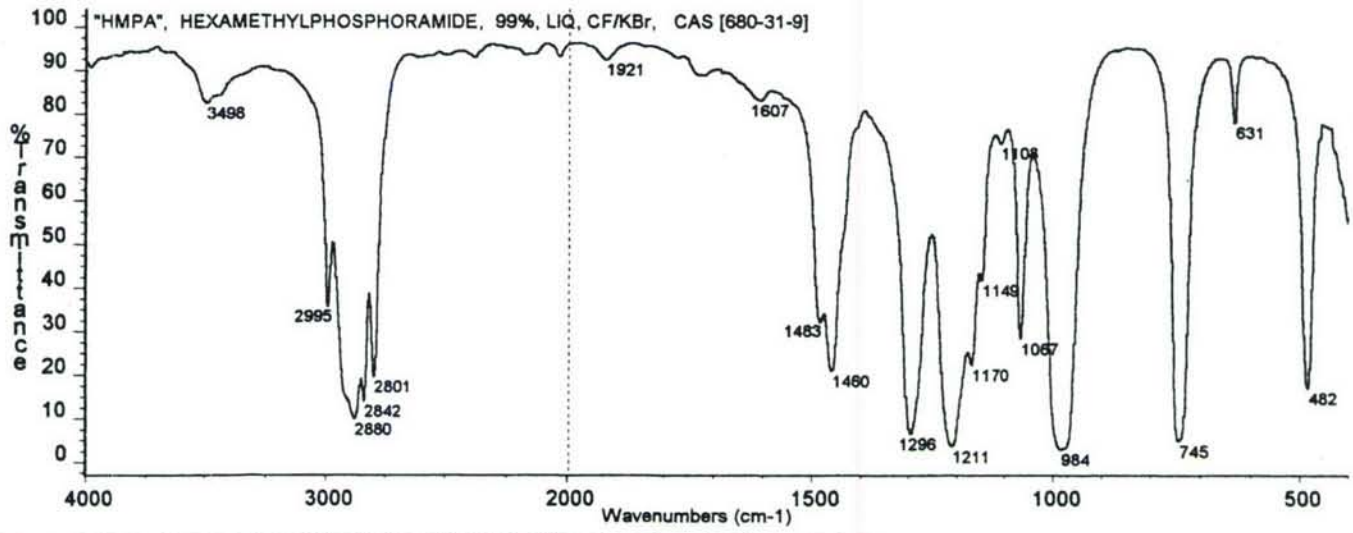

Figure 357 HEXAMETHYLPHOSPHORAMIDE (HMPA), 99%, LIQUID, CF/KBr

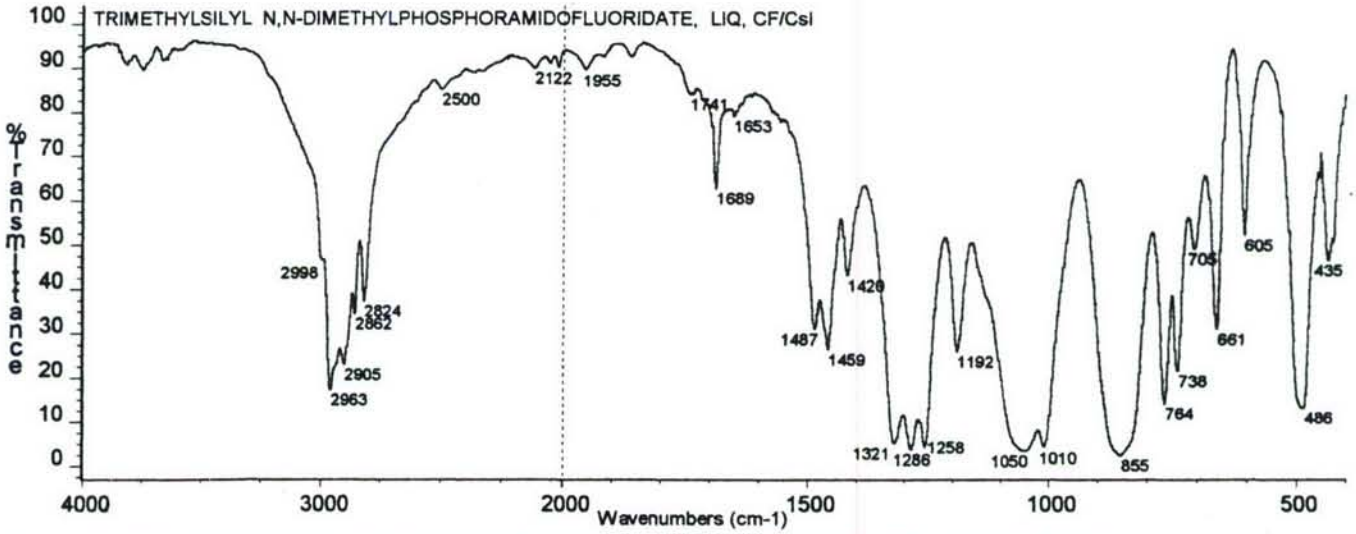

Figure 358 TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI

and 1459 cm^{-1} m [δ CH_3 from $N(CH_3)_2$], 1420 cm^{-1} w (δ_{as} Si-CH_3), 1321 cm^{-1} s [$PN(CH_3)_2$], 1286 s (ν P=O, *calculated* value is 1302 cm^{-1}), 1258 cm^{-1} s (δ_{as} Si-CH_3), 1192 cm^{-1} w [$PN(CH_3)_2$], 1050 cm^{-1} s (ν P-O-Si), 1010 cm^{-1} s (ν_{as} P-N-C), 855 cm^{-1} s [possibly composed of the Si-C stretching mode and the CH_3 rocking mode of the $Si(CH_3)_3$ group and the P-F stretching mode], 764 cm^{-1} m [$Si(CH_3)_3$], 705 cm^{-1} w (ν_{sy} P-O-Si ?), 661 cm^{-1} m (ν_{sy} P-N-C), 486 cm^{-1} ms (P=O deformation ?).

The effect of atmospheric moisture on a liquid film of trimethylsilyl N,N-dimethylphosphoramido-

fluoridate between CsI windows is illustrated by the infrared spectra presented in ***Figures 359A*** and ***359B***. After 1.5 hours of exposure to atmospheric moisture the infrared spectrum (***Figure 359A***) shows bands near 3000, 2800 and 2492 cm^{-1} due to the formation of the NH_2^+ group. By 19 hours of exposure (***Figure 359A***), the infrared spectrum shows only one broad band near 1280 cm-1 instead of the original three bands at 1321, 1286 and 1258 cm^{-1}. New bands also appear near 1144 and 1103 cm^{-1}. The P-F stretching vibration still appears to be present near 830 cm^{-1}, unless this band is from a Si-OH vibration.[iii] The bands of the $PN(CH_3)_2$ moiety are gone from the spectrum. As time progresses, the water bands near 3400 and 1640 cm^{-1} become very intense in the spectra. New bands are evident in the spectra after the 19th day (***Figure 359B***) at 1091 and 611 cm^{-1}. The two bands are due to the formation of cesium sulfate, Cs_2SO_4, from the cesium iodide windows used to contain the liquid sample. Perhaps, the hydrolysis of trimethylsilyl N,N-dimethylphosphoramidofluoridate may be summarized as follows:

$(CH_3)_2NP=O(F)[OSi(CH_3)_3]$ -HOH→ $HO\text{-}P=O(F)[OSi(CH_3)_3]$ + $HN(CH_3)_2$ -HOH→ $HOP=O(F)(OH)$ + $HOSi(CH_3)_3$ -HOH→ $HOP=O(OH)_2 + HN(CH_3)_2 \rightarrow [HO\text{-}PO_2^-(OH)](CH_3)_2NH_2^+$.

3.6.19 2,2-Dichlorovinyl N,N-dimethylphosphoramidofluoridate $(CH_3)_2N\text{-}P=O(F)(O\text{-}CH=CCl_2)$

The infrared spectrum of 2,2-dichlorovinyl N,N-dimethylphosphoramidofluoridate as a thin liquid film between sodium chloride windows is presented in ***Figure 360.*** The band assignments are as follows: 3063 cm^{-1} w (ν =C-H), 3001 cm^{-1} vw, 2945 cm^{-1} m, 2921 cm^{-1} sh, 2869 and 2832 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1647 cm^{-1} m (ν C=C), 1489 and 1457 cm^{-1} m (δ CH_3), 1335 cm^{-1} ms [$PN(CH_3)_2$], 1286 cm^{-1} ms (ν P=O), 1185 and 1074 cm^{-1} w-m [$PN(CH_3)_2$], 1144 cm^{-1} s (ν PO-C=), 1015 cm^{-1} (ν P-OC=), 981 cm^{-1} ms (ν_{as} P-N-C), 881 and 848 cm^{-1} ms (ν P-F and ν CCl_2), 814 cm^{-1} sh (=C-H wag), 727 and 714 cm^{-1} m (ν_{sy} P-N-C), 656 cm^{-1} w (CCO deformation?).

3.6.20 Diphenylphosphoryl Azide $N=N=N\text{-}P=O(O\text{-}C_6H_5)_2$

The infrared spectrum of a liquid film of diphenylphosphoryl azide between KBr windows is given

[iii] The Si-OH group has a strong band at 910-830 cm^{-1}. A broad medium -weak band occurs near 1030 cm^{-1} (Si-OH deformation) in the condensed state. Colthup, N.B., Daly, L.H., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", pp. 341,342, Second Edition, Academic Press, New York, 1975.

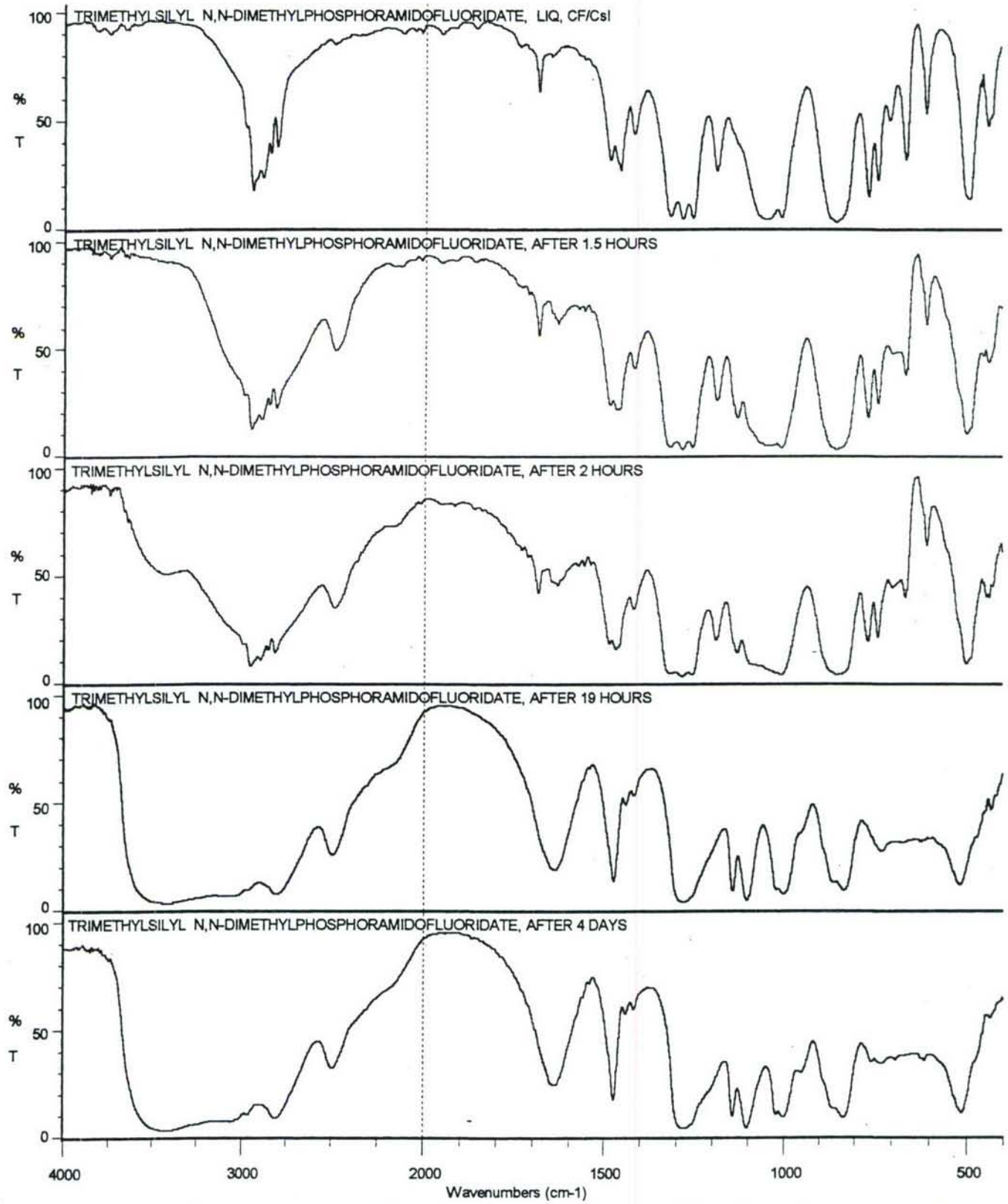

Figure 359A TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

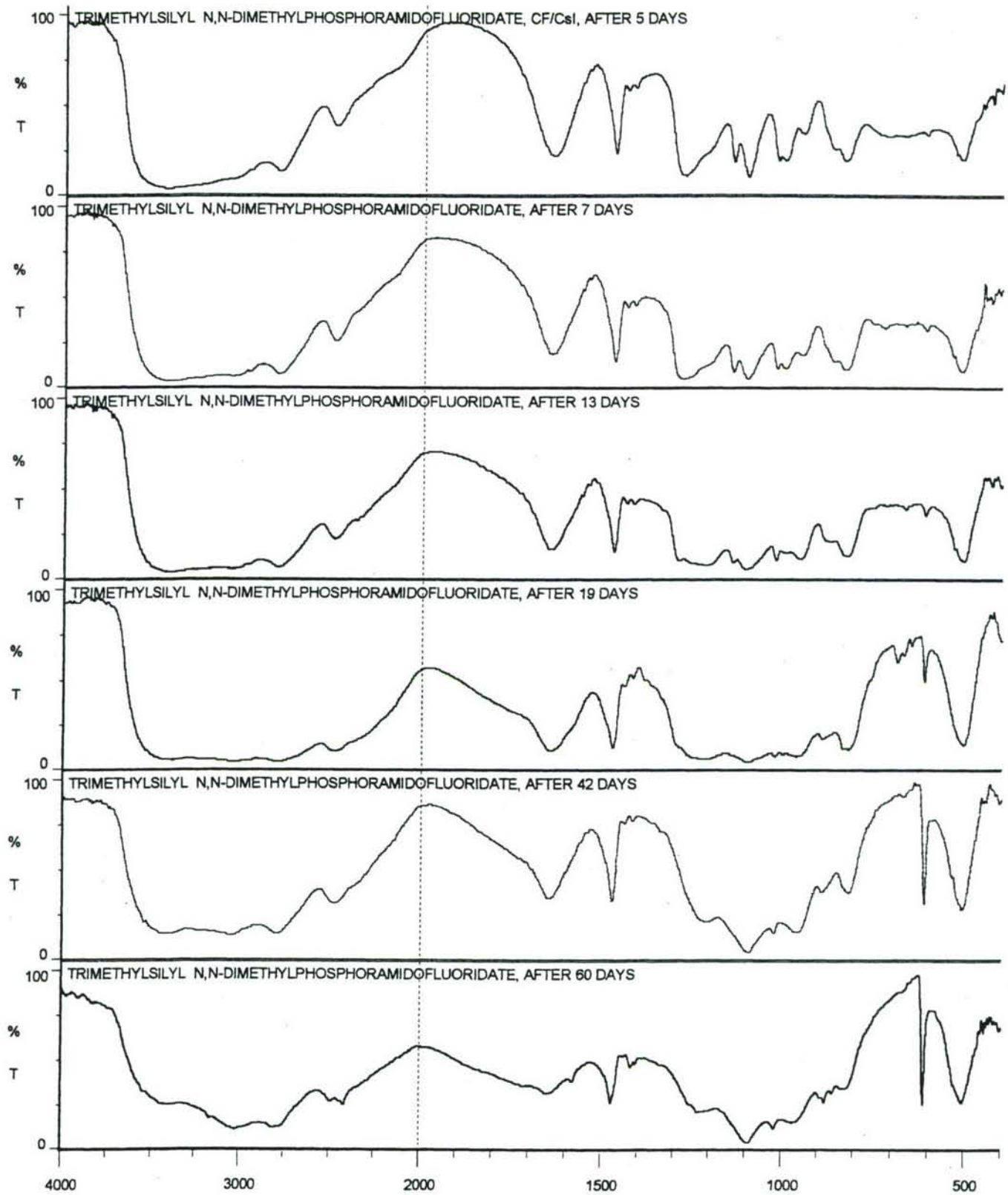

Figure 359B TRIMETHYLSILYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

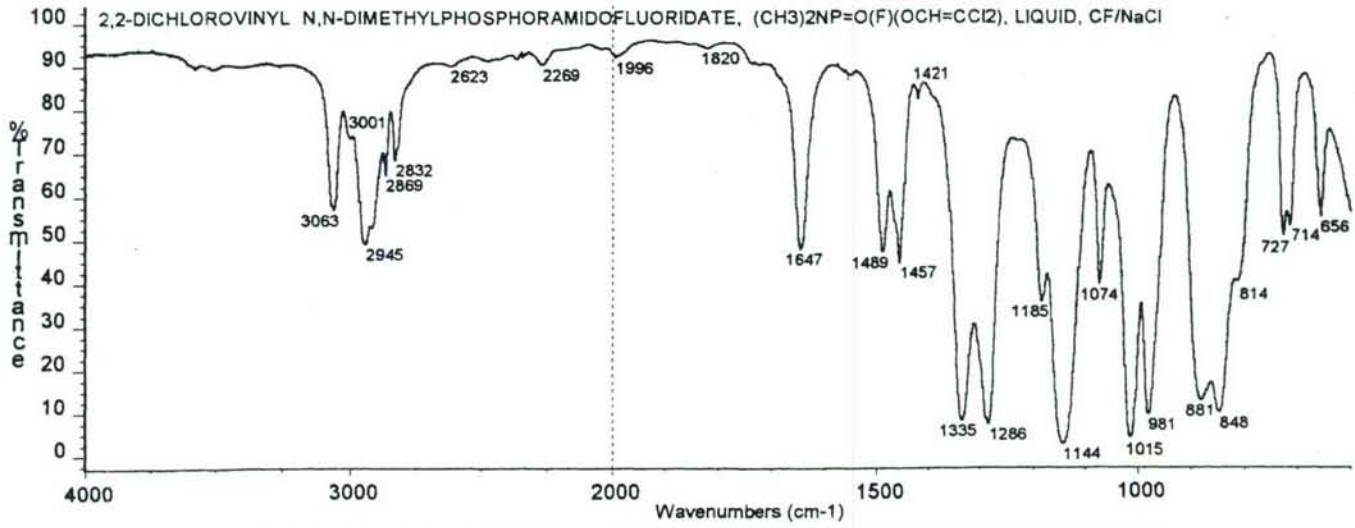

Figure 360 2,2-DICHLOROVINYL N,N-DIMETHYLPHOSPHORAMIDOFLUORIDATE, LIQUID, CF/NaCl

in Figure 361. The band assignments are as follows: 3096 cm^{-1} sh, 3069 cm^{-1} w and 3044 cm^{-1} sh (ν C-H aromatic), 2171 cm^{-1} s ($\nu_{o.o.p.}$ N=N=N),[kkk] 1590 cm^{-1} ms, 1489 cm^{-1} s and 1456 cm^{-1} w (aromatic ring), 1301 cm^{-1} ms (ν P=O, *calculated* value is 1290 cm^{-1}), 1273 cm^{-1} ms ($\nu_{i.p.}$ N=N=N), 1206 and 1183 cm^{-1} s (ν C-O), 1161 cm^{-1} m, 1071 cm^{-1} w, 1025 and 1010 cm^{-1} m (β C-H of mono-substituted aromatic ring), 967 cm^{-1} s (ν P-O), 785 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 688 cm^{-1} ms (mono-substituted aromatic ring deformation).

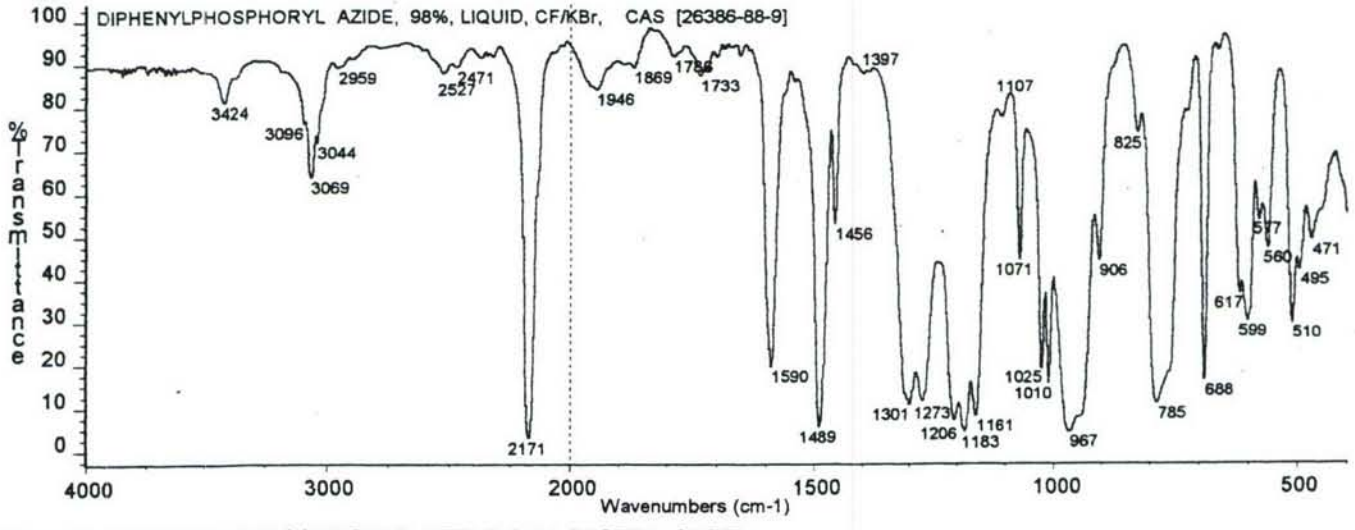

Figure 361 DIPHENYLPHOSPHORYL AZIDE, 98%, LIQUID, CF/KBr

[kkk] Azides have an out-of-phase N=N=N stretching vibration in the region of 2169-2080 cm^{-1} (*vs*). The in-phase mode occurs as a weak band in the region of 1343-1177 cm^{-1}. Lin-Vien, D., Colthup, N.B., Fateley, W.G., and Grasselli, J.G., "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules", p 221 Academic Press, Inc., San Diego, CA, 1991.

3.6.21 2-Cyanoethyl N,N,N',N'-tetraisopropylphosphorodiamidite $N\equiv C\text{-}CH_2\text{-}CH_2\text{-}O\text{-}P[N(i\text{-}C_3H_7)_2]_2$

The infrared specrtrum of a liquid film of 2-cyanoethyl N,N,N',N'-tetraisopropylphosphorodiamidite or bis(diisopropylamino)(2-cyanoethoxy)phosphine between KBr windows is given in ***Figure 362***. The band assignments are as follows: 2968 cm^{-1} s, 2931 cm^{-1} ms, and 2872 cm^{-1} m (ν CH_3 and ν CH_2), 2720 and 2610 cm^{-1} vw [these two bands seem to appear when the N(isopropyl)$_2$ moiety is present],[lll] 2253 cm^{-1} w (ν C≡N), 1459 cm^{-1} m (δ CH_2, CH_3), 1414 cm^{-1} vw (δ CH_2-C≡N), 1392 cm^{-1} m (ω OCH_2), 1379 and 1363 cm^{-1} m-ms (δ_{sy} CH_3), 1218 cm^{-1} sh, 1184 cm^{-1} s, 1157 cm^{-1} m, 1118 cm^{-1} ms [PN(isopropyl)$_2$],[mmm] 1060 cm^{-1} ms (ν P-O-C), 955 cm^{-1} s (ν_{as} P-N-C), 890 cm^{-1} m (CH_3 rock of isopropyl group), 868 cm^{-1} m (ν C-C of $POCH_2CH_2C{\equiv}N$?), 846 cm^{-1} w (POC ?), 720 cm^{-1} m (ν_{sy} P-N-C).

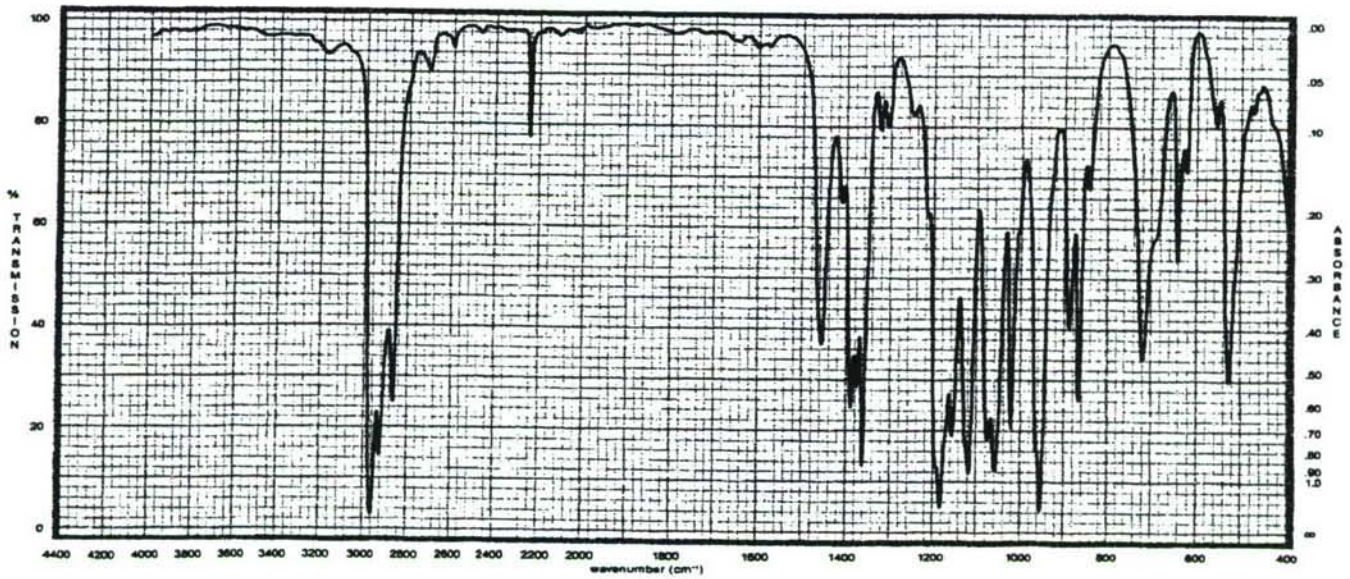

Figure 362 2-CYANOETHYL N,N,N',N'-TETRAISOPROPYLPHOSPHORODIAMIDITE, 98%, LIQUID, CF/KBr

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[lll] Compounds containing the N(isopropyl)$_2$ moiety are discussed in "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part II. V-Agents and Related Compounds", Piffath, R.J. , 1999, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, Unpublished data.

[mmm] L.C. Thomas in "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 125, Heyden & Son Ltd., 1974, lists the PN(isopropyl)$_2$ group as having bands near 1200, 1183, 1160, 1139 (sh) and 1129 cm^{-1}. The P-N vibration is assigned to the 1000-971 cm^{-1} region.

3.6.22 Isopropyl Methylphosphonohydrazine [(Isopropoxymethylphosphinyl)hydrazine)]

$CH_3P{=}O[O\text{-}CH(CH_3)_2](NH\text{-}NH_2)$

The infrared spectrum of isopropyl methylphosphonohydrazine [(isopropoxymethylphosphinyl)hydrazine] as a solid between CsI discs (windows) is given in ***Figure 363***. Band assignments are as follows: 3328 cm^{-1} w (ν_{as} NH_2), 3294 cm^{-1} vw (2 x 1641 = 3281 cm^{-1}), 3199 cm^{-1} m (ν N-H), 3158 cm^{-1} w (ν_{sy} NH_2), 2988 cm^{-1} sh, 2971 cm^{-1} w, 2930 cm^{-1} vw, 2869 and 2836 cm^{-1} vw (ν CH_3), 1641 cm^{-1} w (δ NH_2), 1466, 1450 cm^{-1} vw (δ_{as} CH_3), 1424 cm^{-1} vw (δ_{as} P-CH_3), 1387 and 1372 cm^{-1} w (δ_{sy} CH_3), 1339 cm^{-1} vw (δ -C-H ?), 1304 cm^{-1} m (δ_{sy} P-CH_3), 1188 cm^{-1} s (ν P=O, *calculated* value is 1200 cm^{-1} assuming a π value of 1.9 for the -NH-NH_2 group), 1108 cm^{-1} m (from isopropyl part of P-O-isopropyl), 1001 cm^{-1} m (ν P-O-C), 931 cm^{-1} m (ν P-N), 907 cm^{-1} m (P-CH_3 rock), 766 cm^{-1} w (POC ?), 702 cm^{-1} w (ν P-C), 510 cm^{-1} w (P=O deformation ?).

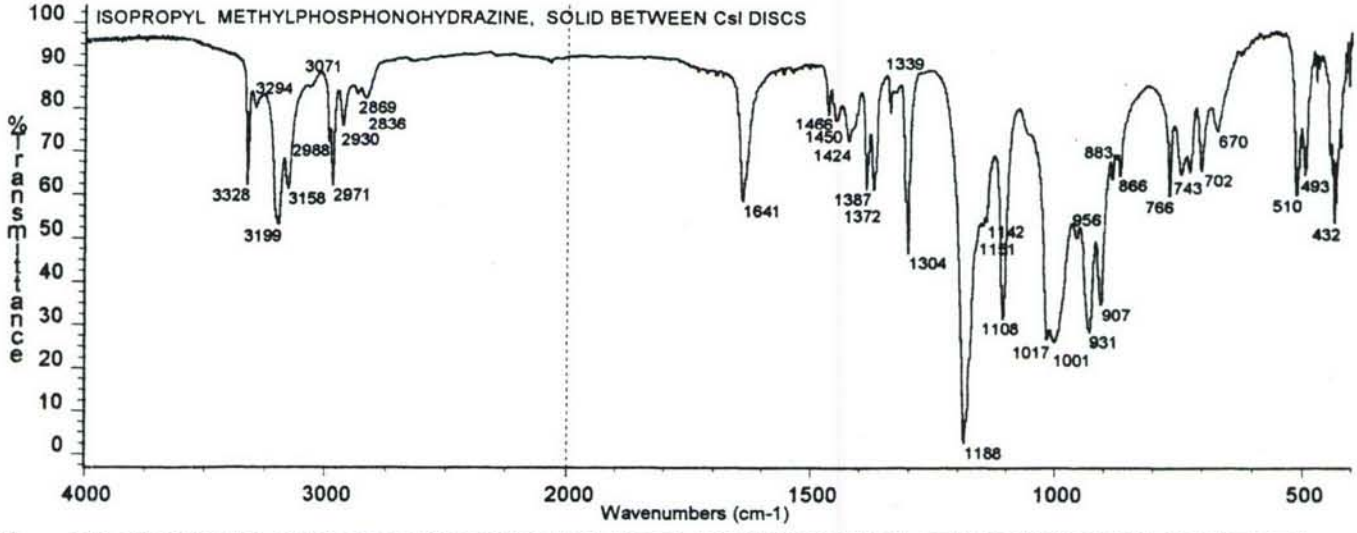

Figure 363 ISOPROPYL METHYLPHOSPHONOHYDRAZINE [ISOPROPOXYMETHYLPHOSPHINYL)HYDRAZINE] , SOLID BETWEEN CsI DISCS (WINDOWS)

3.6.23 Diethyl Phosphoramidate (Diethyl Amidophosphate) $H_2N\text{-}P{=}O(O\text{-}CH_2\text{-}CH_3)_2$

The infrared spectrum of diethyl phosphoramidate (diethyl amidophosphate) as a KBr pellet and as a solid between KBr discs (windows) is given in ***Figure 364***. Band assignments for the sample determined as a KBr pellet are as follows: 3340 and 3255 cm^{-1} w (ν_{as} and ν_{sy} NH_2), 3147 cm^{-1} w (2 x 1572 = 3144 cm^{-1}), 2984 cm^{-1} w (ν_{as} CH_3), 2941 cm^{-1} vvw (ν_{as} CH_2), 2906 cm^{-1} vw (ν_{sy} CH_3), 2873 cm^{-1} vvw (ν_{sy} CH_2), 1572 cm^{-1} m

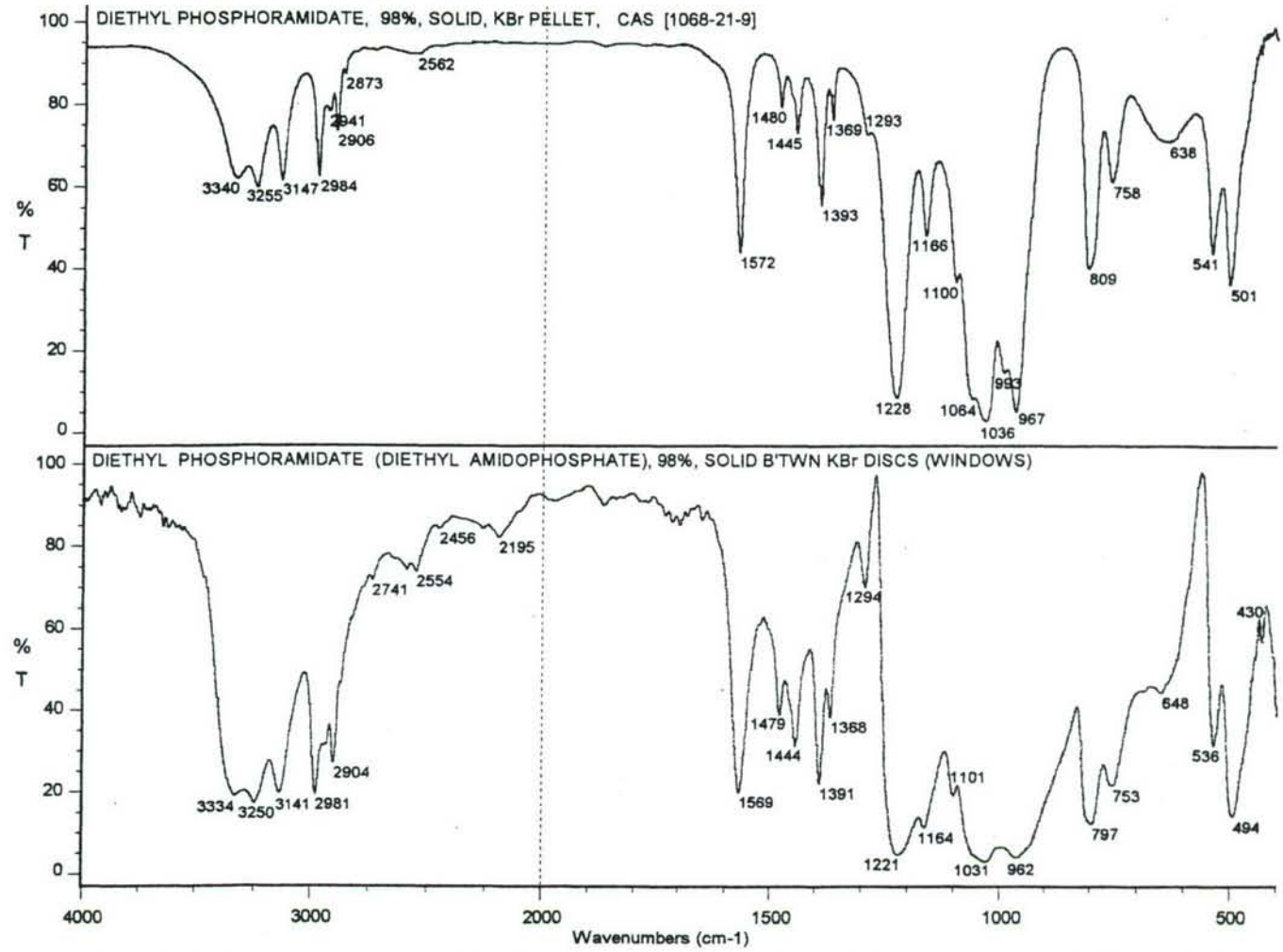

Figure 364 DIETHYL PHOSPHORAMIDATE (DIETHYL AMIDOPHOSPHATE), 98%, *UPPER SPECTRUM*--**KBr PELLET,** *LOWER SPECTRUM*--**AS A SOLID BETWEEN KBr DISCS (WINDOWS)**

(δ NH_2), 1480 cm^{-1} vw (δ OCH_2), 1445 cm^{-1} vw (δ_{as} CH_3), 1393 cm^{-1} w (ω OCH_2), 1369 cm^{-1} vw (δ_{sy} CH_3), 1228 cm^{-1} ms (ν P=O, *calculated* value is 1232 cm^{-1}), 1166 and 1100 cm^{-1} w (CH_3 rock of POEt, characteristic), 1064 cm^{-1} sh and 1036 cm^{-1} s (ν P-O-C), 998 cm^{-1} sh (ν P-N), 967 cm^{-1} ms (ν C-C of POEt), 809 cm^{-1} m and 758 cm^{-1} w (POC, the 758 band may be due to P-N),[nnn] 638 cm^{-1} w and broad (ω NH_2), 541 cm^{-1} m (CCO bending ?), 501 cm^{-1} m (P=O deformation).

Figure 365 depicts the infrared spectra of diethyl phosphoramidate after exposure of the compound

[nnn] Corbridge, D. E. C., "The Infrared Spectra of Organophosphorus Compounds" , in Topics in Phosphorus Chemistry (Eds. Grayson, M. and Griffith, E.), Vol. 6, p. 343, Table XXXIV, John Wiley & Sons, Inc., New York, 1969, lists the P-N band as occurring at 749 cm^{-1} , no higher frequency band is given.

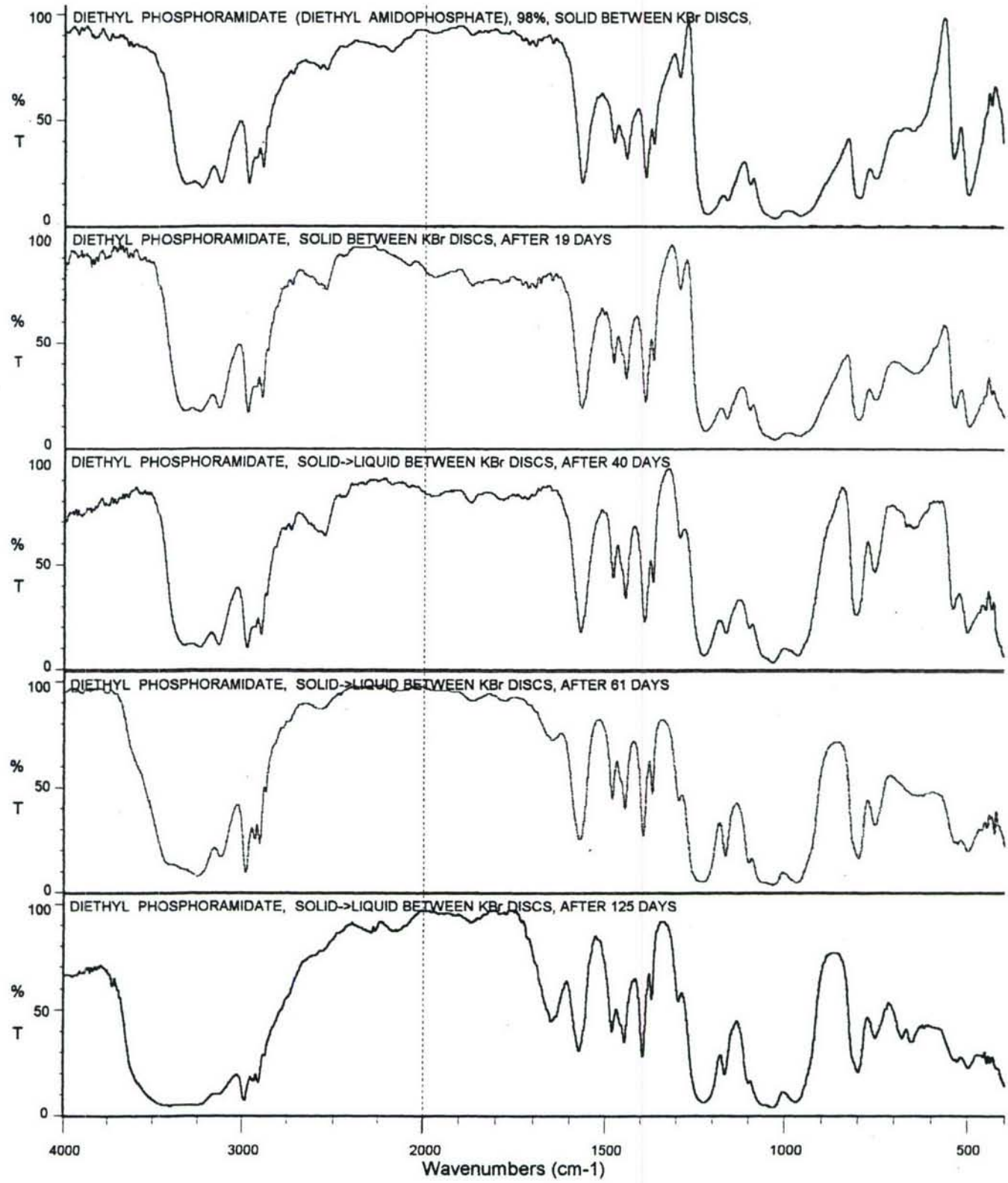

Figure 365 DIETHYL PHOSPHORAMIDATE (DIETHYL AMIDOPHOSPHATE), AS A SOLID BETWEEN KBr DISCS (WINDOWS), AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

to atmospheric moisture for a period of 125 days. The compound shows little change over the 125 day period save for the large amount of water as indicated by the bands near 3400 and 1650 cm^{-1}.

3.6.24 Phenyl Phosphorodiamidate $C_6H_5O\text{-}P{=}O(NH_2)_2$

The infrared spectrum of phenyl phosphorodiamidate as a KBr pellet and a solid between KBr discs (windows) is presented as ***Figure 366***. Band assignments for the KBr pellet infrared spectrum are as follows: 3369 cm^{-1} ms (ν_{as} NH_2), 3231 cm^{-1} m (ν_{sy} NH_2), 3120 cm^{-1} w (2 x 1569 = 3138 cm^{-1}), 1593 cm^{-1} m, 1491 cm^{-1} ms and 1454 cm^{-1} w (aromatic ring), 1569 cm^{-1} w (δ NH_2), 1401 cm^{-1} vw (NH_4^+ from hydrolysis ?), 1233 cm^{-1} (ν C-O), 1183 cm^{-1} s (ν P=O, *calculated* value is 1198 cm^{-1}), 1164, 1149, 1069, and 1025 cm^{-1} w (β C-H mono-substituted aromatic ring), 974 cm^{-1} m and 953 cm^{-1} ms (ν P-O and P-N), 774 and 766 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 732 cm^{-1} w (P-N ?), 616 cm^{-1} vw (ω NH_2), 501 cm^{-1} w (P=O deformation ?).

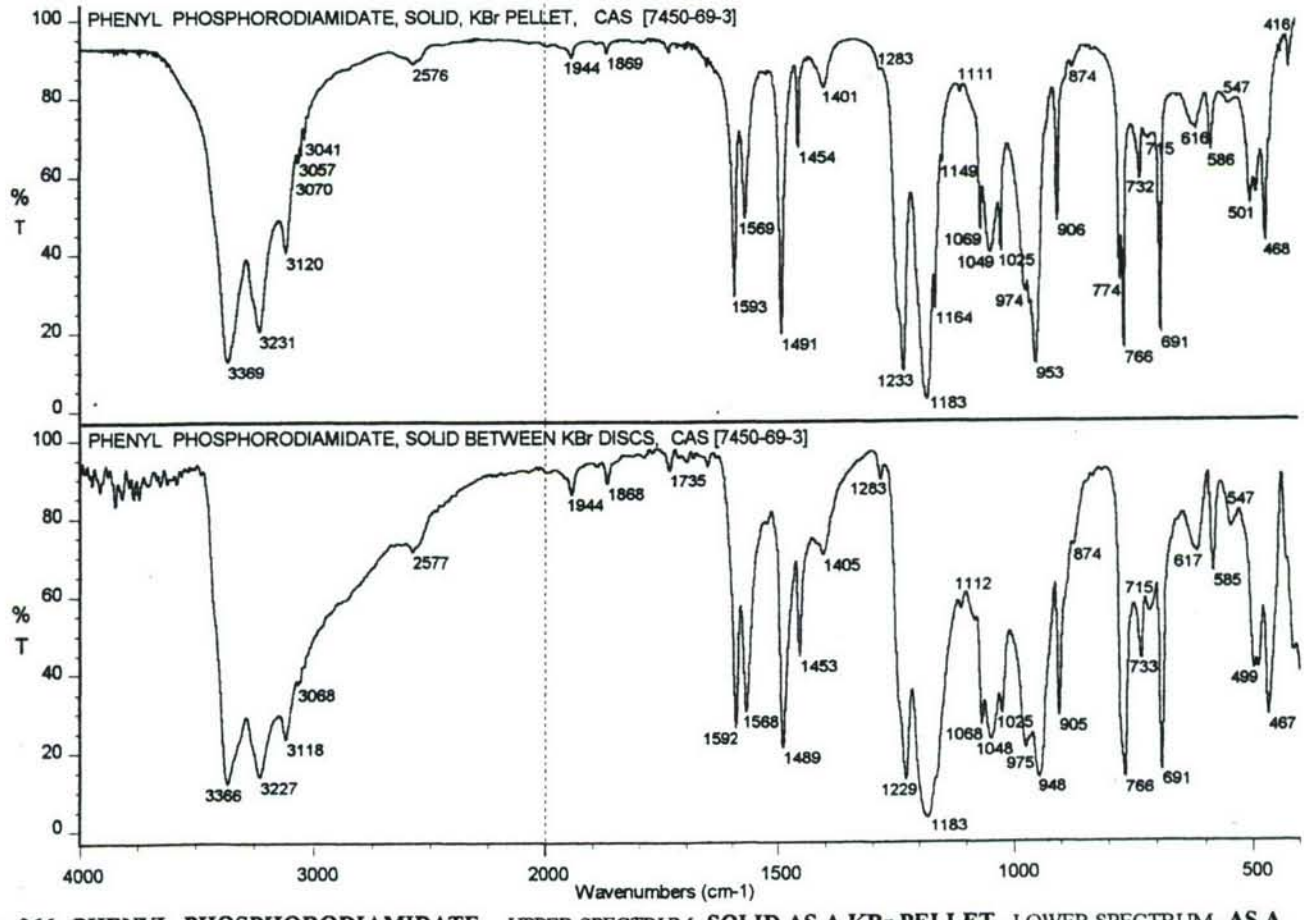

Figure 366 PHENYL PHOSPHORODIAMIDATE, UPPER SPECTRUM--**SOLID AS A KBr PELLET,** LOWER SPECTRUM--**AS A SOLID BETWEEN KBr DISCS (WINDOWS)**

The effect of atmospheric moisture on phenyl phosphorodiamidate is illustrated by the infrared spectra presented in ***Figure 367A*** (KBr pellet), and ***Figures 367B*** and ***367C*** (solid between KBr windows). The sample determined as a KBr pellet (***Figure 367A***) remains essentially unchanged except for a band near 1400 cm^{-1} that gradually increases in intensity over the 125 days of the study. The band at 1400 cm^{-1} can be assigned to a deformation mode of the NH_4^+ moiety. This band is more evident in the spectra pertaining to the sample determined as a solid between KBr windows (***Figure 367B***). By the 325th day of exposure to atmospheric moisture (***Figure 367B***) the band at 1400 cm^{-1} is quite strong. The POphenyl group still appears to be present as indicated by the bands at 1595, 1490, 1454, 755 and 689 cm^{-1}. Two bands appear near 1146 and 1071 cm^{-1} that can be assigned to the PO_2^- group. The resultant compound can perhaps be expressed as follows:

$C_6H_5O\text{-}P{=}O(NH_2)_2$ -HOH→ $C_6H_5O\text{-}P{=}O(OH)(NH_2)$ -HOH→ $C_6H_5O\text{-}P{=}O(OH)(OH)$ + NH_3

→ $[C_6H_5O\text{-}PO_2^-(OH)]NH_4^+$.

3.6.25 Diphenyl Phosphoramidate (Diphenyl Amidophosphate) $H_2N\text{-}P{=}O(O\text{-}C_6H_5)_2$

The infrared spectrum of diphenyl phosphoramidate as a KBr pellet and a solid between CsI discs (windows) is presented as ***Figure 368***. Band assignments for the KBr pellet are as follows: 3431 cm^{-1} ms (ν_{as} NH_2), 3242 cm^{-1} m (ν_{sy} NH_2), ca 3108 cm^{-1} vvw (2 x 1546 = 3092 cm^{-1}), 3070, 3058 and 3042 cm^{-1} vvw (ν C-H aromatic), 1593 cm^{-1} m, 1493 cm^{-1} ms and 1455 cm^{-1} w (aromatic ring C≈C), 1546 cm^{-1} w (δ NH_2), 1399 cm^{-1} vw (NH_4^+ from hydrolysis), 1256 cm^{-1} ms (ν C-O), 1221 cm^{-1} s (ν P=O, calculated value is 1244 cm^{-1}), 1166, 1160, 1069, 1025, 1012 and 1012 cm^{-1} w (β C-H mono-substituted aromatic ring), 984 cm^{-1} w (P-N), 957 cm^{-1} s (ν P-O), 774 cm^{-1} ms (γ C-H mono-substituted ring), 689 cm^{-1} m (mono-substituted ring deformation), 626 cm^{-1} vw (ω NH_2), 502 cm^{-1} m (P=O deformation ?).

The effect of atmospheric moisture on diphenyl phosphoramidate (diphenyl amidophosphate) as a KBr pellet and as a solid between CsI windows is illustrated by the infrared spectra presented in ***Figure 369A*** and ***Figure 369B*** respectively. The infrared spectra for diphenyl phosphoramidate as a KBr pellet show little change over the period of 54 days. Only a very weak band, assignable to NH_4^+, is visible at 1400 cm^{-1}. This band is due

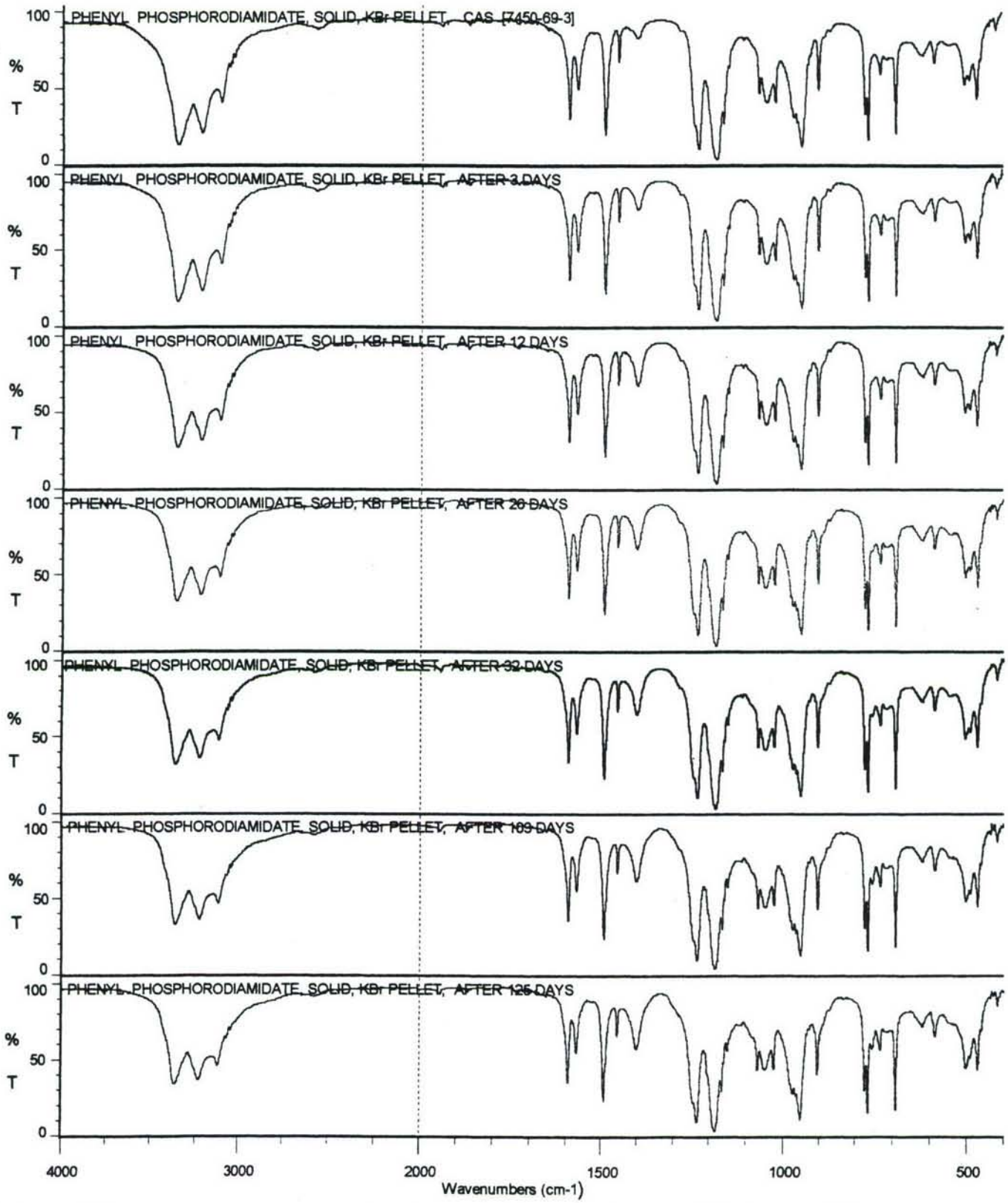

Figure 367A PHENYL PHOSPHORODIAMIDATE, SOLID, KBr PELLET, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

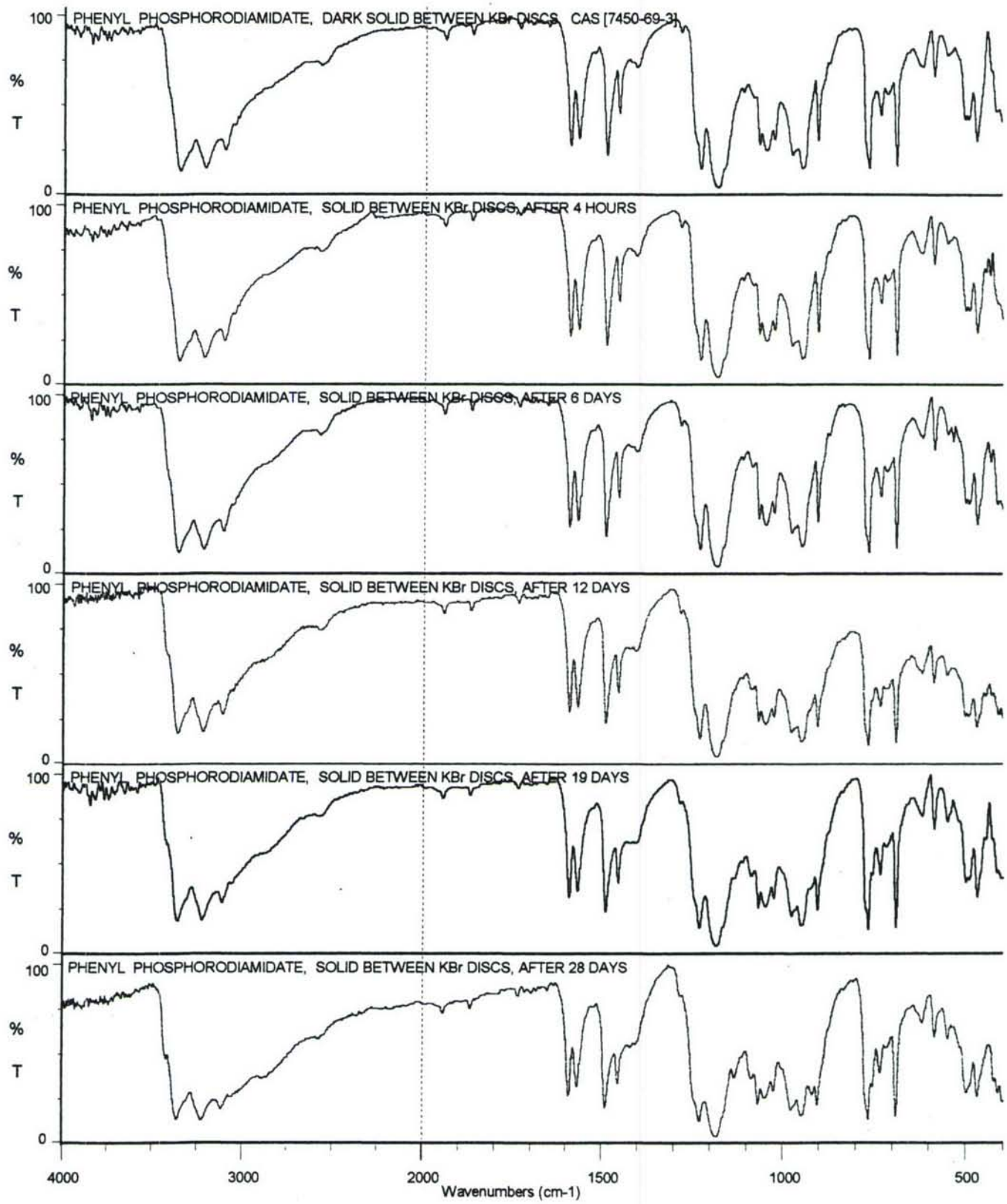

Figure 367B PHENYL PHOSPHORODIAMIDATE, SOLID BETWEEN KBr DISCS (WINDOWS), AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

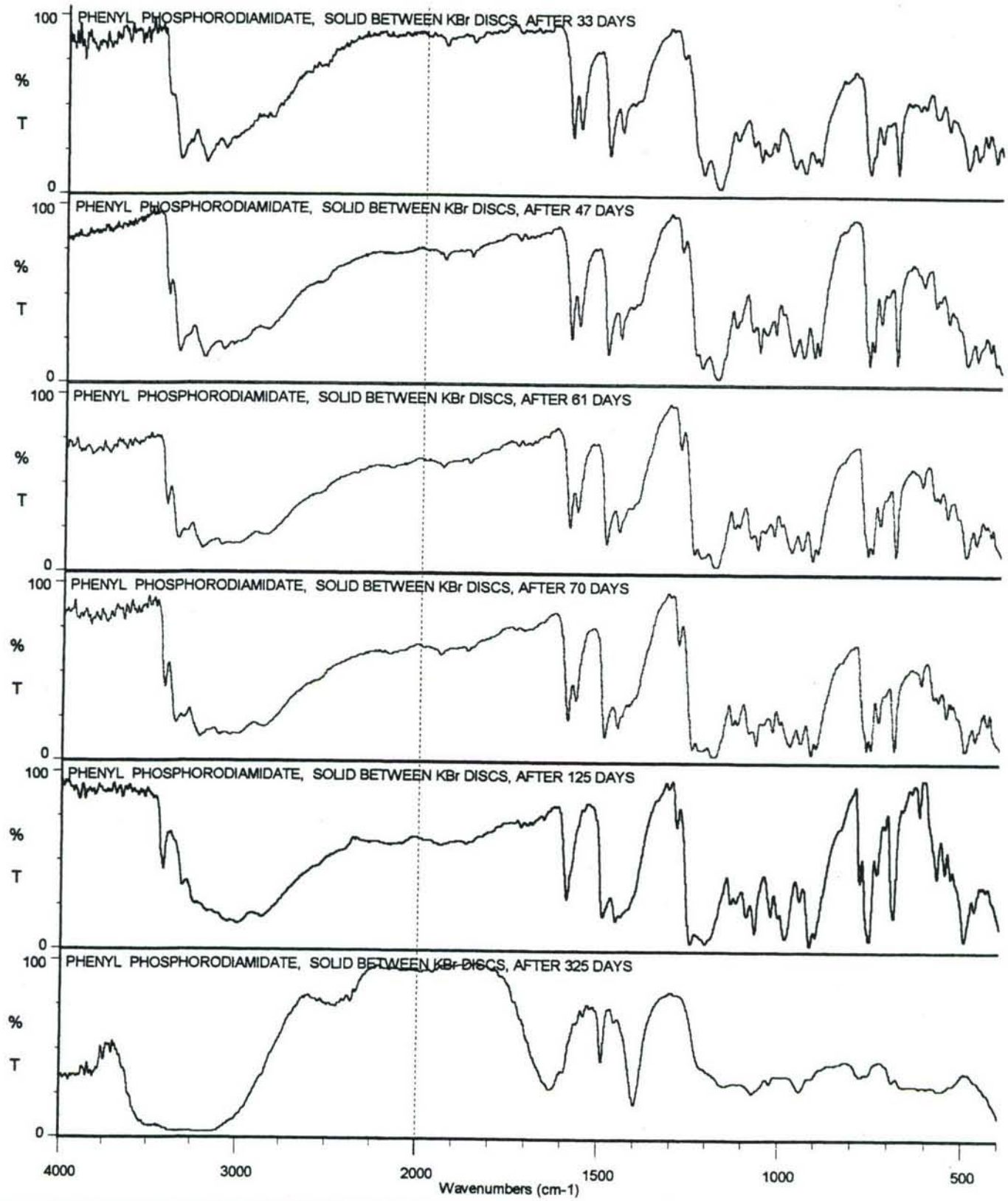

Figure 367C PHENYL PHOSPHORODIAMIDATE, SOLID BETWEEN KBr DISCS (WINDOWS), AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

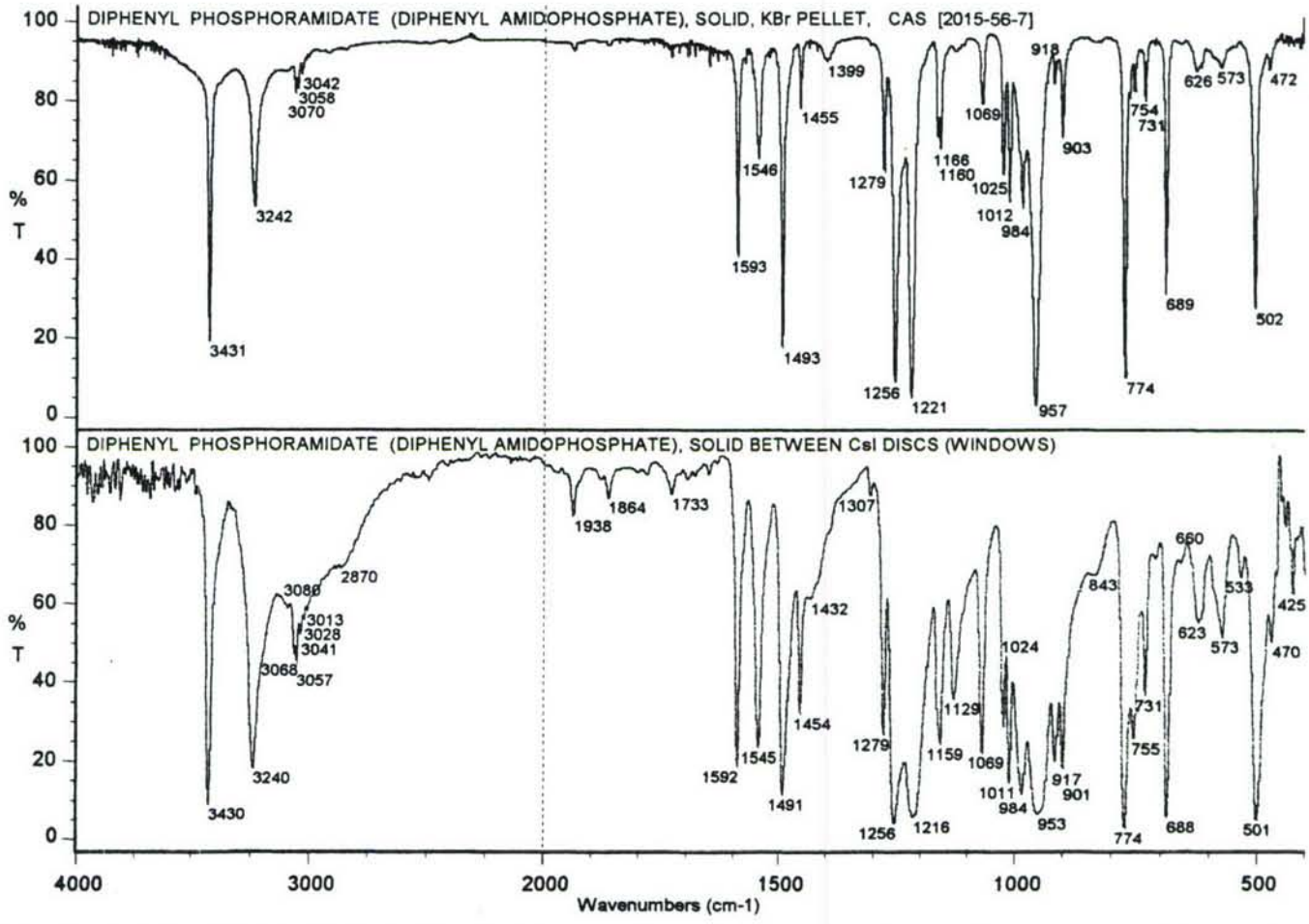

Figure 368 DIPHENYL PHOSPHORAMIDATE (DIPHENYL AMIDOPHOSPHATE), SOLID. UPPER SPECTRUM–**AS A KBr PELLET,** LOWER SPECTRUM–**AS A SOLID BETWEEN KBr DISCS (WINDOWS)**

to a small amount of hydrolysis in the original compound that does not seem to increase in the KBr pellet with time.

The infrared spectra of diphenyl phosphoramidate, detetermined as a solid between cesium iodide windows (***Figure 369B***), show little change when the compound is exposed to atmospheric moisture over a period of 120 days. Some NH_4^+ absorption may be present in the 1400 cm^{-1} region, but this absorption does not seem to increase to any appreciable degree by the 120th day of exposure to atmospheric moisture. However, absorption does seem to occur near 1360 and 843 cm^{-1} and may be indicative of cesium nitrate ($CsNO_3$) formation from the cesium iodide windows. Bands also appear at 1091 and 612 cm^{-1} and can be assigned to the formation of cesium sulfate (Cs_2SO_4) from the same cesium iodide windows.

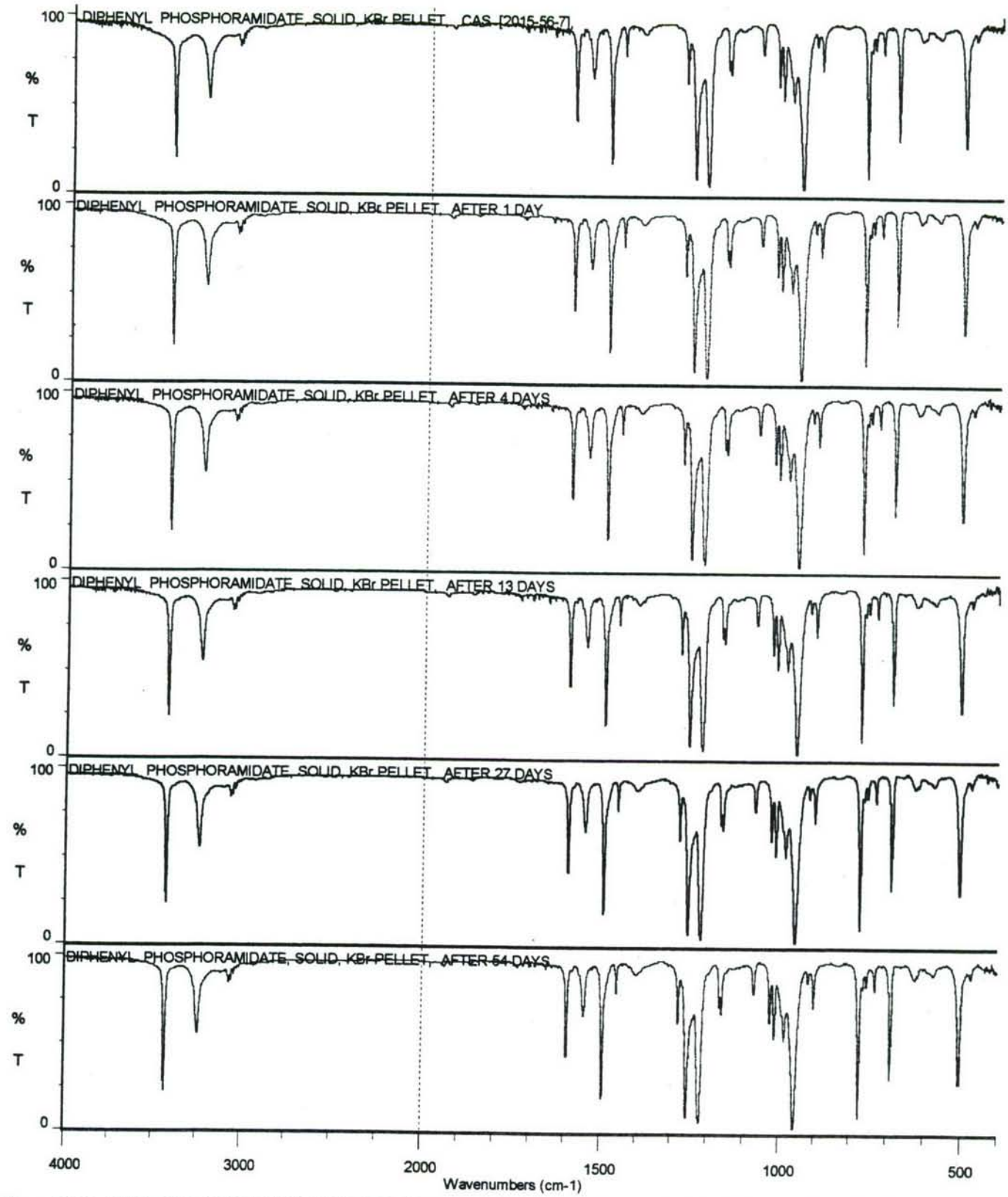

Figure 369A DIPHENYL PHOSPHORAMIDATE (DIPHENYL AMIDOPHOSPHATE), SOLID AS A KBr PELLET, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

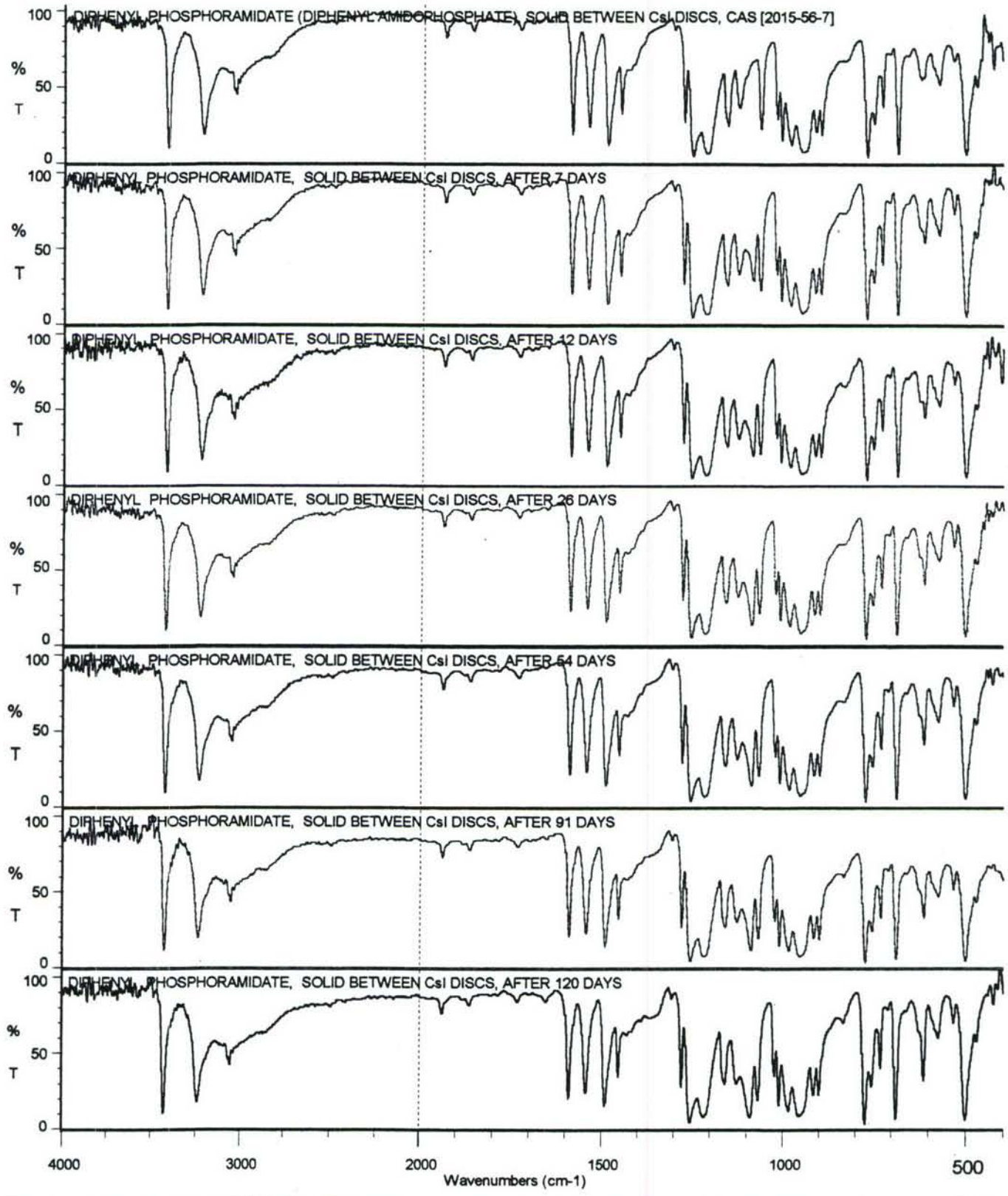

Figure 369B DIPHENYL PHOSPHORAMIDATE (DIPHENYL AMIDOPHOSPHATE), AS A SOLID BETWEEN CsI DISCS (WINDOWS), AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.6.26 Diphenylphosphinamide $(C_6H_5)_2P{=}O(NH_2)$

The infrared spectrum of diphenylphosphinamide as a solid between KBr discs (windows) is given as ***Figure 370***. Band assignments are as follows: 3296 cm^{-1} ms (ν_{as} NH_2), 3253 cm^{-1} ms (ν_{sy} NH_2), 3135 cm^{-1} ms (2 x 1576 = 3152 cm^{-1}), 3076, 3059, and 3038 vw (ν C-H aromatic), 2920 cm^{-1} vw (1483 + 1437 = 2920 cm^{-1}), 1621 cm^{-1} w, 1483 cm^{-1} w 1437 cm^{-1} ms (aromatic ring C≈C), 1576 cm^{-1} m (δ NH_2), 1177 cm^{-1} s (ν P=O, the *calculated* value is 1172 cm^{-1}), 1125 and 1108 cm^{-1} ms (phenyl-P), 1071, 1026 and 997 cm^{-1} vw-w (β C-H mono-substituted aromatic ring), 913 cm^{-1} ms (ν P-N), 757 and 748 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 724 and 695 cm^{-1} s (mono-substituted aromatic ring deformation), 645 cm^{-1} w (ω NH_2), 539 and 514 cm^{-1} ms (aromatic ring), 468 cm^{-1} w (P=O deformation ?).

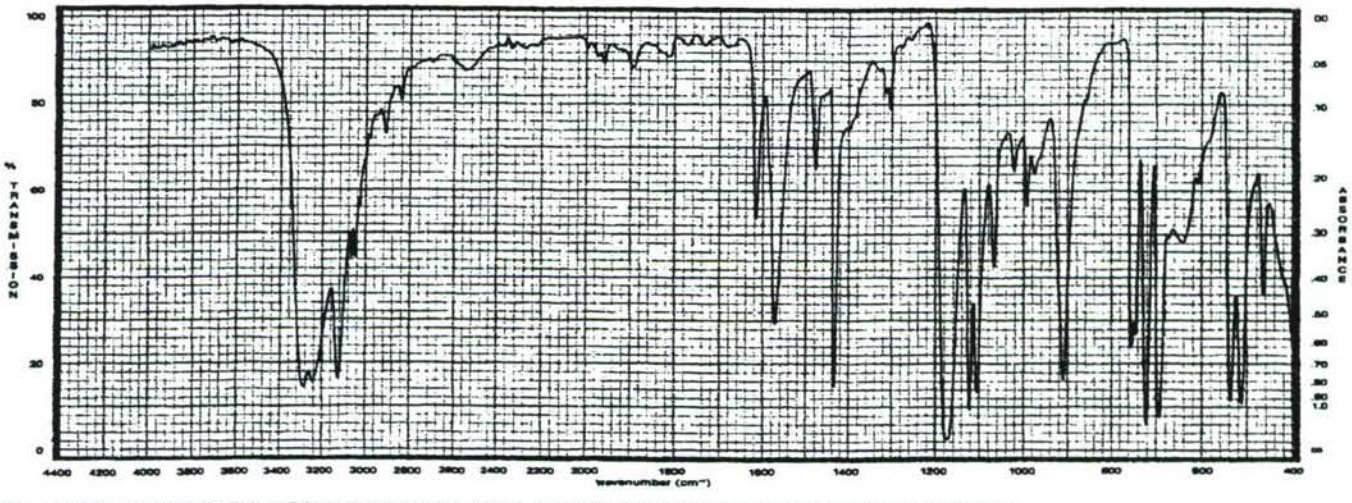

Figure 370 DIPHENYLPHOSPHINAMIDE, 98%, SOLID BETWEEN KBr DISCS (WINDOWS)

3.6.27 Diethyl Phenethylphosphoramidate (Diethyl Phenethylamidophosphate)

C_6H_5-CH_2-CH_2-NH-P=O(O-CH_2-CH_3)$_2$

The infrared spectra of diethyl phenethylphosphoramidate (diethyl phenethylamidophosphate) as a liquid film between KBr discs (windows) is reproduced as ***Figure 371***. Band assignments are as follows: 3219 cm^{-1} m (ν N-H), 3086, 3062 and 3026 cm^{-1} vw-w (ν C-H aromatic), 2980 cm^{-1} m (ν_{as} CH_3), 2930 cm^{-1} w (ν_{as} CH_2), 2904 cm^{-1} w (ν_{sy} CH_3), 2870 cm^{-1} w (ν_{sy} CH_2), 1604 cm^{-1} vw, 1584 cm^{-1} vvw, 1497 cm^{-1} w (aromatic ring

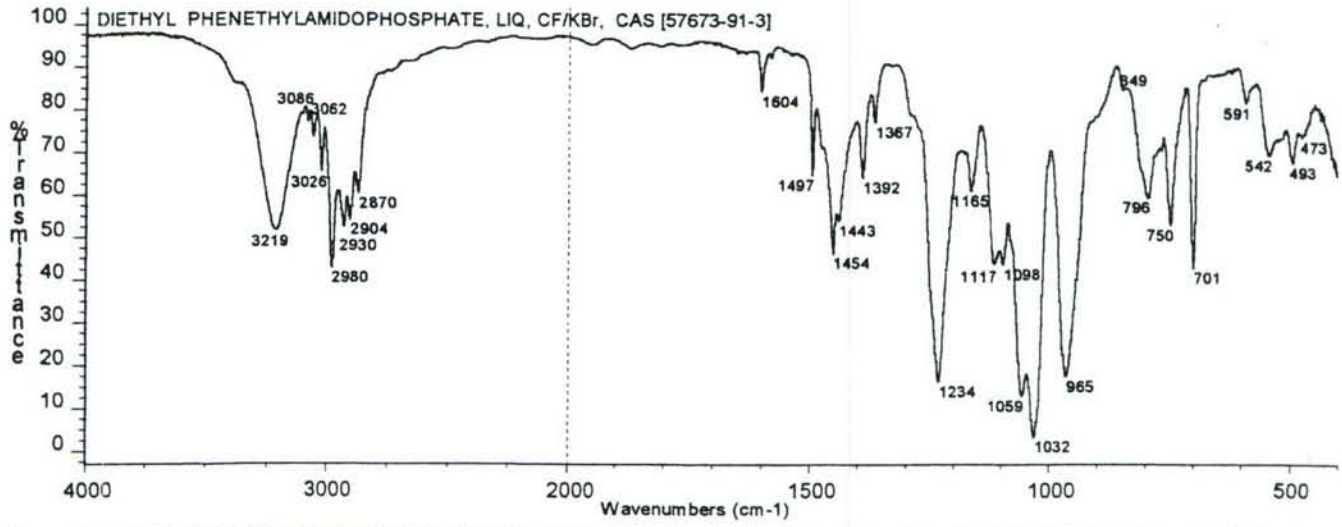

Figure 371 DIETHYL PHENETHYLPHOSPHORAMIDATE (DIETHYL PHENETHYLAMIDOPHOSPHATE), LIQUID, CF/KBr

C≈C), 1477 cm^{-1} sh (δ OCH_2), 1454 cm^{-1} m and 1443 cm^{-1} sh (aromatic ring and δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2), 1367 cm^{-1} vw (δ_{sy} CH_3), 1234 cm^{-1} ms (ν P=O, the *calculated* value is 1238 cm^{-1}), 1165 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1117 cm^{-1} w (ν C-N), 1059 cm^{-1} ms and 1032 cm^{-1} s (ν P-O-C), 965 cm^{-1} ms (ν C-C of POEt, ν P-N ?),[ooo] 796 cm^{-1} w (POC), 750 cm^{-1} m (γ C-H mono-substituted aromatic ring), 701 cm^{-1} m (mono-substituted aromatic ring deformation), 542 cm^{-1} w (P=O deformation ?).

3.7 Thiono (P=S) and Thiolo (P=S) Organophosphorus Compounds

A great deal of confusion has occurred over the assignment of the absorption bands characteristic of the P=S (thiono, thiophosphoryl) group. The P=S band, unlike the P=O vibration, which always shows a strong infrared band, varies in intensity, thus making its identification difficult and lending itself to the ensuing confusion. Early investigators[ppp] assigned the P=S stretching vibration to two different regions, 840-780 cm^{-1} and below 770 cm^{-1}.

[ooo] The vibrational frequencies correlated with the PNH-alkyl moiety are 3316-3125 cm^{-1} (ν N-H), 1144-1099 cm^{-1} (ν C-N) and 1040-873 (ν P-N). The P-N band can be difficult to assign, being of variable intensity and often obscured by other stronger bands. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 117, Heyden & Son Ltd., London, 1974.

[ppp] **Above** 770 cm^{-1}: McIvor, R.A., Grant, G.A. and Hubley, C.E., Can. J. Chem. **34,**1611 (1956). McIvor, R.A., and Hubley, C.E., Can. J. Chem., **37**, 869 (1959). **Below** 770 cm^{-1}: Gore, R.C., Discussions Faraday Soc., **No. 9**, 138 (1950). Daasch, L.W. and Smith, D.C., Anal. Chem., **23**, 853 (1951). Corbridge, D.E.C., J. Appl. Chem., **6**, 456 (1956). Hooge, F.N. and Christen, P.J., Rec. Trav. Chim., **77**, 911 (1958).

Chittenden and Thomas[qqq] proposed that the P=S group appeared to have two infrared bands associated with it. They designated these two bands as P=S(I) and P=S(II) having the ranges 862-685 cm^{-1} and 730-550 cm^{-1} respectively. On the isomerization of phosphorothionates (1) to phosphorothiolates (1a) two bands dissappeared from the spectrum.

$$(RO)_2P{=}S(OR) \rightarrow (RO)_2P{=}O(SR)$$
$$(1) \qquad\qquad (1a)$$

The P=S stretching vibration is believed to be associated with the P=S(II) band. The P=S stretching vibration is not a pure vibration, but is strongly coupled to other vibrations in a molecule. The P=S(I) band may arise from the vibration of another group in the molecule which is coupled to the P=S vibration. This vibration should change frequency when the coupling is removed (as on isomerization), resulting in the disappeaerance of the band.

Part of the original confusion over the assignment of the band characteristic of the P=S group may be as Thomas states[rrr] due to the failure of many investigators to distinguish between correlation and assignments. The former relating to absorption bands, which are always present in the infrared spectrum of a molecule when a specific molecular group is present in that molecule, and the latter (assignments) designating frequencies as characteristic of specific molecular vibrations. Thomas further states that he never made the suggestion that the P=S bond had two stretching vibration frequencies.

Cothup, Daly and Wiberley[sss] give the region for the P=S group as 750-580 cm^{-1} and further state that the P=S band, unlike the P=O vibration which always gives a strong infrared band, varies in intensity making infrared detection difficult. The P=S stretaching vibration should interact mechanically with attached P-O and P-C stretching vibrations at 850-650 cm^{-1} to a greater degree than the P=O stretching vibrations. This they suggest is the probable reason why two regions have been given by Thomas as being characteristic for the P=S group. The

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[qqq] Chittenden, R.A. and Thomas, L.C., Spectrochim. Acta, **20**, 1679 (1964).

[rrr] Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 129-130, Heyden & Son Ltd., London, 1974.

[sss] Colthup, N.B., Daly, L.H. and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", pp 347-349, Second Edition, Academic Press, New York, 1975.

electronegativities of the substituents on the P atom do not affect the force constant of the P=S group as much as they do that of the P=O group. P=S frequency shifts are mostly due to mechanical effects. The P=S stretching vibration (ca 675 cm^{-1}) interacts with the PX_3 symmetrical stretching vibration giving rise to two bands, where each band to some extent, involves both the P=S stretch and the symmetrical PX_3 stretch (in-phase and out-of phase). If the P=S is vibrating in-phase with the PX_3 group the *P=S* frequency is lowered below the 675 cm^{-1} value. If the *P=S* band has a higher frequency than 675 cm^{-1} then the P=S group is vibrating out-of phase with the PX_3 group, which raises the *P=S* frequency. The closer the P=S and PX_3 frequencies are before interaction, the greater the magnitude of the shift will be. The P=S frequency can be roughly estimated from the following equation, ν**(P=S) = 675 +** $\sum \Delta$, where Δ is an empirical value for various substituents. Δ values (in cm^{-1}) for substituent groups are; Cl +23, S +10, H 0, OR -23, CH_2 -50, phenyl -13, F +7, NR_2 -40, NHR 0. These Δ shift constants vary with both the electronegativity of the substituent on the P-atom and the effects of mechanical interaction.[ttt]

P-S (**thiolo**) stretching bands occur in region 613-400 cm^{-1} as given by Thomas.[uuu] Two absorption bands may occur in this range over the limits of 613-447 cm^{-1} (band I) and 582-440 cm^{-1} (band II) and may be due to different conformers. The P-S band is lower in P=S compounds than in the corresponding P=O compounds. The P-S band is normally of medium-strong intensity; where two bands occur, the bands are usually of comparable intensities. P-S compounds containing a P-CH_3 group have only one P-S band, whereas the corresponding P-Ethyl compounds have two bands. Two P-S bands are also seen in P-Phenyl compounds.

The P-S(H) group shows absorption bands at 548-522 cm^{-1} (I) and 526-490 cm^{-1} (II). The S-H stretching vibrations occur in the range 2480-2440 cm^{-1} for compounds of the type $(RO)_2PS(SH)$. In dithiophosphinic acids of the type $R_2PS(SH)$, in the condensed state, the S-H band absorbs broadly over the range 2420-

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[ttt] Colthup, N.B., Daly, L.H. and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", pp 347-349, Second Edition, Academic Press, New York, 1975.
Lin-Vien, D., Colthup, N.B., Fateley, W.G. and Grasselli, J.G., "The Handbook of Infrared and Raman Characteristic Frequencies of Orgasnic Molecules", pp 266- 268, Academic Press, Inc., San Diego, CA, 1991.

[uuu] Thomas, L.C. "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 146, Heyden & Son Ltd., London, 1974.

2300 cm^{-1}.[vvv]

Compounds containing P=O and P-SH groups do not exist as such, but exist as the isomeric thionic acid form, O=P-SH → S=P-OH.[www] Here the P=S bands occur over the ranges 810-749 cm^{-1} (I) and 655-584 cm^{-1} (II).

3.7.1 Thiophosphoryl Chloride (Phosphorus Sulfochloride) $Cl_3P=S$

The infrared spectrum of thiophosphoryl chloride (phosphorus sulfochloride) as a thin liquid film between KBr windows is reproduced as ***Figure 372***. The band assignments are as follows: 1506 cm^{-1} vvw (2 x 751 = 1502 cm^{-1}), 1384 cm^{-1} vvw (KNO_3 from KBr windows ?), 1302 cm^{-1} vw (ν P=O from $POCl_3$?), 1181 cm^{-1} vw (751 + 430 = 1181 cm^{-1} ?), 965 cm^{-1} vw (534 + 430 = 964 cm^{-1}), 751 cm^{-1} s (ν P=S), 589 and 492 cm^{-1} w (ν_{as} and ν_{sy} PCl_3 from $POCl_3$?), 534 cm^{-1} s (ν_{as} PCl_3), 430 cm^{-1} ms (ν_{sy} PCl_3).

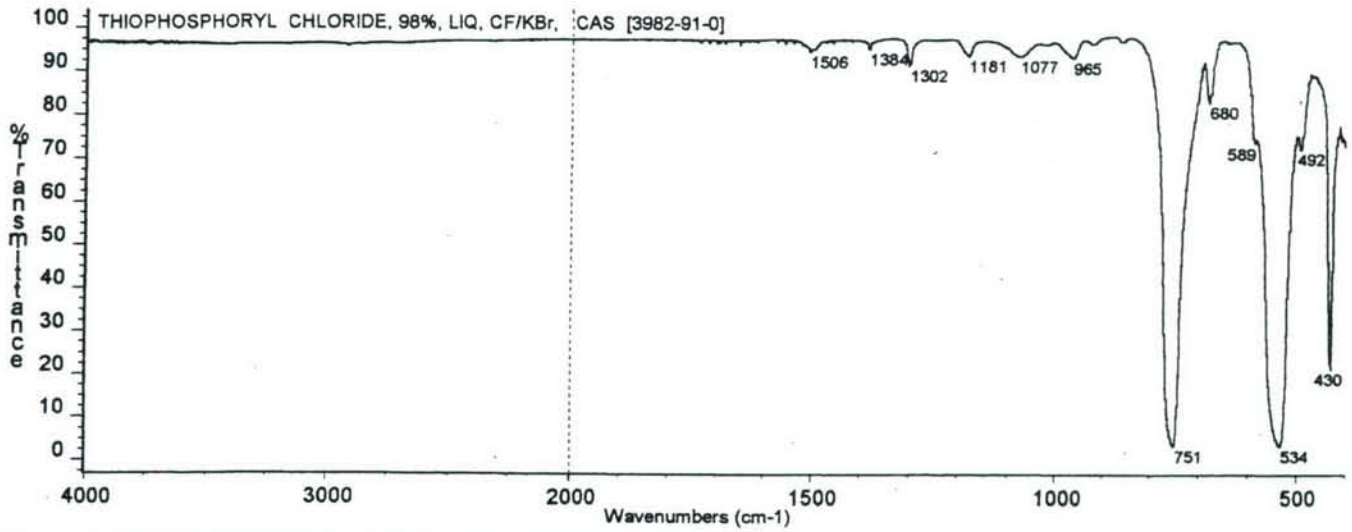


Figure 372 THIOPHOSPHORYL CHLORIDE (PHOSPHORUS SULFOCHLORIDE), 98%, LIQUID, CF/KBr

3.7.2 Methylphosphonothioic Dichloride (**TDC**) $CH_3-P=S(Cl)_2$

The infrared spectrum of a liquid film of methylphosphonothioic dichloride (**TDC**) between KBr windows is given in ***Figure 373***. The band assignments are as follows: 2994 cm^{-1} vw (ν_{as} CH_3), 2914 cm^{-1}

[vvv] Colthup, N.B., Daly, L.H. and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy",p. 349, Second Edition, Academic Press, New York, 1975.

[www] Thomas. L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 147,131, Heyden & Son Ltd., London, 1974.

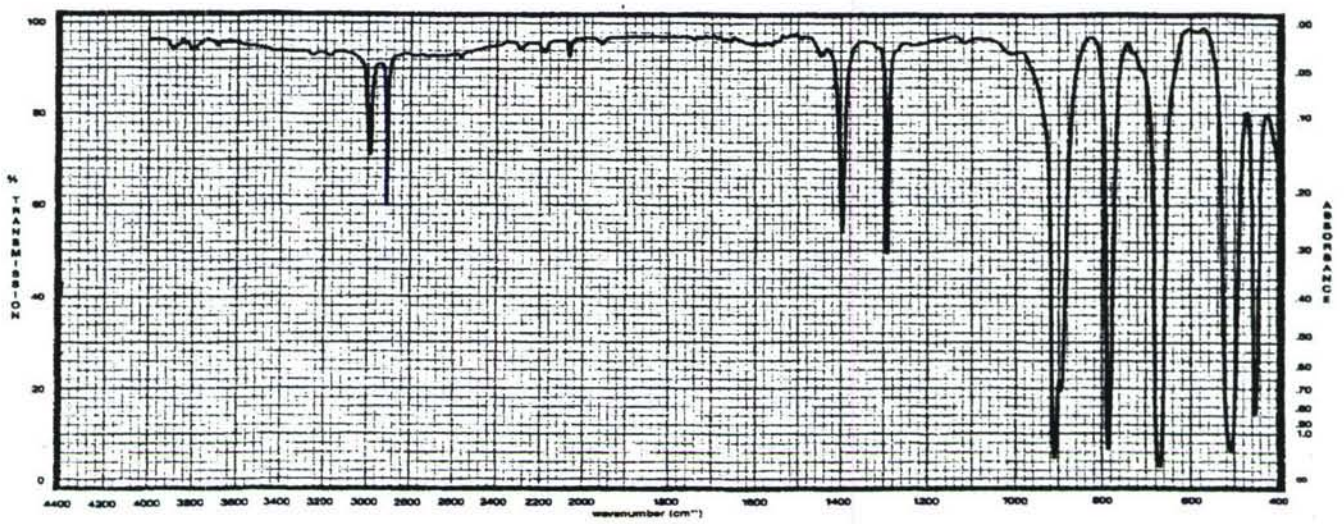


Figure 373 METHYLPHOSPHONOTHIOIC DICHLORIDE (TDC), LIQUID, CF/KBr

w (ν_{sy} CH_3), 1399 cm^{-1} m(δ_{as} P-CH_3), 1293 cm^{-1} m (δ_{sy} P-CH_3), 909 cm^{-1} ms and 894 cm^{-1} sh (P-CH_3 rock),[xxx] 785 cm^{-1} ms (P=S I band),[xxx] 669 cm^{-1} s (P=S II band),[xxx] 509 cm^{-1} s (ν_{as} PCl_2), 451 cm^{-1} ms (ν_{sy} PCl_2).

The effect of atmospheric moisture on a liquid film of methylphosphonothioic dichloride (**TDC**) is illustrated by the spectra given in ***Figures 374 A-C***. After 19 hours of exposure to atmospheric moisture the infrared spectrum (***Figure 374A***) showed the presence of the original compound (**TDC**) plus bands near 2900, 2300 and 1680 cm^{-1} assignable to the POH group, 1317 cm^{-1} w (δ_{as} P-CH_3), 1160 cm^{-1} m (ν P=O), ca 1000 cm^{-1} sh and 940 cm^{-1} s (ν P-OH), 718 cm^{-1} w (ν P-C). After 27 hours of exposure to atmospheric moisture, the spectrum (***Figure 374B***) was that of mainly a P-acid moiety. After 7 days of exposure, the infrared spectrum (***Figure 374C***) resembled that of methylphosphonic acid, CH_3-P=O$(OH)_2$. The compound, CH_3-P=S$(Cl)_2$, apparently undergoes oxidative desulfurization, where the sulfur atom is lost and is replaced by an oxygen atom to form methylphosphonic acid by hydrolysis.

[xxx] The 909 and 894 cm^{-1} bands have been assigned to the symmetric and antisymmetric rocking of the P-CH_3 group. The 785 cm^{-1} band has been assigned to the P-C stretching vibration, while the 669 cm^{-1} band has been assigned to the P=S stretching vibration. Durig, J.R., Block, F., and Levin, I.W., "Vibrational Spectra of CH_3PCl_2, CH_3POCl_2 and CH_3PSCl_2", Spectrochim. Acta, **21**, 1105 (1965).

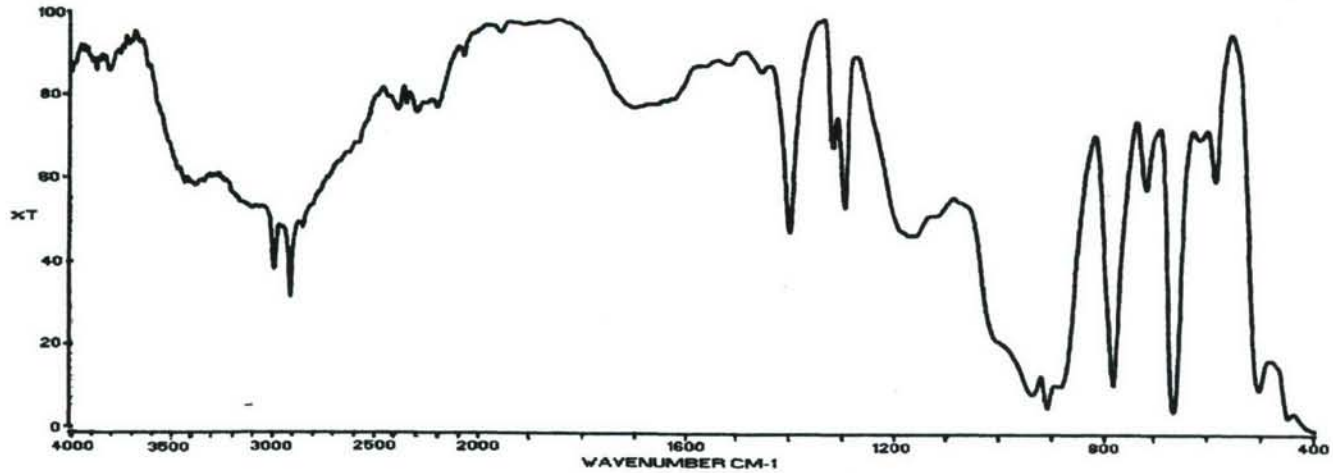


Figure 374A METHYLPHOSPHONOTHIOIC DICHLORIDE, LIQUID, CF/KBr, AFTER 19 HOURS

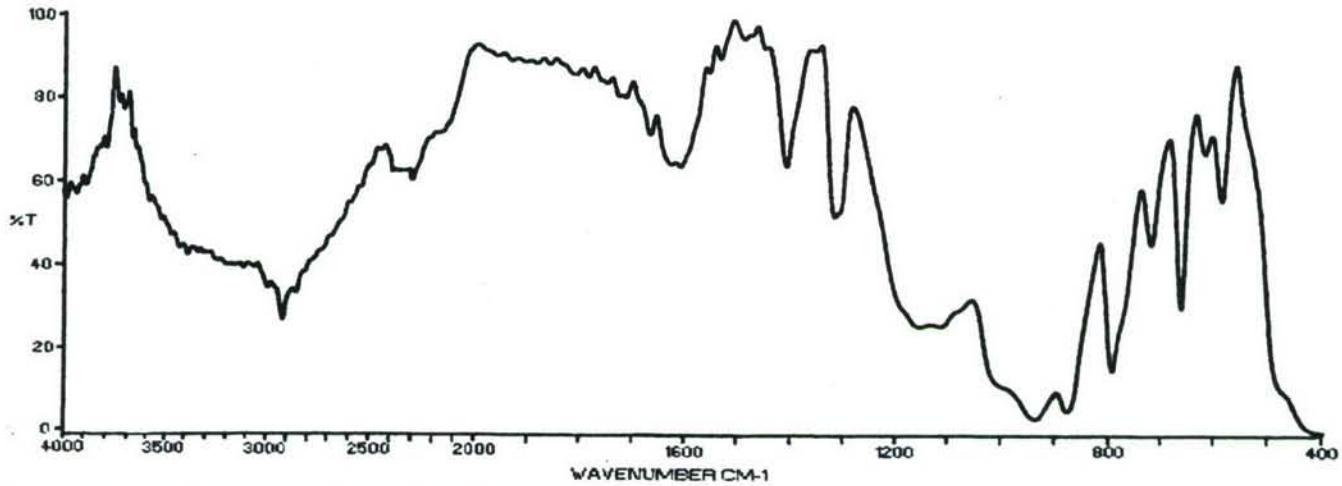


Figure 374B METHYLPHOSPHONOTHIOIC DICHLORIDE, LIQUID, CF/KBr, AFTER 27 HOURS

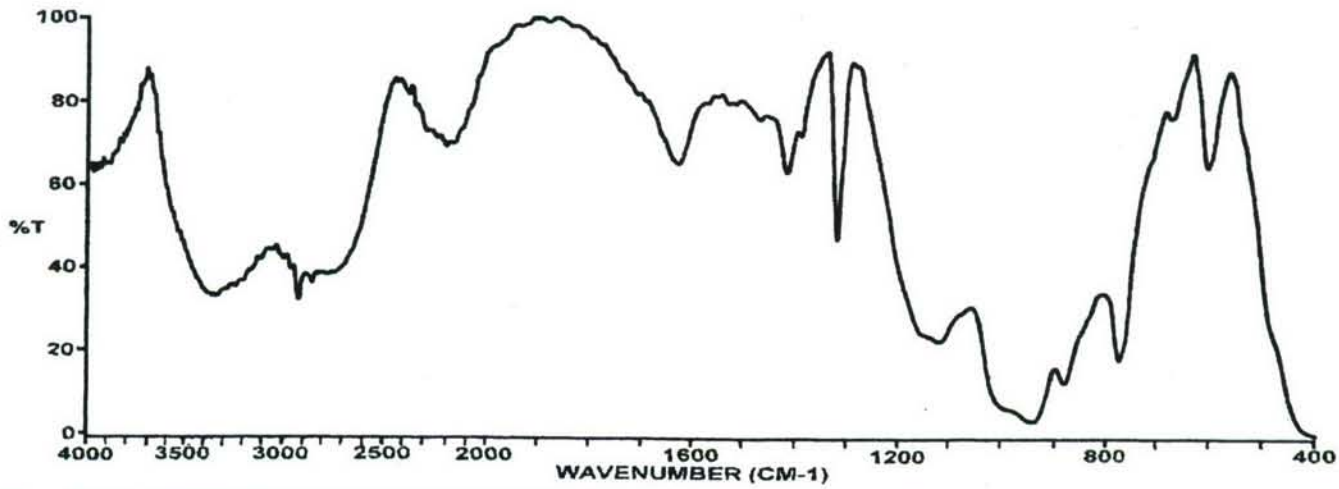


Figure 374C METHYLPHOSPHONOTHIOIC DICHLORIDE, LIQUID, CF/KBr, AFTER 7 DAYS

3.7.3 Dimethylphosphinothioic Chloride $(CH_3)_2P=S(Cl)$

The infrared spectrum of dimethylphosphinothioic chloride as a thin liquid film between KBr discs (windows) is presented as ***Figure 375***. The band assignments are as follows: 2984 cm^{-1} w (ν_{as} CH_3), 2909 cm^{-1} w (ν_{sy} CH_3), 2251 cm^{-1} vvw (2 x 1289 = 2578 cm^{-1}), 2251 cm^{-1} vvw (1299 + 954 = 2253 cm^{-1}), 2216 cm^{-1} vvw (1299 + 916 = 2215 cm^{-1}), 1496 cm^{-1} vvw (2 x 750 = 1500 cm^{-1}), 1408 and 1399 cm^{-1} w (δ_{as} P-CH_3), 1359 cm^{-1} vw (750 + 610 = 1360 cm^{-1}), 1299 cm^{-1} w and 1289 cm^{-1} m (δ_{sy} P-CH_3), 1218 cm^{-1} vvw (2 x 610 = 1220 cm^{-1}), 954 and 916 cm^{-1} ms (P-CH_3 rock, symmetric and asymmetric), 858 cm^{-1} m (ν P-C, asymmetric ?), 750 cm^{-1} ms (P=S I, ν P-C symmetric ?), 610 cm^{-1} s (P=S II), 456 cm^{-1} m (ν P-Cl).

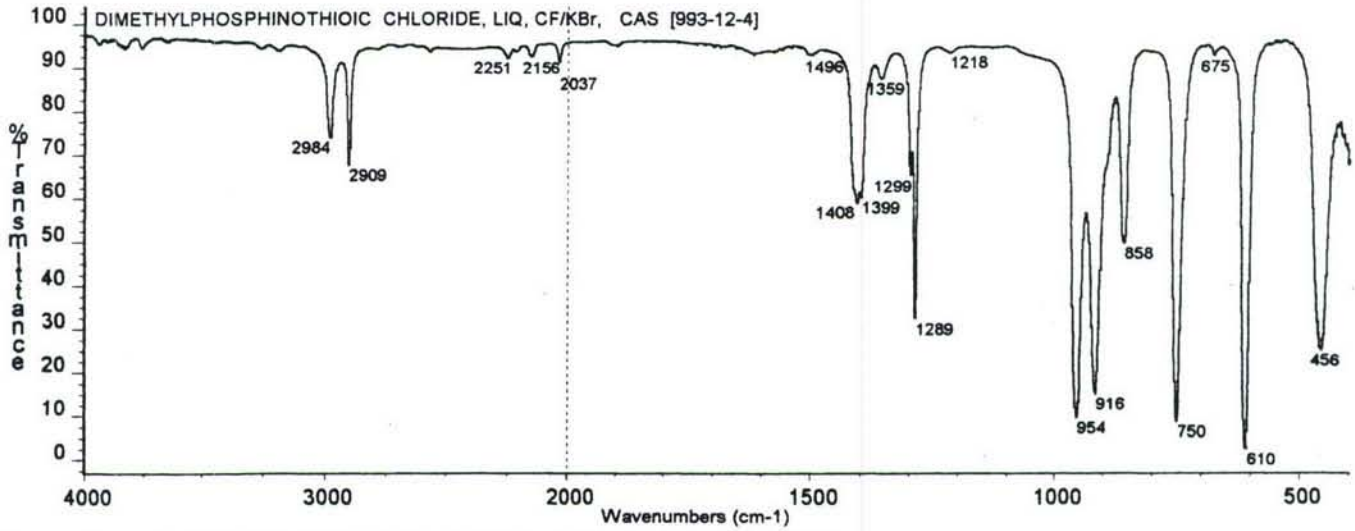


Figure 375 DIMETHYLPHOSPHINOTHIOIC CHLORIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of dimethylphosphinothioic chloride between KBr windows is illustrated by the infrared spectra presented in ***Figures 376A*** and ***376B***. After 1 day of exposure to atmospheric moisture, the infrared spectrum (***Figure 376A***) shows the formation of the POH group near 3000 and 2300 cm^{-1}. The P-Cl stretch at 456 cm^{-1} has become weaker and is gone from the spectrum by the second day. The spectrum now resembles that of a compound containing a P=S(OH) moiety. The P=S bands are now present at 749 cm^{-1} (I) and 596 cm^{-1}. The POH group absorbs near 3000, 2300 and 900 cm^{-1}. The original compound has been hydrolyzed to dimethylphosphinothioic acid, $(CH_3)_2$ P=S(OH).

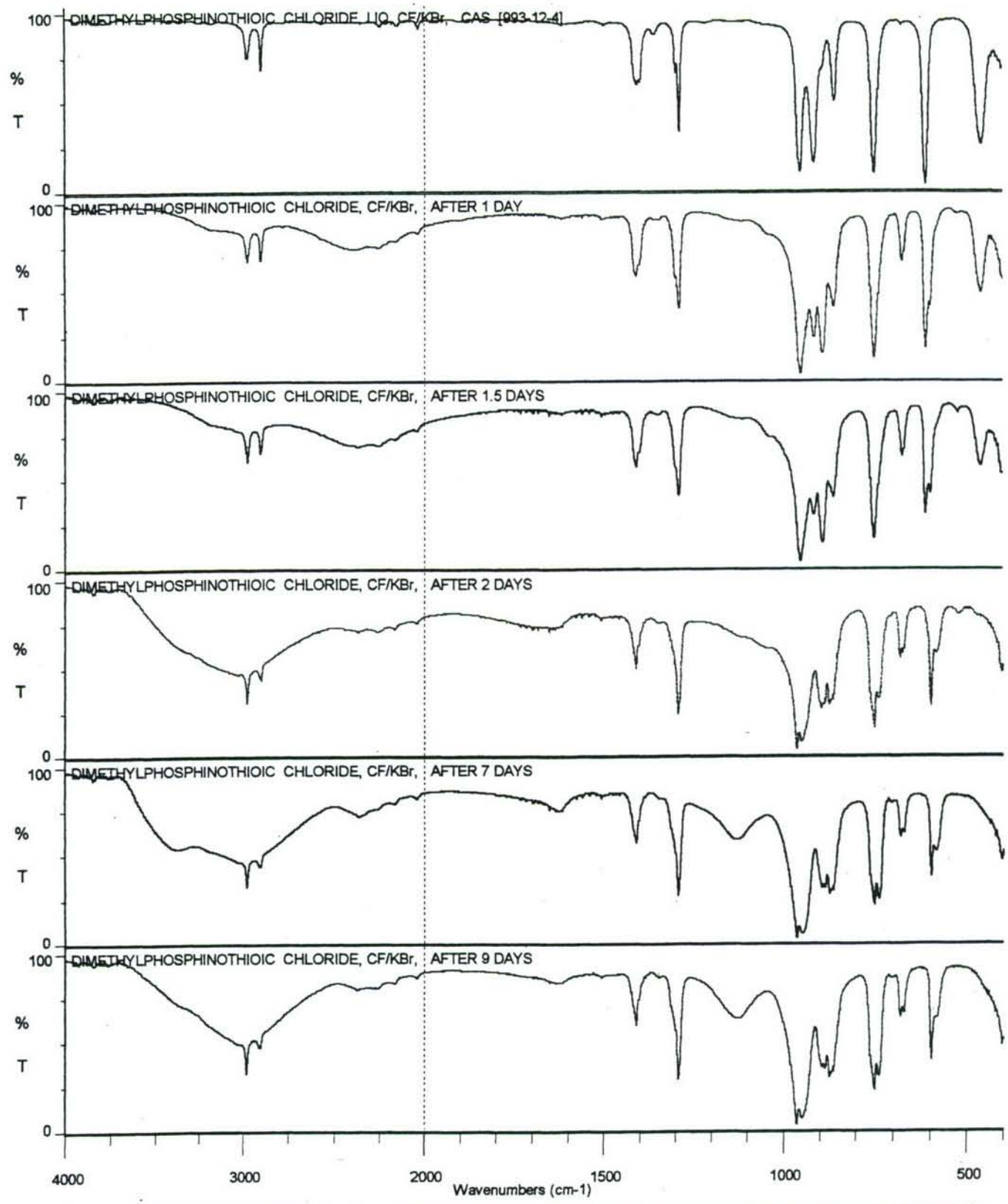


Figure 376A DIMETHYLPHOSPHINOTHIOIC CHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

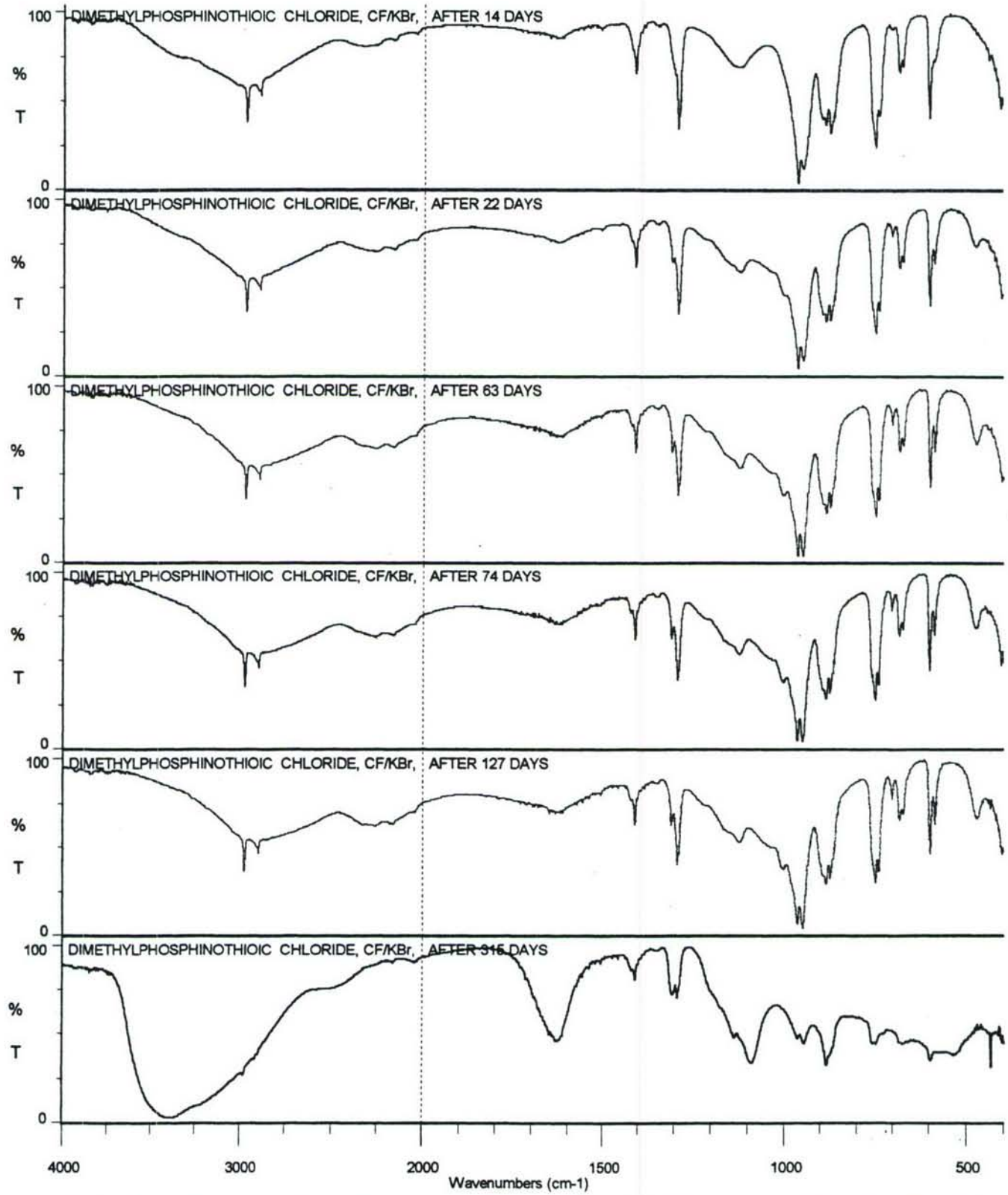


Figure 376B DIMETHYLPHOSPHINOTHIOIC CHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.7.4 Methylphosphonothioic Difluoride **(TDF, Thiono Difluor)** CH_3-P=S$(F)_2$

The infrared spectrum of methylphosphonothioic difluoride (**TDF, Thiono Difluor**) as a liquid film between KBr windows and as a vapor is presented in ***Figure 377***. Methylphosphonothioic difluoride (**TDF, Thiono Difluor**) is a volatile and flammable liquid (b.p. 60-65 °C, fl.p. -5 to -10 °C),[yyy] that fumes when exposed to air. Band assignments for the liquid phase are as follows: 3003 cm^{-1} vw (ν_{as} CH_3), 2926 cm^{-1} vw (ν_{sy} CH_3), 1449 cm^{-1} vvw (816 + 638 = 1454 cm^{-1}), 1408 cm^{-1} w (δ_{as} P-CH_3), 1311 cm^{-1} m (δ_{sy} P-CH_3), 942 cm^{-1} s and 920 cm^{-1} sh (P-CH_3 rocking), 858 and 844 cm^{-1} m (ν_{as} and ν_{sy} PF_2) 816 cm^{-1} s (P=S I), 753 cm^{-1} vvw (ν P-C) and 638 cm^{-1} w (P=S II).

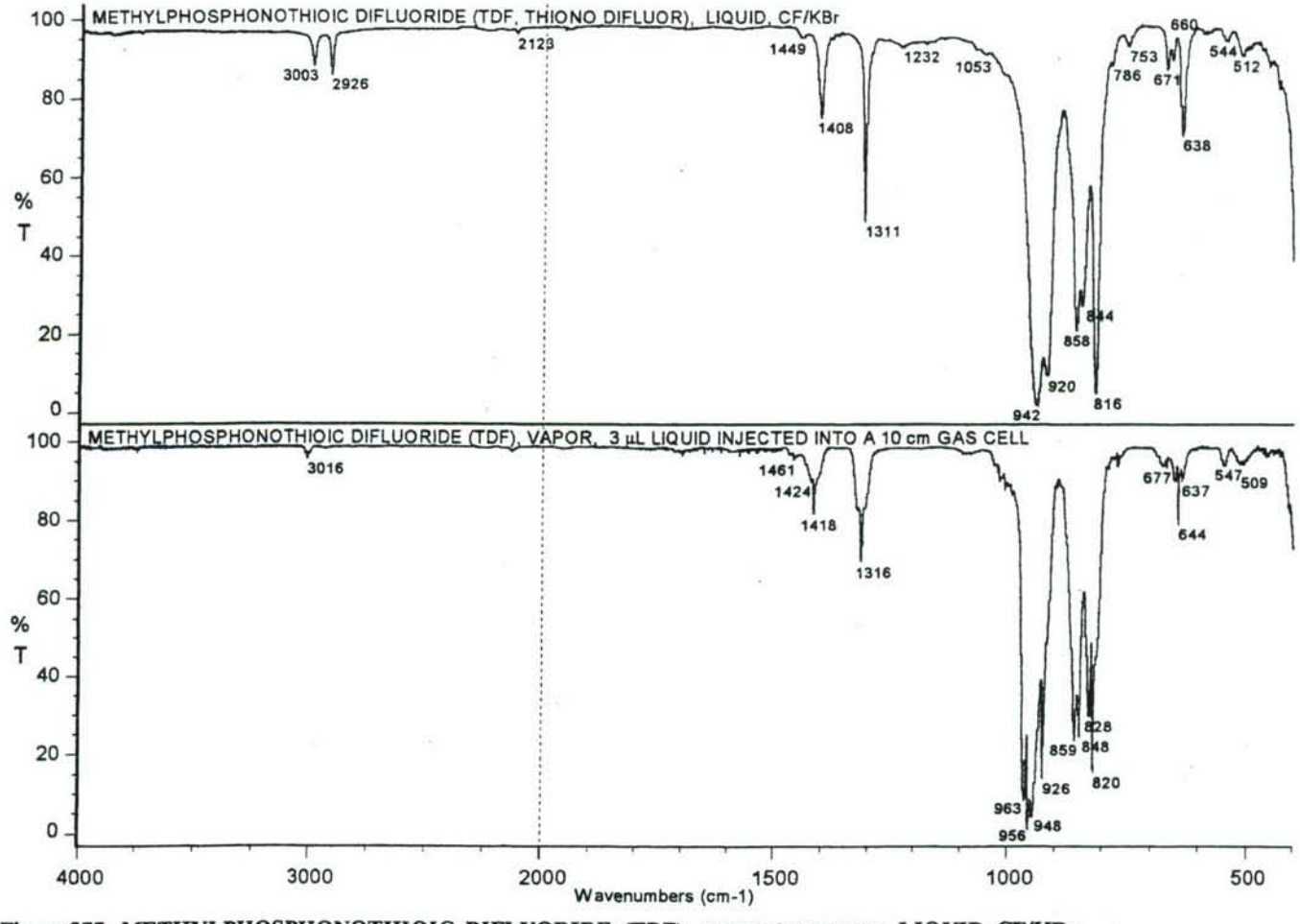


Figure 377 METHYLPHOSPHONOTHIOIC DIFLUORIDE (TDF), *UPPER SPECTRUM*--LIQUID, CF/KBr *LOWER SPECTRUM*--VAPOR PHASE (3 µL OF LIQUID INJECTED INTO AN EVACUATED 10 cm GAS CELL)

[yyy] Fielder, D., and Daasch, L.W., "Reaction of Methylphosphonothioic Difluoride With Air", EATM 2200-2, December 1971. U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, 21010-5423.

The vapor phase spectrum of methylphosphonothioic difluoride was determined in a 10 cm glass body gas cell with KBr windows. The gas cell was evacuated prior to the introduction of the sample. The vapor spectrum (***Figure 377***) showed the following bands: ca 3016 cm^{-1} vw (ν_{as} CH_3), ca 2937 cm^{-1} vvw (ν_{sy} CH_3), ca 1418 cm^{-1} w (δ_{as} P-CH_3), ca 1316 cm^{-1} w (δ_{sy} P-CH_3), 956 and 926 cm^{-1} s (P-CH_3 rocking), 859 and 848 ms cm^{-1} (ν_{as} and ν_{sy} PF_2), 820 cm^{-1} ms (P=S I), 770 cm^{-1} vw (ν P-C) and 644 w cm^{-1} (P=S II). When the stopcock on the gas cell was momentarily opened and then closed, a dense cloud formed and a spectrum (***Figure 378A***) taken within one minute after the addition of air showed the presence of **Difluor** (methyphosphonic difluoride, $CH_3P{=}OF_2$), sulfur dioxide (SO_2), hydrogen chloride (HCl) probably from $CH_3P{=}SCl_2$ present as an impurity, carbon dioxide (CO_2) and water vapor. After six minutes the spectrum (***Figure 378B***) showed the presence of the additional products of silicon tetrafluoride (SiF_4) at 1035 and 1030 cm^{-1}, and potassium hexafluorosilicate (K_2SiF_6) at 734 and 480 cm^{-1}. These two compounds, SiF_4 and K_2SiF_6, would account for the lack of HF in the spectrum. Since any HF formed would have reacted with the glass body of the gas cell as discussed previously with **Difluor**.

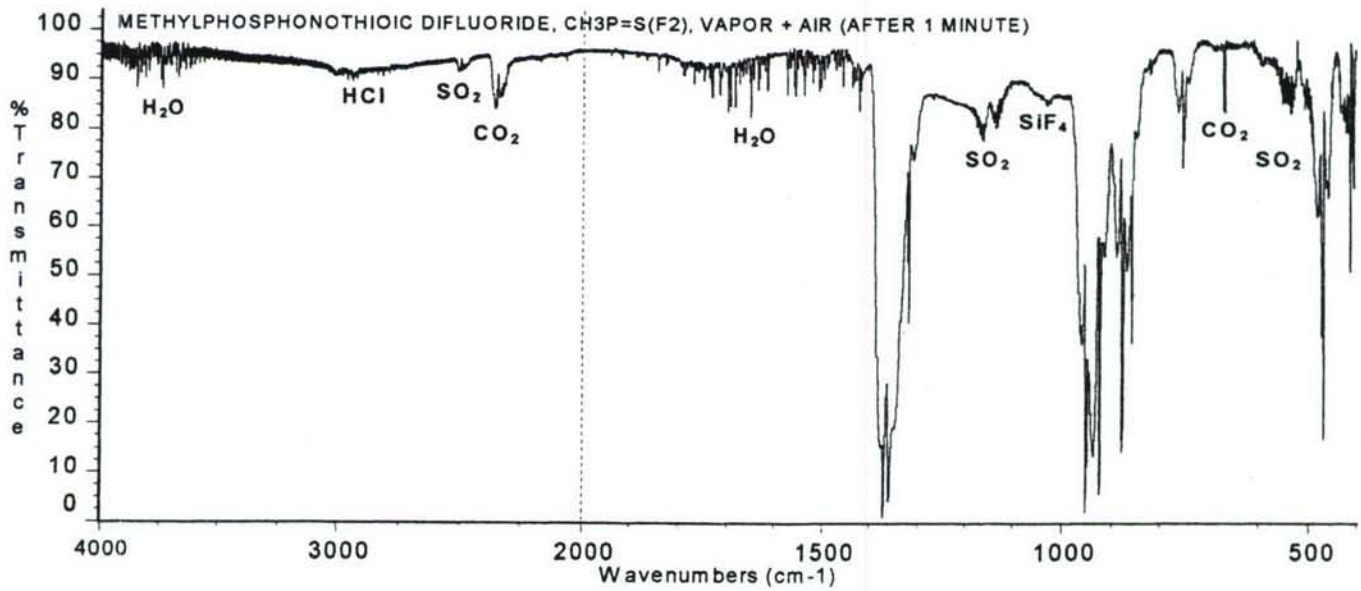


Figure 378A METHYLPHOSPHONOTHIOIC DIFLUORIDE (TDF), VAPOR + AIR, AFTER 1 MINUTE

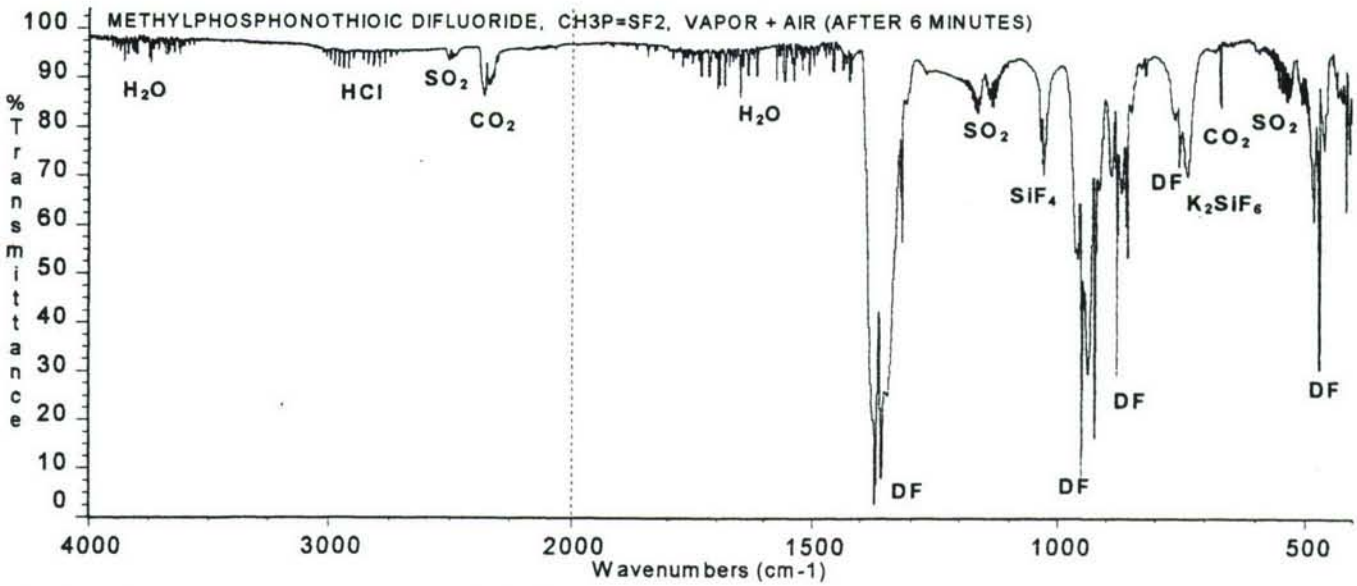


Figure 378B METHYLPHOSPHONOTHIOIC DIFLUORIDE (TDF), VAPOR + AIR AFTER 6 MINUTES

Thus, in air, methylphosphonothioic difluoride undergoes oxidative desulfurization to form **Difluor** and SO_2. Sulfur dioxide is evident in the spectrum by the bands at ca 2500, 1160, 1130 and 540 cm^{-1}; HCl by a series of bands between ca 3000-2700 cm^{-1}; CO_2 (which entered the gas cell when air was admitted) by bands at ca 2350 and 660 cm^{-1}. These results are similar to those obtained by Fielder and Daasch[yyy] who used mass spectrometry to identify the products SO_2, SO_3 and **Difluor**. They showed that the fuming of **TDF** exposed to air is caused by its reaction with atmospheric oxygen.

3.7.5 Ethylphosphonothioic Dichloride (EPTD) $CH_3\text{-}CH_2\text{-}P{=}S(Cl)_2$

The infrared spectrum of ethylphosphonothioic dichloride (**EPTD**) as a liquid film between CsI discs (windows) is given as ***Figure 379***. Band assignments are as follows: 2983 cm^{-1} m (ν_{as} CH_3), 2939 cm^{-1} m (ν_{as} CH_2), 2910 cm^{-1} w (ν_{sy} CH_3), 2878 cm^{-1} w (ν_{sy} CH_2), ca 2650 cm^{-1} vw broad (POH ?), 1455 cm^{-1} ms (δ_{as} CH_3), 1394 cm^{-1} w (δ P-CH_2), 1382 cm^{-1} m (δ_{sy} CH_3), 1255 and 1230 cm^{-1} w (P-Et, ω, τ CH_2), 1034 and 1010 cm^{-1} ms (ν C-C of P-Et), 915 cm^{-1} w (ν P-O-P impurity ?), 777 cm^{-1} s and 749 cm^{-1} ms (P=S I, ν P-C, isomers),[zzz]

[zzz] The range of the P=S I and P=S II bands for compounds of the type $RP{=}SCl_2$ is given as 790-775 cm^{-1} (I) and 708-624 cm^{-1} (II). Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p 135, Heyden & Son Ltd., London, 1974.

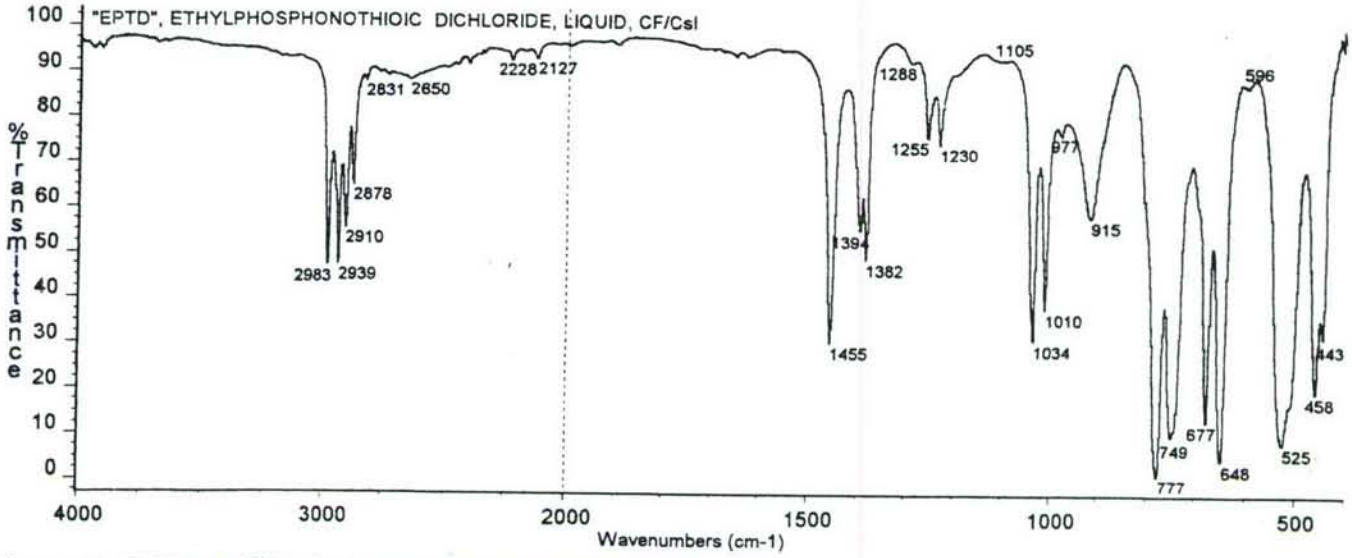


Figure 379 ETHYLPHOSPHONOTHIOIC DICHLORIDE (EPTD), LIQUID, CF/CsI

677 cm^{-1} ms and 648 cm^{-1} s (P=S II, isomers),[zzz] 525 cm^{-1} ms and ca 508 cm^{-1} sh (ν_{as} PCl_2, isomers), 458 cm^{-1} ms and 443 cm^{-1} sh (ν_{sy} PCl_2).

3.7.6 Ethyl Phosphorodichloridothionate (Ethyl Dichlorothiophosphate) CH_3-CH_2-O-P=S$(Cl)_2$

The infrared spectrum of ethyl phosphorodichloridothionate (ethyl dichlorothiophosphate) as a liquid film between CsI windows is reproduced as ***Figure 380***. The band assignments are as follows: 2996 and 2986 cm^{-1} m (ν_{as} CH_3), 2938 cm^{-1} w (ν_{as} CH_2), 2904 cm^{-1} w (ν_{sy} CH_3), 2866 cm^{-1} vw (ν_{sy} CH_2), 1800 cm^{-1} vw (1014 + 795 = 1809 cm^{-1}), 1472 cm^{-1} m (δ OCH_2), 1441 cm^{-1} m (δ_{as} CH_3), 1392 cm^{-1} m (ω OCH_2, some δ_{sy} CH_3), 1286 cm^{-1} w (ν P=O impurity ?), 1157 and 1099 cm^{-1} m-w (CH_3 rock of POEt, characteristic), 1014 cm^{-1} s (ν P-O-C), 976 cm^{-1} ms (ν C-C of POEt), 795 cm^{-1} ms (POC, P=S I),[aaaa] 726 and 699 cm^{-1} s (P=S II),[aaaa] 552 and 529 cm^{-1} m (ν_{as} PCl_2, 2 bands-isomers), 488 and 470 cm^{-1} ms (ν_{sy} PCl_2, 2 bands-isomers).[bbbb]

The effect of atmospheric moisture on a liquid film of ethyl phosphorochloridothionate (ethyl dichlorothiophosphate) is illustrated by the infrared spectra presented in ***Figure 381***. By the 5th day

[aaaa] For compounds of the type ROP=S$(Cl)_2$ the P=S I and P=S II bands occur in the ranges of 826-793 cm^{-1} (I) and 739-677 cm^{-1} (II, two strong bands). Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p 135, Heyden & Son Ltd., London, 1974.

[bbbb] For compounds of the type ROP=S$(Cl)_2$ the ν_{as} and ν_{sy} PCl_2 bands occur over the ranges 555-533 cm^{-1} and 532-473 cm^{-1} respectively. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p 81, Heyden & Son Ltd., London, 1974.

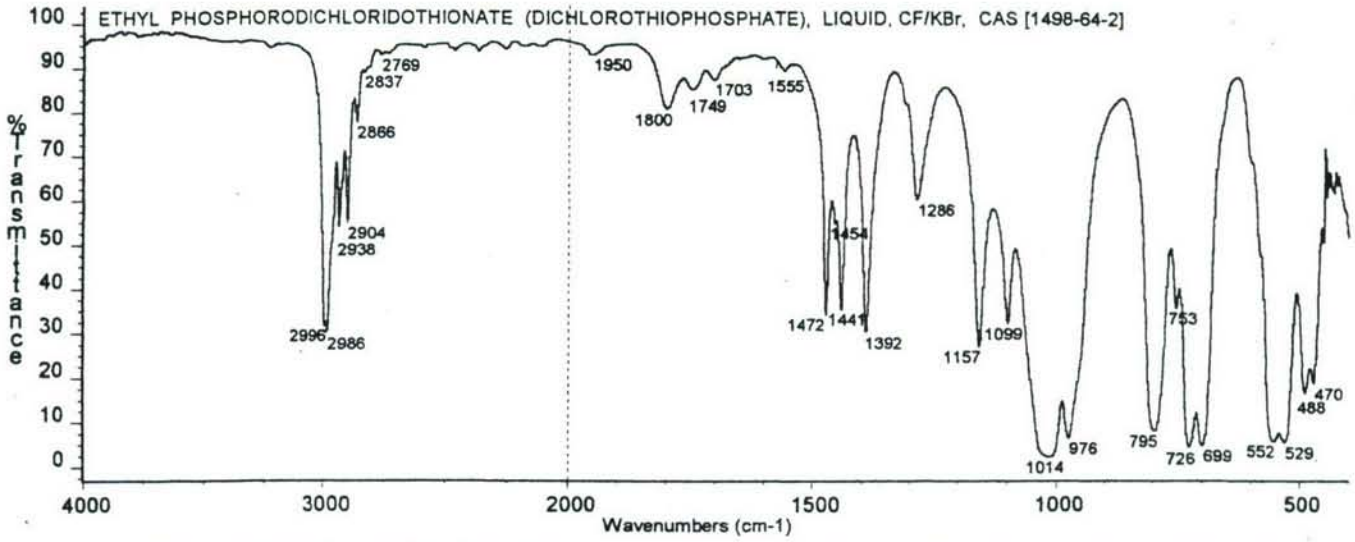


Figure 380 ETHYL PHOSPHORODICHLORIDOTHIONATE (ETHYL DICHLOROTHIOPHOSPHATE), LIQUID, CF/KBr

of exposure to atmospheric moisture, the spectrum shows mainly bands due to POH (ca 2800, 2320, 1650 and 990 cm^{-1}) with very weak bands from the POEthyl moiety still evident. The spectrum may be mostly that of phosphoric acid, H_3PO_4 (***Figure 103***), and some EtO-P=O$(OH)_2$. Not only has the compound hydrolyzed but desulfurization has also occurred to replace the S with oxygen.

3.7.7 Phenylphosphonothioic Dichloride C_6H_5-P=S$(Cl)_2$

The infrared spectrum of phenylphosphonothioic dichloride as a liquid film between KBr windows is given as ***Figure 382***. The band assignments are as follows: 3078 cm^{-1} sh and 3060 cm^{-1} vw (ν C-H aromatic), 1582 cm^{-1} w, 1480 cm^{-1} w and 1439 cm^{-1} ms (aromatic ring C≈C), 1184, 1162, 1027 cm^{-1} vw and 998 cm^{-1} w (β C-H mono-substituted aromatic ring), 1099 cm^{-1} ms (phenyl-P), 748 cm^{-1} s (γ C-H mono-substituted aromatic ring), 689 cm^{-1} s (mono-substituted aromatic ring deformation and P=S), 523 cm^{-1} ms (ν_{as} PCl_2), 499 cm^{-1} ms (ν_{sy} PCl_2).

The effect of atmospheric moisture on phenylphosphonothioic dichloride as a liquid film between KBr windows is illustrated by the infrared spectra presented in ***Figure 383***. After 118 days of exposure to atmospheric moisture, the spectrum shows mainly bands indicative of the POH moiety (2850, 2325, ca 1650 and

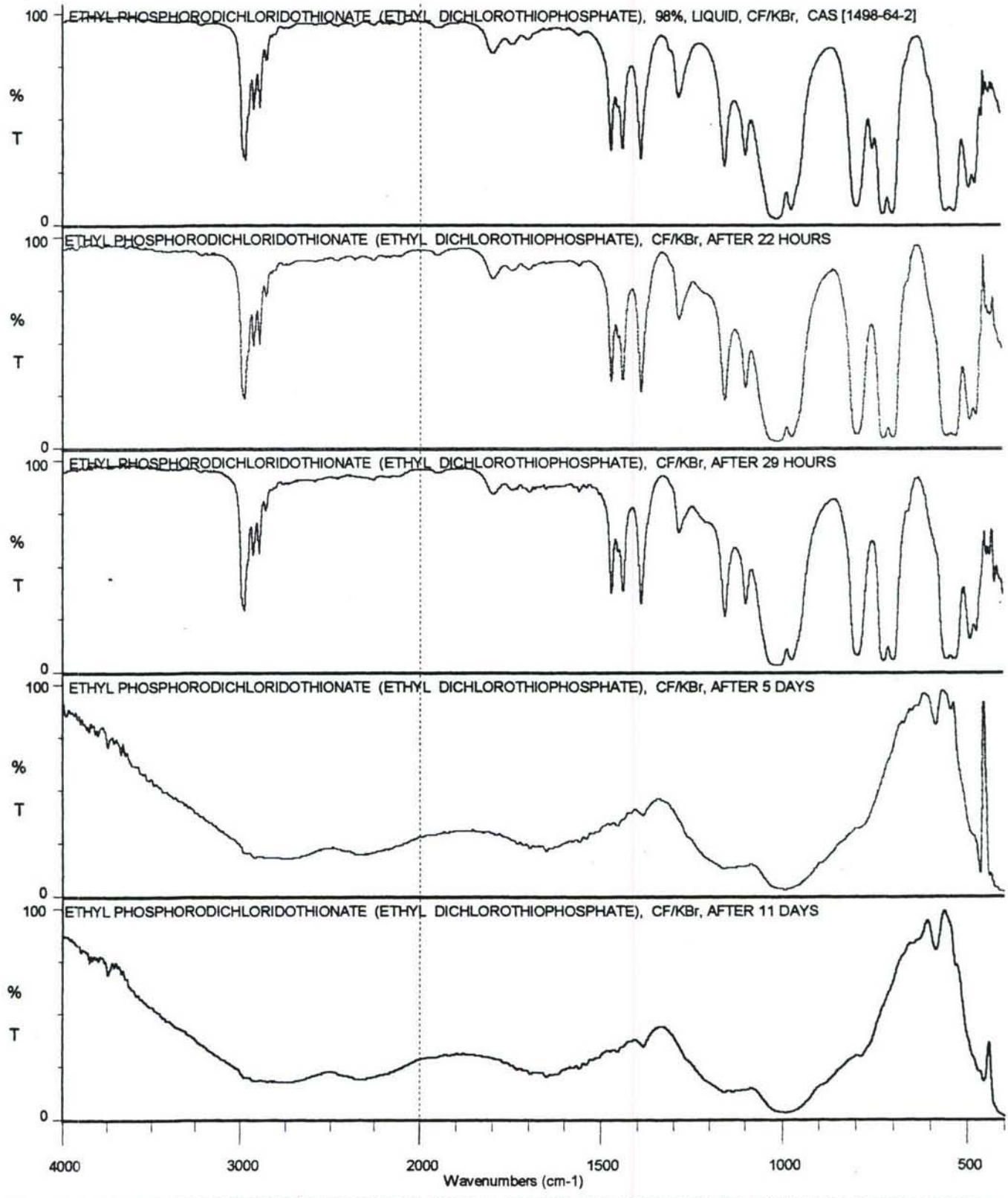


Figure 381 ETHYL PHOSPHORODICHLORIDOTHIONATE (ETHYL DICHLOROTHIOPHOSPHATE), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

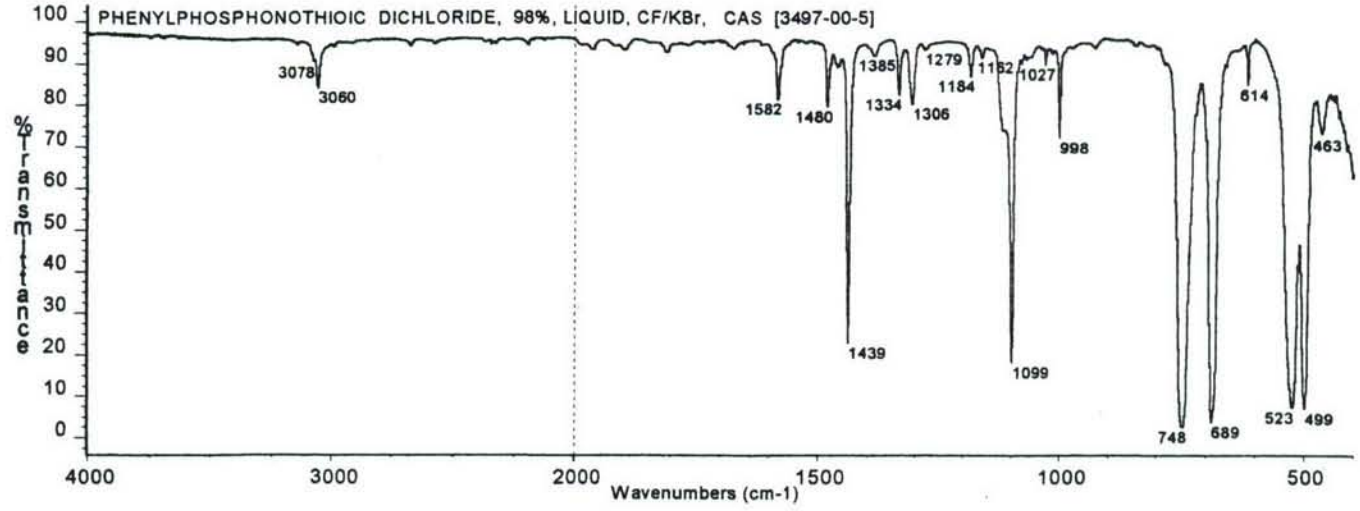


Figure 382 PHENYLPHOSPHONOTHIOIC DICHLORIDE, 98%, LIQUID, CF/KBr

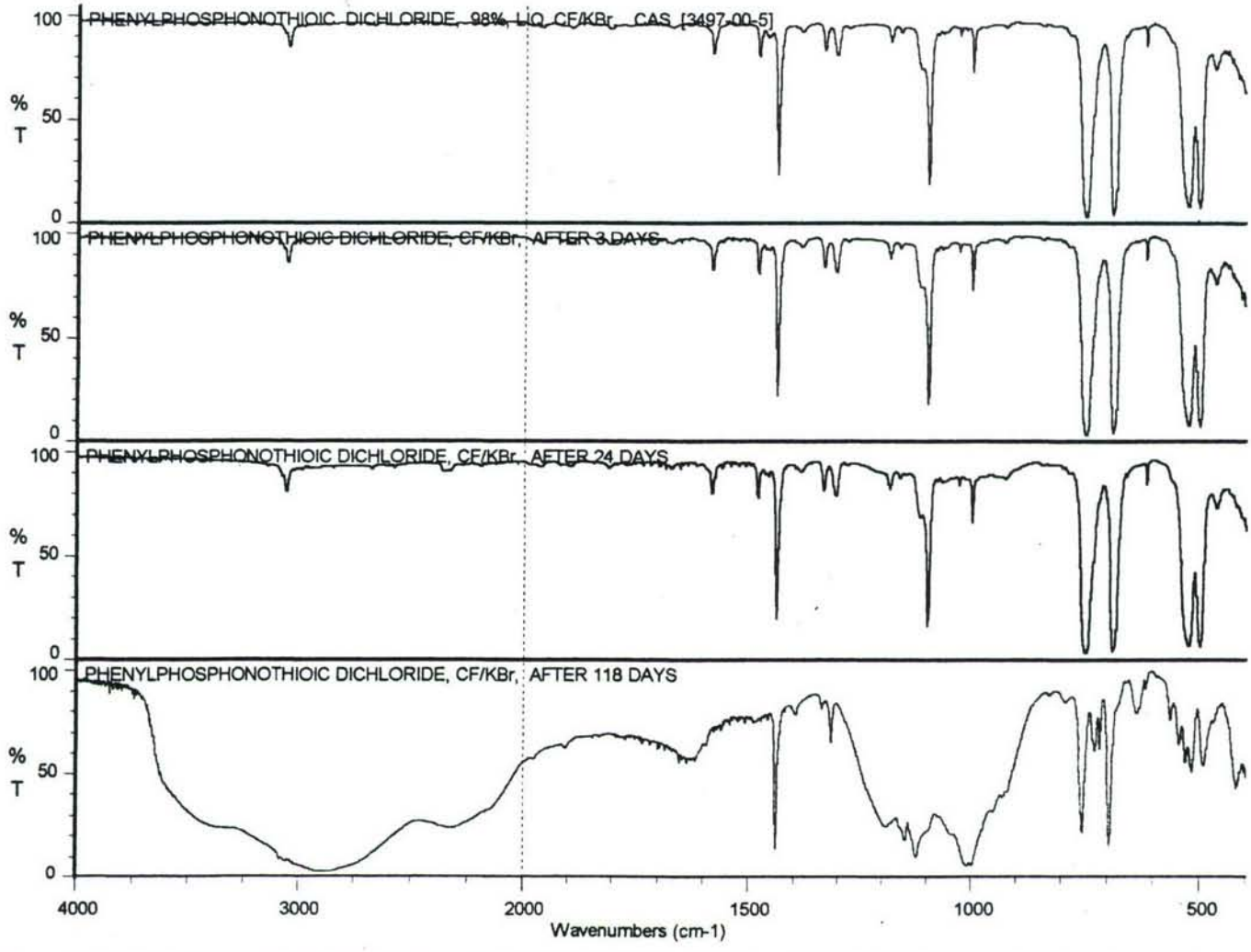


Figure 383 PHENYLPHOSPHONOTHIOIC DICHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

ca 1000 cm^{-1}. Aromatic ring bands are still evident at 3083, 3055, 1439, 754 and 695 cm^{-1}. The original compound, phenylphosphonothioic dichloride, appears to have undergone desulfurization and hydrolysis to form phenylphosphonic acid, C_6H_5-P=O$(OH)_2$ (see ***Figure 135***).

3.7.8 Trimethylphosphine Sulfide $(CH_3)_3P=S$

The infrared spectrum of solid trimethylphosphine sulfide as a KBr pellet is reproduced as ***Figure 384***. The band assignments are as follows: 3436 and ca 1640 cm^{-1} (H_2O), 2975 cm^{-1} m (ν_{as} CH_3), 2904 cm^{-1} vw (ν_{sy} CH_3), 1425 cm^{-1} m, 1422 cm^{-1} sh, 1417 cm^{-1} sh, 1405 cm^{-1} w (δ_{as} P-CH_3), 1304 cm^{-1} m, 1292 and 1285 cm^{-1} ms (δ_{sy} P-CH_3), 978 and 949 cm^{-1} s (P-CH_3 as and sy rock), 745 and 714 cm^{-1} s (ν P-C), 564 cm^{-1} s (ν P=S).

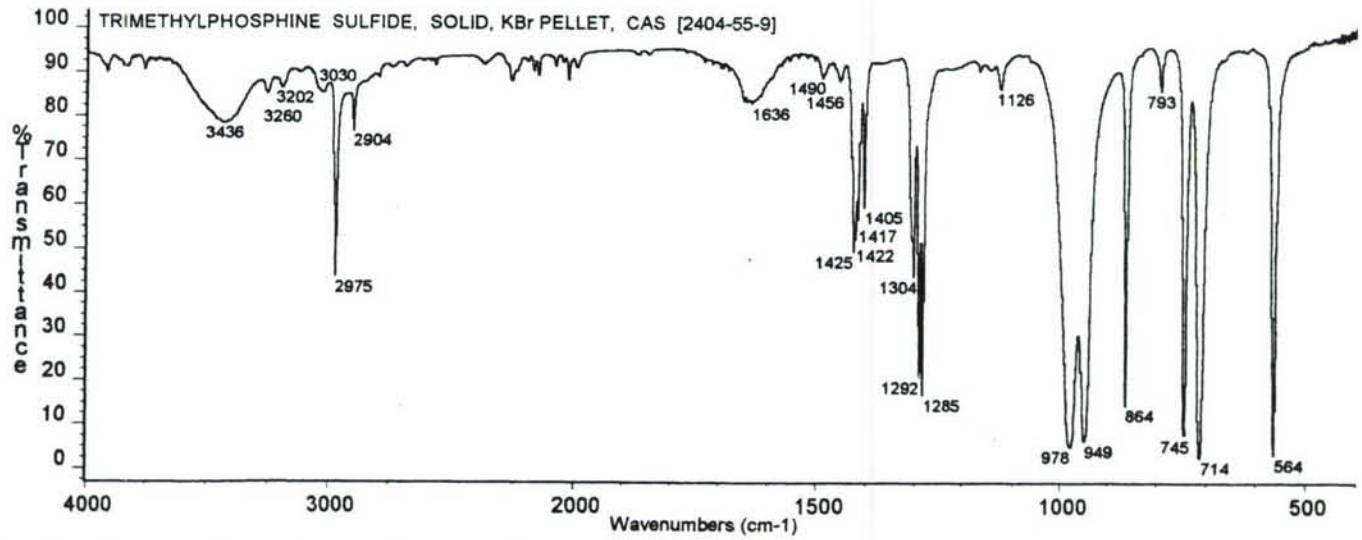


Figure 384 TRIMETHYLPHOSPHINE SULFIDE, SOLID, KBr PELLET

3.7.9 Triethylphosphine Sulfide $(CH_3$-$CH_2)_3P=S$

The infrared spectrum of triethylphosphine sulfide as a solid prepared as a KBr pellet is presented as ***Figure 385***. The band assignments are as follows: 2969 cm^{-1} w (ν_{as} CH_3), 2941 and 2930 cm^{-1} w (ν_{as} CH_2), 2897 cm^{-1} vw (ν_{sy} CH_3), 2880 cm^{-1} w (ν_{sy} CH_2), 1462 cm^{-1} w (δ_{as} CH_3), 1417 and 1403 cm^{-1} w (δ P-CH_2), 1376 cm^{-1} w (δ_{sy} CH_3), 1269 and 1247 cm^{-1} w (ω, τ CH_2 of P-Et), 1046 and 995 cm^{-1} m (ν C-C of P-Et), 771 cm^{-1} s and 762 cm^{-1} sh (CH_2 rock of P-Et, and ν_{as} P-C ?), 692 cm^{-1} w and 673 cm^{-1} m (ν_{sy} P-C), 537 cm^{-1} m (ν P=S).

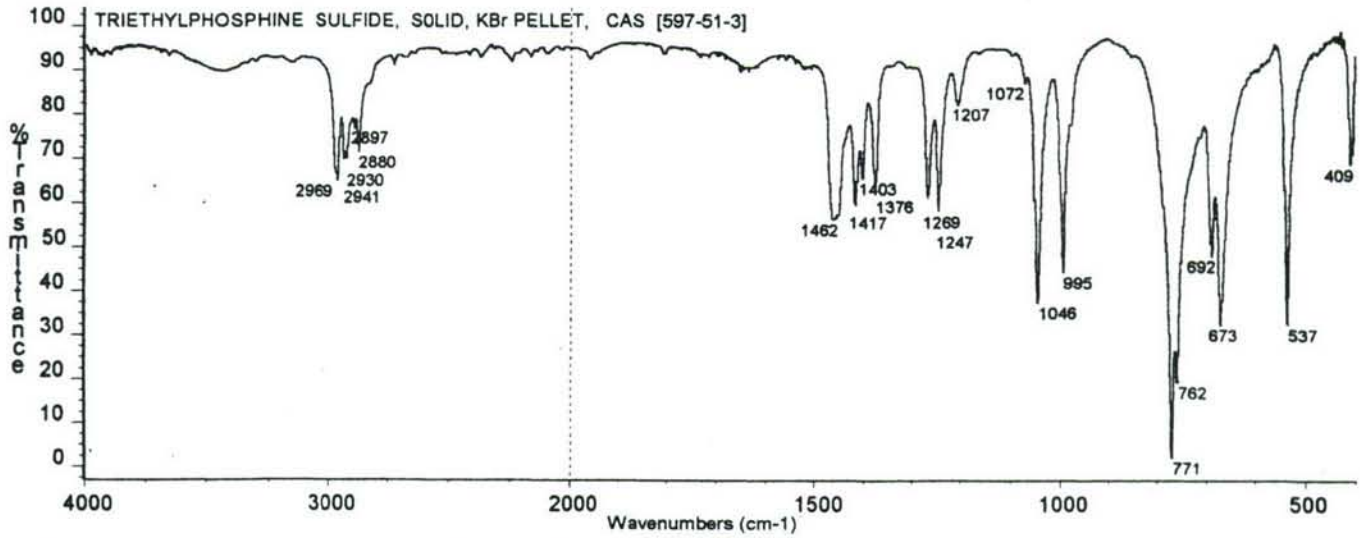


Figure 385 TRIETHYLPHOSPHINE SULFIDE, SOLID, KBr PELLET

3.7.10 Tri-n-butylphosphine Sulfide $(H_9C_4\text{-}n)_3P{=}S$

The infrared spectrum of tri-n-butylphosphine sulfide as a liquid film between KBr windows is reproduced as ***Figure 386***. The band assignments are as follows: 2958 cm^{-1} s (ν_{as} CH_3), 2933 cm^{-1} ms (ν_{as} CH_2), ca 2900 cm^{-1} sh (ν_{sy} CH_3), 2872 cm^{-1} m (ν_{sy} CH_2), 1465 cm^{-1} m (δ CH_2, δ_{as} CH_3), 1407 cm^{-1} w (δ P-CH_2), 1379 cm^{-1} w (δ_{sy} CH_3), 1212, 1183 cm^{-1} w-vw (ω, τ CH_2), 1095 and 1052 cm^{-1} w-vw (ν C-C), 790 cm^{-1} m (P=S I ?), 735 cm^{-1} m (CH_2 rock), 673 cm^{-1} vw (ν P-C ?), 598 and 587 cm^{-1} w (P=S II).

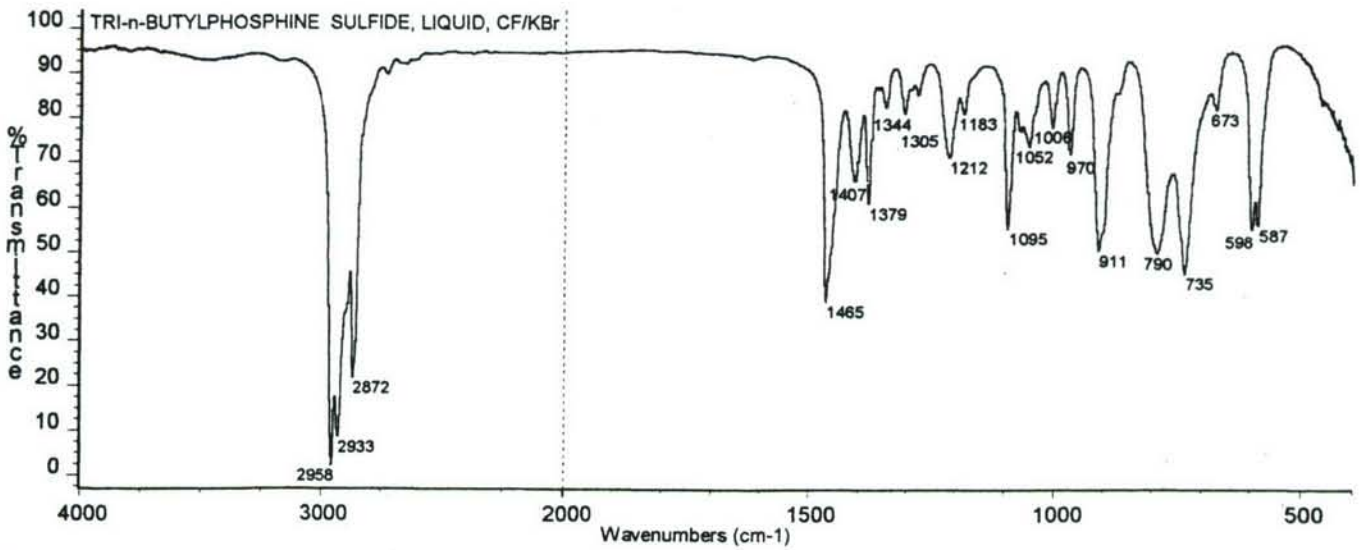


Figure 386 TRI-n-BUTYLPHOSPHINE SULFIDE, LIQUID, CF/KBr

3.7.11 Tricyclohexylphosphine Sulfide $(H_{11}C_6)_3P{=}S$

The infrared spectrum of tricyclohexylphosphine sulfide as a KBr pellet is given in ***Figure 387***. The band assignments are as follows: 3442 and ca 1630 cm^{-1} vw (H_2O), 2935 cm^{-1} sh and 2925 cm^{-1} s (ν_{as} CH_2), 2853 cm^{-1} ms (ν_{sy} CH_2), 1444 cm^{-1} m (δ CH_2), 1004, 900 and 850 cm^{-1} w-m (ring), 749 cm^{-1} ms (P=S I ?), 628 cm^{-1} s (P=S II).

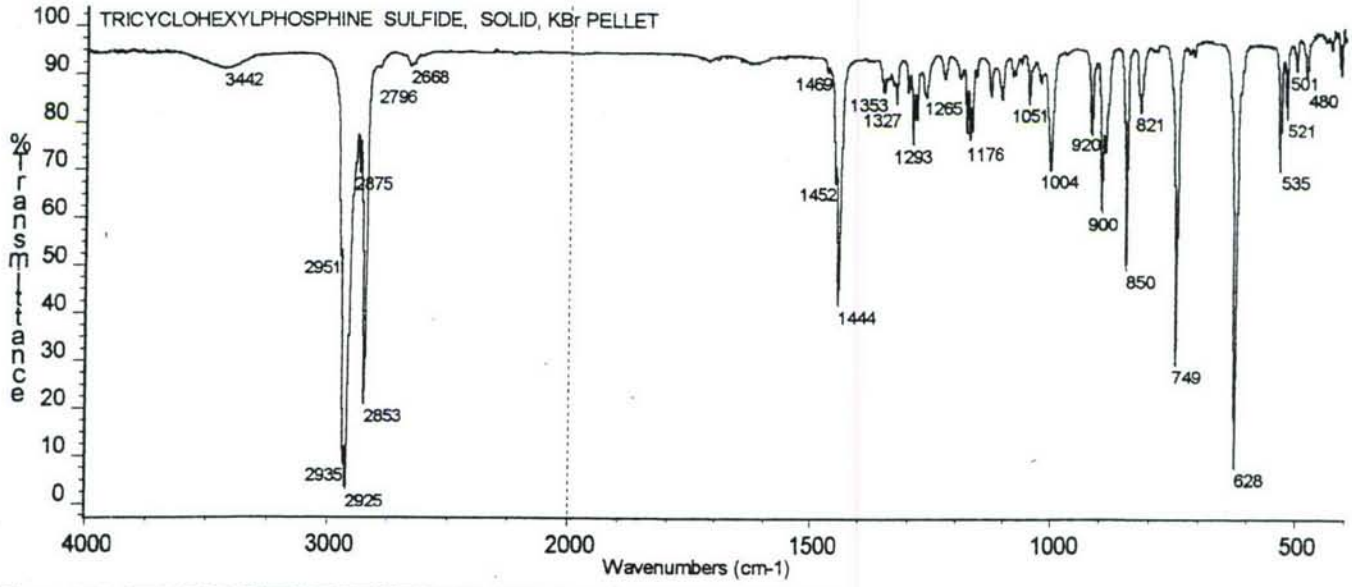


Figure 387 TRICYCLOHEXYLPHOSPHINE SULFIDE, SOLID, KBr PELLET

3.7.12 Triphenylphosphine Sulfide $(H_5C_6)_3P{=}S$

The infrared spectrum of triphenylphosphine sulfide as a KBr pellet is presented as ***Figure 388***. The band assignments are as follows: 3441 and ca 1635 cm^{-1} vw (H_2O), 3072 cm^{-1} sh, 3056 cm^{-1} vw (ν C-H aromatic), 1585 and 1573 cm^{-1} vvw, 1479 cm^{-1} w and 1434 cm^{-1} ms (aromatic ring C≈C), 1182, 1158, 1069, 1026 and 999 cm^{-1} vw-w (β C-H mono-substituted aromatic ring), 1104 cm^{-1} ms (phenyl-P), 753 and 747 cm^{-1} m (γ C-H mono-substituted aromatic ring), 692 cm^{-1} s (mono-substituted aromatic ring deformation), 638 cm^{-1} (ν P=S), 517, 510 cm^{-1} ms (mono-substituted aromatic ring). The infrared spectrum for triphenylphosphine sulfide may be compared to the spectrum (KBr pellet) for triphenylphosphine oxide (***Figure 164***).

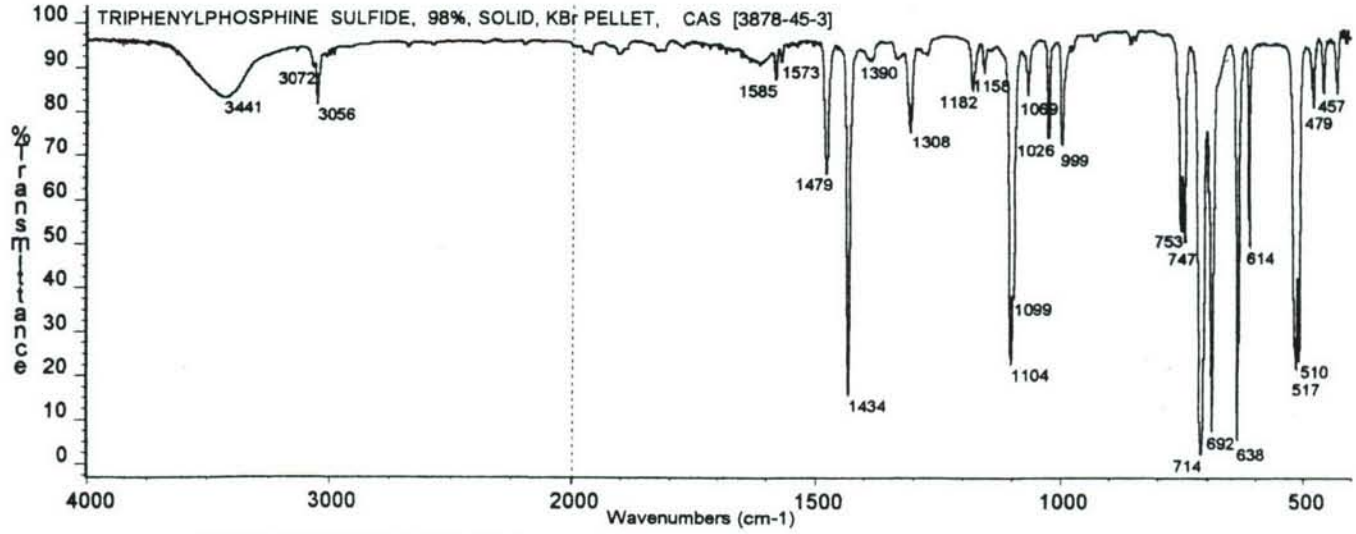


Figure 388 TRIPHENYLPHOSPHINE SULFIDE, 98%, SOLID, KBr PELLET

3.7.13 Tetramethyldiphosphine Disulfide $(CH_3)_2P=S-P=S(CH_3)_2$

The infrared spectrum of tetramethyldiphosphine disulfide as a KBr pellet is given in ***Figure 389***. The band assignments are as follows: 3417 and ca 1650 cm^{-1} w (H_2O), 2989 cm^{-1} vw, 2969 cm^{-1} w (ν_{as} CH_3), 2899 cm^{-1} w (ν_{sy} CH_3), 1403 cm^{-1} m and 1393 cm^{-1} w (δ_{as} P-CH_3), 1284 cm^{-1} ms (δ_{sy} P-CH_3), 941 and 882 cm^{-1} ms-s (P-CH_3 rock), 747 cm^{-1} m and 734 cm^{-1} ms (ν P-C, P=S I), 569 cm^{-1} s (P=S II).[cccc]

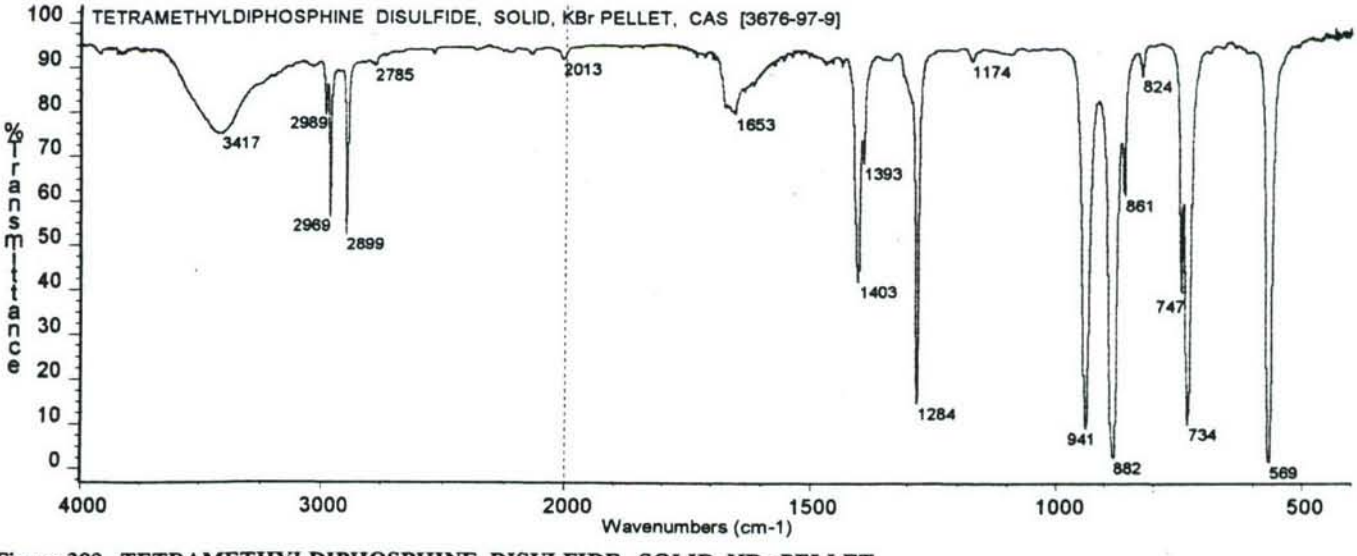


Figure 389 TETRAMETHYLDIPHOSPHINE DISULFIDE, SOLID, KBr PELLET

[cccc] Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 130, 133, Heyden & Son Ltd., London, 1974. The P=S I and P=S II bands are listed as occurring in the ranges 784-683 cm^{-1} (I) and 584-549 cm^{-1} (II).

3.7.14 Tetraethyldiphosphine Disulfide $(CH_3CH_2)_2P(=S)\text{-}P=S(CH_2CH_3)_2$

The infrared spectrum of tetraethyldiphosphine disulfide as a KBr pellet is reproduced in ***Figure 390***. The band assignments are as follows: 3420 cm^{-1} vw and ca 1630 cm^{-1} vvw (H_2O), 2986 cm^{-1} sh and 2976 cm^{-1} w (ν_{as} CH_3), 2937 cm^{-1} w (ν_{as} CH_2), 2905 cm^{-1} vw (ν_{sy} CH_3), 2877 cm^{-1} vw (ν_{sy} CH_2), 1461 cm^{-1} sh and 1457 cm^{-1} w (δ_{as} CH_3), 1405 cm^{-1} vw (δ P-CH_2), 1380 cm^{-1} m (δ_{sy} CH_3), 1265 cm^{-1} vvw and 1237, 1230 cm^{-1} vw (ω, τ CH_2 of P-Et), 1037 and 1024 cm^{-1} m (ν C-C of P-Et), 774 cm^{-1} s (CH_2 rock ?), 738 cm^{-1} m (P=S I), 685 cm^{-1} s (ν P-C), 549 cm^{-1} ms (P=S II, ν P=S), 437 cm^{-1} w (P-P ?).

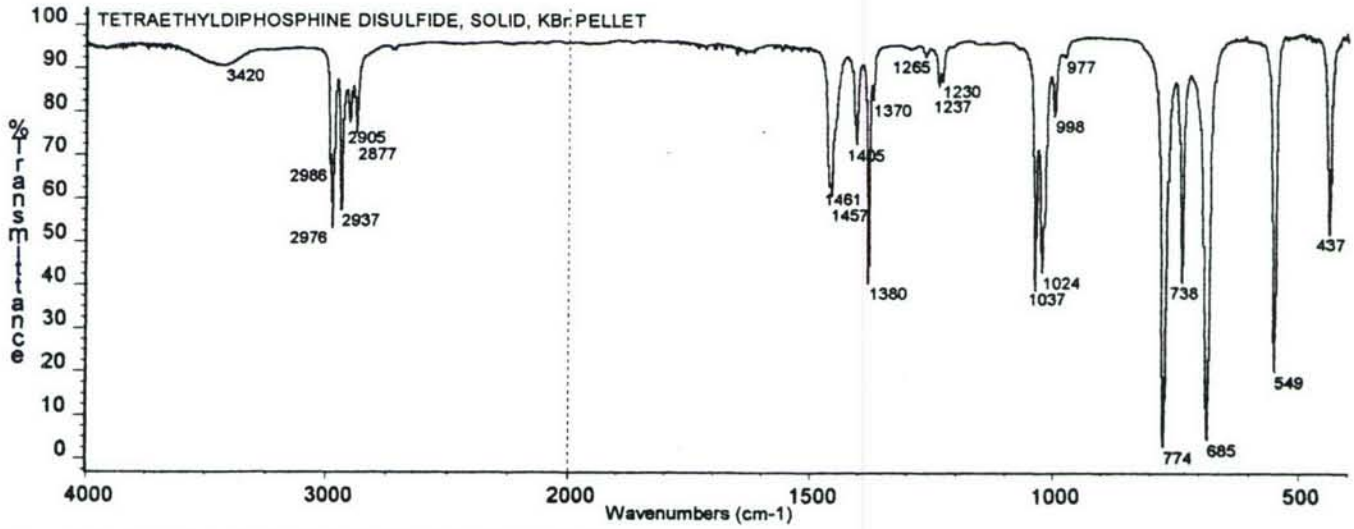


Figure 390 TETRAETHYLDIPHOSPHINE DISULFIDE, SOLID, KBr PELLET

3.7.15 Tetrabutyldiphosphine Disulfide $(H_9C_4)_2P(=S)\text{-}P=S(C_4H_9)_2$

The infrared spectrum of tetrabutyldiphosphine disulfide as a KBr pellet is presented as ***Figure 391***. The band assignments are as follows: 3437 cm^{-1} w and ca 1630 cm^{-1} vw (H_2O), 2957 cm^{-1} ms (ν_{as} CH_3), 2931 cm^{-1} m (ν_{as} CH_2), 2900 cm^{-1} sh (ν_{sy} CH_3), 2872 cm^{-1} m (ν_{sy} CH_2), 1466 cm^{-1} m (δ CH_2, δ_{as} CH_3), 1393 cm^{-1} w (δ P-CH_2), 1379 cm^{-1} w (δ_{sy} CH_3), 1213 cm^{-1} w and 1199 cm^{-1} sh (ω, τ CH_2), 1089 and 1046 cm^{-1} w (ν C-C), 786 cm^{-1} w (P=S I ?), 744 cm^{-1} m (CH_2 rock), 703 cm^{-1} w (ν P-C), 584 cm^{-1} s (P=S II, ν P=S), 434 cm^{-1} vvw (P-P ?).

3.7.16 Tetraphenyldiphosphine Disulfide $(H_5C_6)_2P(=S)\text{-}P=S(C_6H_5)_2$

The infrared spectrum of tetraphenyldiphosphine disulfide as a KBr pellet is give as ***Figure 392***. The

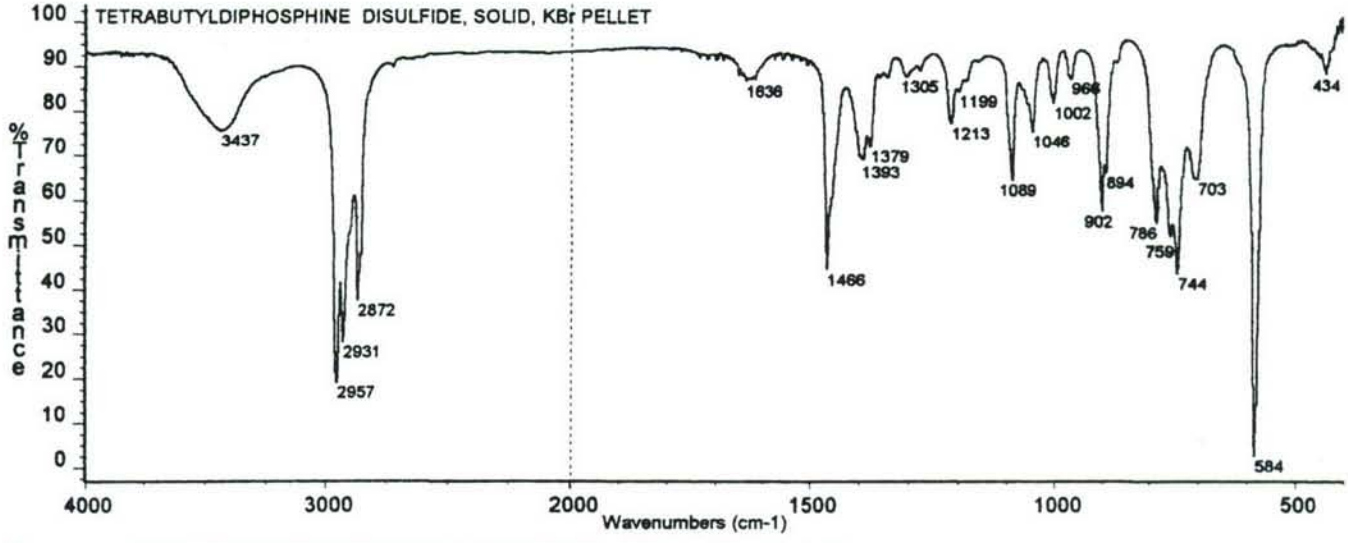


Figure 391 TETRABUTYLDIPHOSPHINE DISULFIDE, SOLID, KBr PELLET

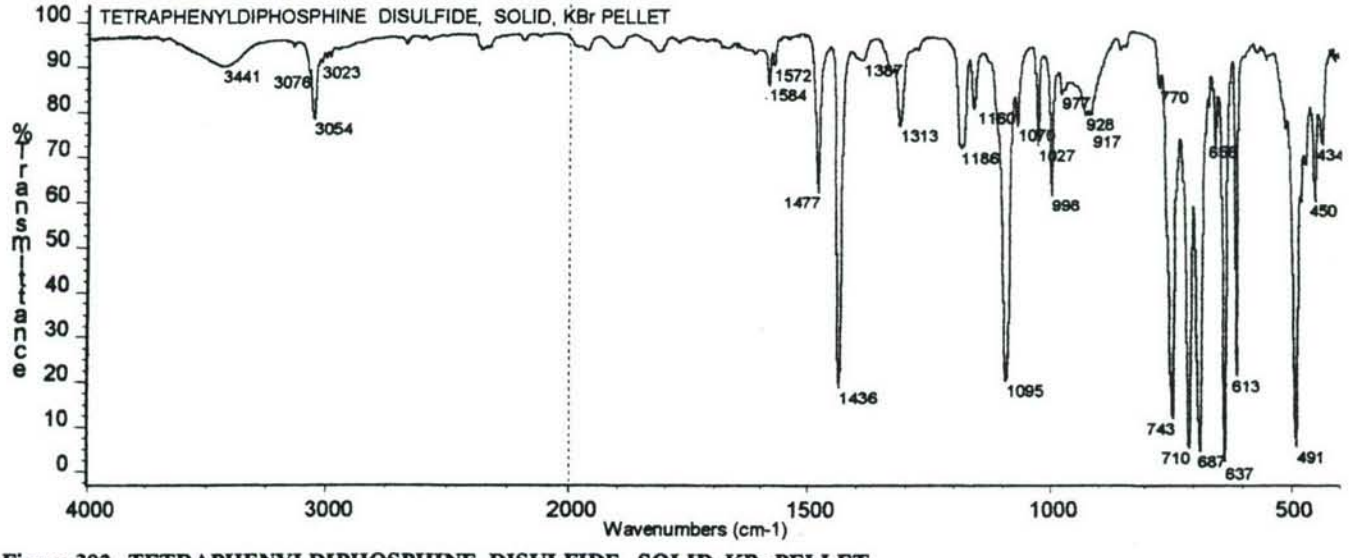


Figure 392 TETRAPHENYLDIPHOSPHINE DISULFIDE, SOLID, KBr PELLET

band assignments are as follows: 3441 cm^{-1} vw (H_2O), 3076 cm^{-1} sh, 3054 cm^{-1} w, 3023 cm^{-1} vvw (ν C-H aromatic), 1584 and 1572 cm^{-1} vw, 1477 cm^{-1} m and 1436 cm^{-1} ms (aromatic ring C≈C), 1186, 1160, 1070, 1027 and 998 cm^{-1} w-m (β C-H mono-substituted aromatic ring), 1095 cm^{-1} ms (phenyl-P), 748 cm^{-1} ms (γ C-H mono-substituted aromatic ring), 710, 687 cm^{-1} s (mono-substituted aromatic ring deformation), 637 cm^{-1} s (P=S II, ν P=S), 491 cm^{-1} s (mono-substituted ring), 434 cm^{-1} w (P-P ?).

3.7.17 Trimethyl Thiophosphate (Trimethyl Phosphorothionate) $(CH_3O)_3P=S$

The infrared spectrum of trimethyl thiophosphate (trimethyl phosphorothionate) as a liquid film between KBr windows is given in ***Figure 393***. The band assignments are as follows: 2952 cm^{-1} m (ν_{as} CH_3), 2848 cm^{-1} w (ν_{sy} CH_3), 1866 cm^{-1} vw (1032 + 827 = 1859 cm^{-1}), 1646 cm^{-1} vw (2 x 827 = 1654 cm^{-1}), 1457 and 1444 cm^{-1} m (δ CH_3), 1284 cm^{-1} vw [possible ν P=O of $(CH_3O)_3P=O$, which has a *calculated* value of 1278 cm^{-1} and an actual value of 1283 cm^{-1}, see ***Figure 291***], 1183 cm^{-1} m (CH_3 rock of $POCH_3$, characteristic), 1032 cm^{-1} s (ν P-O-C), 827 cm^{-1} ms (POC, P=S I), 620 and 599 cm^{-1} w (P=S II, ν P=S, two bands-isomers).[dddd]

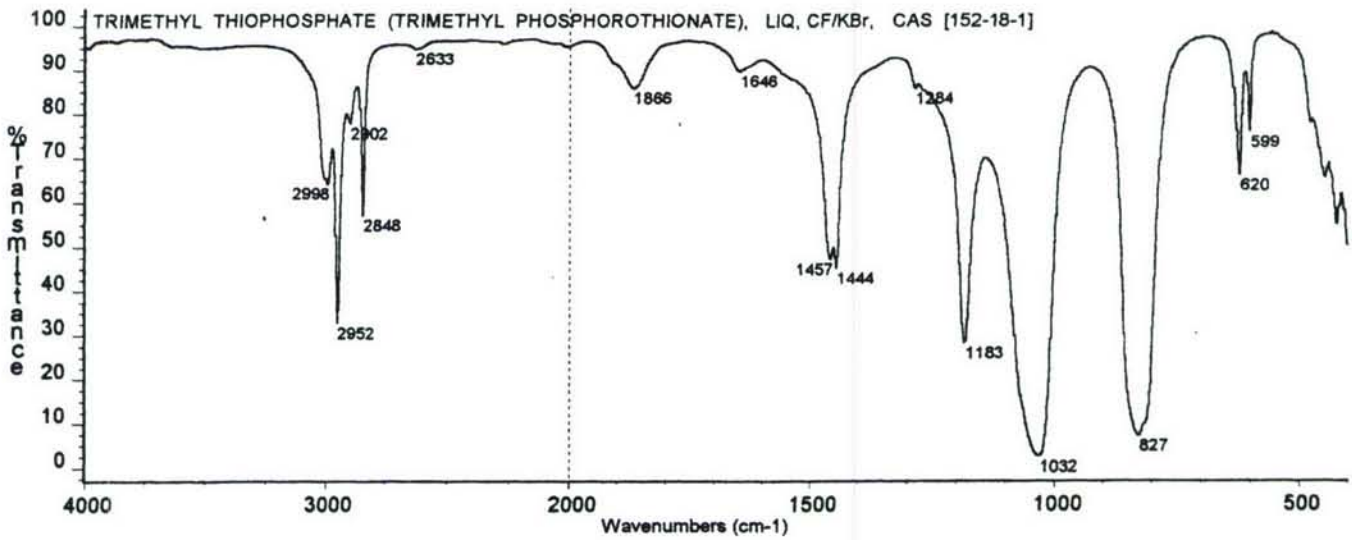


Figure 393 TRIMETHYL THIOPHOSPHATE (TRIMETHYL PHOSPHOROTHIONATE), LIQUID, CF/KBr

3.7.18 Tri-*p*-tolyl Thiophosphate (Tri-*p*-tolyl Phosphorothionate) $(CH_3\text{-}C_6H_4\text{-}O)_3P=S$

The infrared spectrum of tri-*p*-tolyl thiophosphate (tri-*p*-tolyl phosphorothionate) as a KBr pellet is presented as ***Figure 394***. The band assignments are as follows: 3066 and 3036 cm^{-1} vvw-vw (ν C-H aromatic ring), 2924 cm^{-1} vw and 2868 cm^{-1} vvw (ν CH_3), 1602 cm^{-1} vw, 1503 cm^{-1} ms (aromatic ring C≈C), 1457 cm^{-1} vw (aromatic ring and δ_{as} CH_3), 1383 cm^{-1} vvw (δ_{sy} CH_3), 1186 cm^{-1} ms (ν C-O), 1103 and 1018 cm^{-1} w (β C-H of *para*-disubstituted aromatic ring), 957 cm^{-1} s (ν P-O), 826 cm^{-1} m (γ C-H *para*-disubstituted aromatic ring), 752

[dddd] Compounds of the type $(RO)_3P=S$ have the P=S I band in the range 844-800 cm^{-1} and the P=S II band in the range 713-602 cm^{-1}. The splitting of the P=S II band into two bands has been shown to be due to conformational isomers. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 130, 133, Heyden & Son Ltd., London, 1974.

cm^{-1} m (P=S I ?), 642, 615 cm^{-1} w (P=S II), 492 cm^{-1} m (out-of-plane ring quadrant bending, *para*-disubstituted aromatic ring ?).

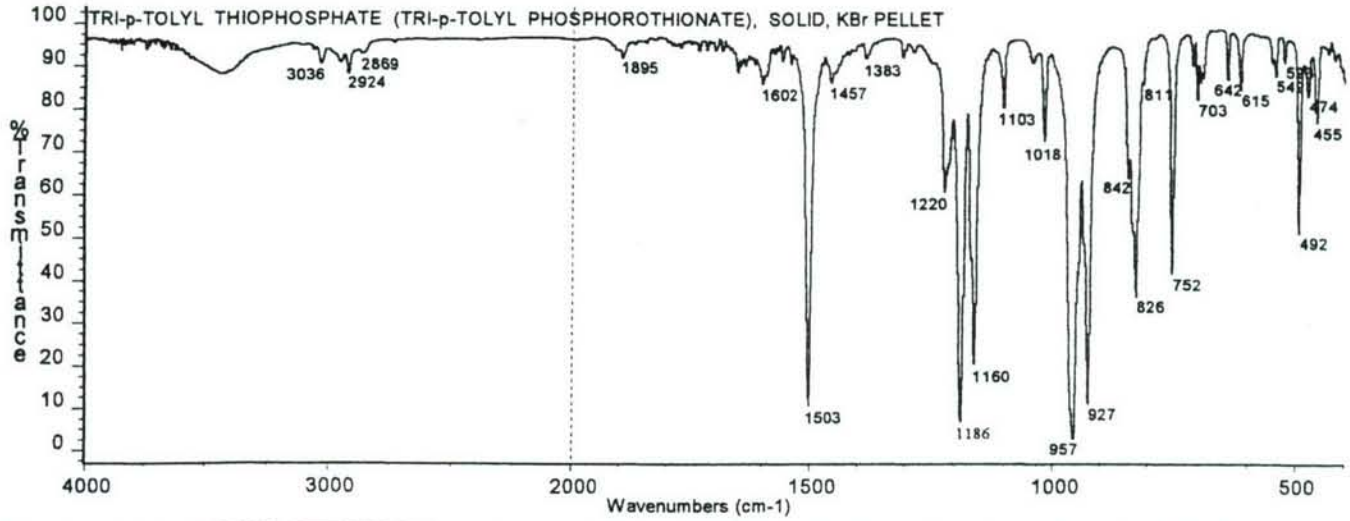


Figure 394 TRI-*p*-TOLYL THIOPHOSPHATE (TRI-*p*-TOLYL PHOSPHOROTHIONATE), SOLID, KBr PELLET

3.7.19 O,O-Diethyl O-*p*-Nitrophenyl Phosphorothioate (**Parathion**) $O_2N\text{-}C_6H_4\text{-}O\text{-}P{=}S(OCH_2CH_3)_2$

The infrared spectrum O,O-diethyl O-*p*-nitrophenyl phosphorothioate (diethyl *p*-nitrophenyl phosphorothionate, **Parathion**) as a thin liquid film between KBr windows is presented as ***Figure 395***. The band

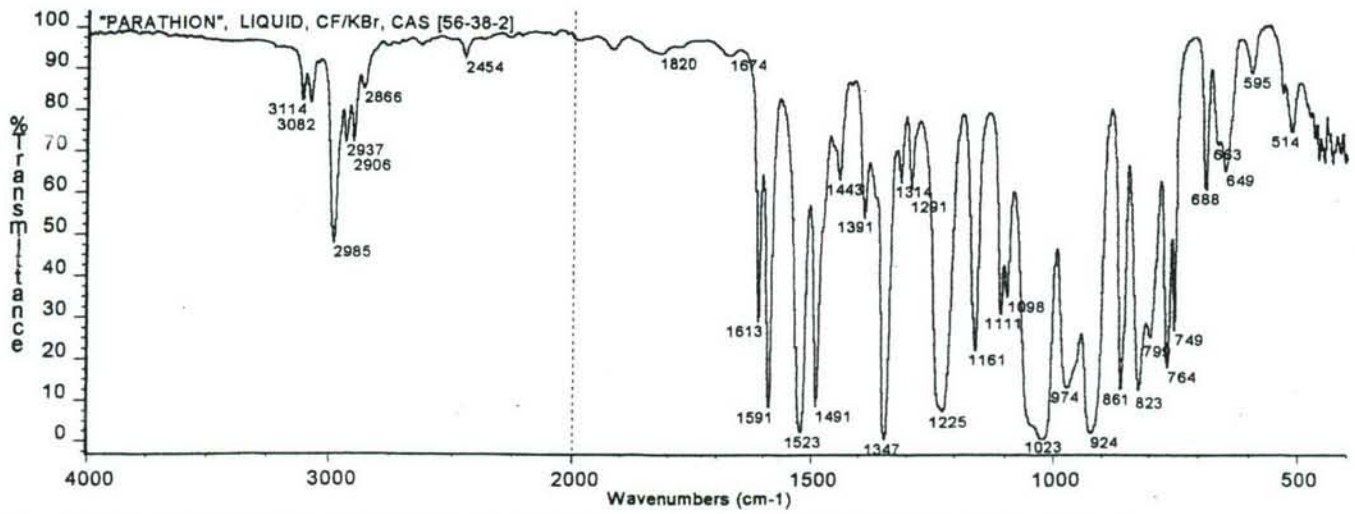


Figure 395 PARATHION, O,O-DIETHYL O-*p*-NITROPHENYL PHOSPHOROTHIONATE, LIQUID, CF/KBr

assignments are as follows: 3114 and 3082 cm^{-1} vw (ν C-H aromatic ring), 2985 cm^{-1} m (ν_{as} CH_3), 2937 cm^{-1} w (ν_{as} CH_2), 2906 cm^{-1} w (ν_{sy} CH_3), 2866 cm^{-1} vw (ν_{sy} CH_2), 2454 cm^{-1} vvw (2 x 1225 = 1450 cm^{-1}), 1613 cm^{-1} m

and 1591 cm^{-1} ms (aromatic ring C≈C), 1523 s cm^{-1} s (ν_{as} NO_2), 1491 cm^{-1} ms (aromatic ring C≈C and δ OCH_2), 1443 cm^{-1} w (aromatic ring C≈C and δ_{as} CH_3), 1391 cm^{-1} w (ω OCH_2), 1347 cm^{-1} s (ν_{sy} NO_2), 1225 cm^{-1} ms (ν aryl C-O), 1161 and 1098 cm^{-1} m (CH_3 rock of POEt, characteristic), 1111 cm^{-1} m (β C-H of *para*-disubstituted aromatic ring), 1023 cm^{-1} s (ν P-O-C aliphatic), 974 cm^{-1} ms (ν C-C of POEt), 924 cm^{-1} s (ν P-O aromatic), 866 and 823 cm^{-1} ms (NO_2 scissors deformation and γ C-H of *para*-disubstituted aromatic ring), 799 cm^{-1} w (POC aliphatic), 764 cm^{-1} ms (NO_2 moiety), 649 cm^{-1} w (ν P=S).

3.7.20 Ethyl Hydrogenmethylphosphinothionate CH_3-P=S(H)(OCH_2CH_3)

The infrared spectrum of a thin liquid film of ethyl hydrogenmethylphosphinothionate between KBr windows is reproduced as ***Figure 396***. The band assignments are as follows: 2982 cm^{-1} m (ν_{as} CH_3), 2936 cm^{-1} w (ν_{as} CH_2), 2899 cm^{-1} w (ν_{sy} CH_3), ca 2870 cm^{-1} sh (ν_{sy} CH_2), 2344 cm^{-1} w (ν P-H), 1475 cm^{-1} vw (δ OCH_2), 1444 cm^{-1} vw (δ_{as} CH_3), 1406 cm^{-1} w (δ_{as} P-CH_3), 1391 cm^{-1} w (ω OCH_2), 1293 cm^{-1} m (δ_{sy} P-CH_3), 1160 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1046 and 1013 cm^{-1} ms (ν P-O-C), 949 cm^{-1} s (P-H deformation and ν C-C of POEt), 882 cm^{-1} w (P-CH_3 rock), 819 cm^{-1} m (POC), 752 cm^{-1} ms (ν P-C, P=S I ?), 617 cm^{-1} m (P=S II, ν P=S).

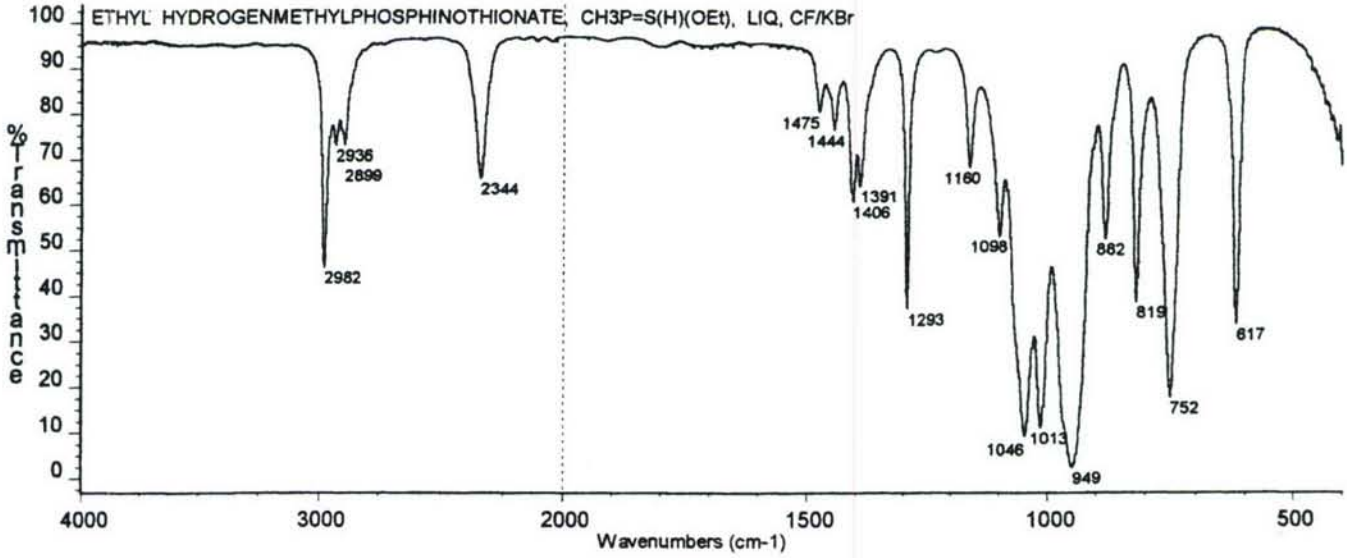


Figure 396 ETHYL HYDROGENMETHYLPHOSPHINOTHIONATE, LIQUID, CF/KBr

3.7.21 Diphenylphosphine Sulfide $(C_6H_5)_2P{=}S(H)$

The infrared spectrum of diphenylphosphine sulfide as a KBr pellet is given in ***Figure 397***. The band assignments are as follows: 3439 cm^{-1} vw (H_2O), 3071, 3049, 3018 cm^{-1} vvw (ν C-H aromatic), 2359 and 2348 cm^{-1} vw (ν P-H), 1586 and 1574 cm^{-1} vvw, 1481 cm^{-1} w and 1437 cm^{-1} ms (aromatic ring C≈C), 1182, 1158, 1069, 1027 and 999 cm^{-1} vw (β C-H mono-substituted aromatic ring), 1109 cm^{-1} m (phenyl-P), 930, 914,903, 882 cm^{-1} m-ms (P-H deformation), 750, 739 cm^{-1} m-ms (γ C-H mono-substituted aromatic ring), 711, 690 cm^{-1} s-ms (mono-substituted aromatic ring deformation), 636 cm^{-1} s (ν P=S), 504 cm^{-1} m (mono-substituted aromatic ring).

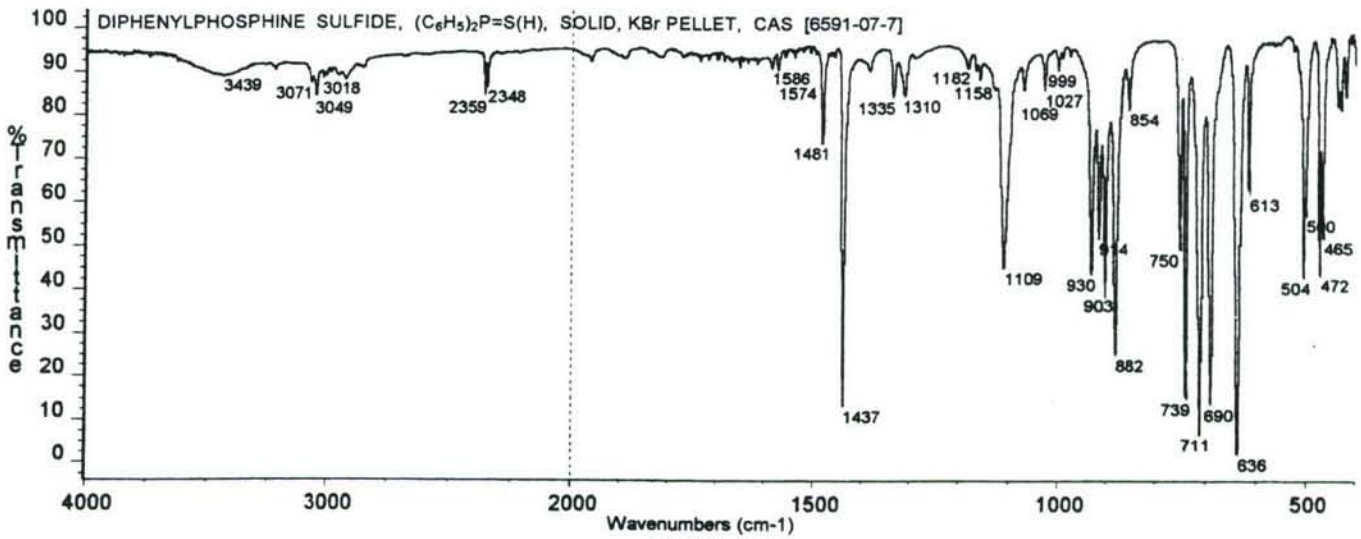


Figure 397 DIPHENYLPHOSPHINE SULFIDE, SOLID, KBr PELLET

3.7.22 Diethyl Dithiophosphate (O,O-Diethyl Dithiophosphoric Acid, Diethyl Phosphorothiolothionic Acid, O,O-Diethyl S-Hydrogen Phosphorothiolothionate) $HS{-}P{=}S(OCH_2CH_3)_2$

The infrared spectrum of diethyl dithiophosphate (O,O-diethyl dithiophosphoric acid) as a liquid film between KBr windows is given in ***Figure 398***. The band assignments are as follows: 2982 cm^{-1} m (ν_{as} CH_3), 2936 cm^{-1} w (ν_{as} CH_2), 2901 cm^{-1} w (ν_{sy} CH_3), 2867 cm^{-1} vw (ν_{sy} CH_2), 2525 cm^{-1} sh, 2459 cm^{-1} w (ν S-H),[eeee] 1474 cm^{-1} w (δ OCH_2), 1442 cm^{-1} w (δ_{as} CH_3), 1390 cm^{-1} m (ω OCH_2), ca 1375 cm^{-1} sh (δ_{sy} CH_3), 1290 cm^{-1} vw

[eeee] The 2525 cm^{-1} band is given as being due to the free S-H while the 2459 cm^{-1} band is listed as being due to bonded S-H. Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S., "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)", p. 37 IR No. 45, Kluwer Academic Publishers, Boston, 1990.

(ω, τ CH_2), 1161 and 1099 cm^{-1} m (CH_3 rock of POEt, characteristic), 1014 cm^{-1} s (ν P-O-C), 964 cm^{-1} ms (ν C-C of POEt), 848 cm^{-1} m (S-H bending),[fffff] 767 cm^{-1} m (POC), 656 cm^{-1} ms (P=S II, ν P=S),[ggggg] 540 and 508 cm^{-1} w (ν P-SH).[hhhhh]

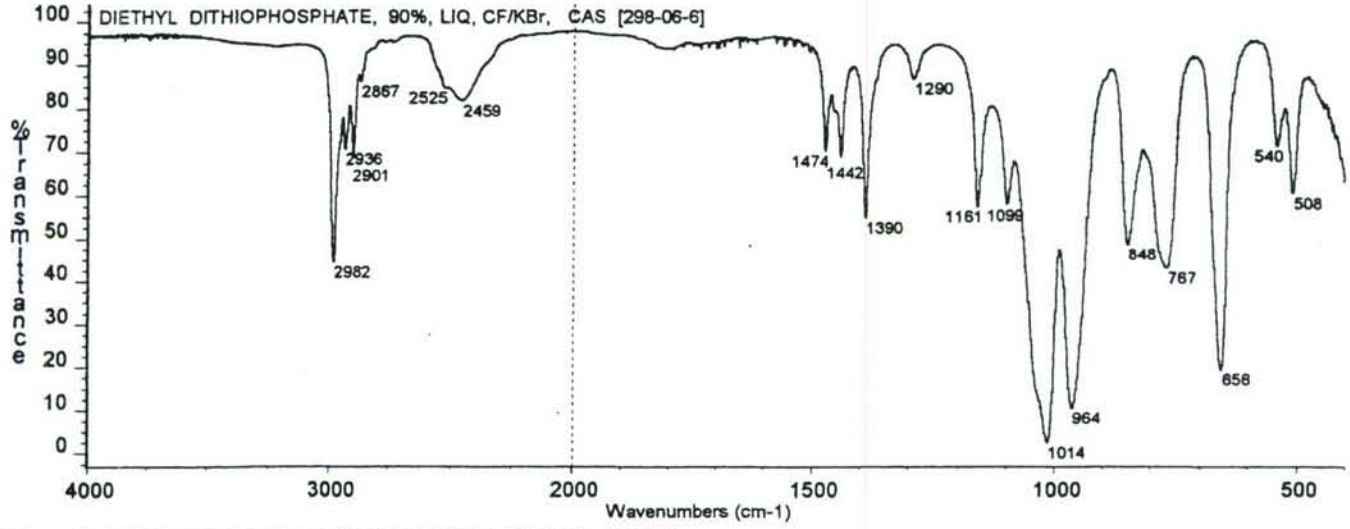


Figure 398 DIETHYL DITHIOPHOSPHATE, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of diethyl dithiophosphate (O,O-diethyl dithiophosphoric acid) between KBr windows is illustrated by the infrared spectra presented in ***Figures 399A*** and ***399B***. As the time of exposure to atmospheric moisture approaches the 10th day (***Figure 399A***), the bands due to the P-SH moiety (540 and 508 cm^{-1}) have just about disappeared from the spectrum. The P=S band near 656 cm^{-1} gradually decreases in intensity, being replaced by two bands near 630 and 584 cm^{-1} by the 17th day. The PS-H band near 2459 cm^{-1} has been replaced by bands near 3000 and 2300 cm^{-1} (POH from S=P-OH and O=P-OH moieties). A broad band has occurred near 1200 cm^{-1} and may be assigned to a P=O stretching vibration. Bands

[fffff] A band in the range of 865-835 cm^{-1} is listed as being due to S-H bending. Colthup, N.B., Daly, L.H. and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", p. 349, Academic Press, New York, 1975. For compounds of the type, $(RO)_2P=S(SH)$, the P=S (I) band is listed as occurring in the range of 857-730 cm^{-1}, Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 137, Heyden & Son Ltd., London, 1974.

[ggggg] The P=S II band (ν P=S) is listed by Thomas as occurring over the range of 671-649 cm^{-1} for $(RO)_2P=S(SH)$ compounds. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 137, Heyden & Son Ltd., London, 1974.

[hhhhh] The P-SH vibration, in compounds of the type $(RO)_2P=S(SH)$, is listed as having bands at 548-524 cm^{-1} and 526-490 cm^{-1}, assigned as isomer I and isomer II respectively. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 148, Heyden & Son Ltd., London, 1974.

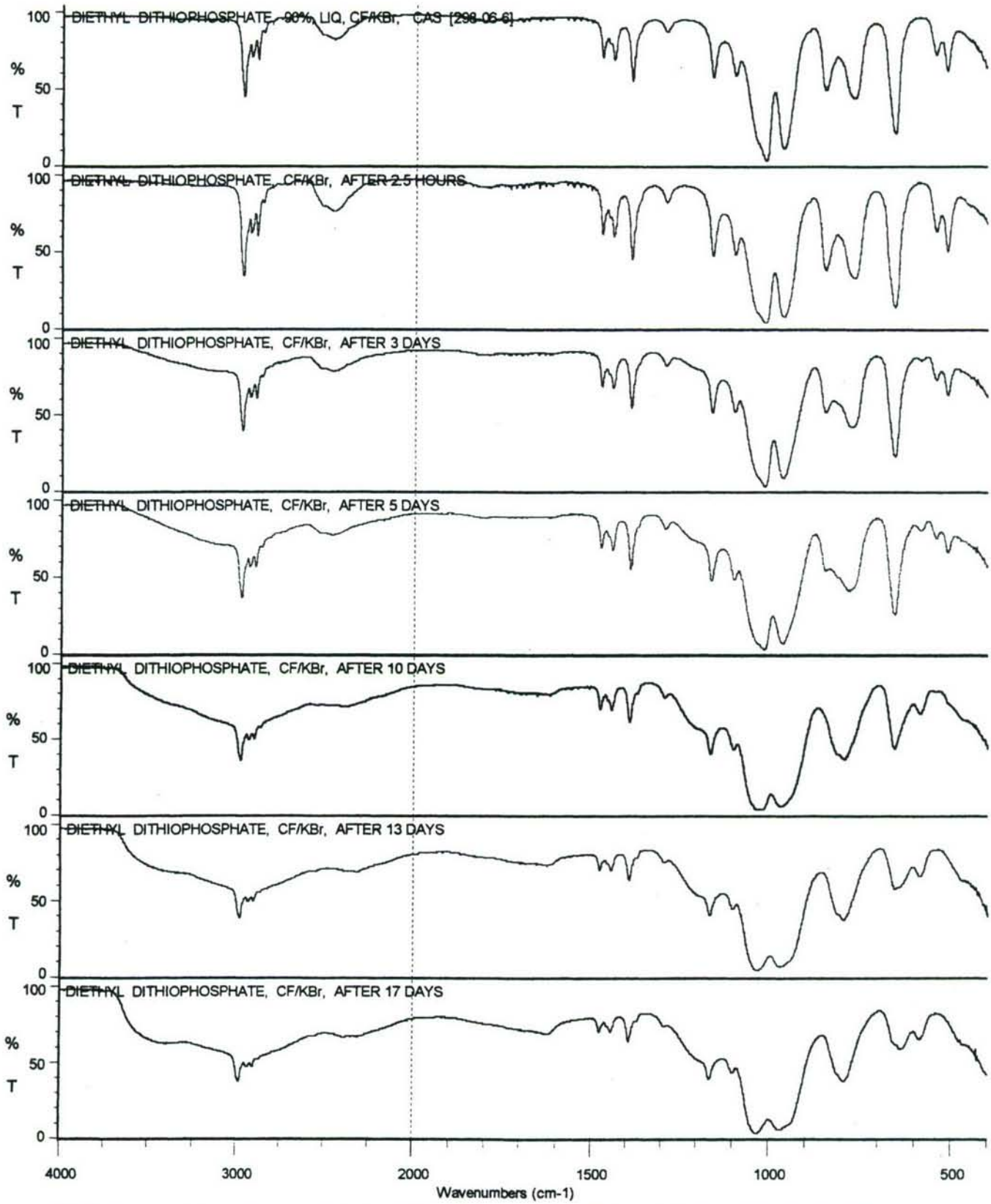


Figure 399A DIETHYL DITHIOPHOSPHATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

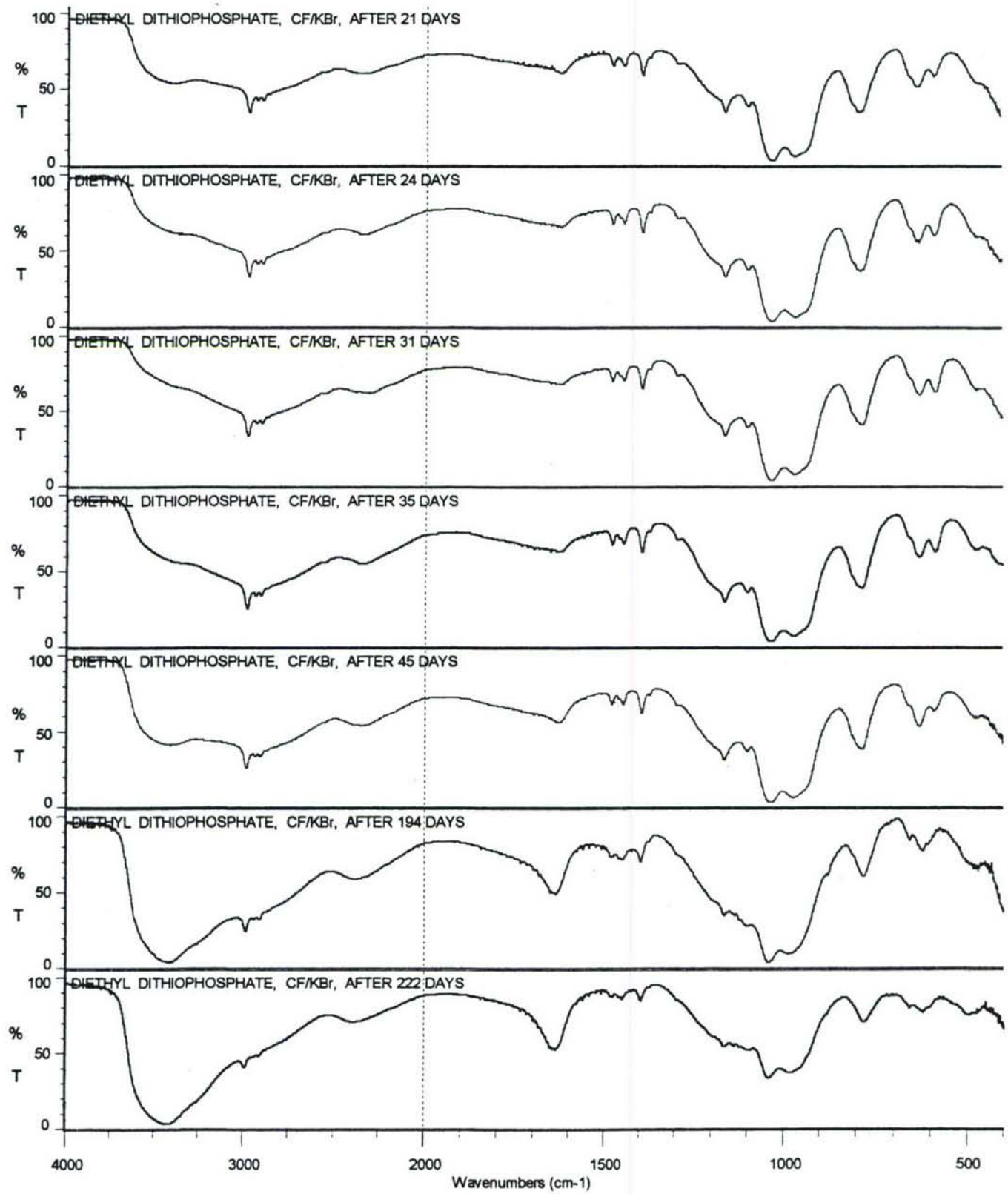


Figure 399B DIETHYL DITHIOPHOSPHATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

near 1030 and 972 cm^{-1} may be due to POC and P-OH (and ν C-C from POEt) respectively. The bands due to the POEt moiety become weaker as time progresses to the 222nd day of observation (***Figure 399B***). The compound appears to have undergone hydrolysis followed by desulfurization which may be depicted as follows:

$(EtO)_2P{=}S(SH)$ -HOH→ $(EtO)_2P{=}S(OH)$ + $H_2S\uparrow$ -DESULFURIZATION→ $(EtO)_2P{=}O(OH)_2$.

3.7.23 Diethyl Dithiophosphate, Ammonium Salt $(CH_3CH_2O)_2P{=}S(S^-)NH_4^+$

The infrared spectrum of diethyl dithiophosphate, ammonium salt (diethyl phosphorothiolothionic acid, ammonium salt), as a solid between cesium iodide discs (windows), is presented as ***Figure 400***. The band assignments are as follows: 3107 cm^{-1} ms (ν NH_4^+), 2979 cm^{-1} ms, 2931 cm^{-1} sh, 2894 cm^{-1} sh, 2850 cm^{-1} sh (ν CH_3 and ν CH_2), 2807 cm^{-1} m (2x 1408 = 2816 cm^{-1}), 1466 cm^{-1} vw (δ CH_2, CH_3), 1408 ms (δ NH_4^+), 1158 and 1096 cm^{-1} w (CH_3 rock of POEt, characteristic), 1042 cm^{-1} sh and 1018 cm^{-1} s (ν P-O-C), 930 cm^{-1} s (ν C-C of POEt), 753 cm^{-1} ms (POC), 679 cm^{-1} s (ν_{as} PS_2^-), 546 cm^{-1} w (ν_{sy} PS_2^-).[iiii]

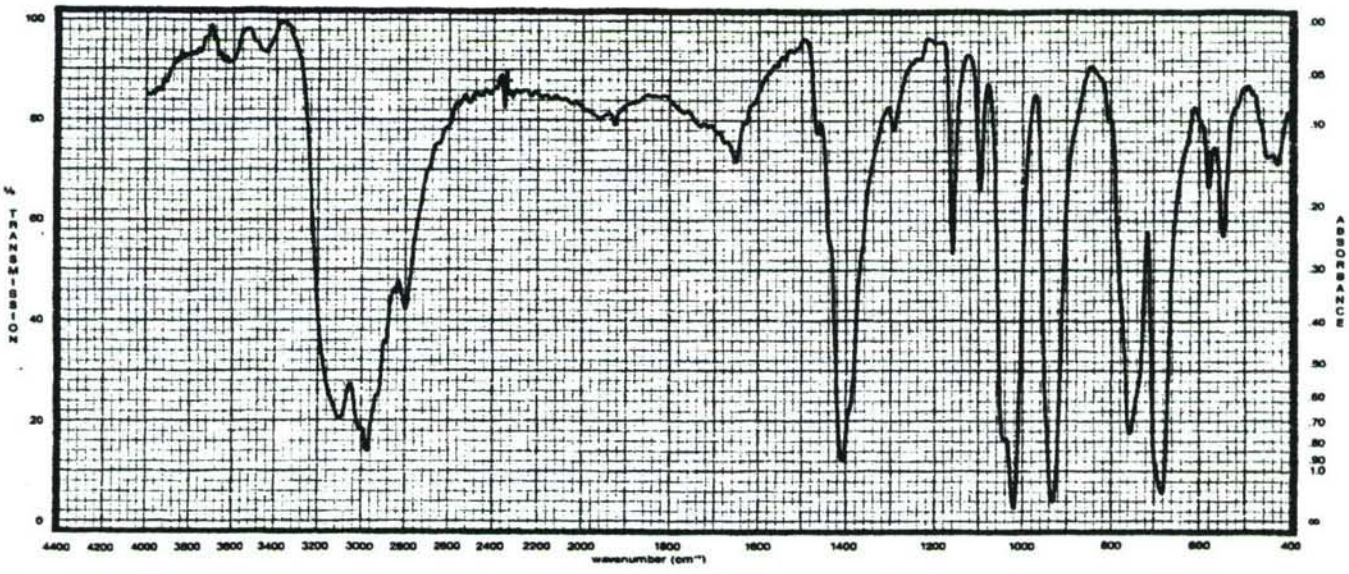


Figure 400 DIETHYL DITHIOPHOSPHATE, AMMONIUM SALT, 95%, SOLID BETWEEN CsI DISCS (WINDOWS)

[iiii] The PS_2^- anion in diesters of phosphorothiolothionic acid, $(RO)_2PS_2^-$, is characterized by two bands occurring in the ranges 720-625 cm^{-1} strong (ν_{as} PS_2^-) and 575-501 cm^{-1} weak-medium (ν_{sy} PS_2^-). Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 172, Heyden & Son Ltd., London, 1974.

3.7.24 Diphenylphosphinodithioic Acid (Diphenylphosphinothiolothionic Acid) $(C_6H_5)_2P=S(SH)$

The infrared spectrum of diphenylphosphinodithioic acid (diphenylphosphinothiolothionic acid) as a KBr pellet is reproduced as ***Figure 401***. The band assignments are as follows: 3438 cm^{-1} w (H_2O), 3074 and 3051 cm^{-1} vw, 3017 cm^{-1} vvw (ν C-H aromatic), 2333 cm^{-1} w (ν S-H), 1583 and 1573 cm^{-1} vvw, 1483 cm^{-1} w and 1435 cm^{-1} m (aromatic ring C≈C), 1182, 1158, 1071, 1027 cm^{-1} all vw and 998 cm^{-1} w (β C-H mono-substituted aromatic ring), 1103 cm^{-1} sh and 1098 cm^{-1} m (phenyl-P), 753 and 743 cm^{-1} m (γ C-H mono-substituted aromatic ring), 709 and 690 cm^{-1} s (mono-substituted aromatic ring deformation), 639 cm^{-1} s (ν P=S), 542 cm^{-1} ms (ν P-S).

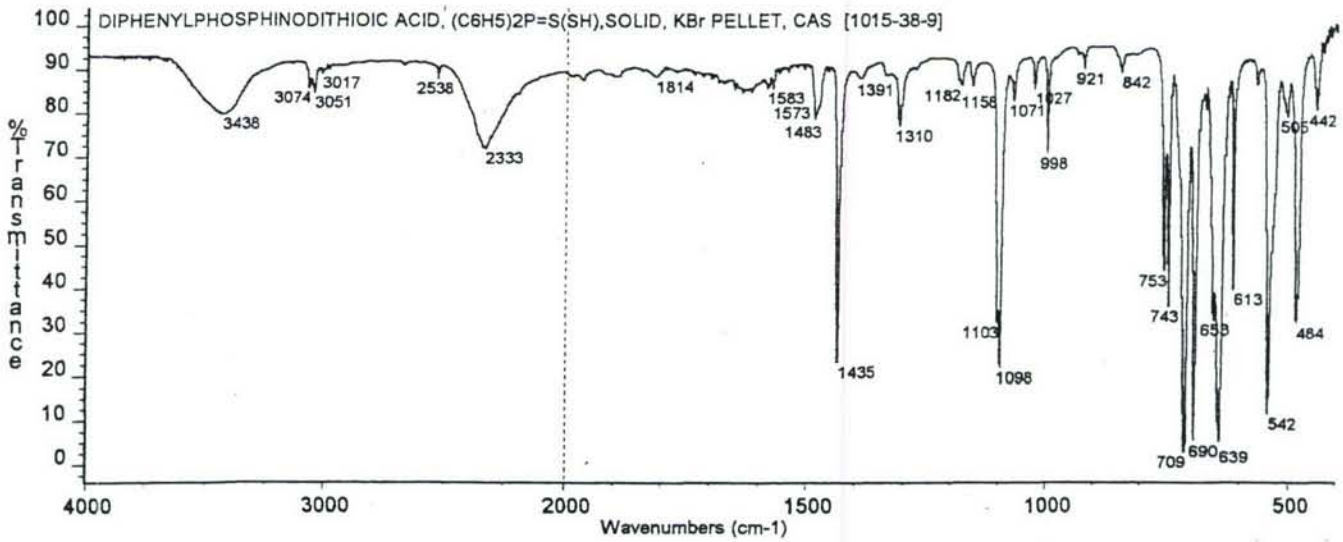


Figure 401 DIPHENYLPHOSPHINODITHIOIC ACID (DIPHENYLPHOSPHINOTHIOLOTHIONIC ACID), SOLID, KBr PELLET

3.7.25 Dicyclohexylphosphinodithioic Acid (Dicyclohexylphosphinothiolothionic Acid) $(H_{11}C_6)_2P=S(SH)$

The infrared spectrum of dicyclohexylphosphinodithioic acid (dicyclohexylphosphinothiolothionic acid) as a KBr pellet is presented as ***Figure 402***. The band assignments are as follows: 3437 and ca 1628 cm^{-1} vw (H_2O), 2932 cm^{-1} ms (ν_{as} CH_2), 2851 cm^{-1} m (ν_{sy} CH_2), 2346 cm^{-1} w (ν S-H), 1452 cm^{-1} m (δ CH_2), 738 cm^{-1} m (P=S I), 634 cm^{-1} s (P=S II, ν P=S), 524 cm^{-1} m (ν P-SH).

3.7.26 Di-*n*-butylphosphinothionic Acid $(H_9C_4\text{-}n)_2P=S(OH)$

The infrared spectrum of di-*n*-butylphosphinothionic acid as a thin liquid film between KBr windows is presented in ***Figure 403***. The band assignments are as follows: ca 3026 cm^{-1} sh and ca 2218 cm^{-1} vw broad

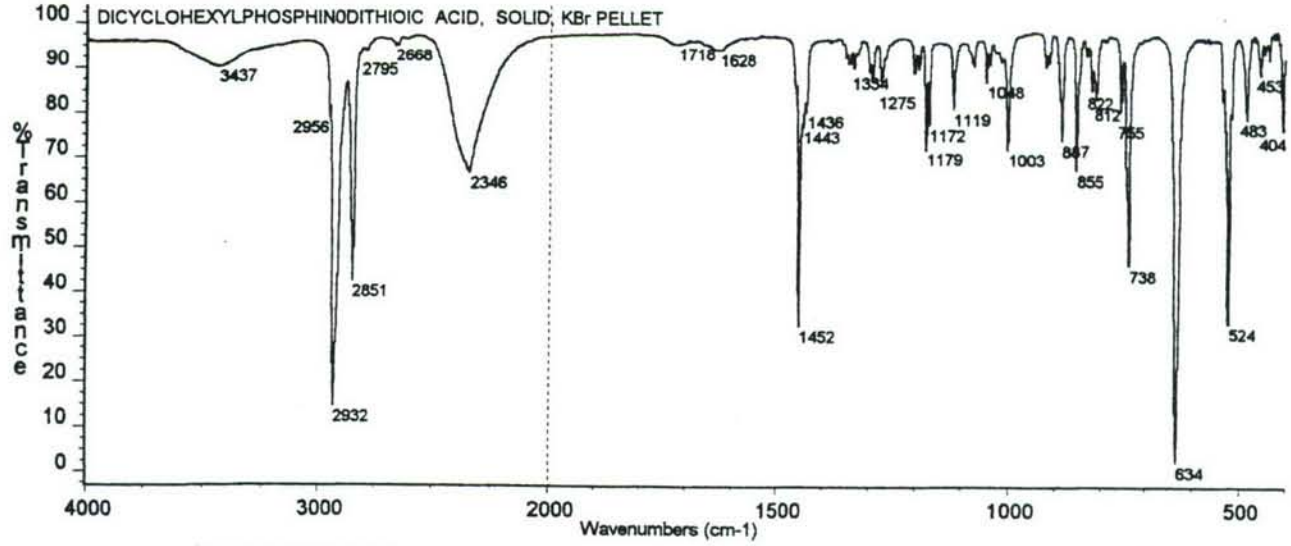


Figure 402 DICYCLOHEXYLPHOSPHINODITHIOIC ACID (DICYCLOHEXYLPHOSPHINOTHIOLOTHIONIC ACID), SOLID, KBr PELLET

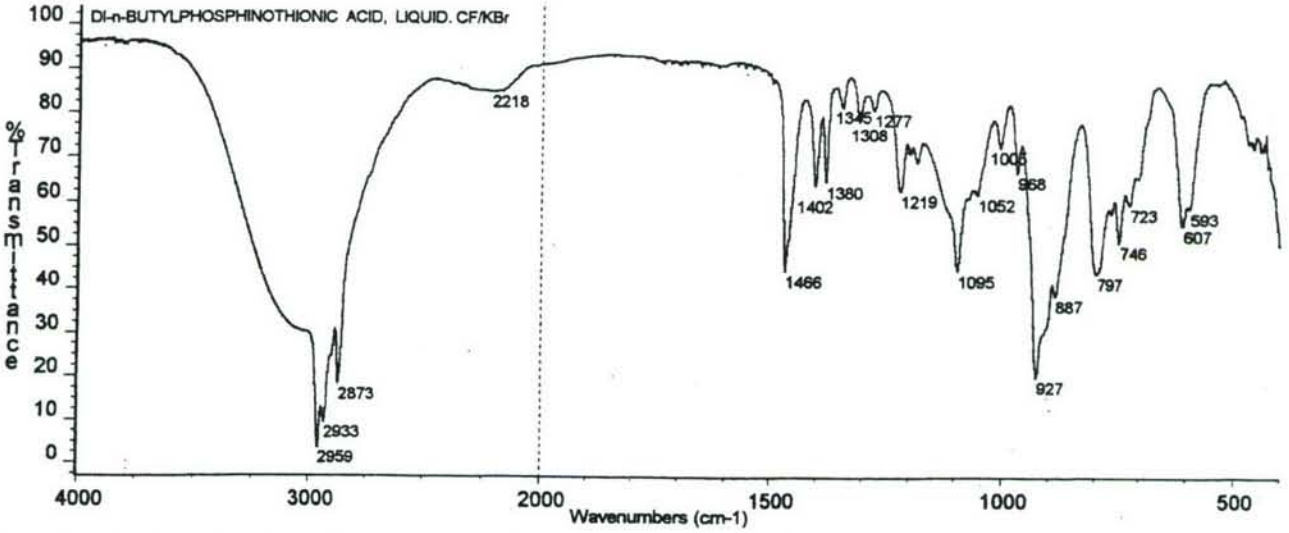


Figure 403 DI-*n*-BUTYLPHOSPHINOTHIONIC ACID (DI-*n*-BUTYLPHOSPHINOTHIONIC ACID), LIQUID, CF/KBr

(POH),[iiii] 2959 cm^{-1} s (ν_{as} CH_3), 2933 cm^{-1} ms (ν_{as} CH_2), ca 2901 cm^{-1} sh (ν_{sy} CH_3), 2873 cm^{-1} m (ν_{sy} CH_2), 1466 cm^{-1} m (δ CH_2, δ_{as} CH_3), 1402 cm^{-1} w (δ P-CH_2), 1380 cm^{-1} w (δ_{sy} CH_3), 1308 cm^{-1} vw, 1219 cm^{-1} w (ω, τ CH_2),

[iiii] The HO-P=S group is characterized by diffuse bands in the regions 3100-3000 cm^{-1} and 2360-2200 cm^{-1}. The P-O-H band occurs in the region 932-909 cm^{-1}. The higher value for the O-H vibration indicates that the intermolecular hydrogen bond to sulfur is weaker than that to oxygen. The P-OH in HO-P=O compounds is characterized by bands in the regions of 2725-2525 cm^{-1}, 2350-2080 cm^{-1}, 1740-1600 cm^{-1}, 1040-917 cm^{-1} (ν P-OH). Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp 40-42, Heyden & Son Ltd., London, 1974.

927 cm^{-1} ms (ν P-OH), 797 cm^{-1} m (P=S I), 746 cm^{-1} w (CH_2 rock), 723 cm^{-1} vw (ν P-C ?), 607 cm^{-1} (P=S II, ν P=S).

3.7.27 Diphenylphosphinothionic acid $(H_5C_6)_2P=S(OH)$

The infrared spectrum of diphenylphosphinothionic acid (diphenylphosphinothioic acid) as a KBr pellet is given in ***Figure 404***. The band assignments are as follows: 3416 cm^{-1} w (H_2O), 3075, 3058, 3020 and 3008 cm^{-1} vvw (ν C-H aromatic), ca 3000 cm^{-1} ms broad and 2131 cm^{-1} vw (POH), 1602 and 1589 cm^{-1} vw, 1481 cm^{-1} w and 1437 cm^{-1} ms (aromatic ring C≈C), 1181, 1160, 1071, 1029 and 998 cm^{-1} vw-w (β C-H mono-substituted aromatic ring), 1123 and 1114 cm^{-1} ms (phenyl-P), 895 cm^{-1} s (ν P-OH), 759, 754 and 749 cm^{-1} m (γ C-H mono-substituted aromatic ring), 721 and 691 cm^{-1} s-ms (mono-substituted aromatic ring deformation), 634 cm^{-1} s (P=S II, ν P=S), 505 cm^{-1} ms (mono-substituted aromatic ring, quadrant out-of-plane bending ?).

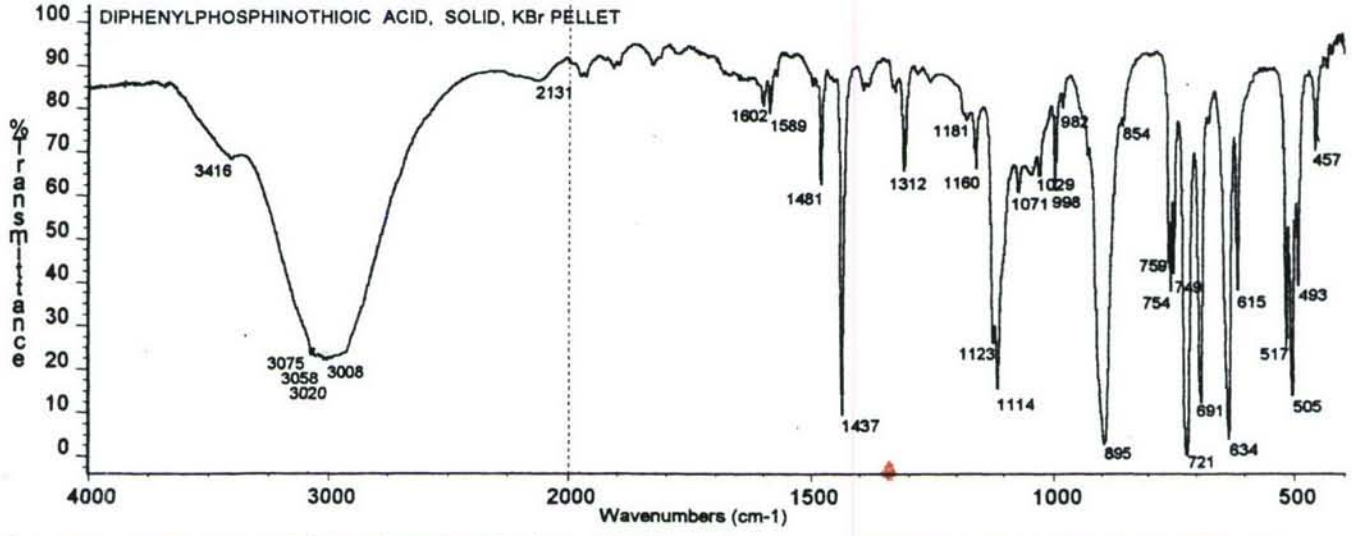


Figure 404 DIPHENYLPHOSPHINOTHIONIC ACID (DIPHENYLPHOSPHINOTHIOIC ACID), SOLID, KBr PELLET

3.7.28 Diethyl Phosphorothionic Acid $(H_5C_2O)_2P=S(OH)$

The infrared spectrum of diethyl phosphorothionic acid (diethyl hydrogen phosphorothionate, diethyl hydrogen thiophosphate, O,O-diethyl thiophosphoric acid) as a liquid film between KBr windows is reproduced as ***Figure 405.*** The band assignments are as follows: 3064 cm^{-1} m broad and 2333 cm^{-1} vw broad (POH), 2985 cm^{-1} m (ν_{as} CH_3), 2939 cm^{-1} w (ν_{as} CH_2), 2907 cm^{-1} w (ν_{sy} CH_3), 2873 cm^{-1} sh (ν_{sy} CH_2), 1837 cm^{-1} vvw (1028 +

812 = 1840 cm^{-1}), 1477 cm^{-1} vw (δ OCH_2), 1444 cm^{-1} vw (δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2), 1369 cm^{-1} vvw (δ_{sy} CH_3), 1293 cm^{-1} vvw, 1217 cm^{-1} w (ω,τ CH_2; perhaps the 1217 cm^{-1} band may be due to the ν P=O from an impurity ?), 1164 and 1099 cm^{-1} m (CH_3 rock of POEt, characteristic), 1028 cm^{-1} s (ν P-O-C), 971 cm^{-1} ms (ν C-C of POEt), 812 cm^{-1} sh and 788 cm^{-1} m (POC, and P=S I),[kkkk] 647 and 616 cm^{-1} w (P=S II, ν P=S).[kkkk]

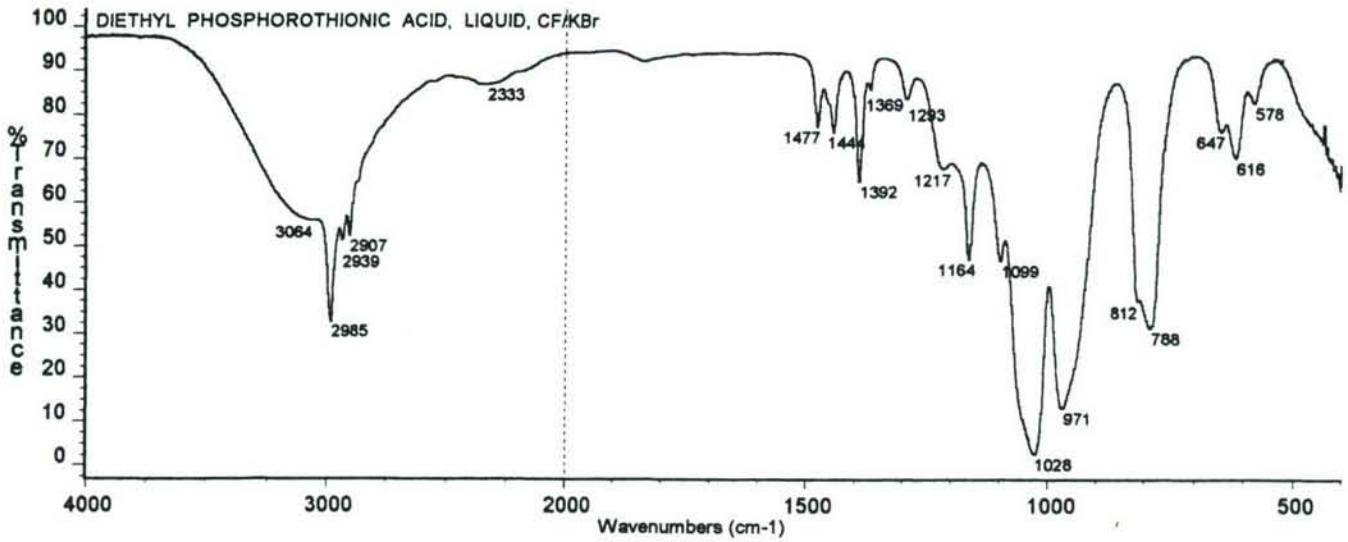


Figure 405 DIETHYL PHOSPHOROTHIONIC ACID (DIETHYL HYDROGEN PHOSPHOROTHIONATE), LIQUID, CF/KBr

3.7.29 Isopropyl Methylphosphonothionic Acid CH_3-P=S(OH)[O-CH(CH_3)$_2$]

The infrared spectrum (**grating**) of isopropyl methylphosphonothionic acid (isopropyl hydrogen methylphosphonothionate), as a liquid film between sodium chloride windows is given as ***Figure 406***. The band assignments are as follows: ca 3370 cm^{-1} sh and 1622 cm^{-1} w (H_2O), ca 3060 cm^{-1} ms and ca 2375 cm^{-1} w broad (POH), 2978 cm^{-1} m, 2933 cm^{-1} w and 2876 cm^{-1} vw (ν CH_3), 1464 and 1451 cm^{-1} w (δ_{as} CH_3), 1409 cm^{-1} m (δ_{as} P-CH_3), 1385 and 1374 cm^{-1} ms (δ_{sy} CH_3 isopropyl), 1302 cm^{-1} ms (δ_{sy} P-CH_3), 1177, 1140 and 1105 cm^{-1} ms (triplet characteristic of P-O-isopropyl), 988 cm^{-1} s (ν P-O-C), 951 cm^{-1} ms (ν P-OH), 906 cm^{-1} s (P-CH_3 rock), 877 cm^{-1} m (CH_3 rock isopropyl), 781 cm^{-1} s (POC, P=S I), 738 cm^{-1} ms (ν P-C), ca 600 cm^{-1} (P=S II, ν P=S, unfortunately this sample was presented to the author as a liquid film between sodium chloride windows, thus not

[kkkk] The frequency limits for the P=S bands in compounds of the type, $(RO)_2P=S(OH)$ where R is alkyl, are 810-783 cm^{-1} (P=S **I**) and 645 + 618 cm^{-1} (P=S **II**). Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 131, Heyden & Son Ltd., London, 1974.

allowing the P=S II band to be definitely determined, since the band is below the cutoff point for NaCl).[IIII]

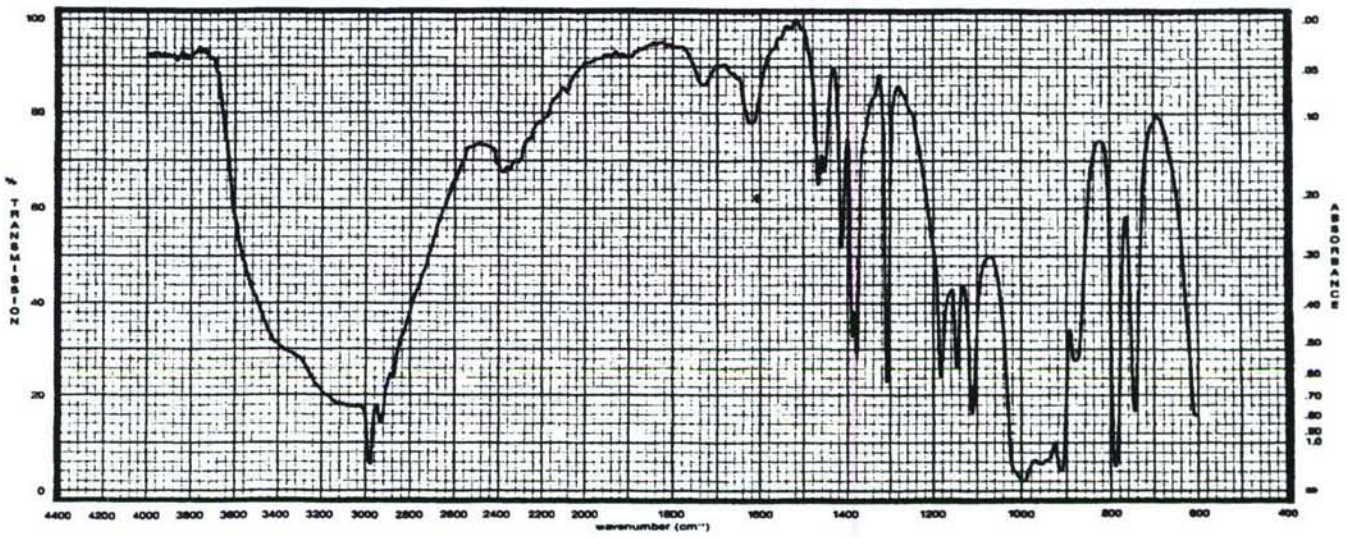


Figure 406 ISOPROPYL METHYLPHOSPHONOTHIONIC ACID (ISOPROPYL HYDROGEN METHYLPHOSPHONOTHIONATE), LIQUID, CF/NaCl

3.7.30 Ethyl N,N-dimethylphosphoramidothionic Fluoride $(CH_3)_2N\text{-}P{=}S(F)(O\text{-}CH_2\text{-}CH_3)$

The infrared spectrum of ethyl N,N-dimethylphosphoramidothionic fluoride as liquid film between cesium iodide windows is presented in ***Figure 407***. The band assignments are as follows: 2980 cm^{-1} m, 2935 cm^{-1} m, 2901 cm^{-1} m and 2854 cm^{-1} w (ν CH_3 and ν CH_2), 2817 cm^{-1} w (N-CH_3), 1476 cm^{-1} w (δ OCH_2), 1455 cm^{-1} m (δ_{as} CH_3), 1389 cm^{-1} w (ω OCH_2), 1367 cm^{-1} vvw (δ_{sy} CH_3), 1302 cm^{-1} m [$PN(CH_3)_2$], 1177 cm^{-1} m [$PN(CH_3)_2$], 1095 cm^{-1} w (CH_3 rock of POEt, the 1160 cm^{-1} band is lost in the 1177 cm^{-1} band), 1037 cm^{-1} s (ν P-O-C), 998 cm^{-1} s (ν_{as} P-N-C), 969 cm^{-1} ms (ν C-C of POEt), 851 cm^{-1} ms (ν P-F), 826 cm^{-1} sh, 811 cm^{-1} ms, 794 cm^{-1} sh (POC, and P=S I bands), 757 cm^{-1} ms (ν_{sy} P-N-C), 607 cm^{-1} w (P=S II, ν P=S).

3.7.31 S,S-Dimethyl N,N-dimethylphosphoramidodithiolate $(CH_3)_2N\text{-}P{=}O(S\text{-}CH_3)_2$

The infrared spectrum of S,S-dimethyl N,N-dimethylphosphoramidodithiolate as a liquid film between cesium iodide windows is presented in ***Figure 408***. The band assignments are as follows: 3000 cm^{-1} w,

[IIII] The P=S I and P=S II bands for compounds of the type, (RO)(R)P=S(OH), occur in the ranges 800-762 cm^{-1} and 610-589 cm^{-1} respectively. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 131, Heyden & Son Ltd., London, 1974.

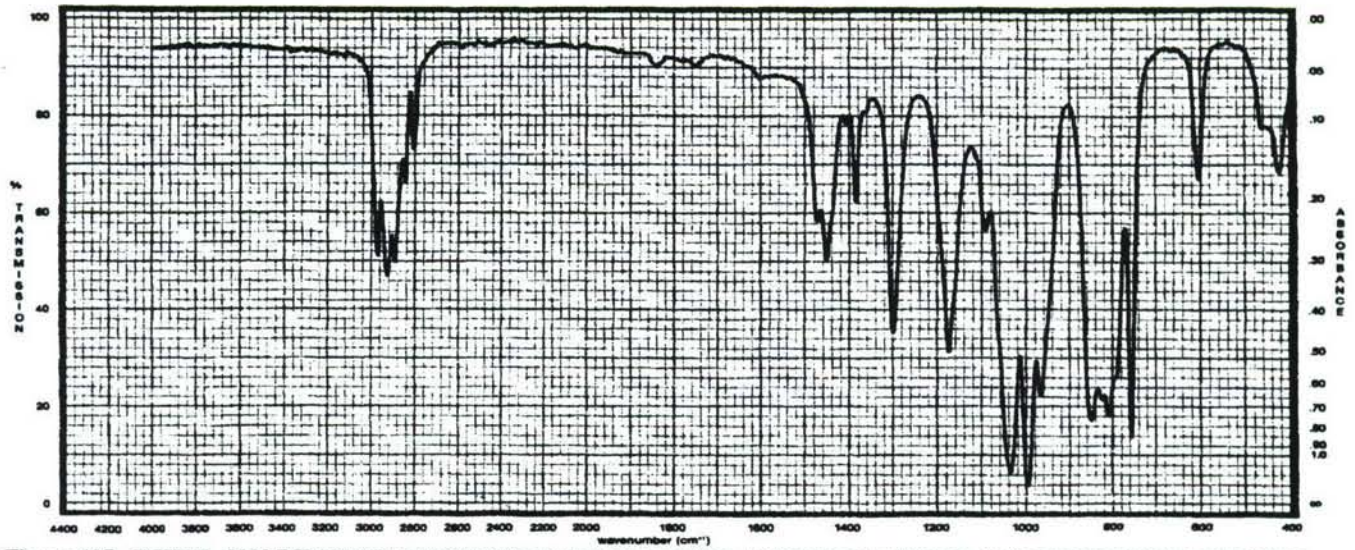


Figure 407 ETHYL N,N-DIMETHYLPHOSPHORAMIDOTHIONIC FLUORIDE (ETHYL N,N-DIMETHYLTHIO PHOS - PHORAMIDIC FLUORIDE), LIQUID, CF/CsI

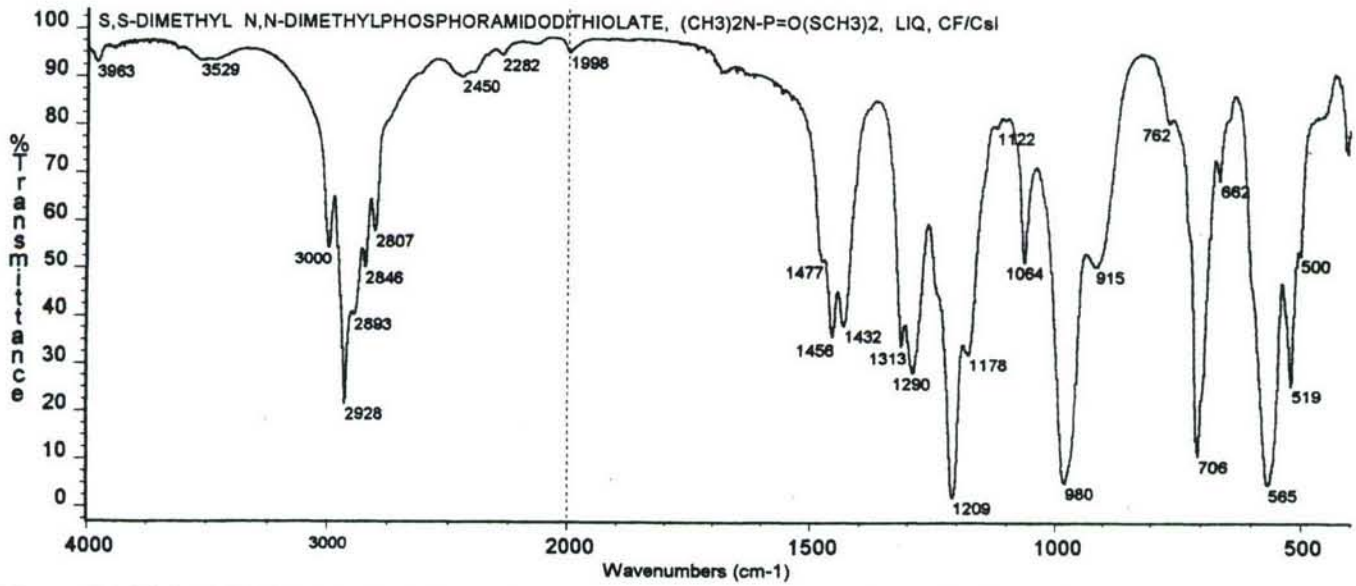


Figure 408 S,S-DIMETHYL N,N-DIMETHYLPHOSPHORAMIDODITHIOLATE, LIQUID, CF/CsI

2928 cm^{-1} ms, 2893 cm^{-1} sh, 2846 cm^{-1} w and 2807 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1477 cm^{-1} sh and 1456 cm^{-1} m (δ N-CH_3), 1432 cm^{-1} m (δ_{as} S-CH_3), 1313 cm^{-1} m (δ_{sy} S-CH_3), 1290 cm^{-1} m [$P(NCH_3)_2$], 1209 cm^{-1} s (ν P=O, *calculated* value is 1218 cm^{-1}), 1178 cm^{-1} m and 1064 cm^{-1} w [$P(NCH_3)_2$], 980 cm^{-1} s (ν_{as} P-N-C), 915 cm^{-1} w (S-CH_3 rock ?), 706 cm^{-1} ms (ν_{sy} P-N-C), 662 cm^{-1} vw (ν C-S ?), 565 cm^{-1} s and 519 cm^{-1} m (ν P-SC).

3.7.32 Tris(N,N-dimethylamino)phosphine Sulfide $[(CH_3)_2N]_3P=S$

The infrared spectrum of tris(N,N-dimethylamino)phosphine sulfide as a liquid film between KBr windows is reproduced as ***Figure 409***. The band assignments are as follows: 2995 cm^{-1} m, 2920 cm^{-1} sh, 2877 cm^{-1} ms, 2837 cm^{-1} w and 2796 cm^{-1} m (ν_{as} and ν_{sy} CH_3), 2007 cm^{-1} vvw (1285 + 722 = 2007 cm^{-1}), 1701 cm^{-1} vw (976 + 722 =1698 cm^{-1} and 963 + 741 = 1704 cm^{-1}), 1456 cm^{-1} m (δ CH_3), 1285, 1188 and 1064 cm^{-1} m [$PN(CH_3)_2$], 976 and 963 cm^{-1} s (ν_{as} P-N-C), 866 cm^{-1} vvw (P=S I ?), 741 and 722 cm^{-1} ms (ν_{sy} P-N-C), 565 cm^{-1} m (P=S II, ν P=S).

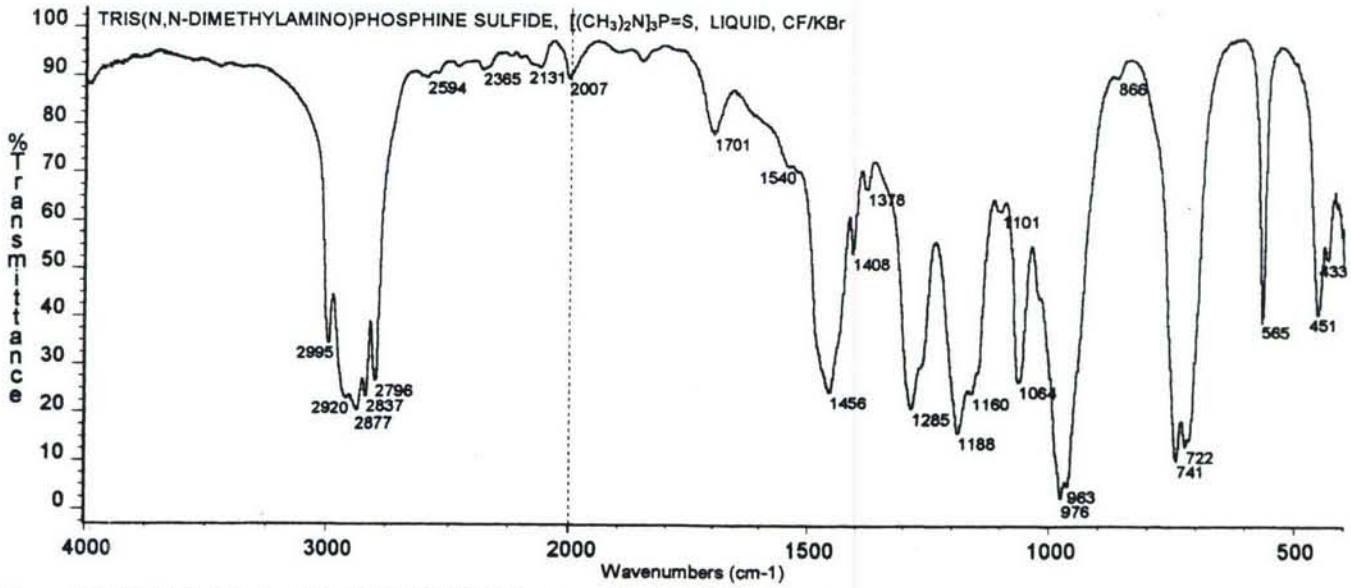


Figure 409 TRIS(N,N-DIMETHYLAMINO)PHOSPHINE SULFIDE, LIQUID, CF/KBr

3.7.33 Diethyl Methylphosphonothionate (TRS) CH_3-P=S$(O\text{-}CH_2CH_3)_2$

The infrared spectrum of diethyl methylphosphonothionate (**TRS**) as a liquid film between KBr windows and as a vapor spectum is given in ***Figure 410***. The band assignments for the liquid film are as follows: 2982 cm^{-1} m (ν_{as} CH_3), 2935 cm^{-1} w (ν_{as} CH_2), 2902 cm^{-1} w (ν_{sy} CH_3), 2873 cm^{-1} vw (ν_{sy} CH_2), 1476 cm^{-1} vw (δ OCH_2), 1444 cm^{-1} vw (δ_{as} CH_3), 1410 cm^{-1} vw (δ_{as} P-CH_3), 1389 cm^{-1} w (ω OCH_2), 1367 cm^{-1} vvw (δ_{sy} CH_3), 1301 cm^{-1} m (δ_{sy} P-CH_3), 1161 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1055 cm^{-1} ms and 1029 cm^{-1} s (ν P-O-C), 959 cm^{-1} ms (ν C-C of POEt), 906 cm^{-1} ms (P-CH_3 rock), 796 cm^{-1} m (P=S I), 753 cm^{-1} m (POC),

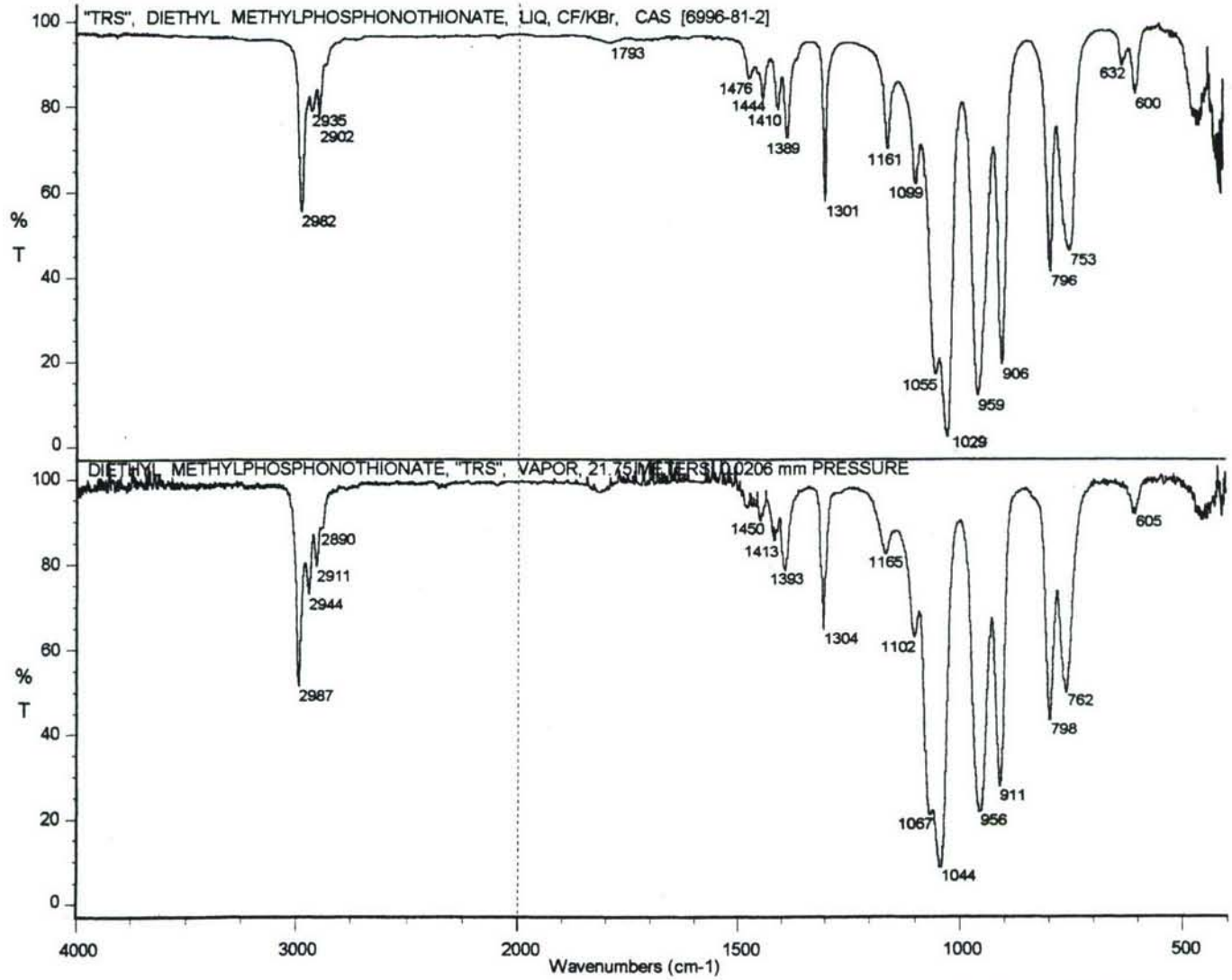


Figure 410 DIETHYL METHYLPHOSPHONOTHIONATE (TRS), *UPPER SPECTRUM*--**AS A LIQUID FILM BETWEEN KBr WINDOWS,** *LOWER SPECTRUM*--**AS A VAPOR IN A 21.75 METERS GAS CELL AT 0.0206 mm PRESSURE**

600 cm^{-1} vw (P=S II, ν P=S).[mmmm]

The effect of the environment on a thin liquid film of diethyl methylphosphonothionate (**TRS**) is illustrated by the infrared spectra presented in ***Figures 411A*** and ***411B***. An extremely weak band can be seen

[mmmm] The frequency ranges for the P=S I and P=S II bands in compounds of the type R-P=S$(OR)_2$, where R is alkyl, are 803-770 cm^{-1} and 650-589 cm^{-1} respectively. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 133, Heyden & Son Ltd., London, 1974.

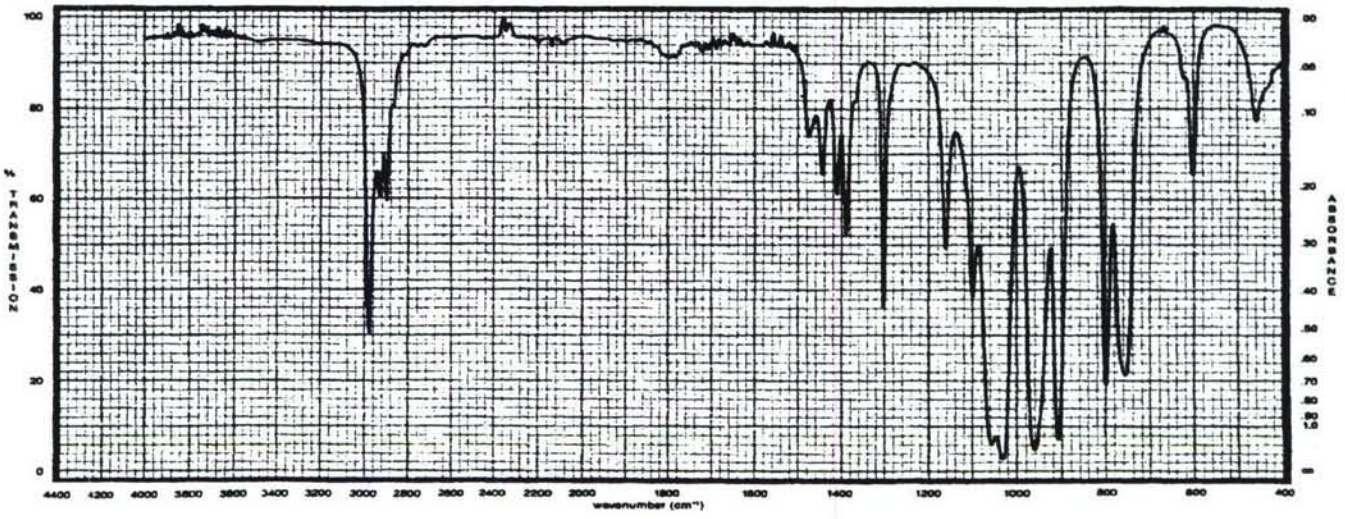


Figure 411A DIETHYL METHYLPHOSPHONOTHIONATE (TRS), LIQUID, CF/CsI

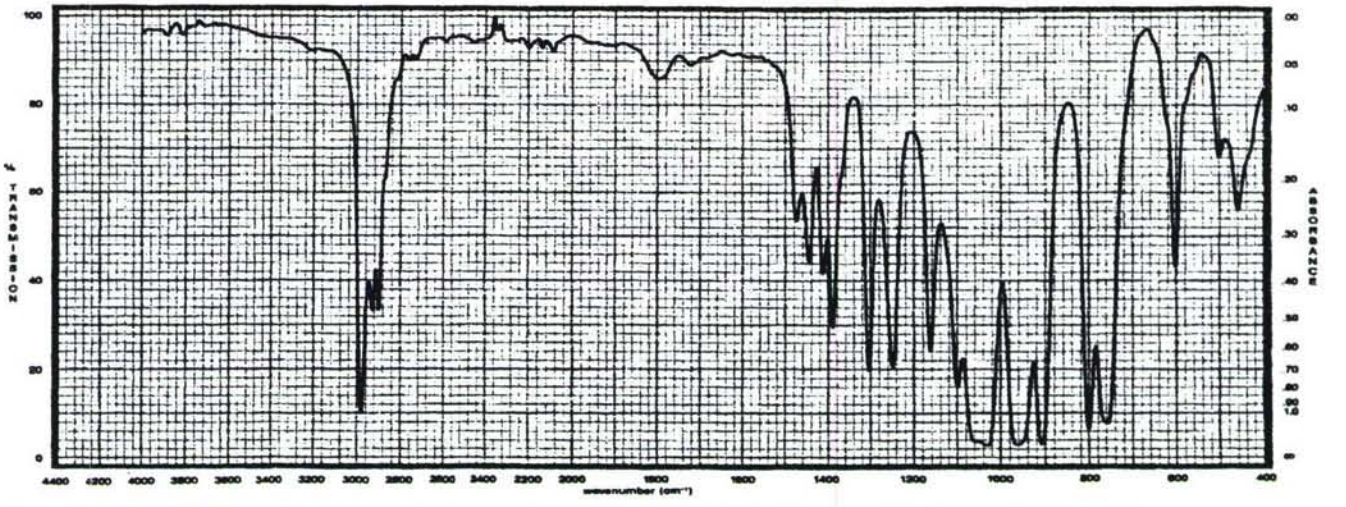


Figure 411B DIETHYL METHYLPHOSPHONOTHIONATE (TRS), LIQUID, CF/CsI, AFTER 24 HOURS

near 1245 cm^{-1} in ***Figure 411A***. After 24 hours (***Figure 411B***) this band becomes more evident and may be assigned to the P=O stretching vibration of diethyl methylphosphonate (**TRO**, **DEMP**), CH_3-P=O$(OEt)_2$. An authentic spectrum for **TRO** (**DEMP**) may be found at ***Figure 204***. The sample of **TRS** apparently undergoes oxidative desulfurization to form diethyl methylphosphonate (**DEMP**, **TRO**).

3.7.34 <u>O,S-diethyl Methylphosphonothiolate (**OSDMP**)</u> CH_3-P=O$(O\text{-}CH_2CH_3)(S\text{-}CH_2CH_3)$

The infrared spectrum of O,S-diethyl methylphosphonothiolate (**OSDMP**) as a thin liquid film

between KBr windows is presented as Figure 412. The band assignments are as follows: 3536 and 3482 cm^{-1} w (H_2O), 2982 cm^{-1} ms (ν_{as} CH_3), 2931 cm^{-1} m (ν_{as} CH_2), 2905 cm^{-1} sh ($\nu_{sy}CH_3$), 2873 cm^{-1} w (ν_{sy} CH_2), 1478 cm^{-1} vw (δ OCH_2), 1450 cm^{-1} w (δ_{as} CH_3), 1408 cm^{-1} vw (δ_{as} P-CH_3, δ S-CH_2 ?), 1390 cm^{-1} w (ω OCH_2), 1378 cm^{-1} sh (δ_{sy} CH_3), 1301 cm^{-1} ms (δ_{sy} P-CH_3), 1268 cm^{-1} m (ω S-CH_2), 1224 cm^{-1} s (ν P=O, *calculated* value is 1224 cm^{-1}), 1162 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1033 cm^{-1} s (ν P-O-C), 957 cm^{-1} ms (ν C-C of POEt), 894 and 882 cm^{-1} ms (P-CH_3 rock), 779 cm^{-1} m (POC), 742 cm^{-1} m (ν P-C ?), 650 cm^{-1} v w (ν C-S), 530 cm^{-1} ms (ν P-SC), 461 (ν P-SC isomer ?).

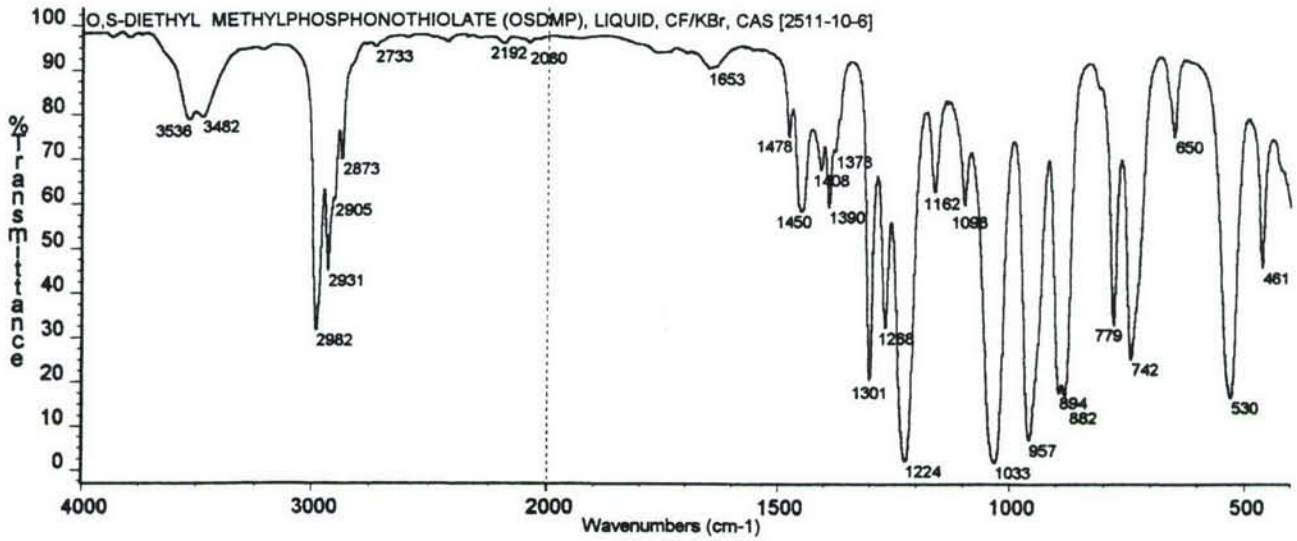


Figure 412 O,S-DIETHYL METHYLPHOSPHONOTHIOLATE (OSDMP), LIQUID, CF/KBr

The effect of atmospheric moisture on a liquid film of O,S-diethyl methylphosphonothiolate (**OSDMP**), is illustrated by the infrared spectra presented in ***Figures 413A*** and ***413B***. The compound remains pretty much intact through 19 days of exposure to atmospheric moisture (***Figures 413 A*** and ***B***). After 23 days of exposure to moisture, the infrared specrum (***Figure 413B***) begins to show changes. Broad bands occur near 2770, 2300 and 1650 cm^{-1} and are assigned to the POH moiety. The P=O stretching band near 1224 cm^{-1} begins to broaden and a new band appears near 1000 cm^{-1}. The P-SC band at 530 cm^{-1} is decreasing in intensity. By the 28th day the presence of a P-acid is even more evident. The 530 cm^{-1} P-SC band has greatly decreased in intensity. The spectrum now resembles that for ethyl methylphosphonic acid (**EMPA**), CH_3P=O(OH)(OEt). An

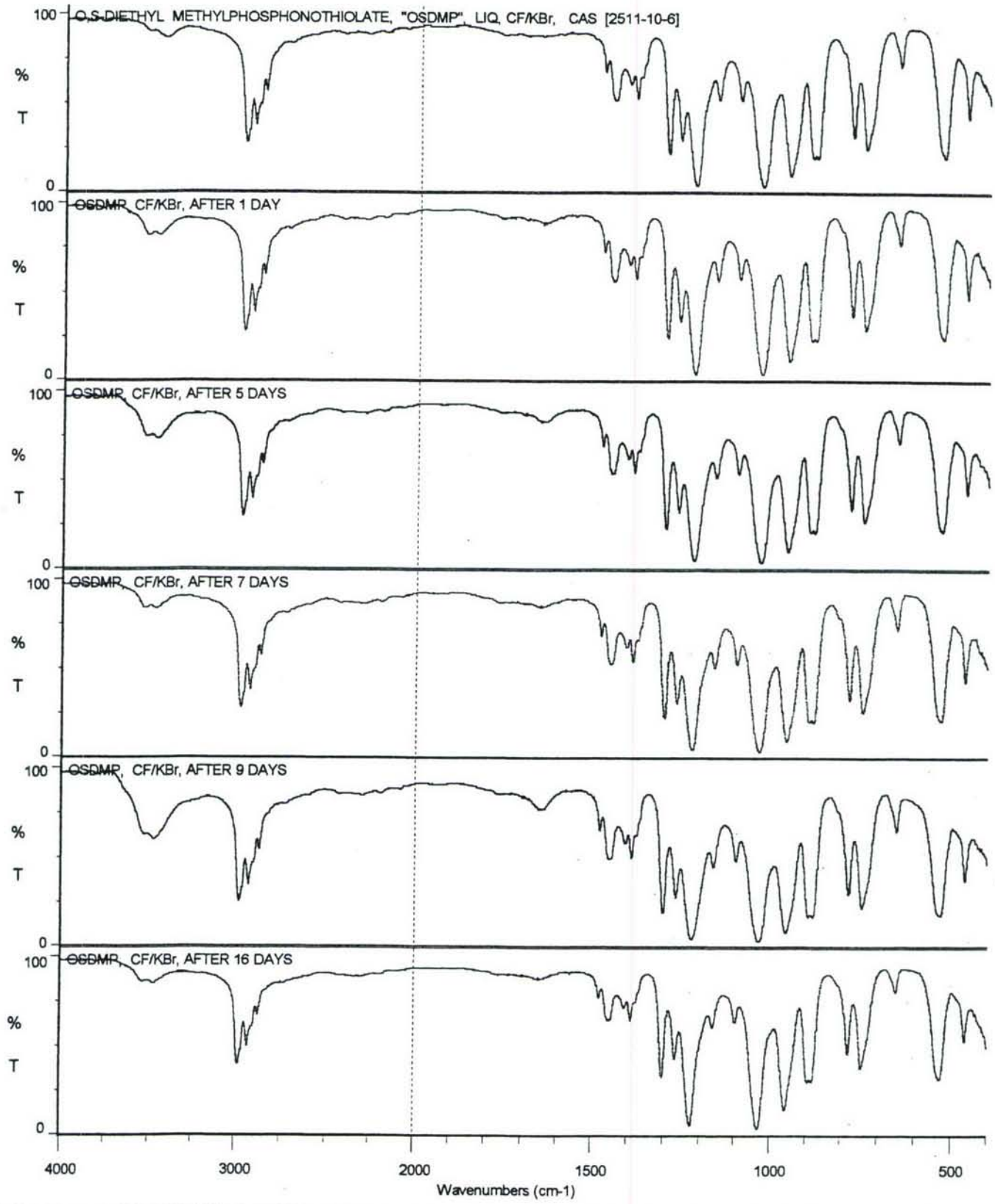


FIGURE 413A O,S-DIETHYL METHYLPHOSPHONOTHIOLATE (OSDMP), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

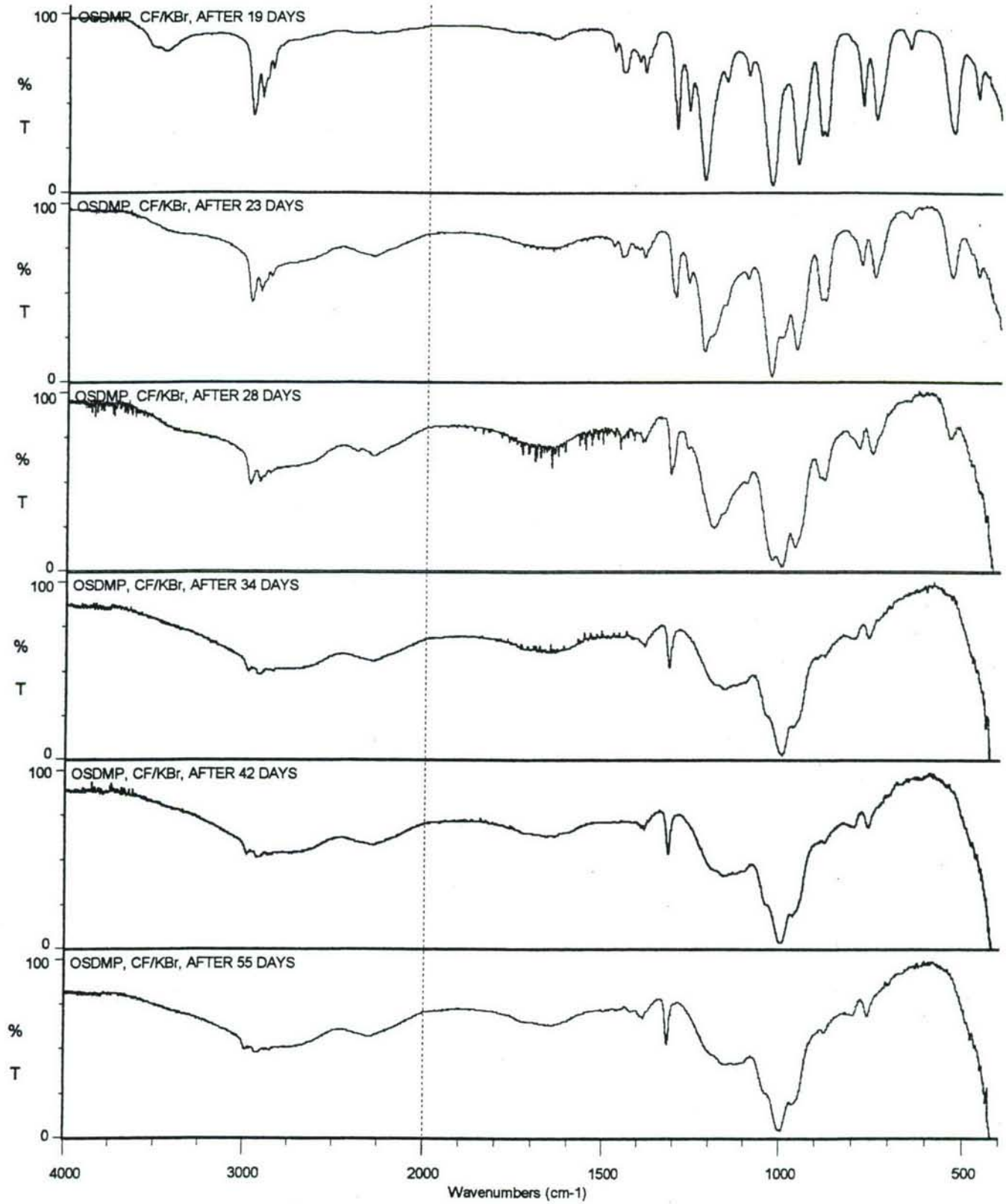


Figure 413B O,S-DIETHYL METHYLPHOSPHONOTHIOLATE (OSDMP), LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

authentic infrared spectrum of **EMPA** was given as ***Figure 143***. By the 55th day of exposure to atmospheric moisture, the infrared spectrum (***Figure 413B***) shows extremely weak CH stretching bands, POH bands and a more diffuse P=O stretching band near 1150 cm^{-1}. The compound has undergone further hydrolysis to form methylphosphonic acid (**MPA**), $CH_3P{=}O(OH)_2$. An authentic spectrum of **MPA** was presented as ***Figure 106***. The hydrolysis of O,S-diethyl methylphosphonothiolate (**OSDMP**) may be summarized as follows:

$CH_3P{=}O(OEt)(SEt)$ $\xrightarrow{-HOH}$ $CH_3P{=}O(OH)(OEt)$ $\xrightarrow{-HOH}$ $CH_3P{=}O(OH)_2$

(OSDMP) **(EMPA)** **(MPA)**

3.7.35 Ethyl S-(2,2-Dichlorovinyl) Methylphosphonothiolate $CH_3\text{-}P{=}O(OCH_2CH_3)(S\text{-}HC{=}CCl_2)$

The infrared spectrum of ethyl S-(2,2-dichlorovinyl) methylphosphonothiolate as a liquid film between KBr windows is presented as ***Figure 414***. The band assignments are as follows: 3048 cm^{-1} w (ν C-H aromatic), 2985 cm^{-1} m (ν_{as} CH_3), 2938 cm^{-1} w (ν_{as} CH_2), 2907 cm^{-1} sh (ν_{sy} CH_3), 2870 cm^{-1} vw (ν_{sy} CH_2), 1563 cm^{-1} w (ν C=C, lowered by the attached S and Cl), 1476 cm^{-1} w (δ OCH_2), 1443 cm^{-1} w (δ_{as} CH_3), 1407 cm^{-1} w (δ_{as} P-CH_3), 1391 cm^{-1} w (ω OCH_2), 1369 cm^{-1} vw (δ_{sy} CH_3), 1302 cm^{-1} m (δ_{sy} P-CH_3), 1246 cm^{-1} ms (ν P=O), 1161 cm^{-1} w and 1108 cm^{-1} m (CH_3 rock of POEt, characteristic), 1029 cm^{-1} s (ν P-O-C), 963 cm^{-1} ms (ν C-C of POEt), 911 cm^{-1} ms (P-CH_3 rock), 816 cm^{-1} m (ω =C-H), 785, 766 and 742 cm^{-1} ms (POC, ν_{as} CCl_2, ν P-C), 625 cm^{-1} m (ν_{sy} CCl_2 ?), 523 cm^{-1} m (ν P-SC).

3.7.36 Ethyl S-(2-Ethoxycarbonyl)vinyl Methylphosphonothiolate

$CH_3\text{-}P{=}O(OCH_2CH_3)[S\text{-}CH{=}CH\text{-}C(=O)OCH_2CH_3$

The infrared spectrum of ethyl S-(2-ethoxycarbonyl)vinyl methylphosphonothiolate as a liquid film between KBr windows is reproduced as ***Figure 415***. The band assignments are as follows: 3038 cm^{-1} vw (ν C-H olefinic), 2983 cm^{-1} m (ν_{as} CH_3), 2937 cm^{-1} w (ν_{as} CH_3), 2916 cm^{-1} w (ν_{sy} CH_3), 2873 cm^{-1} vw (ν_{sy} CH_2), 1707 cm^{-1} s (ν C=O, lowered by conjugation to C=C), 1585 cm^{-1} ms (ν C=C, lowered by the heavy S and by conjugation to the C=O), 1476 cm^{-1} w (δ OCH_2), 1465 cm^{-1} vw and 1445 cm^{-1} w (δ_{as} CH_3), 1392 cm^{-1} w (ω OCH_2),

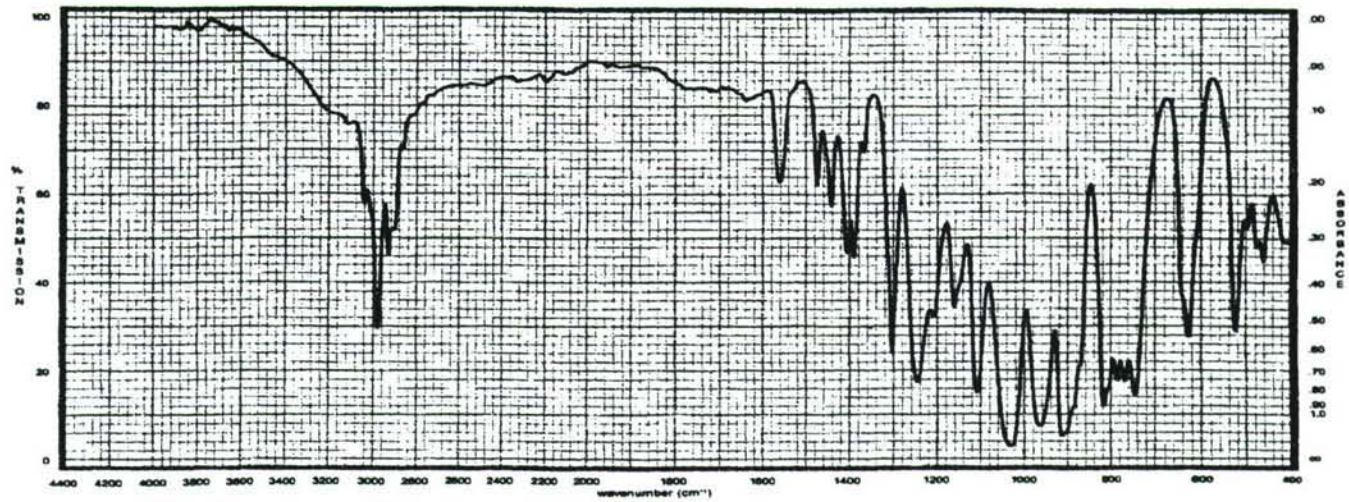


Figure 414 ETHYL S-(2,2-DICHLOROVINYL) METHYLPHOSPHONOTHIOLATE, LIQUID, CF/KBr

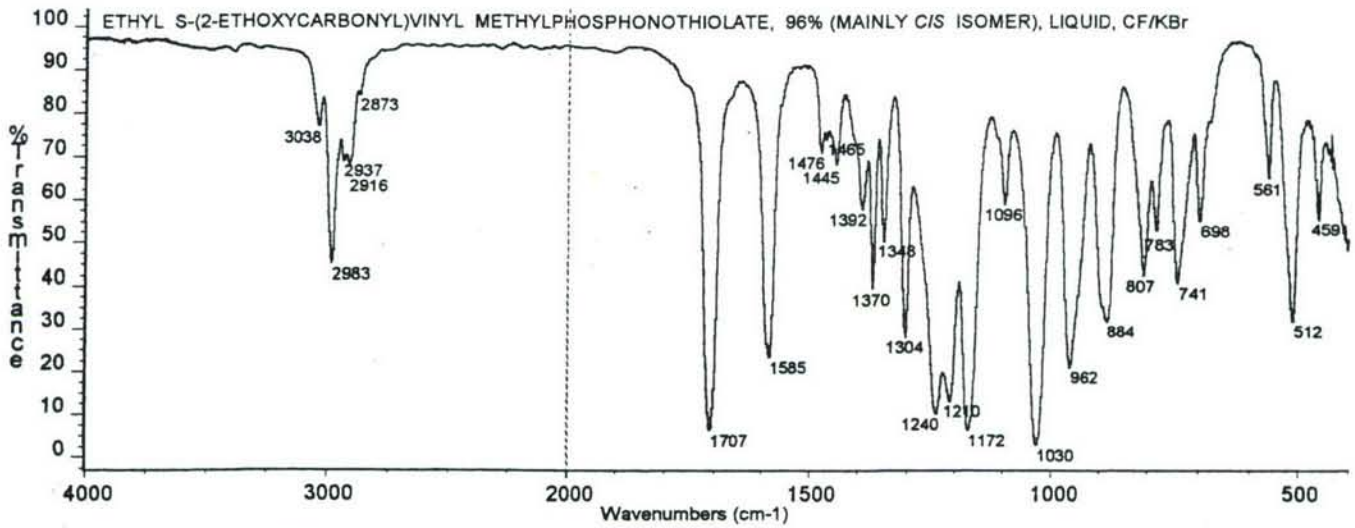


Figure 415 ETHYL S-(2-ETHOXYCARBONYL)VINYL METHYLPHOSPHONOTHIOLATE, 96%, (mainly *cis* isomer) LIQUID, CF/KBr

1370 cm^{-1} m (δ_{sy} CH_3), 1348 cm^{-1} w (=C-H rock?), 1304 cm^{-1} m (δ_{sy} P-CH_3, δP-CH_3), 1240 and 1172 cm^{-1} s (ν :C-O), 1210 cm^{-1} ms (ν P=O), 1096 cm^{-1} w [one of two characteristic bands (ca 1167-1155 and 1105-1095 cm^{-1}) due to CH_3 rock from POEt, the other band is hidden by the strong 1172 cm^{-1} band],[nnnn] 1030 cm^{-1} s (v P-O-C), 962 cm^{-1} w (v C-C of POEt), 884 cm^{-1} m (P-CH_3 rock), 807 cm^{-1} m (POC ?), 741 or 698 cm^{-1} m-w (*cis* CH wag), 512 cm^{-1} m (v P-SC).

[nnnn] Lin-Vien, D., Colthup, N.B., Fateley, W.G., and Grasselli, J.G., "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules", p. 271, Academic Press, Inc., San Diego, CA, 1991.

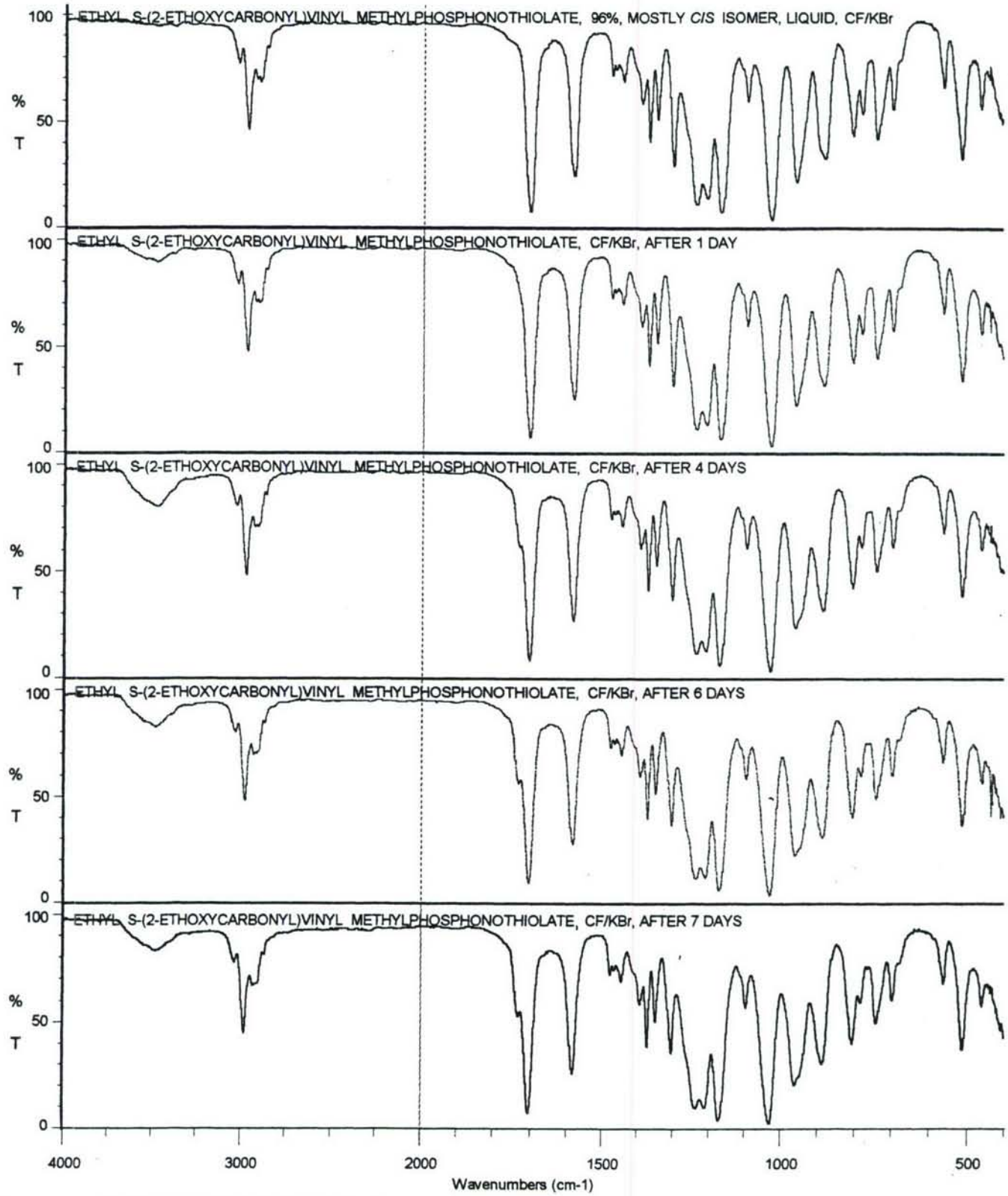


Figure 416A ETHYL S-(2-ETHOXYCARBONYL)VINYL METHYLPHOSPHONOTHIOLATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

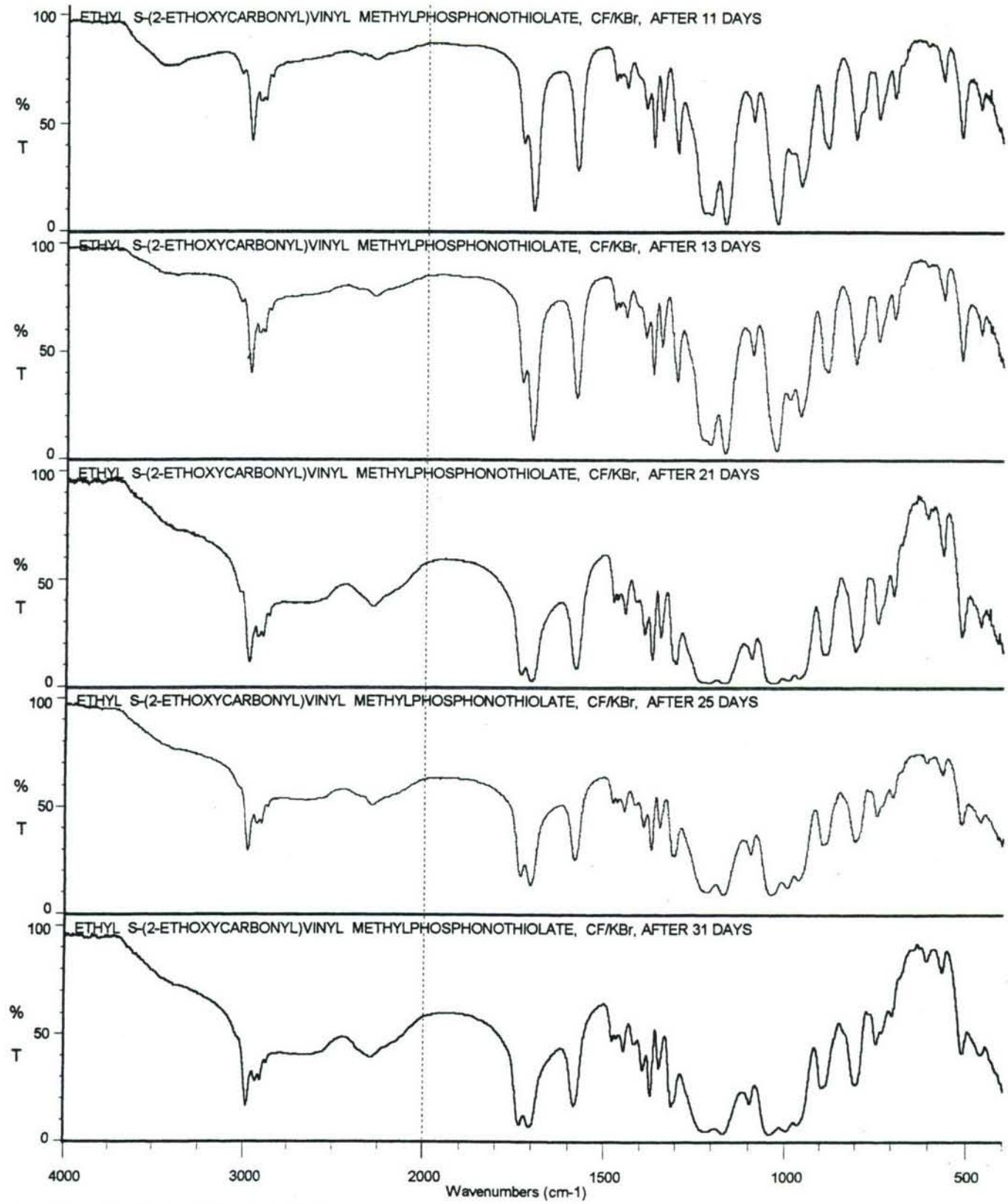


Figure 416B ETHYL S-(2-ETHOXYCARBONYL)VINYL METHYLPHOSPHONOTHIOLATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

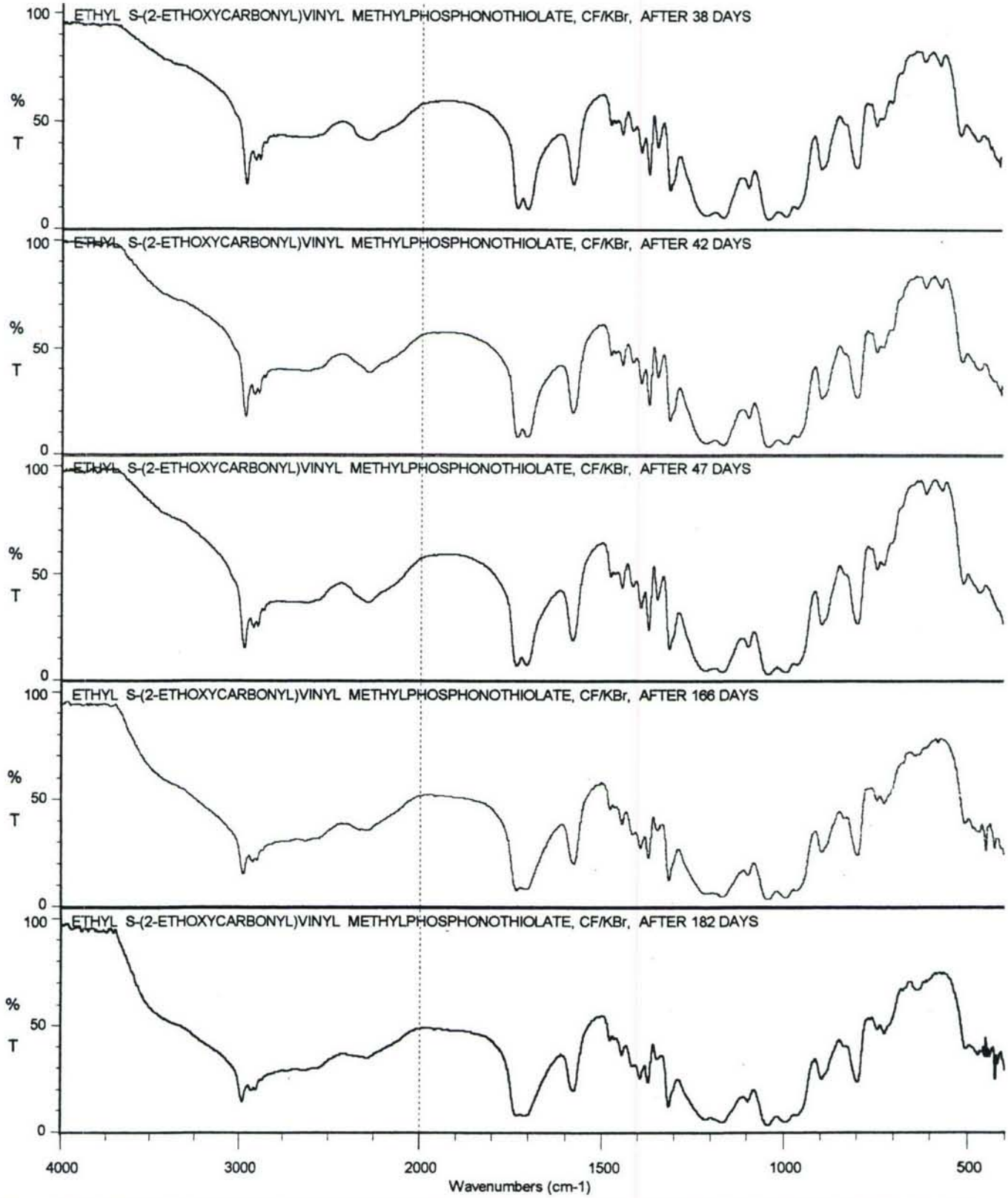


Figure 416C ETHYL S-(2-ETHOXYCARBONYL)VINYL METHYLPHOSPHONOTHIOLATE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

The effect of atmospheric moisture on a thin liquid film of ethyl S-(2-ethoxycarbonyl)vinyl methylphosphonothiolate between KBr windows is illustrated by the infrared spectra presented in ***Figures 416A*** through ***416C***. After 4 days of exposure to atmospheric moisture, the infrared spectum (***Figure 416A***) shows a new band forming near 1733 cm^{-1} (new ν C=O). By 11 days of exposure (***Figure 416B***) new bands are forming near 2700 and 2280 cm^{-1} indicative of the POH moiety. These POH bands increase in intensity with time. The carbonyl stretching region shows two distinct bands at 1735 and 1707 cm^{-1}. The P=O stretching band is now a broader band near 1214 cm^{-1}. The C=C stretching band is still evident at 1579 cm^{-1}. The spectrum has the appearance of being partly composed of **EMPA**, ethyl methylphosphonic acid, $CH_3P{=}O(OH)(OEt)$. An authentic spectrum of **EMPA** was previously presented as ***Figure 143***. The P-S band at 512 cm^{-1} has disappeared from the spectrum, having been replaced by a band near 504 cm^{-1} that may be attributed to **EMPA**. Infrared spectra for the compound after 182 days of exposure and **EMPA** are compared in ***Figure 417***. The hydrolysis of ethyl S-(2-ethoxycarbonyl)vinyl methylphosphonothiolate may be summarized as follows:

CH_3-P=O(OEt)[S-CH=CH-C(=O)OEt $\xrightarrow{-HOH}$ $CH_3P{=}O(OH)(OEt)$ + HS-CH=CH-C(=O)OEt

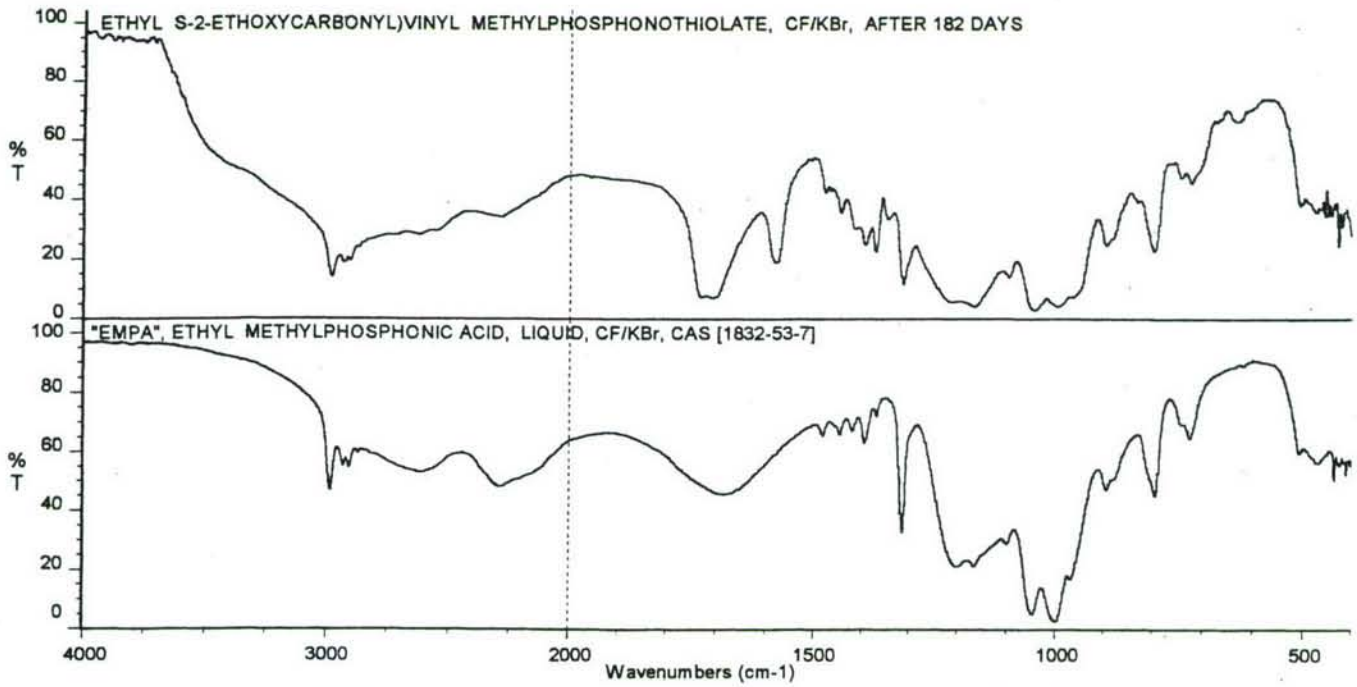


Figure 417 *UPPER SPECTRUM* **ETHYL S-(2-ETHOXYCARBONYL)VINYL METHYLPHOSPHONOTHIOLATE, CF/KBr, AFTER 182 DAYS OF EXPOSURE TO ATMOSPHERIC MOISTURE**
LOWER SPECTRUM **ETHYL METHYLPHOSPHONIC ACID (EMPA), LIQUID, CF/KBr**

3.8 P=Se Compounds

3.8.1 Triethyl Selenophosphate $(CH_3CH_2O)_3P{=}Se$

The infrared spectrum of triethyl selenophosphate as a thin liquid film between KBr windows is given in ***Figure 418***. The band assignments are as follows: 2982 cm^{-1} m (ν_{as} CH_3), 2935 cm^{-1} w (ν_{as} CH_2), 2903 cm^{-1} w (ν_{sy} CH_3), 2870 cm^{-1} vw (ν_{sy} CH_2), 1476 cm^{-1} w (δ OCH_2), 1443 cm^{-1} w (δ_{as} CH_3), 1391 cm^{-1} w (ω OCH_2), 1367 cm^{-1} vw (δ_{sy} CH_3), 1293 cm^{-1} vw (ω, τ CH_2), 1163 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1024 cm^{-1} s (ν P-O-C), 968 cm^{-1} ms (ν C-C of POEt), 772 cm^{-1} m (has shoulders near 810 and 793 cm^{-1}, POC), 575 and 532 cm^{-1} w (ν P=Se, two bands-rotational isomers).[oooo]

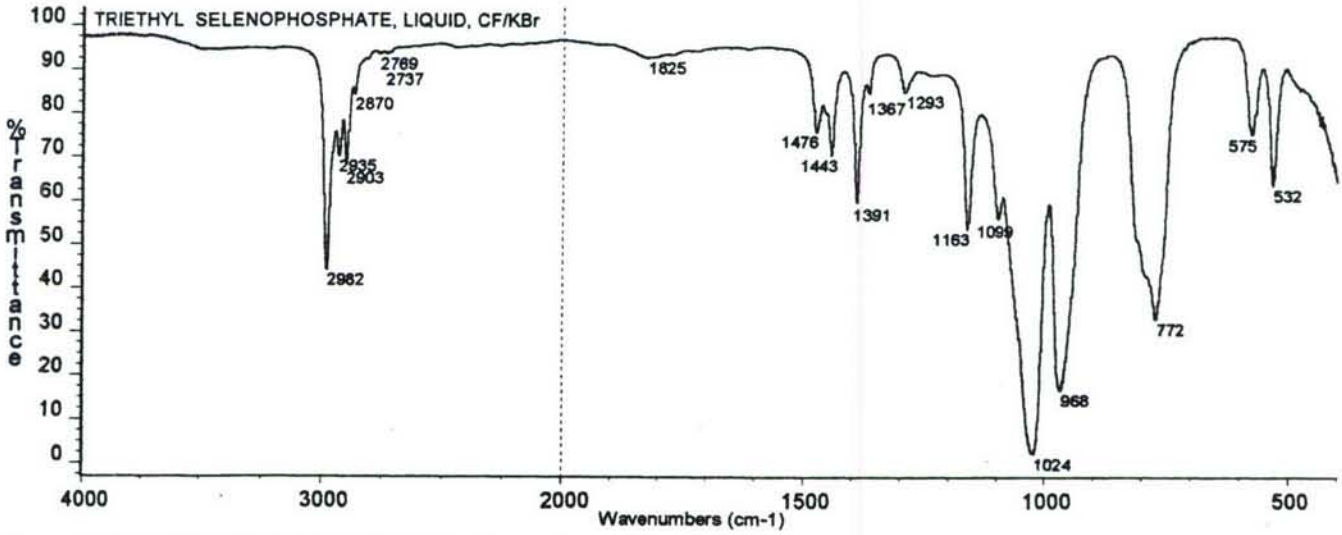


Figure 418 TRIETHYL SELENOPHOSPHATE, LIQUID, CF/KBr

3.8.2 Triphenylphosphine Selenide $(H_5C_6)_3P{=}Se$

The infrared spectrum of triphenylphosphine selenide as a solid between KBr discs (windows) is reproduced as ***Figure 419***. The band assignments are as follows: 3073 cm^{-1} vw and 3054 cm^{-1}

[oooo] The P=Se valence vibration has two bands associated with it due to rotational isomerism. For P=Se compounds of the type $(RO)_3P{=}Se$, isomer I occurs in the range 577-565 cm^{-1}, while isomer II occurs in the 535-504 cm^{-1} range. Thomas, L.C.,"Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 154. Heyden & Son Ltd., London, 1974.
The ranges for the P=Se stretching bands are also given as 600-420 cm^{-1} and 540-470 cm^{-1}. Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S., "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)", p. 6 and p. 282 IR Nos. 521 and 522, Kluwer Academic Publishers, Boston, 1990.

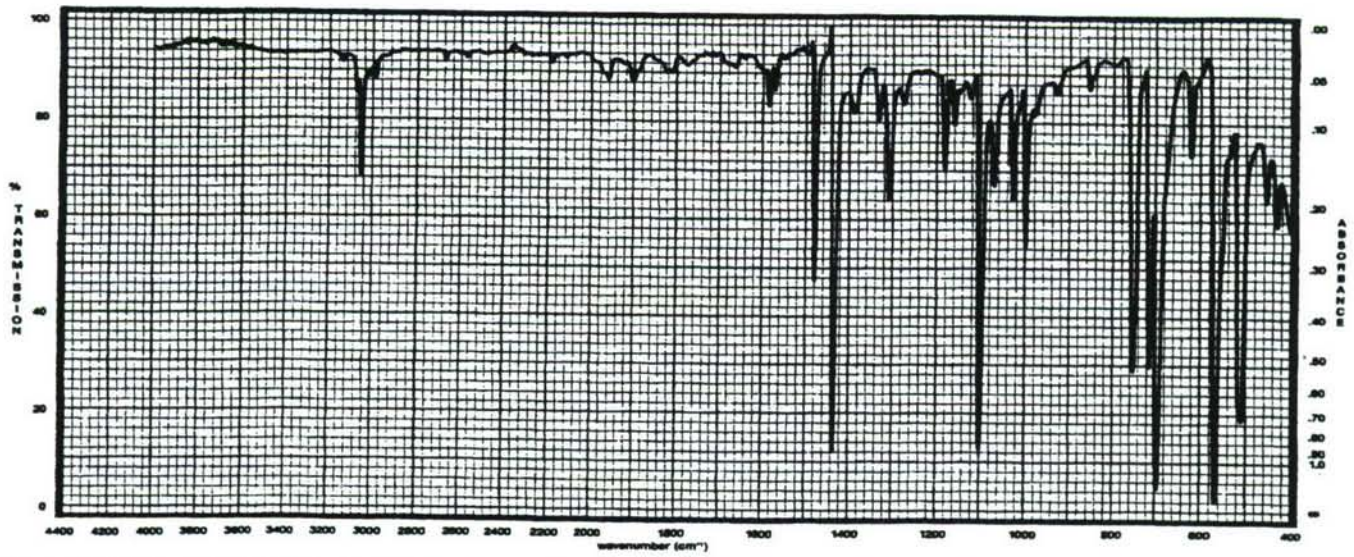


Figure 419 TRIPHENYLPHOSPHINE SELENIDE, SOLID BETWEEN KBr DISCS (WINDOWS)

w (ν C-H aromatic), 1584 and 1572 cm^{-1} vw, 1478 cm^{-1} m and 1434 cm^{-1} ms (aromatic ring C=C, 1180 cm^{-1} w, 1158 cm^{-1} vw, 1068, 1026 and 997 cm^{-1} w (β C-H mono-substituted aromatic ring), 1098 cm^{-1} ms (phenyl-P), 749 cm^{-1} m (γ C-H mono-substituted aromatic ring), 692 cm^{-1} s (mono-substituted aromatic ring deformation), 562 cm^{-1} s (ν P=Se), 506 cm^{-1} ms (mono-substituted aromatic ring).

3.9 Pyro Compounds (P-O-P)

3.9.1 Tetraethyl Pyrophosphite $(CH_3CH_2O)_2P\text{-}O\text{-}P(OCH_2CH_3)_2$

The infrared spectrum of tetraethyl pyrophosphite as a liquid film between KBr windows is given as ***Figure 420***. The band assignments are as follows: 2980 cm^{-1} m (ν_{as} CH_3), 2932 cm^{-1} w (ν_{as} CH_2), 2902 cm^{-1} w (ν_{sy} CH_3), ca 2885 cm^{-1} sh (ν_{sy} CH_2), 2428 cm^{-1} vvw [ν P-H impurity from hydrolysis , probably from $(EtO)_2P{=}O(H)$], 1478 cm^{-1} vw (δ OCH_2), 1443 cm^{-1} vw (δ_{as} CH_3), 1388 cm^{-1} w (ω OCH_2), 1370 cm^{-1} vvw (δ_{sy} CH_3), 1262 cm^{-1} w [ν P=O, probably from $(EtO)_2P{=}O(H)$, which would have a *calculated* value of 1258 cm^{-1}], 1163 and 1098 cm^{-1} w (CH_3 rock from POEt, characteristic), 1027 cm^{-1} s (ν P-O-C), 975 cm^{-1} w (P-H deformation), 946 cm^{-1} sh (ν C-C of POEt), 924 cm^{-1} m (ν P-O-P), 847 cm^{-1} m (ν C-C of $P^{+3}OEt$?), 758 and 735 cm^{-1} m (POC), ca 660 cm^{-1} vw (pyro).

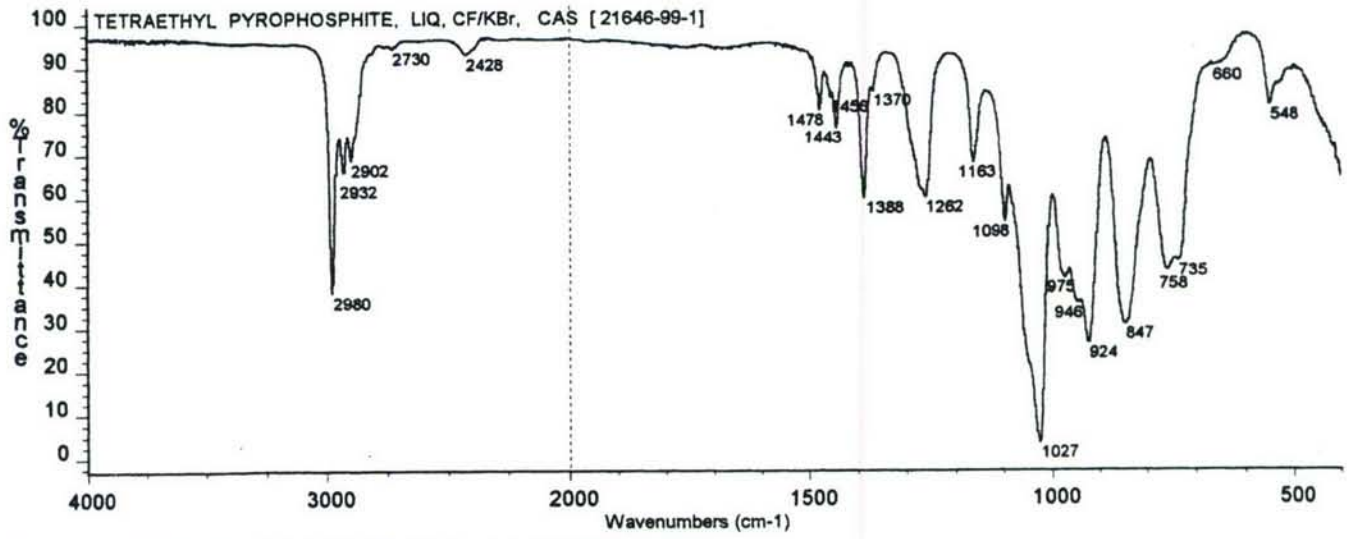


Figure 420 TETRAETHYL PYROPHOSPHITE, LIQUID, CF/KBr

The effect of atmospheric moisture on a liquid film of tetraethyl pyrophosphite while between KBr windows is illustrated by the infrared spectra reproduced in ***Figures 421A*** and ***421B***. After 4 hours of exposure to atmospheric moisture, the infrared spectrum (***Figure 421A***) shows bands indicative of a PH moiety at 2426 cm^{-1} (ν P-H) and 978 cm^{-1} (P-H deformation and ν C-C of P^{+5} OEt). The P=O stretching band at 1261 cm^{-1}, originally present in the compound, is now much stronger. The original compound has hydrolyzed to form diethyl phosphite, $(EtO)_2P{=}O(H)$, an authentic spectrum of which was given previously as ***Figure 183***. After 2 days of exposure the spectrum shows signs of the formation of the POH group, 2730, 2317 and ca 1650 cm^{-1}. The P=O stretching band has fallen in value from 1262 to 1215 cm^{1}. As time progresses the spectrum takes on the appearance of a P-acid, EtO-P=O(H)(OH), ethyl hydrogenphosphonic acid (ethyl hydrogen hydrogenphosphonate). By the 7th through 155th days (***Figure 421B***) the bands indicative of the POEt group have become quite weak, although the spectrum still retains the overall appearance of a P-Acid. Perhaps some phosphonic acid, $HP{=}O(OH)_2$ is forming from the hydrolysis of EtO-P=O(H)(OH). Thus, the hydrolysis of tetraethyl pyrophosphite may be summarized as follows:

$(EtO)_2P\text{-}O\text{-}P(OEt)_2$ -HOH→ $(EtO)_2P{=}O(H)$ -HOH→ EtO-P=O(H)(OH) -HOH→ $H\text{-}P{=}O(OH)_2$ (?)

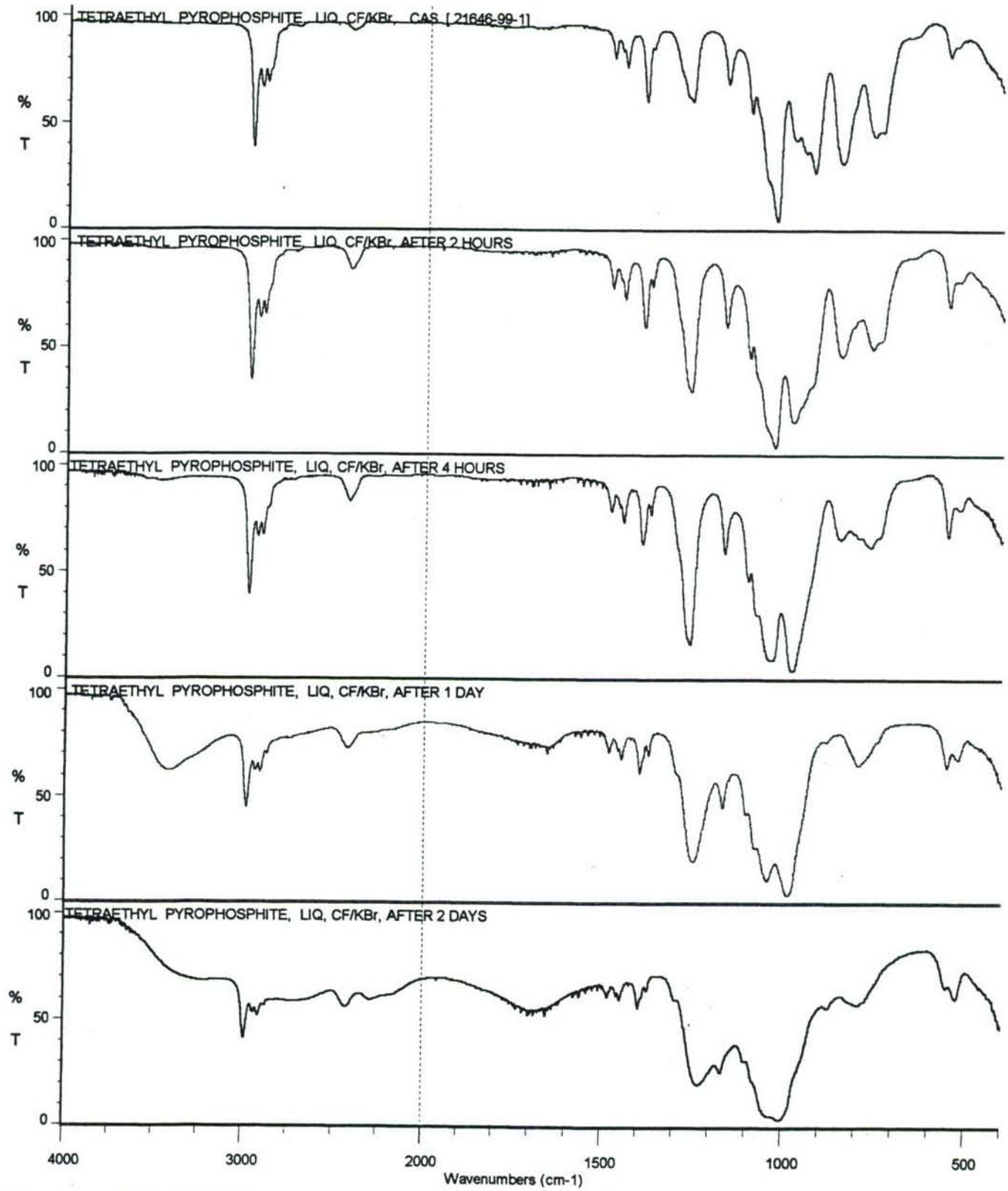


Figure 421A TETRAETHYL PYROPHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

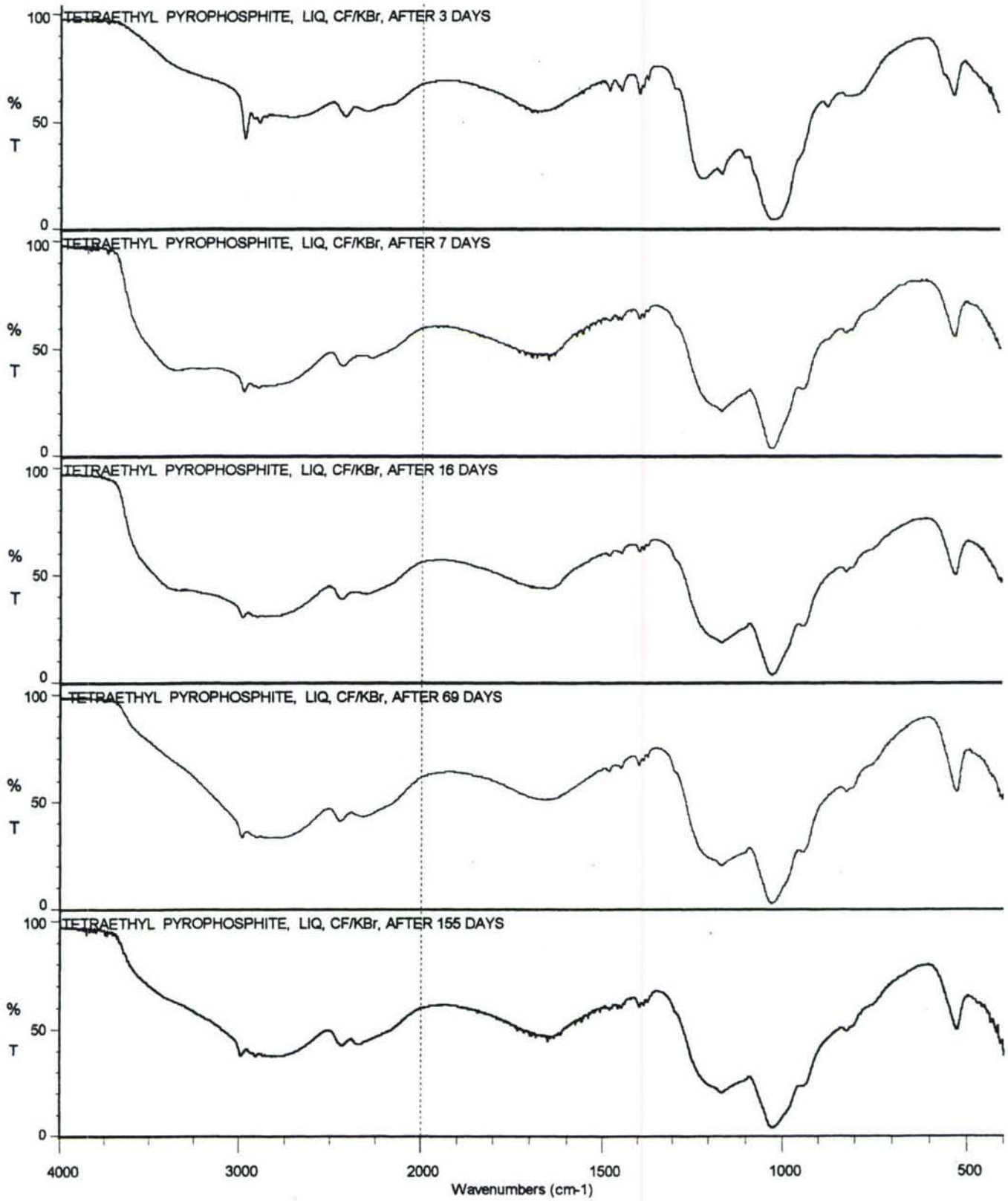


Figure 421B TETRAETHYL PYROPHOSPHITE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE (CONTINUED)

3.9.2 Methylphosphonic Anhydride $(HO)CH_3P(=O)\text{-}O\text{-}P(=O)CH_3(OH)$

The infrared spectrum of methylphosphonic anhydride (Dihydrogen Dimethylpyrophosphonate) is reproduced in ***Figure 422***. The band assignments are as follows: 3006 cm^{-1} vw and 2929 cm^{-1} vw (ν_{as} and ν_{sy} CH_3), 2633 cm^{-1}, 2305 cm^{-1} and 1679 cm^{-1} all weak and broad (POH), 1424 cm^{-1} vw (δ_{as} P-CH_3), 1311 cm^{-1} m (δ_{sy} P-CH_3), 1213 cm^{-1} ms (ν P=O), 1009 cm^{-1} ms (ν P-OH), 951 cm^{-1} ms (ν P-O-P), 894 cm^{-1} ms (P-CH_3 rock), 775 s (ν P-C), 525 w, 504 m, 468 m, 445 ms cm^{-1} (P=O deformations ?).

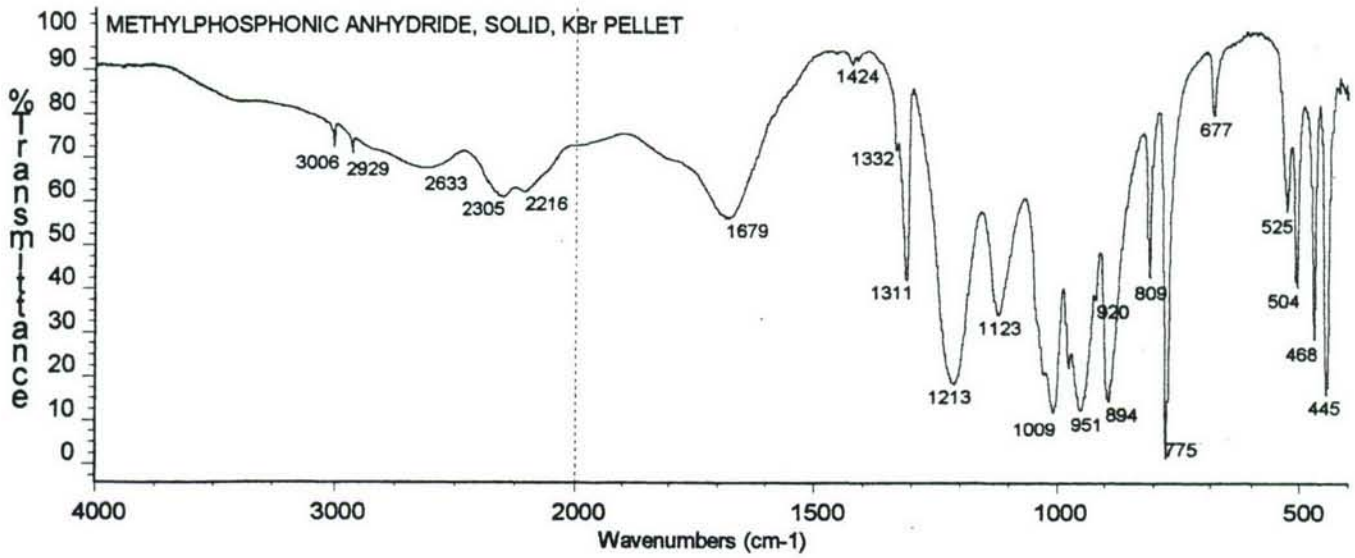


Figure 422 METHYLPHOSPHONIC ANHYDRIDE, SOLID, KBr PELLET

In ***Figure 423***, the effect of grinding on the solid/KBr matrix is illustrated. The top most spectrum is from a freshly prepared pellet. The next spectrum is from another freshly prepared pellet. Note the differences in the band intensities between the two spectra. The third spectrum down shows the previous pellet reground and re-pressed. Note this spectrum appears to lie between the two previous spectra. The last spectrum in the group, shows the effect of moisture on the pellet after it had been sitting in the air for 6 days. This last pellet now seems to resemble the spectrum for methylphosphonic acid (***Figure 106***).[pppp]

[pppp] The last spectrum in ***Figure 423*** for methylphosphonic anhydride best resembles the infrared spectrum for methyl phosphonic acid (***Figure 48***, IR labeled grinding #3) given in "Infrared Spectroscopic Observations on the Fate of Organophosphorus Compounds Exposed to Atmospheric Moisture. Part I. G-Agents and Related Compounds", Piffath, R.J., U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD 21010-5423, 1999.

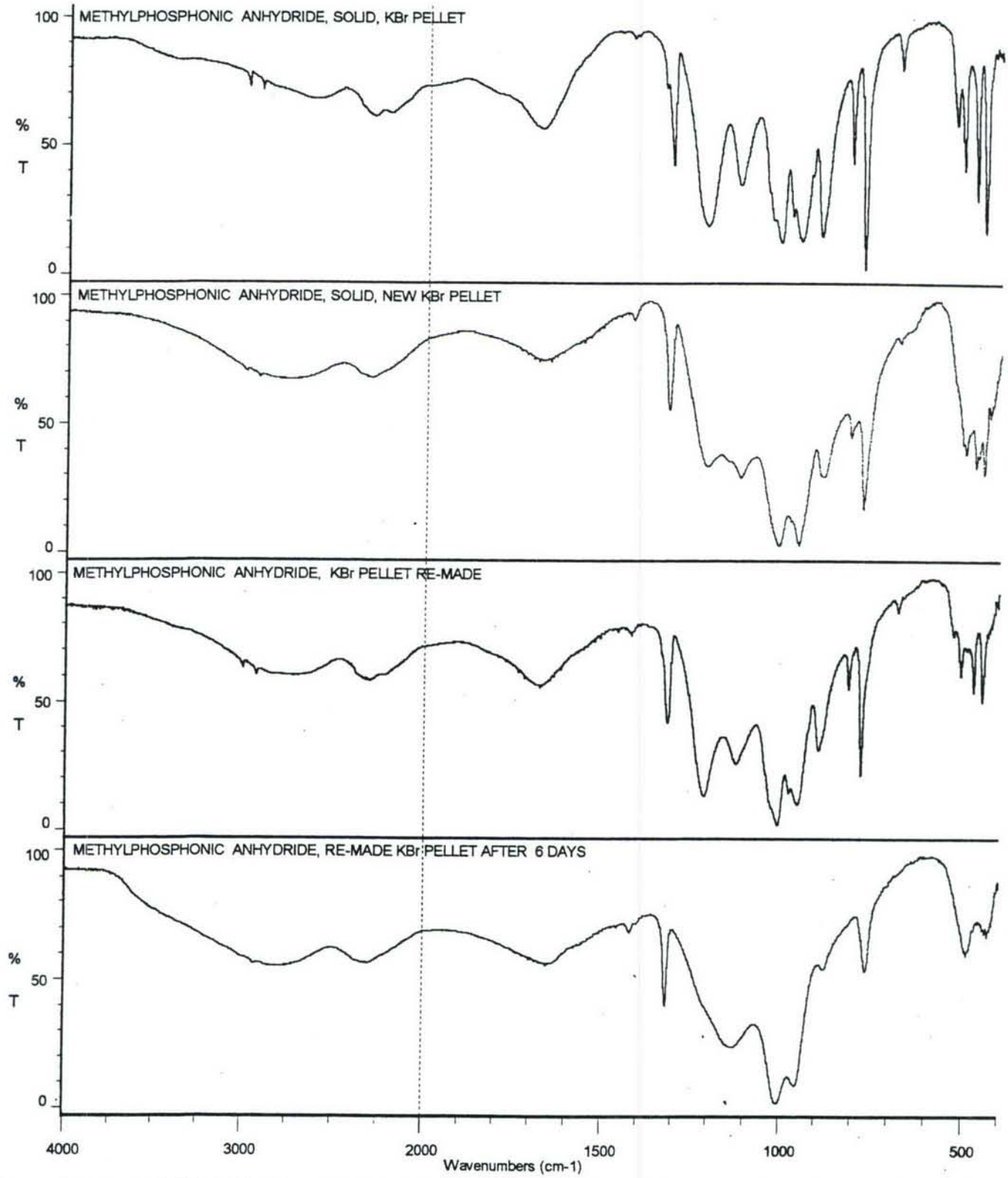


Figure 423 METHYLPHOSPHONIC ANHYDRIDE, SOLID, KBr PELLET. THE SPECTRA ILLUSTRATE THE EFFECT OF GRINDING ON THE SAMPLE/KBr MATRIX. THE BOTTOM SPECTRUM SHOWS THE CONVERSION TO METHYLPHOSPHONIC ACID.

3.9.3 Disodium Dimethylpyrophosphonate (**Na_2PYRO**) $(NaO)CH_3P(=O)\text{-}O\text{-}P(=O)CH_3(ONa)$

The infrared spectrum of disodium dimethylpyrophosphonate as a KBr pellet is presented as ***Figure 424***. The band assignments are as follows: 3432 cm^{-1} w and 1623 cm^{-1} vw (H_2O), 2998 cm^{-1} vw and 2933 cm^{-1} vw (ν_{as} and ν_{sy} CH_3), 1413 cm^{-1} vw (δ_{as} P-CH_3), 1304 cm^{-1} m (δ_{sy} P-CH_3), 1205 cm^{-1} and 1195 cm^{-1} sh (ν_{as} PO_2), 1118 cm^{-1} ms (ν_{sy} PO_2^-), 968 cm^{-1} ms and 942 cm^{-1} ms (ν P-O-P), 874 cm^{-1} ms (P-CH_3 rock), 785 cm^{-1} m and 753 cm^{-1} ms (ν P-C), 452 cm^{-1} m (PO_2^- deformation).

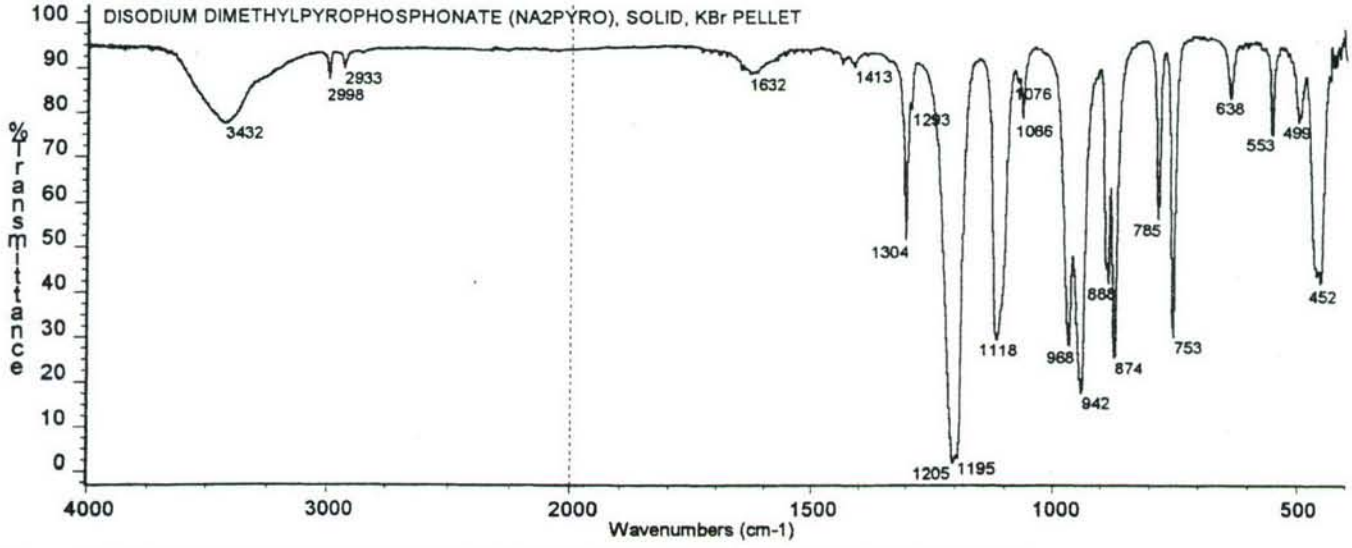


Figure 424 DISODIUM DIMETHYLPYROPHOSPHONATE (Na_2PYRO), SOLID, KBr PELLET

3.9.4 Diethyl Dimethylpyrophosphonate (Diethyl Dimethylphosphonic Anhydride, **VX Pyroester**)

$(EtO)CH_3P(=O)\text{-}O\text{-}P(=O)CH_3(OEt)$

The infrared spectrum of diethyl dimethylpyrophosphonate (diethyl dimethylphosphonic anhydride, **VX Pyroester**) as a thin liquid between CsI discs (windows) is reproduced as ***Figure 425***. The band assignments are as follows: 2988 cm^{-1} m (ν_{as} CH_3), 2928 cm^{-1} w (ν_{as} CH_2), ca 2914 cm^{-1} sh (ν_{sy} CH_3), 2875 cm^{-1} vw (ν_{sy} CH_2), 1480 cm^{-1} vw (δ OCH_2), 1445 cm^{-1} vw (δ CH_3), 1417 cm^{-1} vw (δ_{as} P-CH_3), 1394 cm^{-1} w (ω OCH_2), 1369 cm^{-1} vw (δ_{sy} CH_3), 1316 cm^{-1} ms (δ_{sy} P-CH_3), 1260 cm^{-1} s (ν P=O, *calculated* value is 1260 cm^{-1}), 1165 and 1099 cm^{-1} w (CH_3 rock of POEt, characteristic), 1046 cm^{-1} s (ν P-O-C), 979 cm^{-1} sh (ν C-C of POEt), 942 cm^{-1} s (ν P-O-P), 890 cm^{-1} ms (P-CH_3 rock), 759 cm^{-1} sh and 733 cm^{-1} m (ν P-C), 649 cm^{-1} w (pyro), 510 cm^{-1} m (P=O deformation).

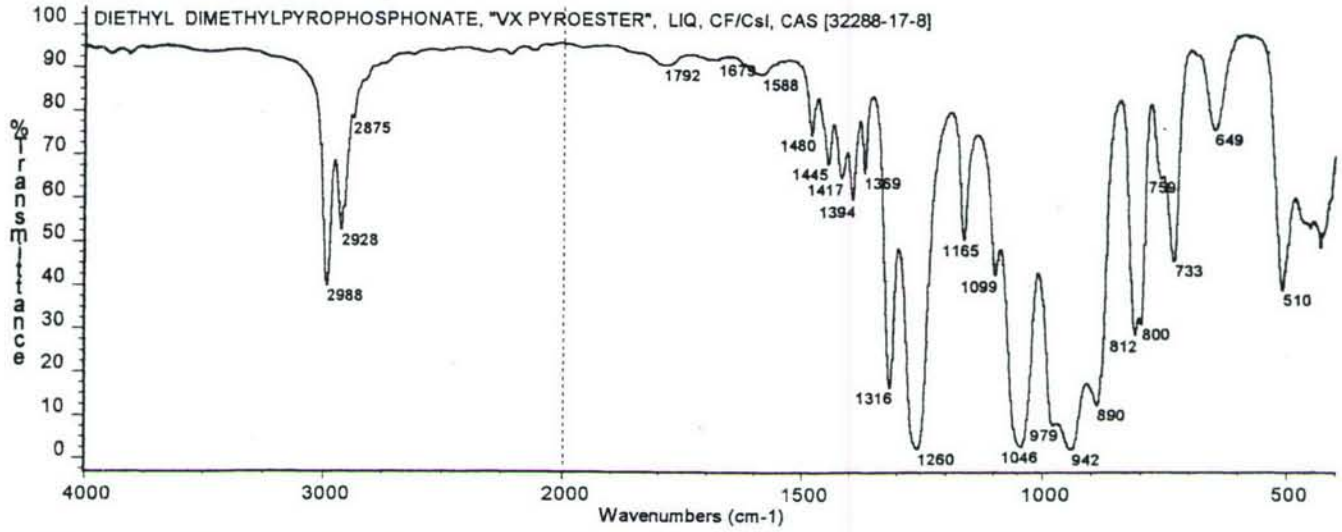


Figure 425 DIETHYL DIMETHYLPYROPHOSPHONATE (VX PYROESTER), LIQUID, CF/CsI

3.9.5 Diisopropyl Dimethylpyrophosphonate (Diisopropyl Dimethylphosphonic Anhydride)

$[(CH_3)_2CHO]CH_3P(=O)\text{-}O\text{-}P(=O)CH_3[OCH(CH_3)_2]$

The infrared spectrum (grating) of diisopropyl dimethylpyrophosphonate (diisopropyl dimethylphosphonic anhydride), **GB Pyroester**, as a liquid film between cesium iodide windows is given in ***Figure 426***. The band assignments are as follows: (the band frequencies are estimated from the spectrum) 2982 cm^{-1} m, 2930 cm^{-1} w and 2867 cm^{-1} vw (ν CH_3), 1470 cm^{-1} vw and 1455 cm^{-1} vvw (δ_{as} CH_3), 1417 cm^{-1} vw (δ_{as} P-CH_3), 1389 and 1377 cm^{-1} w (δ_{sy} CH_3, doublet-isopropyl group), 1354 cm^{-1} sh (δ -C-H), 1314 cm^{-1} m (δ_{sy} P-CH_3), 1261 cm^{-1} ms (ν P=O, *calculated* value is 1256 cm^{-1}), 1180, 1144 and 1108 cm^{-1} w (triplet characteristic of P-O-isopropyl moiety), 1014 cm^{-1} s (ν P-O-C), 946 cm^{-1} ms (ν P-O-P), 888 cm^{-1} m (P-CH_3 rock, CH_3 rock of the isopropyl group) , 806 and 786 cm^{-1} w-m (POC), 728 cm^{-1} vw (ν P-C), 650 cm^{-1} vw (pyro), 514 cm^{-1} w (P=O deformation).

3.9.6 Diethyl Diethylpyrophosphonate (Diethyl Diethylphosphonic Anhydride)

$(CH_3CH_2O)CH_3\ CH_2P(=O)\text{-}O\text{-}P(=O)CH_2CH_3(CH_2CH_3)$

The infrared spectrum of diethyl diethylpyrophosphonate (diethyl diethylphosphonic anhydride) as a liquid film between cesium iodide discs (windows) is given as ***Figure 427***. The band assignments are as follows: 3543 and 3479 cm^{-1} vw (H_2O), 2983 cm^{-1} ms (ν_{as} CH_3), 2944 cm^{-1} m (ν_{sy} CH_2), ca 2915 cm^{-1} sh (ν_{sy} CH_3),

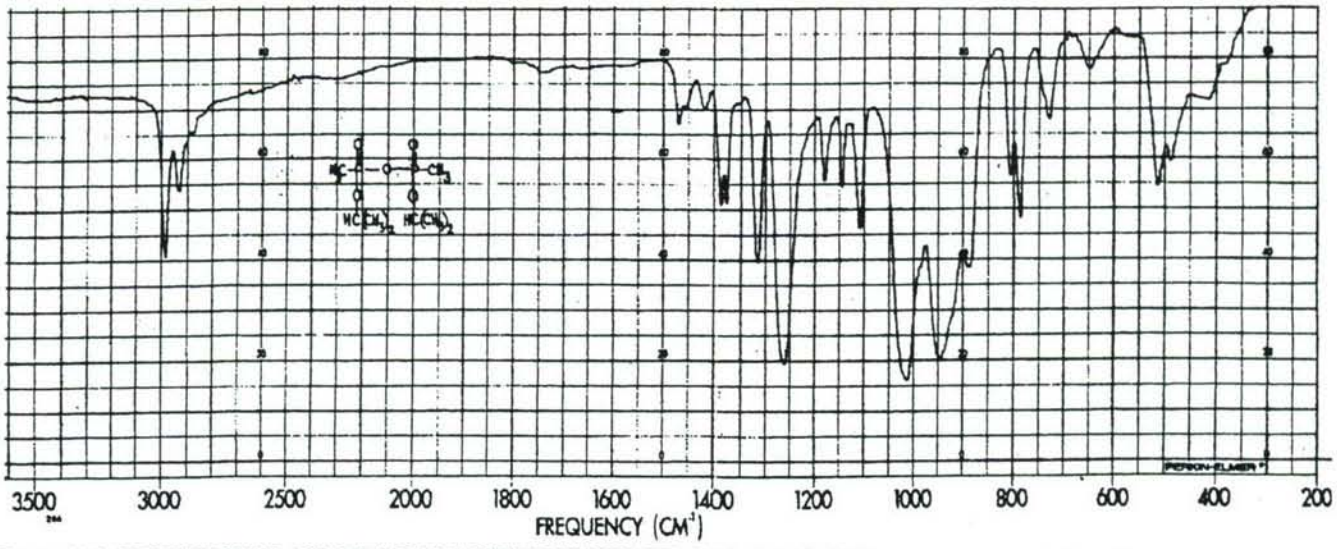


Figure 426 DIISOPROPYL DIMETHYLPYROPHOSPHONATE, LIQUID, CF/CsI (Perkin-Elmer Model 521 Grating Spectrophotometer)

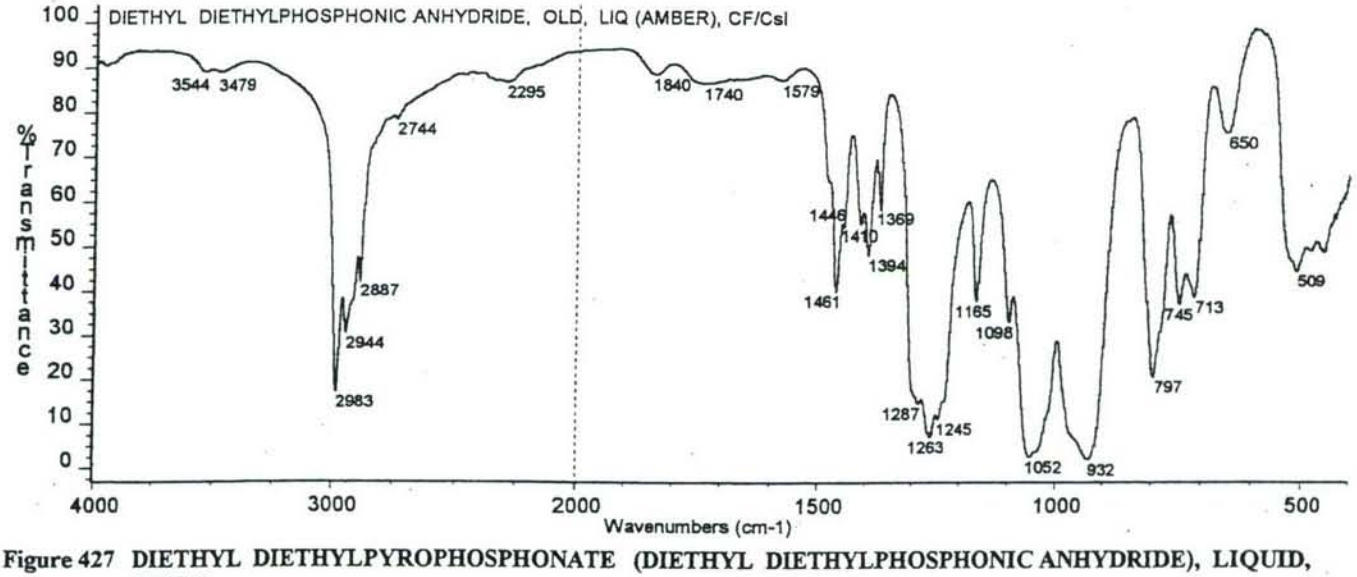


Figure 427 DIETHYL DIETHYLPYROPHOSPHONATE (DIETHYL DIETHYLPHOSPHONIC ANHYDRIDE), LIQUID, CF/CsI

2887 cm^{-1} m (ν_{sy} CH_2), 2295 cm^{-1} vw (POH ?), 1840 cm^{-1} vw (1052 + 797 = 1849 cm^{-1}), 1579 cm^{-1} w (932 + 650 = 1582 cm^{-1}), 1478 cm^{-1} (δ OCH_2), 1461 cm^{-1} m, 1446 cm^{-1} sh (δ_{as} CH_3), 1410 cm^{-1} w (δ P-CH_2), 1394 cm^{-1} w (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1287 and 1245 cm^{-1} shoulders on 1263 cm^{-1} band (P-Et, ω and τ CH_2), 1263 cm^{-1} ms (ν P=O, *calculated* value is 1256 cm^{-1}), 1165 and 1098 cm^{-1} w (CH_3 rock of POEt, characteristic), 1052 cm^{-1} s (ν P-O-C), ca 962 cm^{-1} sh (ν C-C of POEt), 932 cm^{-1} s (ν P-O-P), 797 cm^{-1} ms (POC), 743

cm^{-1} m and 713 cm^{-1} m (CH_2 rock of POEt, and ν P-C), 650 cm^{-1} w (pyro), 509 cm^{-1} m (P=O deformation).

3.9.7 Bis(Ethyl N,N-Dimethylphosphoramidic) Anhydride (GA Pyro)

$(CH_3CH_2O)[(CH_3)_2N]P(=O)\text{-}O\text{-}P(=O)[N(CH_3)_2](OCH_2CH_3)$

The infrared spectrum of bis(ethyl N,N-dimethylphosphoramidic) anhydride [sym-bis(dimethylamido) diethyl pyrophosphate], **GA Pyro**, as a liquid film between cesium iodide windows is reproduced as ***Figure 428***.[qqqq] The band assignments are as follows: 3546 and 3494 cm^{-1} vw (H_2O), 2984, 2935, 2908 cm^{-1} ms and 2857 cm^{-1} m (ν CH_3 and ν CH_2), 2819 cm^{-1} w (N-CH_3), 1483 cm^{-1} m (δ OCH_2), 1458 cm^{-1} m (δ_{as} CH_3), 1393 cm^{-1} w (ω OCH_2), 1369 cm^{-1} w (δ_{sy} CH_3), 1317 cm^{-1} ms [$PN(CH_3)_2$],[rrrr] 1268 cm^{-1} s (ν P=O, *calculated* value is 1272 cm^{-1}), 1190 cm^{-1} m [$PN(CH_3)_2$], 1167 and 1099 cm^{-1} m (CH_3 rock of POEt, characteristic), 1055 cm^{-1} ms (ν P-O-C), 1005 cm^{-1} s (ν_{as} P-N-C), 977 cm^{-1} sh (ν C-C of POEt), 928 cm^{-1} s (ν P-O-P), 816 and 796 cm^{-1} m (POC), 708 cm^{-1} m (ν_{sy} P-N-C), 668 cm^{-1} vw (pyro), 497 cm^{-1} m (P=O deformation).

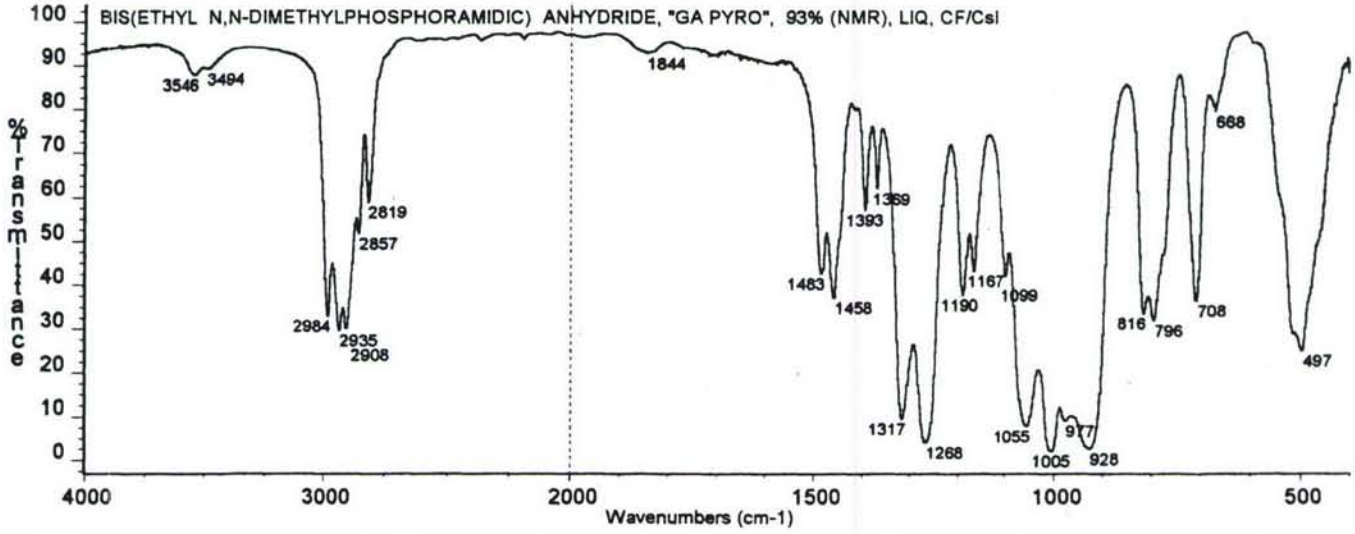


Figure 428 BIS(ETHYL N,N-DIMETHYLPHOSPHORAMIDIC) ANHYDRIDE, [*sym*-BIS(DIMETHYLAMIDO) DIETHYL PYROPHOSPHATE], "GA PYRO", LIQUID, CF/CsI

[qqqq] The infrared spectrum of this pyro compound has been presented previously by Holmstedt, B. and Larsson, L. in "IR Absorption Spectra of Some Organic Phosphoryl Compounds", Acta Chemica Scandinavica **5**, 1179 (1951).

[rrrr] The bands indicative of the P-$N(CH_3)_2$ moiety have been assigned as follows: 1320-1260 cm^{-1} m-s (ν_{as} C-N-C), 1210-1150 cm^{-1}, 1080-1050 cm^{-1} m (CH_3 rock), 1010-970 cm^{-1} m-s (ν_{as} P-N-C), 700-650 cm^{-1} w-m (ν_{sy} P-N-C). Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S., "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms), p. 5, Kluwer Academic Publishers, Boston, 1990.

Figure 429 shows the effect of atmospheric moisture on the infrared spectrum of **GA PYRO**. The compound remains intact in excess of 154 days. At the 175 day mark there is some decrease in the intensities of the bands indicative of the $PN(CH_3)_2$ moiety (namely 1317, 1190, 1005 and 708 cm^{-1}). These decreases continue through the remainder of the observations with the last being at 212 days. After 212 days, some very weak absorption due to the $PN(CH_3)_2$ moiety is still visible at 1316, 1009 and 709 cm^{-1}. Bands are present at 1250 cm^{-1} (ν P=O), 1165 cm^{-1} vw (POEt), 1056 cm^{-1} s (ν P-O-C), 969 cm^{-1} sh (ν C-C of POEt), 923 cm^{-1} ms (ν P-O-P), 795 cm^{-1} w (POC). Bands at 1090 cm^{-1} s and 610 cm^{-1} w are probably due to Cs_2SO_4 from the CsI windows. Perhaps, another pyro compound such as (HO)(OEt)P(=O)-O-P=O(OH)(OEt) is being formed? The phosphoryl stretch of such a compound could occur near 1250 cm^{-1}.[ssss]

3.9.8 1-Propanephosphonic Acid Cyclic Anhydride

The infrared spectrum of 1-propanephosphonic acid cyclic anhydride, (2,4,6-tripropyl-1,3,5,2,4,6-trioxatriphosphorinane 2,4,6-trioxide), as a liquid film (50 wt % in dichloromethane) between KBr windows is presented as ***Figure 430***. The band assignments are as follows: 3057 cm^{-1} w (ν CH_2 solvent), 2970 cm^{-1} ms (ν_{as} CH_3), 2937 cm^{-1} m (ν_{as} CH_2), 2912 cm^{-1} vw (ν_{sy} CH_3), 2879 cm^{-1} m (ν_{sy} CH_2), 2688, 2305 and ca 1660 cm^{-1} w broad (POH some hydrolysis has occurred), 1464 cm^{-1} m (δ CH_2, δ_{as} CH_3), 1404 cm^{-1} w (δ P-CH_2), 1384 cm^{-1} vw (δ_{sy} CH_3), 1350 cm^{-1} w (ω CH_2), 1287 cm^{-1} ms (ω CH_2 solvent and ν P=O), 1243 cm^{-1} w (CH_2 deformation from P-propyl moiety), 997 cm^{-1} s (ν P-O-P), 735 cm^{-1} ms and 703 cm^{-1} w (ν_{as} and ν_{sy} CCl_2).

The effect of atmospheric moisture on 1-propanephosphonic acid cyclic anhydride (50 wt % solution in dichloromethane) determined as a thin liquid film (CH_2Cl_2 solution) between KBr windows is illustrated by the infrared spectra in ***Figure 432***. The spectrum gradually shows the formation of bands indicative of the POH moiety (ca 2740, 2280, 1650 and 1000 cm^{-1}). The effect of moisture on the compound is better illustrated by the spectra given in ***Figure 431***,which shows the material after the solvent (CH_2Cl_2) had been evaporated off the KBr

[ssss] Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 13, Heyden & Son Ltd., London, 1974.

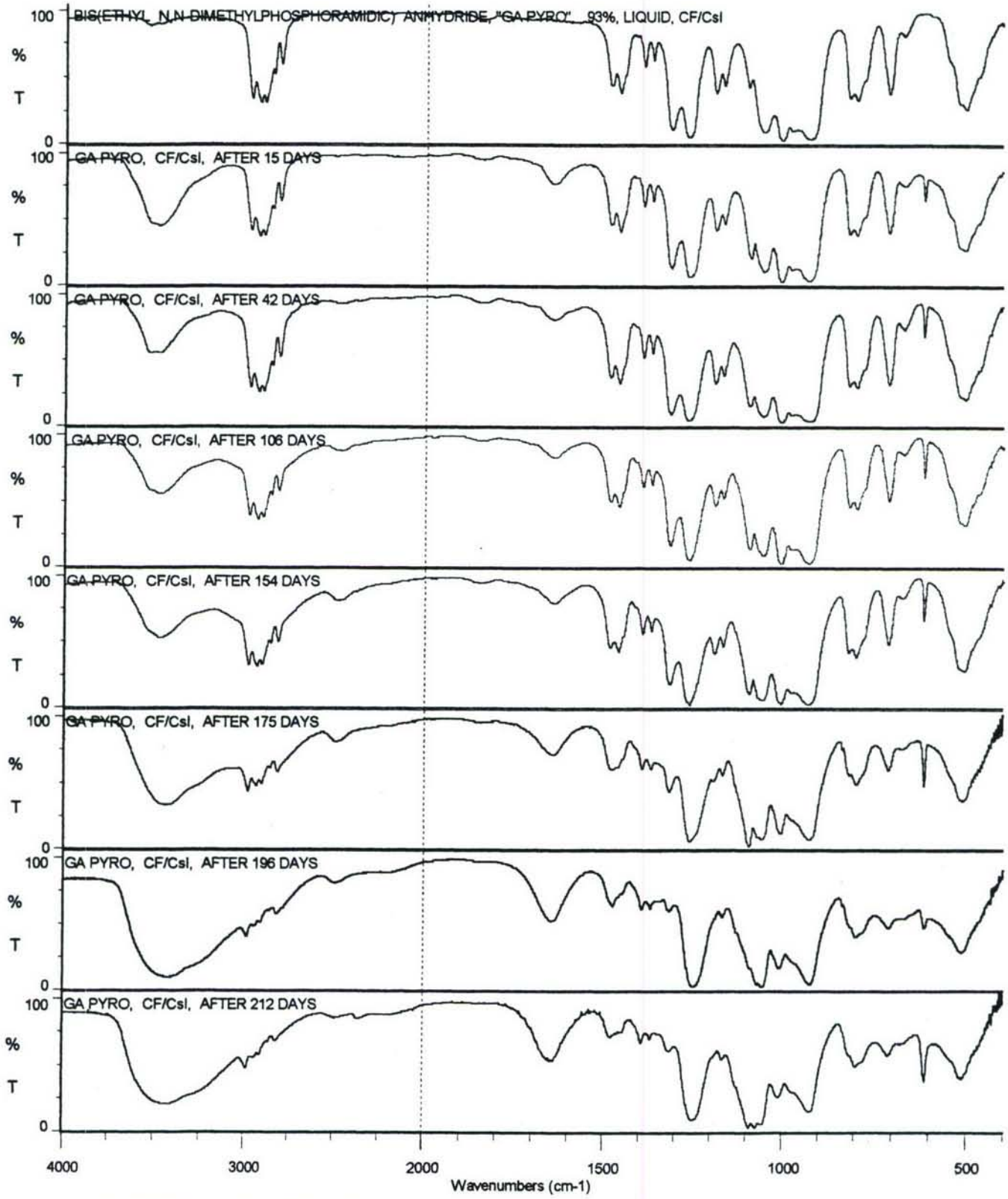


Figure 429 BIS(ETHYL N,N-DIMETHYLPHOSPHORAMIDIC) ANHYDRIDE (GA PYRO), LIQUID, CF/CsI, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

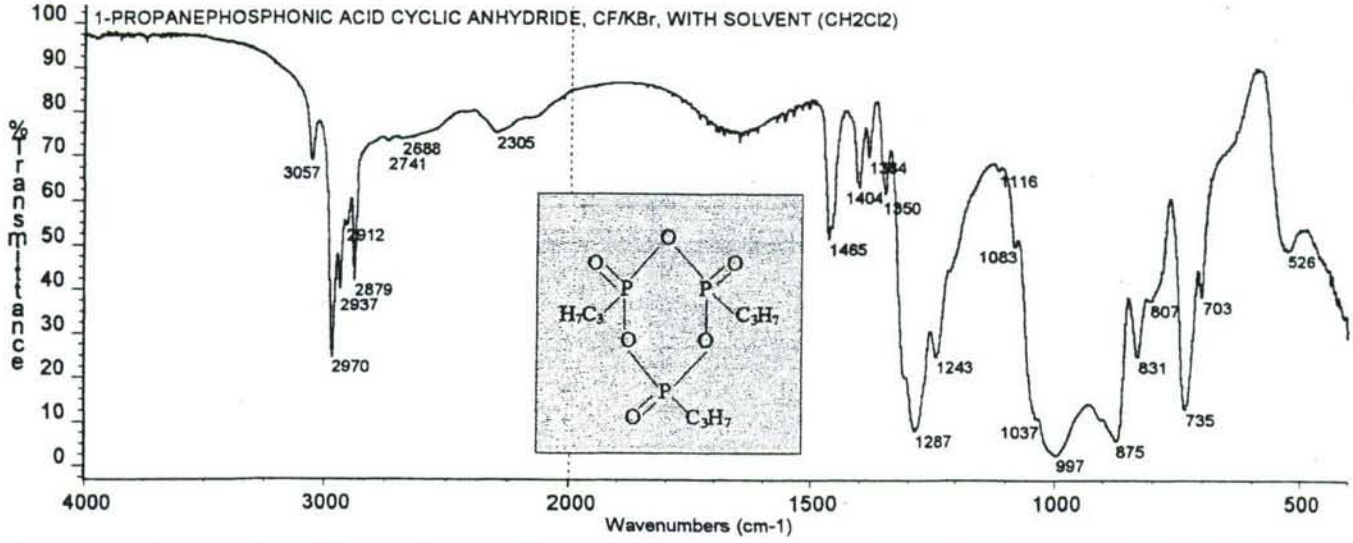


Figure 430 1-PROPANEPHOSPHONIC ACID CYCLIC ANHYDRIDE (or 2,4,6-TRIPROPYL-1,3,5,2,4,6-TRIOXATRIPHOSPHORINANE 2,4,6-TRIOXIDE), A 50 WT % SOLUTION IN DICHLOROMETHANE, CF/KBr

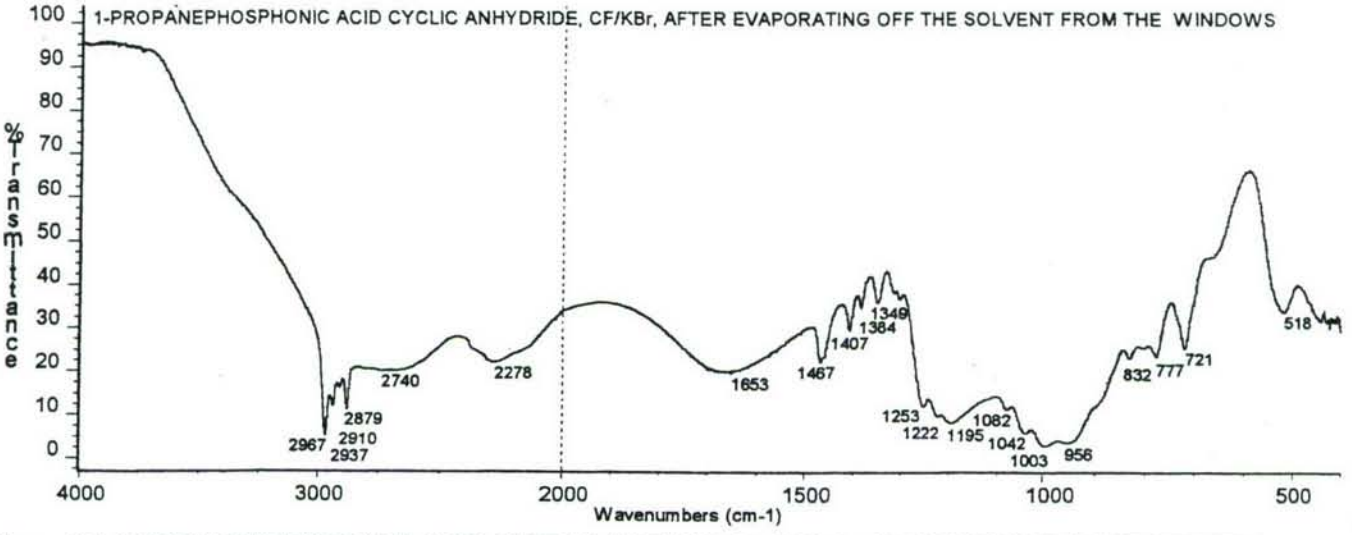


Figure 431 1-PROPANEPHOSPHONIC ACID CYCLIC ANHYDRIDE, CF/KBr, AFTER EVAPORATING OFF THE SOLVENT (CH_2Cl_2) FROM THE KBr WINDOWS

windows. The spectrum (***Figure 431***) shows the formation of POH bands at 2740, 2278, 1650 and 1003 cm^{-1}. The spectrum (***Figure 431***) shows bands at 1253 and 1222 cm^{-1} which may be due to the propyl group (ω, τ CH_2), as may the bands at 1082 and 1042 cm^{-1} (ν C-C, propyl). The band at 1195 cm^{-1} may be assigned to the acid P=O stretching vibration. The bands at 1003 and 956 cm^{-1} may be assigned to P-OH stretching vibrations. The 956 cm^{-1} band may be due to the P-O-P stretch from a compound such as (H_7C_3) (OH)P(=O)O-P=O(C_3H_7)(OH). The spectum could represent a mix of this pyro compound and $C_3H_7P{=}O(OH)_2$, n-propylphosphonic acid.

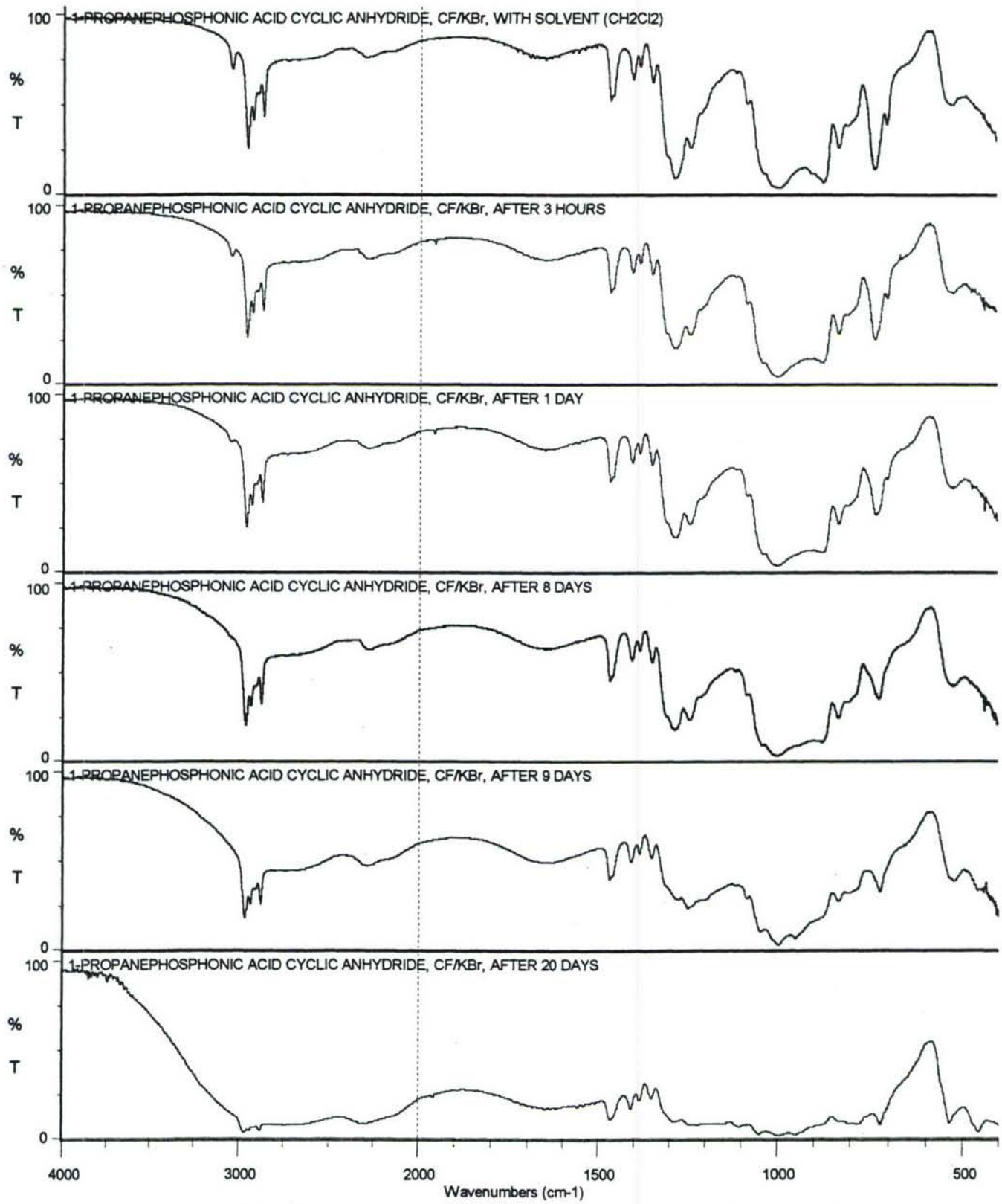


Figure 432 1-PROPANEPHOSPHONIC ACID CYCLIC ANHYDRIDE, WITH SOLVENT (CH_2Cl_2), CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.10 Other Organophosphorus Compounds Of Interest

3.10.1 Diisopropyl Fluorophosphate (DFP) $F\text{-}P{=}O[O\text{-}CH(CH_3)_2]_2$

The infrared spectrum of diisopropyl fluorophosphate (**DFP**) as liquid film between KBr windows is reproduced as ***Figure 433***. The band assignments, based on frequencies estimated from the spectrum, are as follows: 3580, 3520, 1630 cm^{-1} vw (H_2O), 2995 cm^{-1} m, 2944 cm^{-1} w, 2992 cm^{-1} vw and 2930 cm^{-1} vvw (ν CH_3 and ν -CH), 1468 cm^{-1} w (δ_{as} CH_3), 1392 and 1382 cm^{-1} m (doublet, δ_{sy} CH_3), 1359 cm^{-1} vw (δ C-H), 1301 cm^{-1} ms (ν P=O, *calculated* value is 1306 cm^{-1}), 1183, 1146 and 1107 cm^{-1} w (triplet, characteristic of P-O-isopropyl), 1018 cm^{-1} s (ν P-O-C), 902 cm^{-1} m (CH_3 rock), 860 cm^{-1} m (ν P-F), 776 and 744 cm^{-1} w (POC).

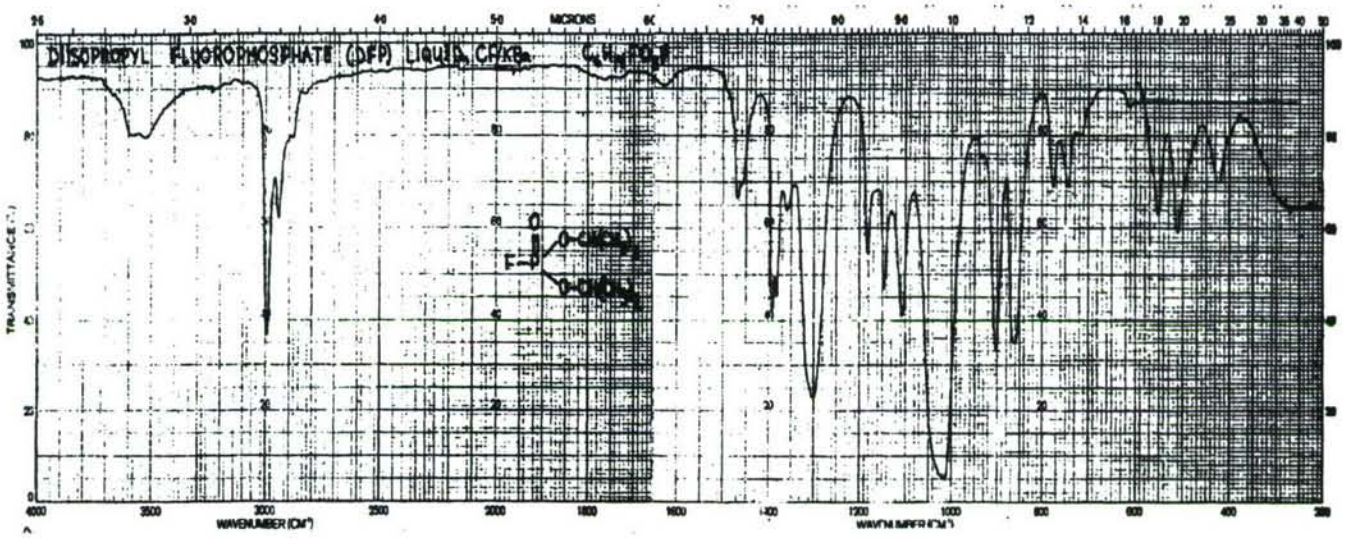


Figure 433 DIISOPROPYL FLUOROPHOSPHATE (DFP), LIQUID, CF/KBr (Perkin-Elmer Model 457 Grating Spectrophotometer)

3.10.2 N,N,N',N'-Tetramethylphosphorodiamidic Fluoride (Dimefox) $F\text{-}P{=}O[N(CH_3)_2]_2$

The infrared spectra of N,N,N',N'-tetramethylphosphorodiamidic fluoride (**Dimefox**) as a liquid film between KBr windows is presented as ***Figure 434***. The band assignments, based on frequencies estimated from the spectrum, are as follows: 3550, 3490 and 1650 cm^{-1} w (H_2O), 2996 cm^{-1} w, 2937 cm^{-1} m, 2905 cm^{-1} m, 2860 cm^{-1} w and 2920 cm^{-1} w (ν_{as} and ν_{sy} CH_3), ca 1770 cm^{-1} vvw (997 + 764 = 1761 cm^{-1}), 1486 and 1460 cm^{-1} m (δ CH_3), 1315 cm^{-1} s [$P(NCH_3)_2$], 1250 cm^{-1} s (ν P=O, *calculated* value is 1278 cm^{-1}), 1185 and 1070 cm^{-1} m [$P(NCH_3)_2$], 997 cm^{-1} s (ν_{as} P-N-C), 836 cm^{-1} s (ν P-F), 764 cm^{-1} s (ν_{sy} P-N-C).

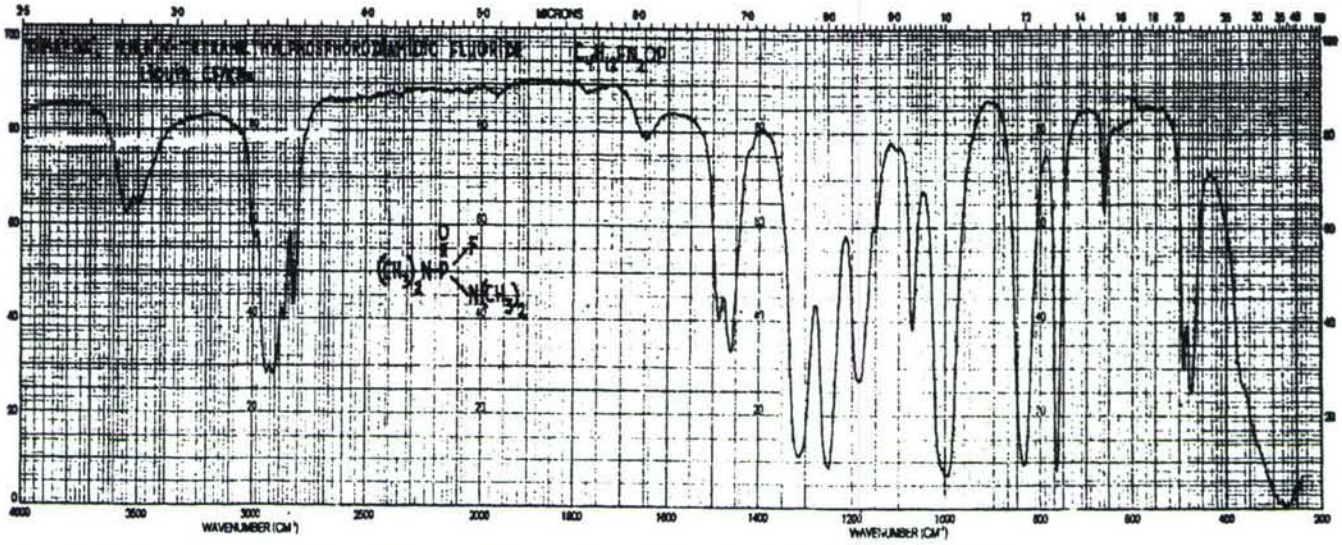
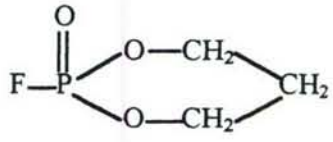


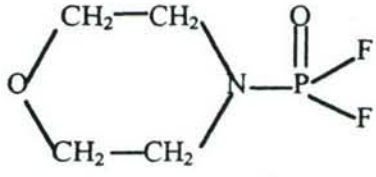
Figure 434 N,N,N',N'-TETRAMETHYLPHOSPHORODIAMIDIC FLUORIDE, LIQUID, CF/KBr (Perkin-Elmer Model 457 Grating Spectrophotometer)

3.10.3 2-Fluoro-1,3,2-dioxaphosphorinane-2-oxide



The infrared spectrum of 2-fluoro-1,3,2-dioxaphosphorinane-2-oxide as a liquid film between KBr discs is given in ***Figure 435***. The band assignments, based on frequencies estimated from the spectrum, are as follows: 3570 and 3510 cm^{-1} vvw (H_2O), 2970 and 2905 cm^{-1} vw (ν_{as} and ν_{sy} CH_2), 1480 and 1467 cm^{-1} vw (δ CH_2), 1328 cm^{-1} s (ν P=O, *calculated* value is 1334 cm^{-1}), 1277 cm^{-1} w, 1236 and 1139 cm^{-1} m (ring vibrations), 1056 cm^{-1} s (ν P-O-C), 981, 935, 893, 830 cm^{-1} ms, 734 cm^{-1} m and 588 cm^{-1} w (ring vibrations), 854 cm^{-1} ms (ν P-F).

3.10.4 Morpholinophosphoramidic Difluoride



The infrared spectrum of morpholinophosphoramidic difluoride as a liquid film between KBr windows is reproduced as ***Figure 436***. The band assignments, based on frequency values estimated from the

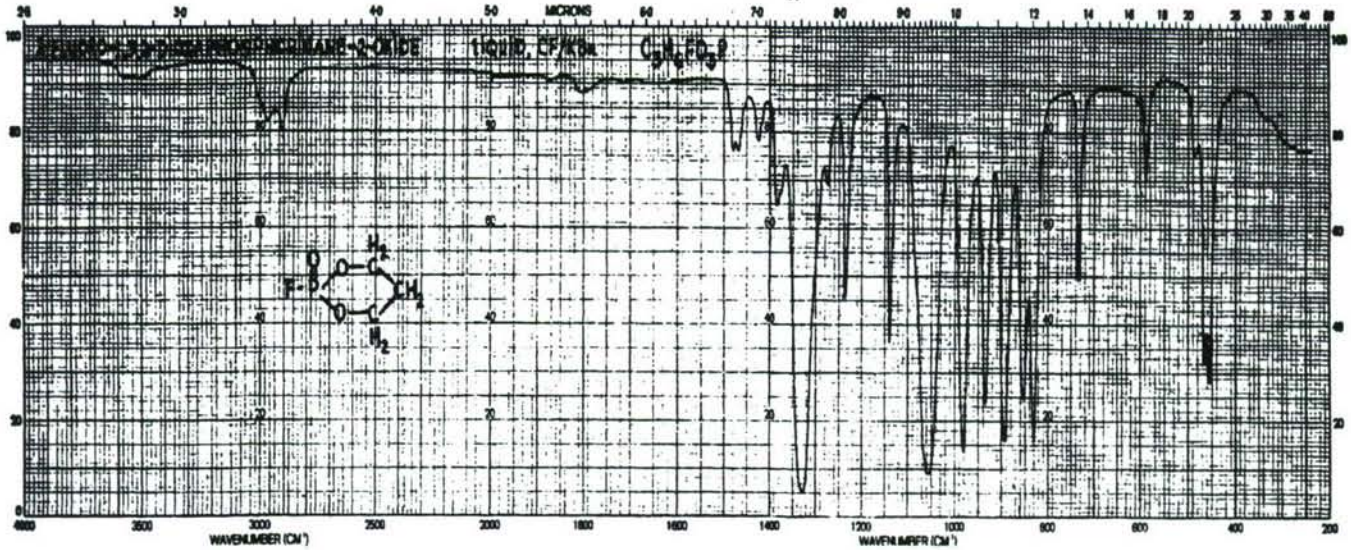


Figure 435 2-FLUORO-1,3,2-DIOXAPHOSPHORINANE-2-OXIDE, LIQUID, CF/KBr (Perkin-Elmer Model 457 Grating Spectrophotometer)

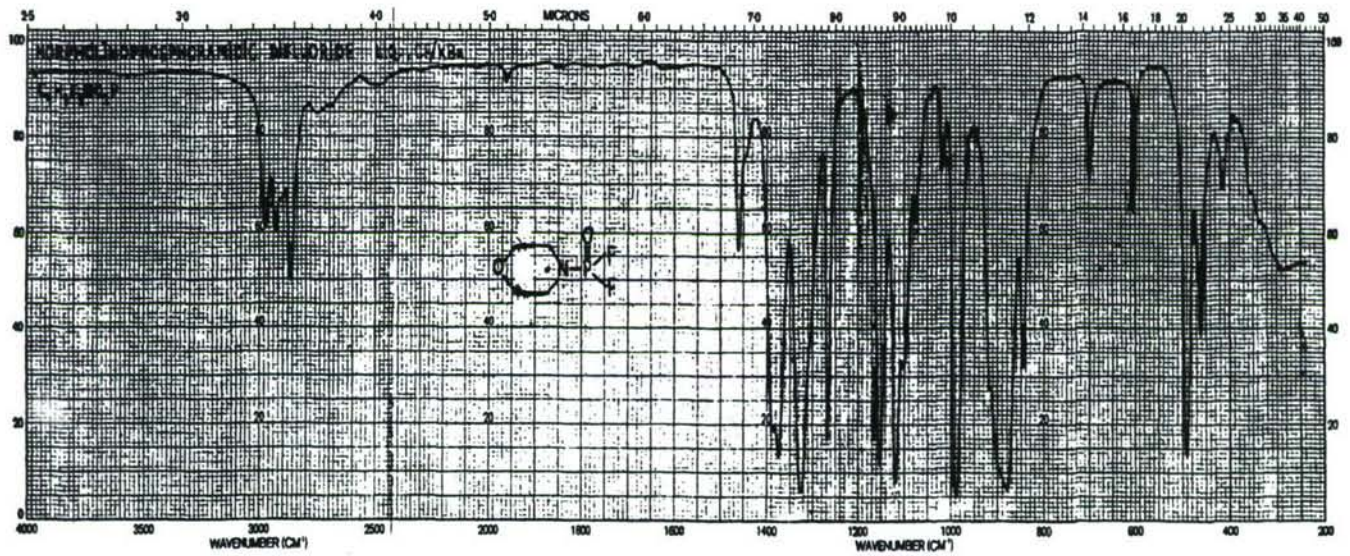


Figure 436 MORPHOLINOPHOSPHORAMIDIC DIFLUORIDE, LIQUID, CF/KBr (Perkin-Elmer Model 457 Grating Spectrophotometer)

spectrum, are as follows: 2980 cm^{-1} w, 2935 cm^{-1} w, 2914 cm^{-1} sh and 2868 cm^{-1} w-m (ν CH_2), 1460 cm^{-1} w (δ CH_2), 1386 cm^{-1} sh and 1375 cm^{-1} ms (morpholino moiety), 1325 cm^{-1} s (ν P=O), 1266 cm^{-1} ms, 1152 cm^{-1} ms, 1118 cm^{-1} s, 1101 cm^{-1} sh, 1075 cm^{-1} w and 1018 cm^{-1} w (morpholino moiety), 988 cm^{-1} s (ν_{as} P-N-C), 916 cm^{-1} sh (morpholino moiety), 880 cm^{-1} m (ν P-F), 490 cm^{-1} ms and 461 cm^{-1} m (PF_2 deformations).

3.10.5 Isopropyl Methylphosphonochloridate (**Chloro GB**) CH_3-P=O(Cl)[O-CH(CH_3)$_2$]

The infrared spectrum of isopropyl methylphosphonochloridate (**Chloro GB**) as a liquid film between CsI windows is reproduced as ***Figure 437***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 2982 cm^{-1} m, 2923 cm^{-1} w, 2875 cm^{-1} vw (ν CH_3 and ν -C-H), 1460, 1447 cm^{-1} vw (δ_{as} CH_3), 1404 cm^{-1} vw (δ_{as} P-CH_3), 1384 and 1372 cm^{-1} w (δ_{sy} CH_3 isopropyl doublet), 1349 cm^{-1} vvw (δ -C-H), 1305 cm^{-1} m (δ_{sy} P-CH_3), 1262 cm^{-1} ms (ν P=O, *calculated* value is 1260 cm^{-1}), 1175, 1138 cm^{-1} vw and 1098 cm^{-1} w (P-O-isopropyl, characteristic), 995 cm^{-1} s (ν P-O-C), 940 cm^{-1} vvw (possible ν P-O-P, impurity), 910 cm^{-1} w (P-CH_3 rock), 885 cm^{-1} w (CH_3 rock, isopropyl moiety), 774 cm^{-1} w (POC), 723 cm^{-1} w (ν P-C), 516 cm^{-1} m (ν P-Cl).

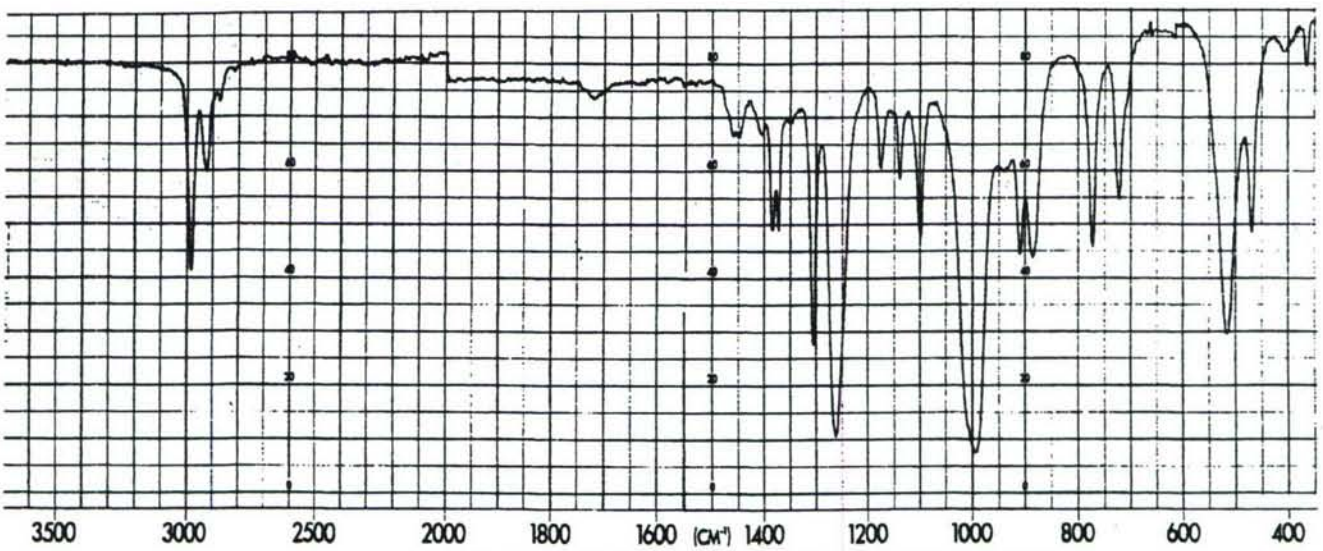


Figure 437 ISOPROPYL METHYLPHOSPHONOCHLORIDATE (CHLORO GB), LIQUID, CF/CsI (Perkin-Elmer Model 521 Grating Spectrophotometer)

3.10.6 Isopropyl Methylphosphonocyanidate CH_3-P=O(C≡N)[O-CH(CH_3)$_2$]

The infrared spectrum of isopropyl methylphosphonocyanidate as a liquid film between cesium bromide windows is presented as ***Figure 438***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 2984 cm^{-1} m, 2930 cm^{-1} w, 2917 cm^{-1} w, 2817 cm^{-1} vw (ν CH_3), 2200 cm^{-1} m (ν C≡N), 2080 cm^{-1} vw (ν C≡N, from H-C≡N, which also is indicated by a shoulder near 3050 cm^{-1}, hydrolysis

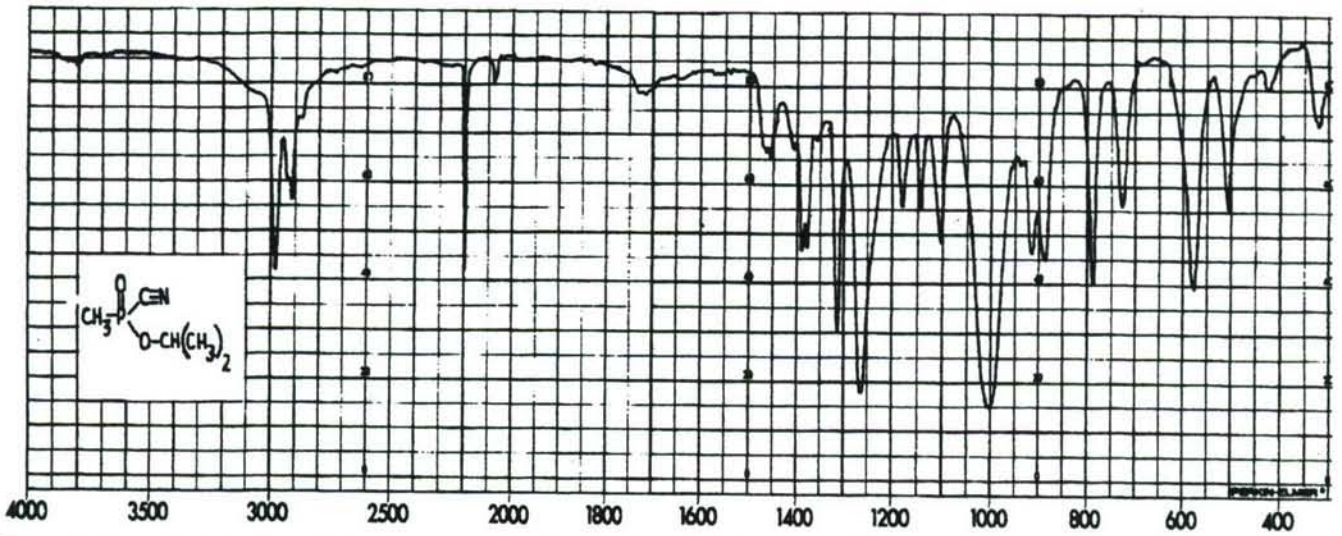


Figure 438 ISOPROPYL METHYLPHOSPHONOCYANIDATE, LIQUID, CF/CsBr (Perkin-Elmer Model 521 Grating Spectrophotometer)

product), 1465 and 1455 cm^{-1} w (δ_{as} CH_3), 1406 cm^{-1} vw (δ_{as} P-CH_3), 1388 and 1378 cm^{-1} m (doublet, δ_{sy} CH_3, isopropyl group), 1356 cm^{-1} vvw (δ -C-H, isopropyl group), 1312 cm^{-1} ms (δ_{sy} P-CH_3), 1262 cm^{-1} s (ν P=O, *calculated* value is 1264 cm^{-1}), 1180, 1144 and 1103 cm^{-1} w (triplet characteristic of P-O-isopropy moiety), 1000 cm^{-1} s (ν P-O-C), 912 cm^{-1} m and 885 cm^{-1} m (P-CH_3 rock and isopropyl CH_3 rock), 786 cm^{-1} m (POC), 728 cm^{-1} w (ν P-C), 575 cm^{-1} m (PCN), 505 cm^{-1} w (P=O deformation).

3.10.7 Isopropyl Hydrogenmethylphosphinate CH_3-P=O(H)[$OCH(CH_3)_2$]

The infrared spectrum of isopropyl hydrogenmethylphosphinate (isopropyl methylphosphinate) as a liquid film between CsI windows is given in ***Figure 439***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 3400 cm^{-1} vw (H_2O), 2975 cm^{-1} m, 2930 cm^{-1} w and 2876 cm^{-1} vw (ν CH_3 and ν -C-H), 2343 cm^{-1} w (ν P-H), 1465 cm^{-1} w, 1451 cm^{-1} vw (δ_{as} CH_3), 1409 cm^{-1} vw (δ_{as} P-CH_3), 1384 and 1373 cm^{-1} m (δ_{sy} CH_3, isopropyl doublet), ca 1355 cm^{-1} sh (δ -C-H), 1298 cm^{-1} ms (δ_{sy} P-CH_3), 1226 cm^{-1} s (ν P=O, *calculated* value is 1224 cm^{-1}), 1176, 1138 and 1104 cm^{-1} w-m (triplet characteristic of P-O-isopropyl), 1036 cm^{-1} ms, 977 cm^{-1} s (ν P-O-C and P-H deformation), 886 cm^{-1} w and 843 cm^{-1} ms (P-CH_3 rock and CH_3 rock of isopropyl group), 756 cm^{-1} w (POC), 708 cm^{-1} w (ν P-C), 489 cm^{-1} w (P=O deformation).

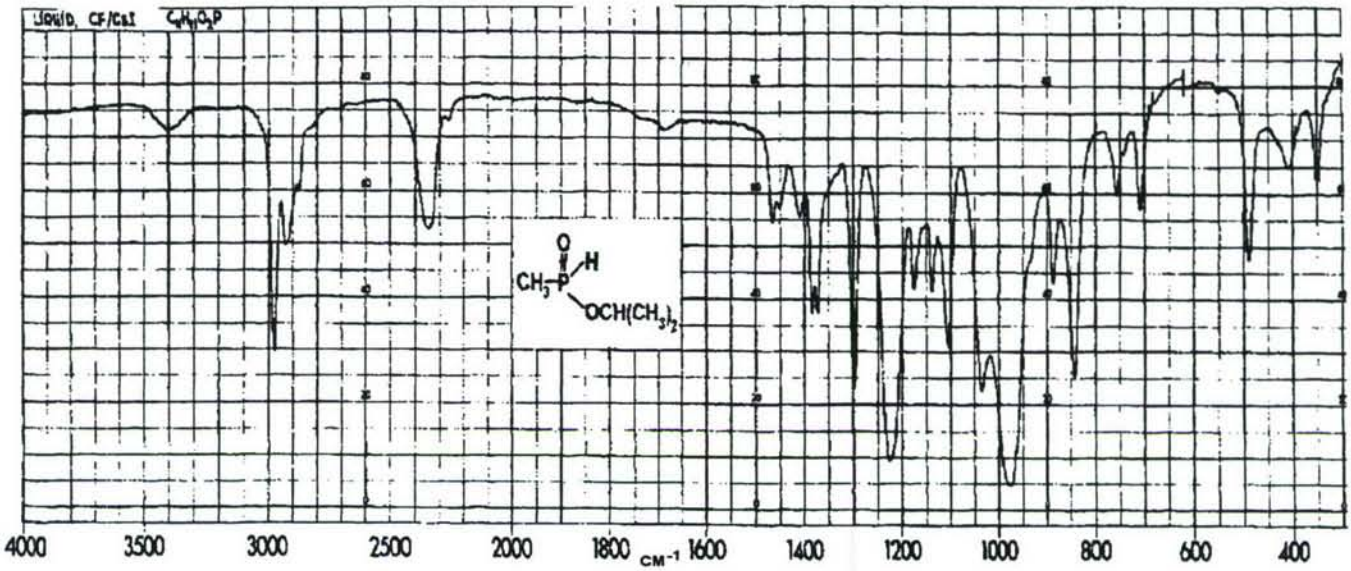


Figure 439 ISOPROPYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/CsI

3.10.8 Cyclopentyl Hydrogenmethylphosphinate $CH_3\text{-}P{=}O(H)(O\text{-}C_5H_9)$

The infrared spectrum of cyclopentyl hydrogenmethylphosphinate (cyclopentyl methylphosphinate) as a liquid between cesium iodide windows is presented in ***Figure 440***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 3400 cm^{-1} vw (H_2O), 2957 cm^{-1} ms, 2917 cm^{-1} sh, 2870 cm^{-1} m (ν_{as} CH_2 and ν_{sy} CH_2 , ν CH_3), 2340 cm^{-1} w (ν P-H), 1470 cm^{-1} vw, 1450 cm^{-1} w, 1433 cm^{-1} w (δ CH_2), 1410 cm^{-1} w (δ_{as} P-CH_3), 1298 cm^{-1} ms (δ_{sy} P-CH_3), 1224 cm^{-1} s (ν P=O, *calculated* value is 1224 cm^{-1}), 1165 cm^{-1} w (ω, τ CH_2), 1037 cm^{-1} ms, 977 cm^{-1} s (ν P-O-C, P-H deformation), 905 cm^{-1} m (cyclopentyl ring), 843 cm^{-1} ms (P-CH_3 rock),[tttt] 727 cm^{-1} vw (ν P-C), 466 cm^{-1} w (P=O deformation ?).

3.10.9 Cyclohexyl Methylphosphonochloridate $CH_3\text{-}P{=}O(Cl)(O\text{-}C_6H_{11})$

The infrared spectrum of cyclohexyl methylphosphonochloridate as a thin liquid film between cesium bromide windows is reproduced as ***Figure 441***. The band assignments, based on frequecies estimated

[tttt] For most P^{+5} organophosphorus compounds the P-CH_3 rocking vibration occurs within the range 935-874 cm^{-1}. In P^{+5} compounds containing both P-CH_3 and P-H groups the P-CH_3 rock occurs in the range 850-842 cm^{-1}. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 95, Heyden & Son Ltd., London, 1974.

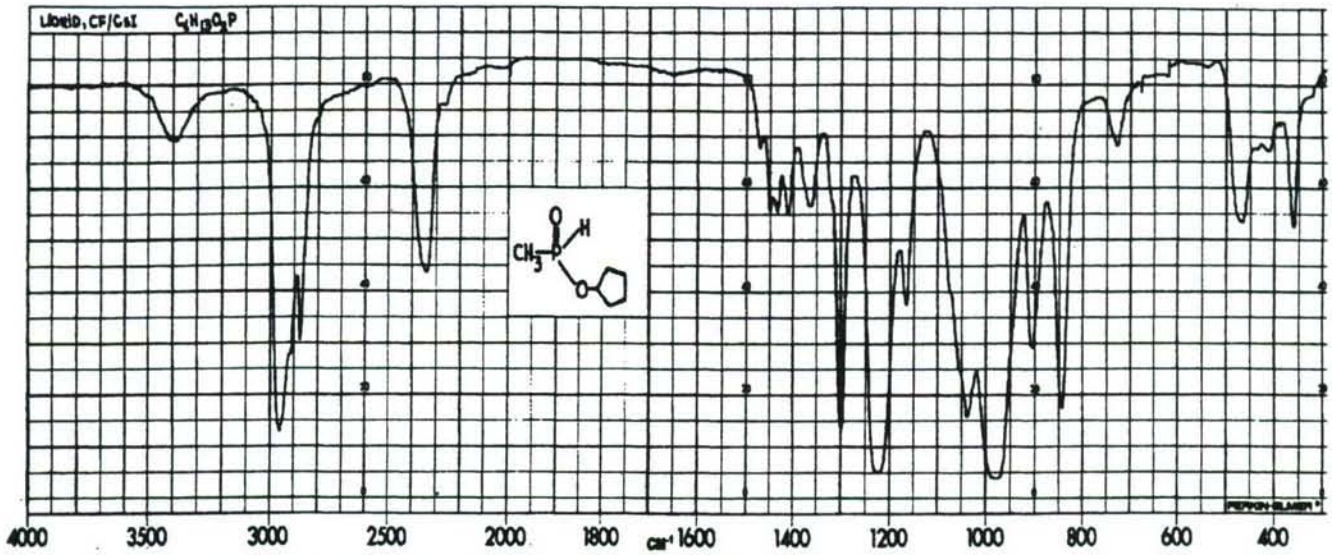


Figure 440 CYCLOPENTYL HYDROGENMETHYLPHOSPHINATE, LIQUID, CF/CsI

from the spectrum (***Figure 441***), are as follows: 2978 cm^{-1} w (ν CH_3), 2936 cm^{-1} ms (ν_{as} CH_2), 2850 cm^{-1} m (ν_{sy} CH_2), 1465 cm^{-1} w and 1448 cm^{-1} m (δ CH_2), 1405 cm^{-1} vw (δ_{as} P-CH_3), 1306 cm^{-1} ms (δ_{sy} P-CH_3), 1258 cm^{-1} s (ν P=O, *calculated* value is 1260 cm^{-1}), 1153 cm^{-1} vw and 1124 cm^{-1} vvw (ω, τ CH_2), 1036 cm^{-1} sh, 998 cm^{-1} s (ν P-O-C), 918 and 896 cm^{-1} m (cyclohexyl ring C-C and P-CH_3 rock), 762 cm^{-1} m (POC, CH_2 rock), 522 cm^{-1} ms (ν P-Cl), 486 cm^{-1} m (P=O deformation).

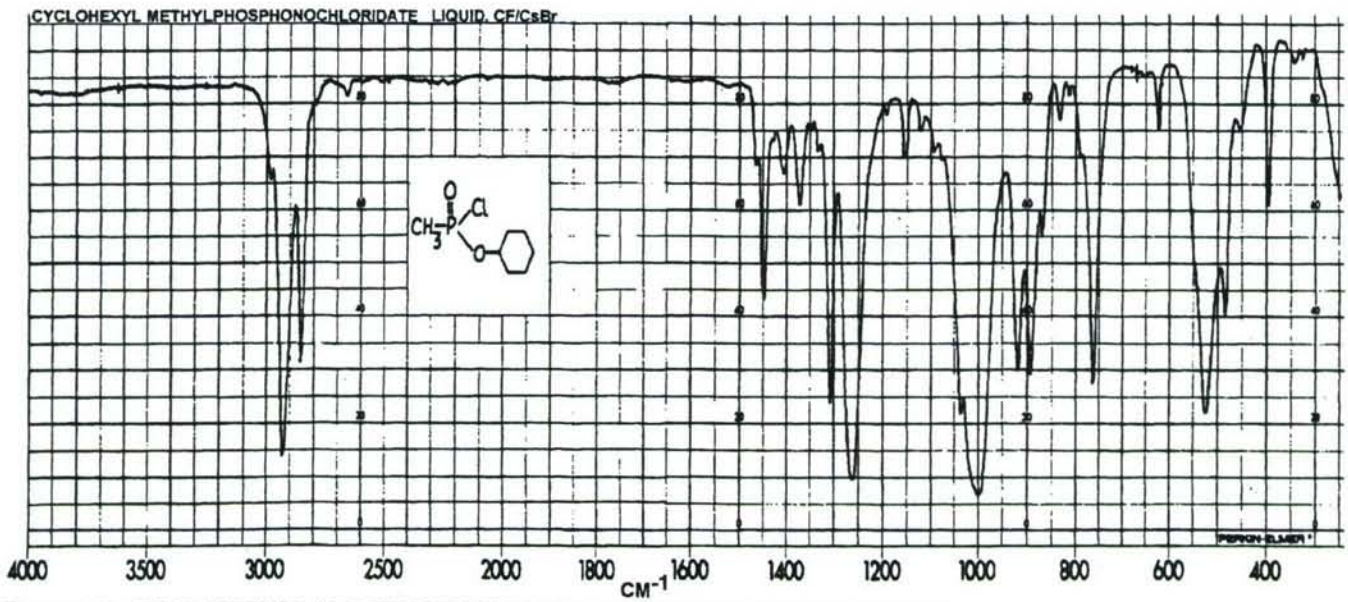


Figure 441 CYCLOHEXYL METHYLPHOSPHONOCHLORIDATE, LIQUID, CF/CsBr

3.10.10 Pinacolyl Methylphosphonofluorothionate (**Thiono GD**) CH_3-P=S(F)[OCH(CH_3)C(CH_3)$_3$]

The infrared spectrum of pinacolyl methylphosphonofluorothionate (**Thiono GD**) as a thin liquid film between CsI windows is presented as ***Figure 442***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 2965 cm^{-1} m, 2918 cm^{-1} sh, 2872 cm^{-1} w (ν_{as} and ν_{sy} CH_3), 1478 cm^{-1} w, 1465 cm^{-1} sh and 1456 cm^{-1} sh (δ_{as} CH_3), 1407 cm^{-1} w (δ_{as} P-CH_3), 1396 cm^{-1} w and 1380 cm^{-1} m [δ_{sy} CH_3 of C(CH_3)], 1365 cm^{-1} m (δ_{sy} CH_3 of C-CH_3), 1345 cm^{-1} vvw (δ -C-H), 1304 cm^{-1} m (δ_{sy} P-CH_3), 1260 cm^{-1} vvw (the ν P=O of the thiolate isomer would have a *calculated* value of 1266 cm^{-1}), 1222 and 1207 cm^{-1} vw [C(CH_3)$_3$], 1115 cm^{-1} w, 1075 cm^{-1} m, 1047 cm^{-1} w and 869 cm^{-1} w (pinacolyl moiety), 1010 cm^{-1} s (ν P-O-C), 982 cm^{-1} s (ν C-C), 915 cm^{-1} s [CH_3 rock of P-CH_3 and C(CH_3)$_3$], 818 cm^{-1} ms (ν P-F), 801 cm^{-1} s, 778 cm^{-1} sh (P=S I band, POC), 629 cm^{-1} m (P=S II band, ν P=S).[uuuu]

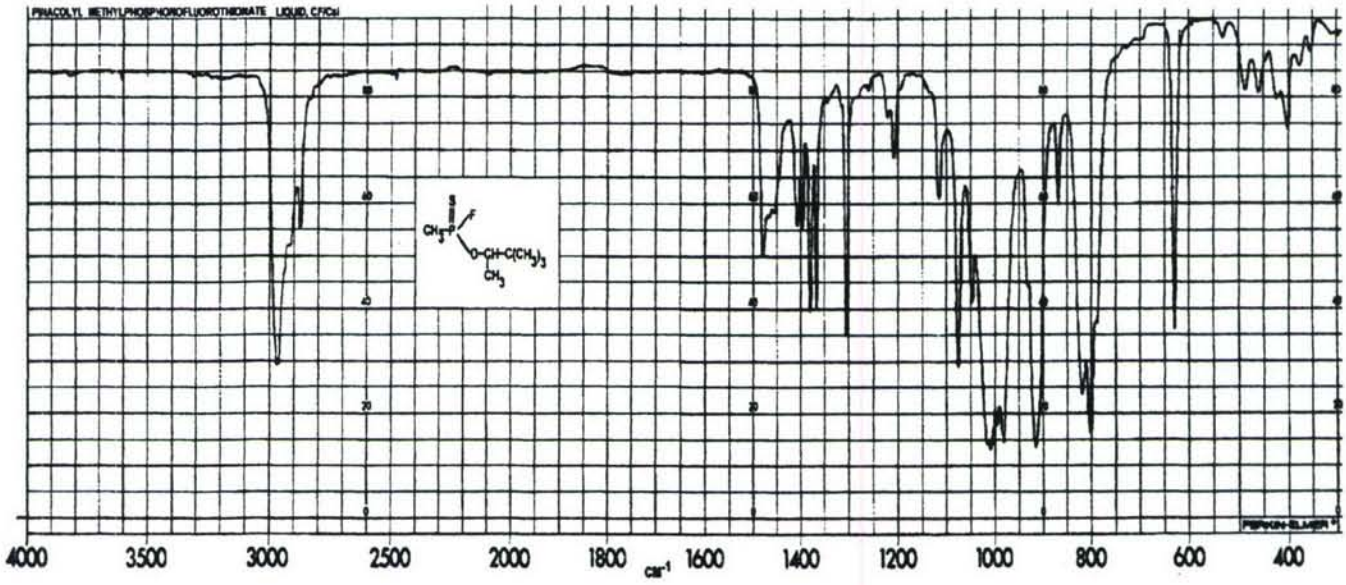


Figure 442 PINACOLYL METHYLPHOSPHONOFLUOROTHIONATE (THIONO GD), LIQUID, CF/CsI (PERKIN-ELMER MODEL 521 GRATING SPECTROPHOTOMETER)

[uuuu] Compounds of the type, RP=S(OR)(F), show the following ranges for the P=S I and P=S II bands, 803-799 cm^{-1} and 629-616 cm^{-1} respectively. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 135, Heyden & Son Ltd., London, 1974.

3.10.11 N,N-Dimethylphosphoramidous Dichloride $(CH_3)_2N\text{-}PCl_2$

The infrared spectrum of N,N-dimethylphosphoramidous dichloride as a liquid film between KBr windows is given in ***Figure 443***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 2972 cm^{-1} w, 2940 cm^{-1} m, 2895 cm^{-1} w, 2845 cm^{-1} w, 2810 cm^{-1} w (ν CH_3), 1470 and 1445 cm^{-1} m (δ CH_3), 1280, 1170 cm^{-1} m and 1057 cm^{-1} w [$PN(CH_3)_2$], 971 cm^{-1} s (ν_{as} P-N-C), 687 cm^{-1} m (ν_{sy} P-N-C), 510 cm^{-1} m and 426 cm^{-1} ms (ν PCl_2).[vvvv]

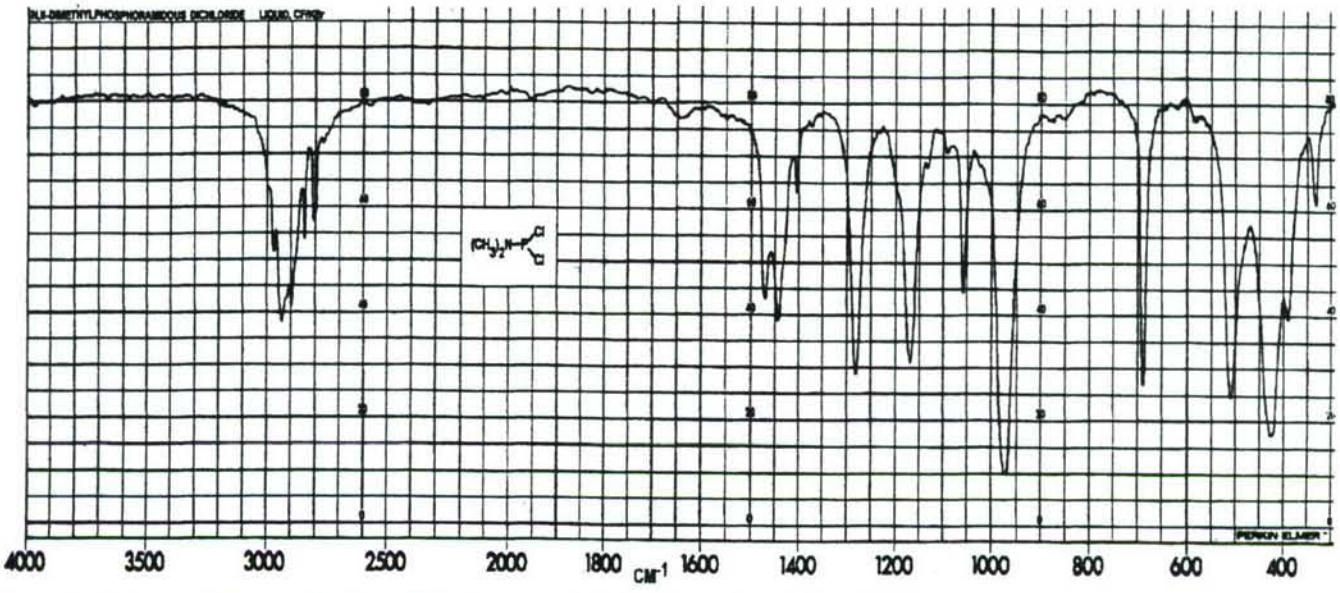


Figure 443 N,N-DIMETHYLPHOSPHORAMIDOUS DICHLORIDE, LIQUID, CF/KBr (PERKIN-ELMER MODEL 521 GRATING SPECTROPHOTOMETER)

3.10.12 N,N-Dimethylphosphoramidothionic Dichloride $(CH_3)_2N\text{-}P{=}S(Cl)_2$

The infrared spectrum of N,N-dimenthylphosphoramidothionic dichloride as a liquid film between cesium iodide windows is presented as ***Figure 444***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 3005 cm^{-1} w, 2928 cm^{-1} w, 2847 cm^{-1} vw and 2817 cm^{-1} vw (ν CH_3), 1472 cm^{-1}, 1451 cm^{-1} w and 1408 cm^{-1} vw (δ CH_3), 1283 cm^{-1} m, 1170 cm^{-1} m and 1060 cm^{-1} w [$PN(CH_3)_2$], 986 cm^{-1} s

[vvvv] The ν_{as} and ν_{sy} for P^{+3} compounds of the type R_2NPCl_2 are given as 515 cm^{-1} and 435 cm^{-1} respectively. Thomas, L.C., "Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 82, Heyden & Son Ltd., London, 1974. Other workers assign the higher band to the ν_{sy} and the lower band to the ν_{as} for P^{+3} organophosphorus compounds. See Shagidullin, R.R., Chernova, A.V., Vinogradova, V.S. and Mukhametov, F.S., "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)", p. 4, Kluwer Academic Publishers, Boston, 1990.

(ν_{as} P-N-C), 764 cm^{-1} s (ν_{sy} P-N-C), 674 cm^{-1} s (ν P=S), 512 cm^{-1} s (ν_{as} PCl_2), 460 cm^{-1} m (ν_{sy} PCl_2).[wwww]

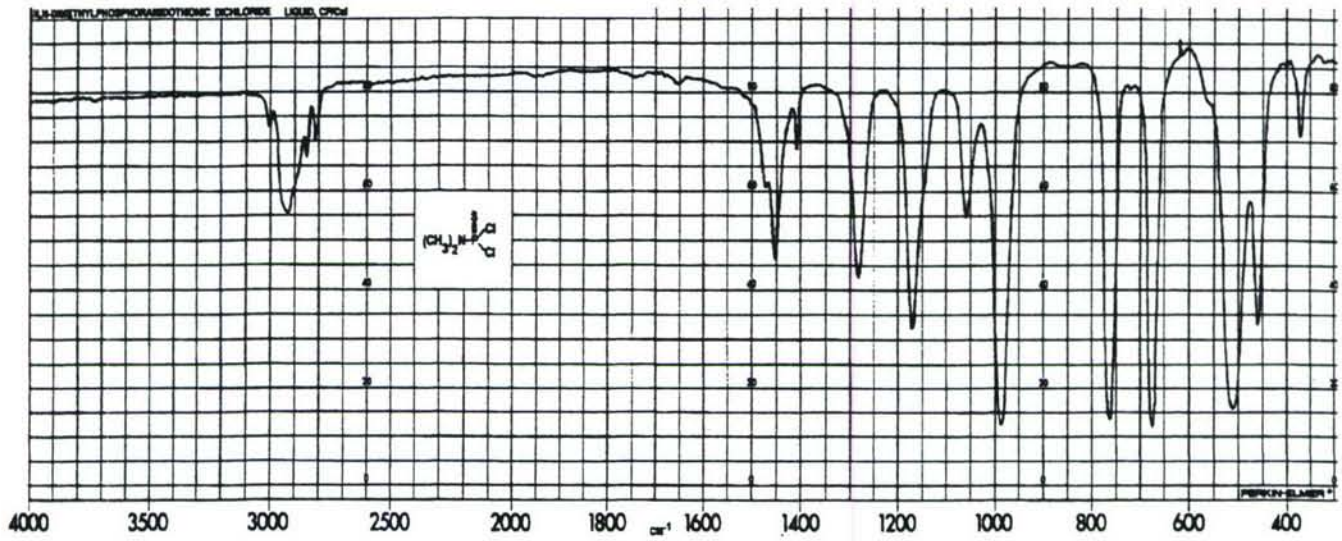


Figure 444 N,N-DIMETHYLPHOSPHORAMIDOTHIONIC DICHLORIDE, LIQUID, CF/CsI (PERKIN-ELMER MODEL 521 GRATING SPECTROPHOTOMETER)

3.10.13 Phenylphosphonothionic Difluoride H_5C_6-P=S$(F)_2$

The infrared spectrum of phenylphosphonothionic difluoride as a liquid film between CsI windows is presented as ***Figure 445***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 3090, 3057 cm^{-1} sh, 3058 cm^{-1} w (ν C-H aromatic), 2000-1650 cm^{-1} vw (series of bands characteristic of a mono-substituted aromatic ring, due to combination and overtone bands), 1587 cm^{-1} m, 1573 cm^{-1} sh, 1476 cm^{-1} vw and 1437 cm^{-1} ms (aromatic ring C≈C), 1126 cm^{-1} s (phenyl-P), 1065, 1025 cm^{-1} vw and 997 cm^{-1} w (β C-H mono-substituted aromatic ring), 890 cm^{-1} s and 860 cm^{-1} ms (ν_{as} and ν_{sy} PF_2), 760 cm^{-1} s (P=S I),[xxxx] 744 cm^{-1} and 684 cm^{-1} ms (γ C-H and ring deformation, mono-substituted aromatic ring), 659 cm^{-1} ms (P=S II), 486 cm^{-1} m, 458 cm^{-1} ms, 402 cm^{-1} m (PF_2 deformations may occur in this region, as may the quadrant out-of-plane

[wwww] For compounds of the type, $R_2NP{=}SCl_2$, the P=S I and P=S II bands occur in the ranges 792-766 cm^{-1} and 725-671 cm^{-1} respectively, while the ν_{as} and ν_{sy} PCl_2 bands occur near 513 and 461 cm^{-1}. See Thomas, L.C.,"Interpretation of the Infrared Spectra of Organophosphorus Compounds", pp. 141, 82 Heyden & Son Ltd., London, 1974.

[xxxx] For compounds of the type $RP{=}SF_2$, the P=S I and P=S II bands occur int the ranges 801-742 cm^{-1} and 658 cm^{-1} respectively. Thomas, L.C.,"Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 136, Heyden & Son Ltd., London, 1974.

bending mode of mono-substituted aromatic rings[yyyy]).

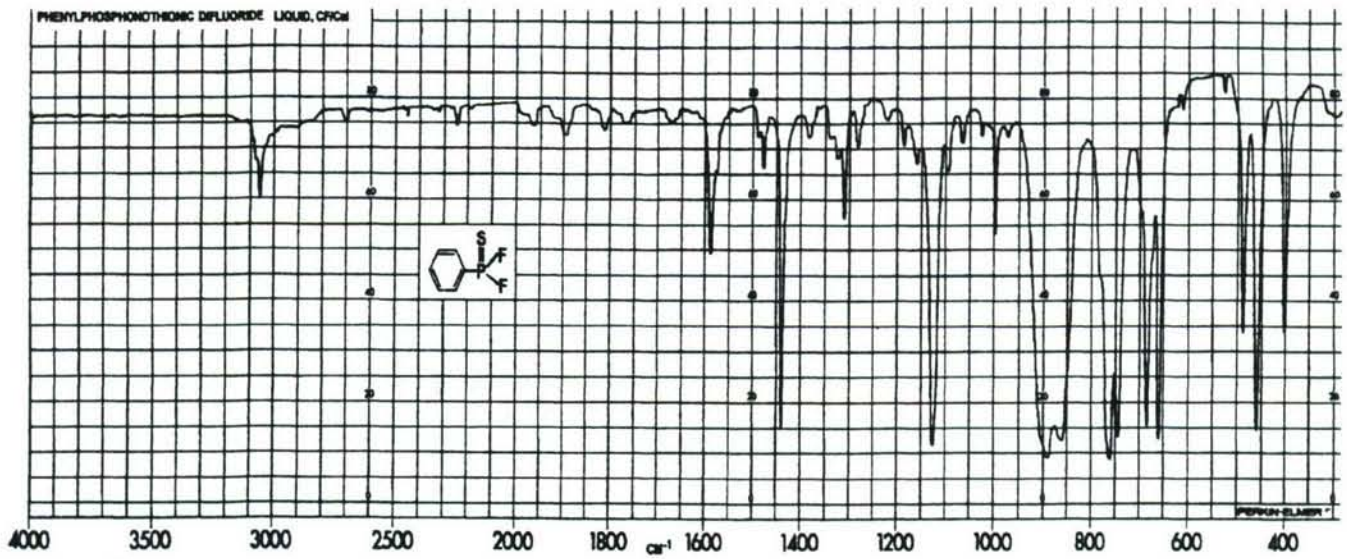


Figure 445 PHENYLPHOSPHONOTHIONIC DIFLUORIDE, LIQUID, CF/CsI

3.10.14 Triethyl Phosphorothionate (Triethyl Thiophosphate) $(CH_3CH_2O)_3P=S$

The infrared spectrum of triethyl phosphorothionate (triethyl thiophosphate) as a thin liquid film between cesium iodide windows is reproduced as ***Figure 446***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 2985 cm^{-1} ms (ν_{as} CH_3), 2939 cm^{-1} m (ν_{as} CH_2), 2907 cm^{-1} m (ν_{sy} CH_3), 2872 cm^{-1} sh (ν_{sy} CH_2), ca 1850 cm^{-1} w broad (1025 + 822 = 1847 cm^{-1}), 1478 cm^{-1} m (δ OCH_2), 1445 cm^{-1} m (δ_{as} CH_3), 1393 cm^{-1} ms (ω OCH_2), 1367 cm^{-1} w (δ_{sy} CH_3), 1294 cm^{-1} w (822 + 470 = 1292 cm^{-1} ?), 1162 and 1098 cm^{-1} ms (CH_3 rock of POEt, characteristic), 1025 cm^{-1} s (ν P-O-C), 967 cm^{-1} s (ν C-C of POEt), 822 cm^{-1} s and 790 cm^{-1} ms (P=S I and POC),[zzzz] 634 cm^{-1} w (P=S II, ν P=S), 470 cm^{-1} w (POC ?).[aaaaa]

[yyyy] The quadrant out-of-plane bending mode of mono-substituted aromatic rings occurs in the region of 560-418 cm^{-1}. Lin-Vien, D., Colthup, N.B., Fateley, W.G. and Grasselli, J.G., "The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules", p. 294, Academic Press, Inc., SanDiego, CA, 1991.

[zzzz] For compounds of the type $(RO)_3P=S$, the P=S I and P=S II bands occur in the ranges of 844-800 cm^{-1} and 713-602 cm^{-1} respectively. Thomas, L.C.,"Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 133, Heyden & Son Ltd., London, 1974.

[aaaaa] An infrared spectrum for triethyl phosphorothionate (triethyl thiophosphate) has also been given by Shagidullin , R.R., Chernova, A.V., Vinogradova, V.S., and Mukhametov, F.S. "Atlas of IR Spectra of Organophosphorus Compounds (Interpreted Spectrograms)", IR No. 513, p. 278, Kluwer Academic Publishers, Boston, 1990.

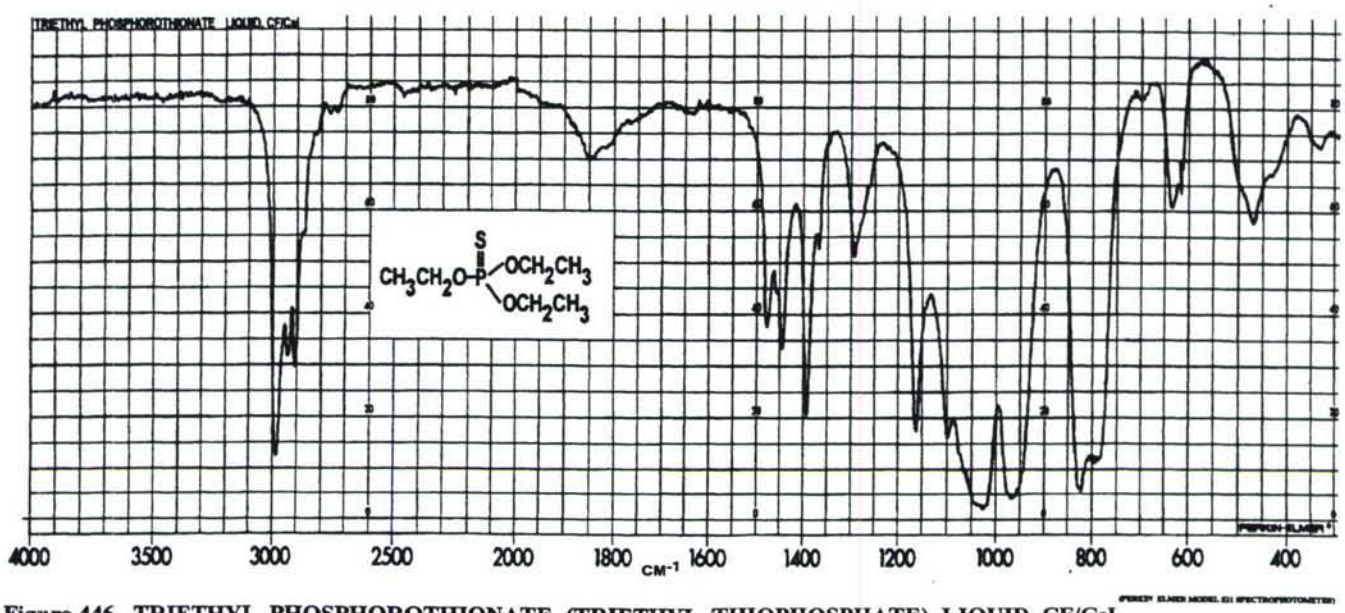


Figure 446 TRIETHYL PHOSPHOROTHIONATE (TRIETHYL THIOPHOSPHATE), LIQUID, CF/CsI

3.10.15 Diethyl S-Ethyl Phosphorothiolate (Diethyl S-Ethyl Thiophosphate) $(CH_3CH_2O)_2P{=}O(S\text{-}CH_2CH_3)$

The infrared spectrum of a thin liquid film of diethyl S-ethyl phosphorothiolate (diethyl S-ethyl thiophosphate) between CsI discs (windows) is given as ***Figure 447***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 3550 and 3500 cm^{-1} vw (H_2O), 2985 cm^{-1} m (ν_{as} CH_3), 2933 cm^{-1} m (ν_{as} CH_2), 2908 cm^{-1} w (ν_{sy} CH_3), 2875 cm^{-1} w (ν_{sy} CH_2), 1478 cm^{-1} w (δ OCH_2), 1446 cm^{-1} w (δ_{as} CH_3), 1393 cm^{-1} w (ω OCH_2), 1375 cm^{-1} sh, 1367 cm^{-1} w (δ_{sy} CH_3), 1270 cm^{-1} sh (ω CH_2-S),[bbbbb] 1253 cm^{-1} ms (ν P=O, *calculated* value is 1254 cm^{-1}), 1162 and 1096 cm^{-1} w (CH_3 rock of POEt, characteristic), 1040 cm^{-1} sh and 1016 cm^{-1} s (ν P-O-C), 968 cm^{-1} ms (ν C-C of POEt), 792 and 755 m (POC, CH_2 rock), 645 cm^{-1} vw (ν C-S),[ccccc] 610 and 575 cm^{-1} m (ν P-SC bands identified as isomers I and II).[ddddd]

[bbbbb] The CH_2-S moiety shows bands near 1435-1410 cm^{-1} w (δ CH_2) and 1270-1220 cm^{-1} s (ω CH_2). Colthup, N.B., Daly, L.H., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", p. 351, Sec. Ed., Academic Press, N.Y., 1975.

[ccccc] It has been suggested that the C-SP vibration occurs as follows: S-Methyl 699 cm^{-1} , S-Ethyl 642 cm^{-1} and S-Butyl 636 cm^{-1}. The band may be weak and not always visible. Laffite, C., "Infrared Spectra of Organophosphorus Compounds", D.Sc. Thesis, University of Montpellier, 1965.

[ddddd] In compounds of the type $(RO)_2P{=}O(SR)$, the Isomer I and II bands occur in the ranges 610-600 cm^{-1} (I) and 575-563 cm^{-1} (II). Thomas, L.C.,"Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 150, Heyden & Son Ltd., London, 1974.

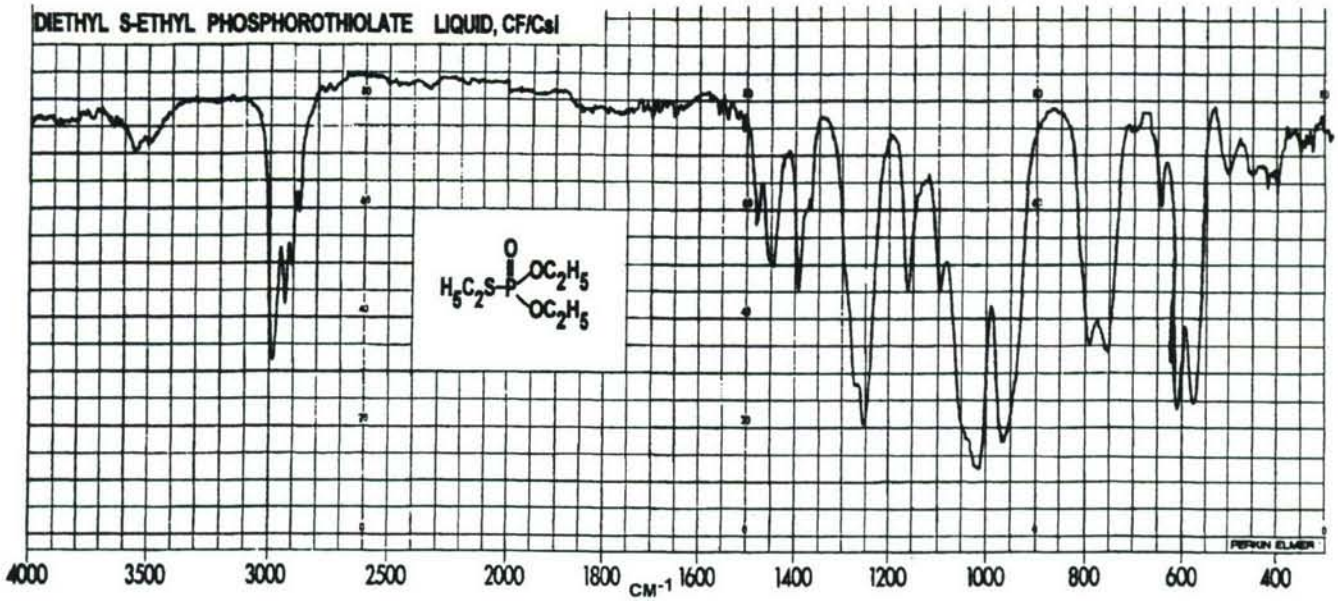


FIGURE 447 DIETHYL S-ETHYL PHOSPHOROTHIOLATE (DIETHYL S-ETHYL THIOPHOSPHATE), LIQUID, CF/CsI

3.10.16 Diethyl S-Methyl Phosphorothiolate (Diethyl S-Methyl Thiophosphate) CH_3-S-P=O$(OCH_2CH_3)_2$

The infrared spectrum of diethyl S-methyl phosphorothiolate (diethyl S-methyl thiophosphate) as a thin liquid film between cesium iodide discs (windows) is reproduced as ***Figure 448***. The band assignments, based on frequency values estimated from the infrared spectrum, are as follows: 3540 and 3480 cm^{-1} vw (H_2O), 2980 cm^{-1} ms (ν_{as} CH_3), 2932 cm^{-1} m (ν_{as} CH_2), 2905 cm^{-1} w (ν_{sy} CH_3), 2868 cm^{-1} vw (ν_{sy} CH_2), 1477 cm^{-1} w (δ OCH_2), 1443 cm^{-1} m (δ_{as} CH_3), 1391 cm^{-1} m (ω OCH_2), 1367 cm^{-1} w (δ_{sy} CH_3), 1322 cm^{-1} w (δ_{sy} CH_3-S), 1250 cm^{-1} s (ν P=O, *calculated* value is 1254 cm^{-1}), 1161 and 1095 cm^{-1} m (CH_3 rock of POEt, characteristic), ca. 1040 cm^{-1} sh and 1015 cm^{-1} s (ν P-O-C), 970 cm^{-1} s (ν C-C, S-CH_3 rock),[eeeee] 788 and 760 cm^{-1} m (POC), 695 cm^{-1} w (ν C-SP),[fffff] 610 and 576 cm^{-1} ms (ν P-SC, isomer I and II).[ggggg]

[eeeee] The S-CH_3 rock occurs in the range 1030-960 cm^{-1}. Colthup, N.B., Daly, L.H., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", p. 352, Sec. Ed., Academic Press, N.Y., 1975.

[fffff] It has been suggested that the C-SP vibration of S-Methyl occurs at 699 cm^{-1}. The band may be weak and not always visible. Laffite, C., "Infrared Spectra of Organophosphorus Compounds", D.Sc. Thesis, University of Montpellier, 1965.

[ggggg] In compounds of the type $(RO)_2P$=O(SR), the Isomer I and II bands occur in the ranges 610-600 cm^{-1} (I) and 575-563 cm^{-1} (II). Thomas, L.C.,"Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 150, Heyden & Son Ltd., London, 1974.

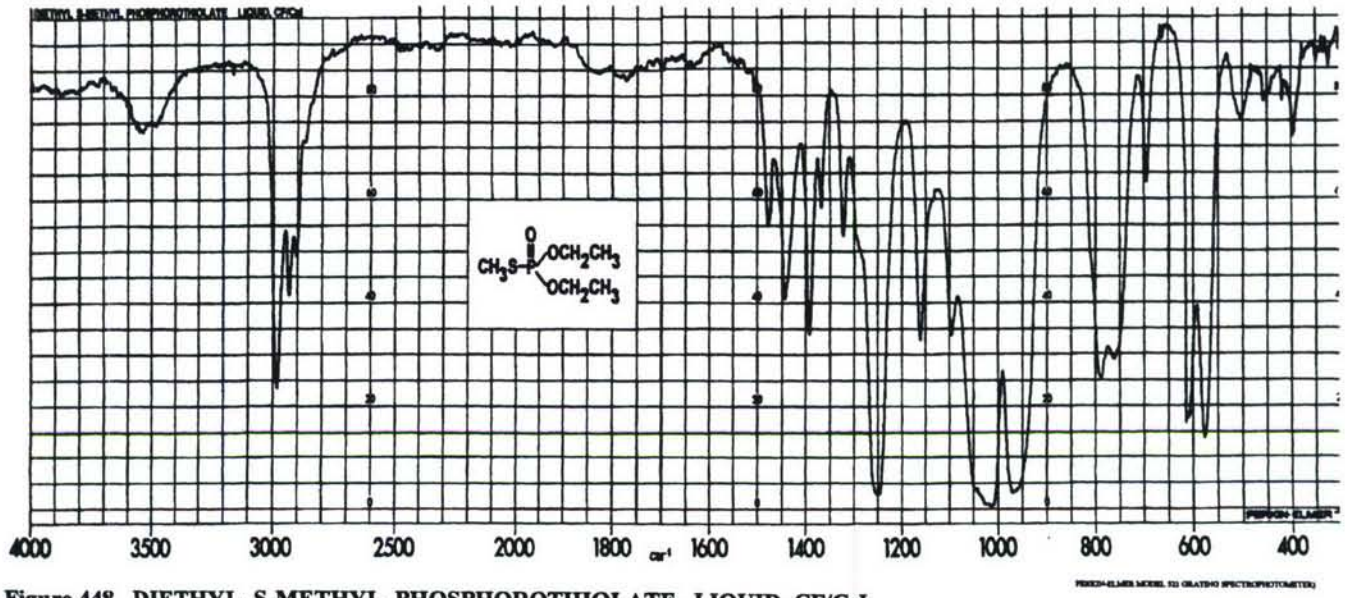


Figure 448 DIETHYL S-METHYL PHOSPHOROTHIOLATE, LIQUID, CF/CsI

3.10.17 2-Diethylaminoethyl Diethyl Phosphite $(CH_3CH_2O)_2P\text{-}O\text{-}CH_2\text{-}CH_2\text{-}N(CH_2\text{-}CH_3)_2$

The infrared spectrum of 2-diethylaminoethyl diethyl phosphite as a thin liquid film between cesium bromide discs (windows) is presented as ***Figure 449***. The band assignments, based on frequency values estimated from the infrared spectrum, are as follows: 2965 cm^{-1} ms, 2925 cm^{-1} m, 2890 cm^{-1} sh and 2870 cm^{-1} m (ν

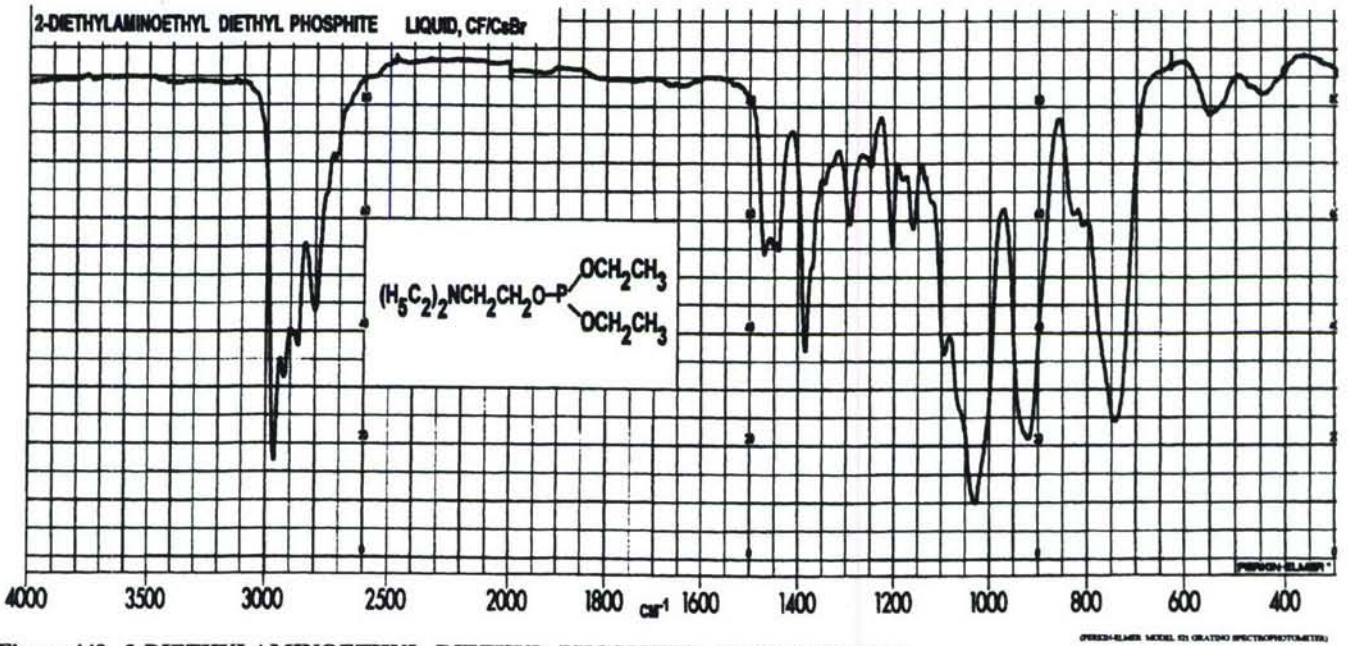


Figure 449 2-DIETHYLAMINOETHYL DIETHYL PHOSPHITE, LIQUID, CF/CsBr

CH_3 and ν CH_2), 2800 cm^{-1} m (ν CH_2-N), 1470 cm^{-1} w, 1452 cm^{-1} vw and 1440 cm^{-1} w (δ O-CH_2, δ_{as} CH_3), 1384 cm^{-1} m (ω OCH_2), 1369 cm^{-1} sh (δ_{sy} CH_3), 1205 cm^{-1} w (ν C-N ?), 1160 cm^{-1} w and 1095 cm^{-1} m (CH_3 rock of POEt, characteristic), 1030 cm^{-1} s (ν P-O-C), 920 cm^{-1} ms (ν C-C of POEt),[hhhhh] 743 cm^{-1} ms (POC).

3.10.18 Tris(Isopropyl Methylphosphonate)Iron (III) $Fe^{+3}[CH_3P(O_2)^-OCH(CH_3)_2]_3$

The infrared spectrum of tris(isopropyl methylphosphonate)iron(III), or the iron (III) salt of GB acid, [iron (III) salt of IMPA], as a KBr pellet is reproduced as ***Figure 450***. The band assignments, based on frequency values estimated from the infrared spectrum, are as follows: 3440 cm^{-1} w and 1625 cm^{-1} vw (H_2O), 2976 cm^{-1} w, 2929 cm^{-1} vw and 2875 cm^{-1} vw (ν CH_3 and ν C-H), 1466 and 1450 cm^{-1} vw (δ CH_3), 1415 cm^{-1} vvw (δ_{as} P-CH_3), 1384 and 1371 cm^{-1} w, doublet (δ_{sy} CH_3), 1301 cm^{-1} m (δ_{sy} P-CH_3), 1174 cm^{-1} sh (P-O-isopropyl, a triplet of bands usually occurs, but the other two bands are covered over by the strong 1117 cm^{-1} band), 1117 cm^{-1} s (ν_{as} PO_2^-), 1063 cm^{-1} ms (ν_{sy} PO_2^-), 1005 cm^{-1} ms (ν P-O-C), 905 cm^{-1} w (P-CH_3 rock, CH_3 rock-isopropyl moiety), 782 cm^{-1} w (POC), 724 cm^{-1} vvw (ν P-C), ca 535 cm^{-1} w, broad (PO_2^- deformation).

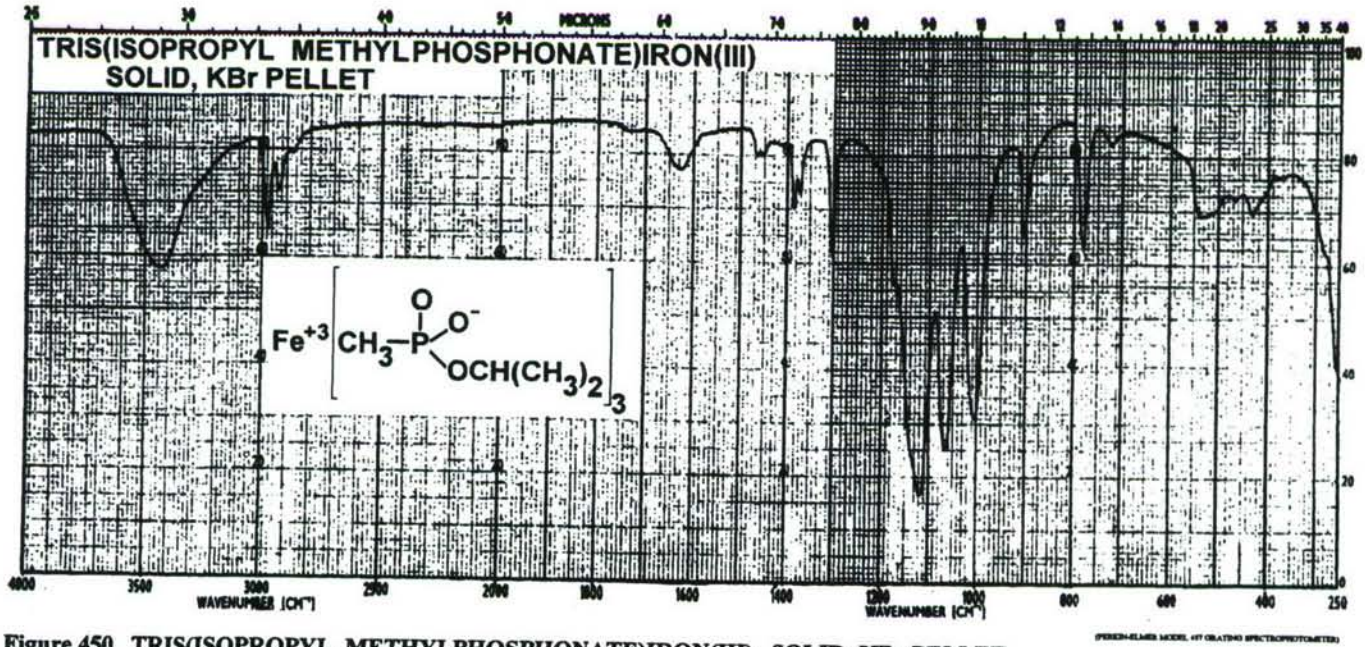


Figure 450 TRIS(ISOPROPYL METHYLPHOSPHONATE)IRON(III), SOLID, KBr PELLET

[hhhhh] For trivalent (P^{+3}) compounds containing a POEt group, the ν C-C band usually appears in the region 925-909 cm^{-1}. In P^{+5}OEt compounds this band occcurs over the range of 982-939 cm^{-1}. Thomas, L.C.,"Interpretation of the Infrared Spectra of Organophosphorus Compounds", p. 53, Heyden & Son Ltd., London, 1974.

3.10.19 Bis(Isopropyl Methylphosphonate)Barium(II) $Ba^{+2}[CH_3P(O)_2^- OCH(CH_3)_2]_2$

The infrared spectrum of bis(isopropyl methylphosphonate)barium(II) or the barium salt of GB acid (barium salt of IMPA), as a KBr pellet is given in ***Figure 451***. The band assignments, based on frequencies estimated from the spectrum, are as follows: 3450 cm^{-1} w and 1630 cm^{-1} vw (H_2O), 2977 cm^{-1} m, 2930 cm^{-1} w and 2876 cm^{-1} vw (ν CH_3 and ν -CH), 1470 cm^{-1} vw and 1447 cm^{-1} vvw (δ_{as} CH_3), 1420 cm^{-1} vvw (δ_{as} P-CH_3), 1382 and 1370 cm^{-1} w, doublet (δ_{sy} CH_3, isopropyl), 1330 cm^{-1} vvw (δ -C-H), 1296 cm^{-1} m (δ_{sy} P-CH_3), 1222 and 1204 cm^{-1} s (ν_{as} PO_2^-), 1180, 1137 and 1127 cm^{-1} w (triplet characteristic of POiPr), 1063 cm^{-1} s (ν_{sy} PO_2^-), 996 cm^{-1} s (ν P-O-C), 889 cm^{-1} ms (P-CH_3 rock), 773 cm^{-1} ms (POC), 717 cm^{-1} w (ν P-C), 517 cm^{-1} m, 488 cm^{-1} m (PO_2^- deformation).

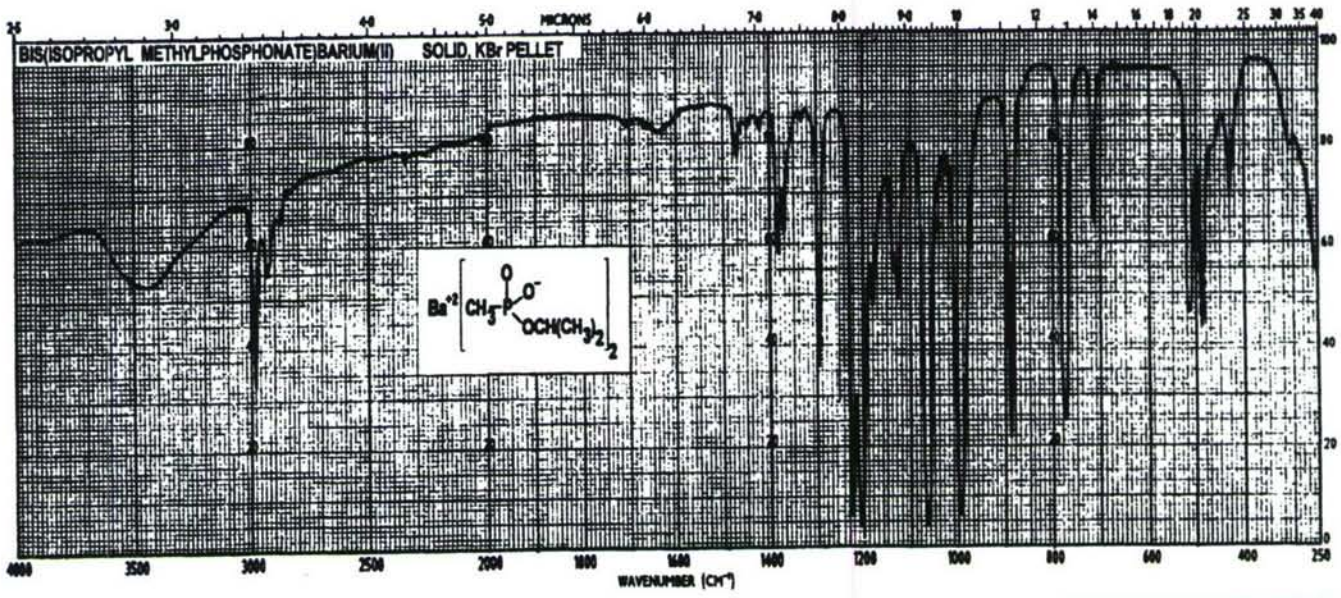


Figure 451 BIS(ISOPROPYL METHYLPHOSPHONATE)BARIUM(II), BARIUM SALT OF GB ACID, SOLID, KBr PELLET

3.10.20 Bis(Isopropyl Methylphosphonate)Calcium(II) $Ca^{+2}[CH_3P(O)_2^- OCH(CH_3)_2]_2$

The infrared spectrum of bis(isopropyl methylphosphonate)calcium(II), or the calcium salt of GB acid (calcium salt of IMPA), is presented as ***Figure 452***. The band assignments, based on frequency values estimated from the spectrum, are as follows: 3450 cm^{-1} m and 1635 cm^{-1} w (H_2O), 2975 cm^{-1} m, 2927 cm^{-1} w and

2875 cm^{-1} vw (ν CH_3 and ν C-H), 1468 cm^{-1} w, 1455 cm^{-1} vw (δ_{as} CH_3), 1425 cm^{-1} vw (δ_{as} P-CH_3), 1385 and 1372 cm^{-1} m, doublet (δ_{sy} CH_3, isopropyl moiety), 1303 cm^{-1} m (δ_{sy} P-CH_3), 1188 cm^{-1} s (ν_{as} PO_2^-), 1175 cm^{-1} sh, 1135 and 1117 cm^{-1} w (triplet characteristic of POiPr), 1068 cm^{-1} s (ν_{sy} PO_2^-), 993 cm^{-1} s (ν P-O-C), 895 m (P-CH_3 rock, CH_3 rock isopropyl moiety), 777 cm^{-1} m (POC), 723 cm^{-1} w (ν P-C), 519 cm^{-1} m (PO_2^- deformation).

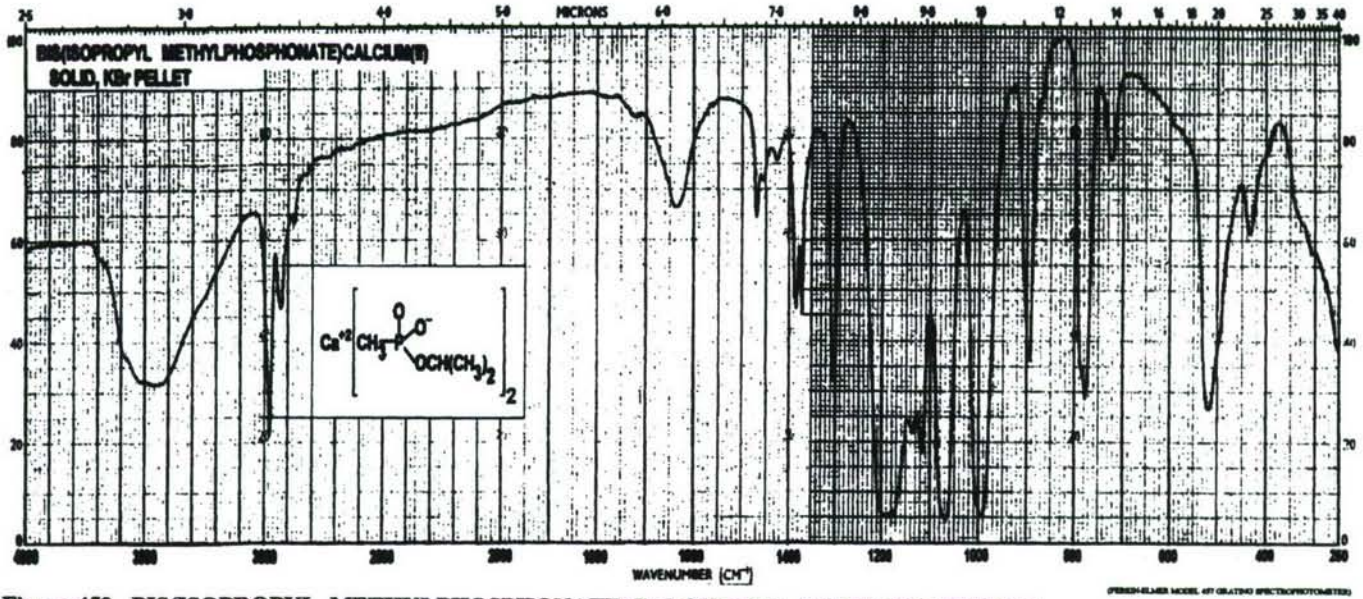


Figure 452 BIS(ISOPROPYL METHYLPHOSPHONATE)CALCIUM(II), SOLID, KBr PELLET

3.10.21 Bis(Diisopropyl Phosphate)Barium(II) $Ba^{+2}[((CH_3)_2CHO)_2P(O_2)^-]_2$

The infrared spectrum of bis(diisopropyl phosphate)barium(II) as a KBr pellet is reproduced as ***Figure 453***. The band assignments, based on frequency values estimated from the infrared spectrum, are as follows: 3440 cm^{-1} m and 1630 cm^{-1} vw (H_2O), 2977 cm^{-1} m, 2930 cm^{-1} w and 2870 cm^{-1} vw (ν CH_3 and ν C-H), 1466 cm^{-1} vw and 1450 cm^{-1} sh (δ_{as} CH_3), 1382 and 1371 cm^{-1} w, doublet (δ_{sy} CH_3), 1355 cm^{-1} vvw (δ -C-H), 1266 cm^{-1} sh and 1218 cm^{-1} s (ν_{as} PO_2^-), 1172, 1137 cm^{-1} w and 1111 cm^{-1} vw (triplet characteristic of POiPr), 1066 cm^{-1} s (ν_{sy} PO_2^-), 1011 cm^{-1} m and 979 cm^{-1} ms (ν P-O-C), 886 cm^{-1} m and 877 cm^{-1} sh (CH_3 rock), 771 cm^{-1} m and 742 cm^{-1} w (POC), 555 cm^{-1} m (PO_2^- deformation).

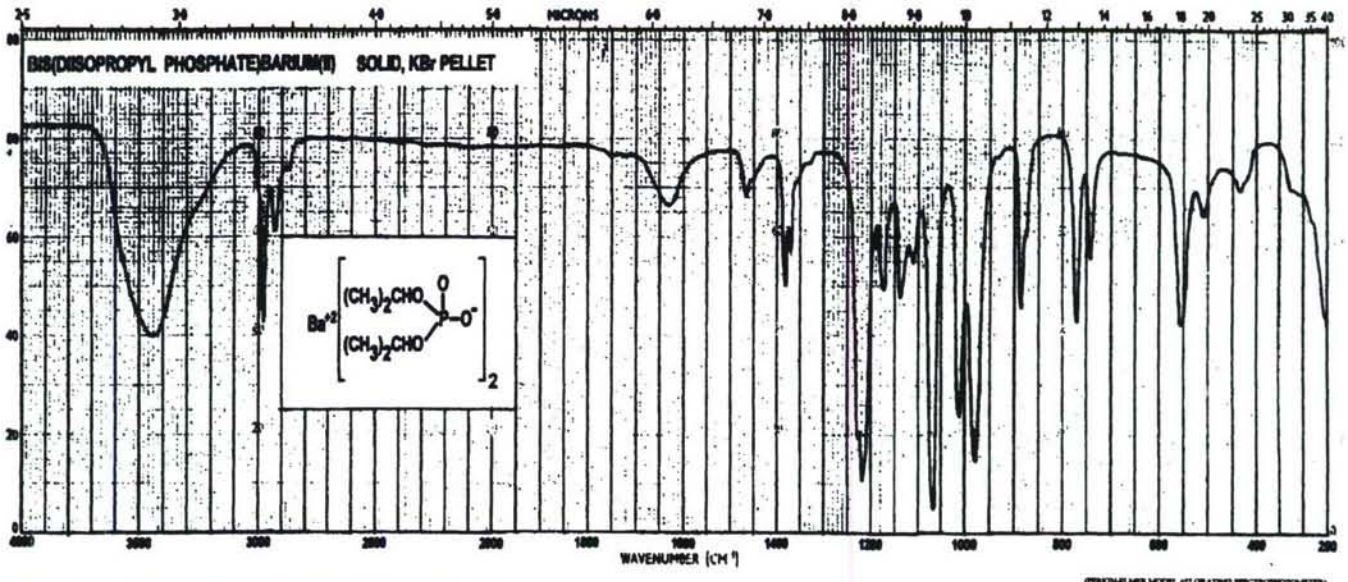


Figure 453 BIS (DIISOPROPYL PHOSPHATE)BARIUM(II), SOLID, KBr PELLET

3.10.22 Tris(Ethyl Methylphosphonate)Iron(III) $Fe^{+3}[CH_3P(O_2^-)OCH_2CH_3]_3$

The infrared spectum of tris(ethyl methylphosphonate)iron(III), the iron (III) salt of ethyl methylphosphonic acid, as a KBr pellet is presented ***as Figure 454***. The band assignments, based on frequency values estimated from the infrared spectrum, are as follows: 3450 cm^{-1} w and 1630 cm^{-1} vw (H_2O), 2985 cm^{-1} w, 2935 cm^{-1} w (ν_{as} CH_3 and ν_{as} CH_2), 2910 cm^{-1} vw and 2875 cm^{-1} vvw (ν_{sy} CH_3 and ν_{sy} CH_2), 1480 cm^{-1} vvw (δ OCH_2), 1443 cm^{-1} vvw (δ_{as} CH_3), 1415 cm^{-1} vvw (δ_{as} P-CH_3), 1395 cm^{-1} vw (ω OCH_2), 1367 cm^{-1} vvw (δ_{sy} CH_3), 1305 cm^{-1} m (δ_{sy} P-CH_3), 1114 cm^{-1} s (ν_{as} PO_2^-), 1076 cm^{-1} ms (ν_{sy} PO_2^-), 1043 cm^{-1} ms (ν P-O-C), 959 cm^{-1} m (ν C-C of POEt), 898 cm^{-1} w (P-CH_3 rock), 790 cm^{-1} m (POC), 751 cm^{-1} vw (ν P-C), 540 cm^{-1} w (PO_2^- ?).

3.10.23 Phosphorus Trichloride PCl_3

The infrared spectrum of phosphorus trichloride as a thin liquid film between KBr windows is given in ***Figure 455***. The band assignments are as follows: 1384 cm^{-1} vvw (KNO_3 from KBr windows), 1301 cm^{-1} wv (possible ν P=O from $POCl_3$, which occurs at 1298 cm^{-1}), 991 cm^{-1} vw (ν P-OH ?), 485 cm^{-1} s (ν_{sy} and ν_{as} PCl_3).

The effect of atmospheric moisture on a liquid film of phosphorus trichloride between KBr windows is illustrated by the infrared spectra reproduced as ***Figure 456***. After 30 minutes of exposure to atmospheric

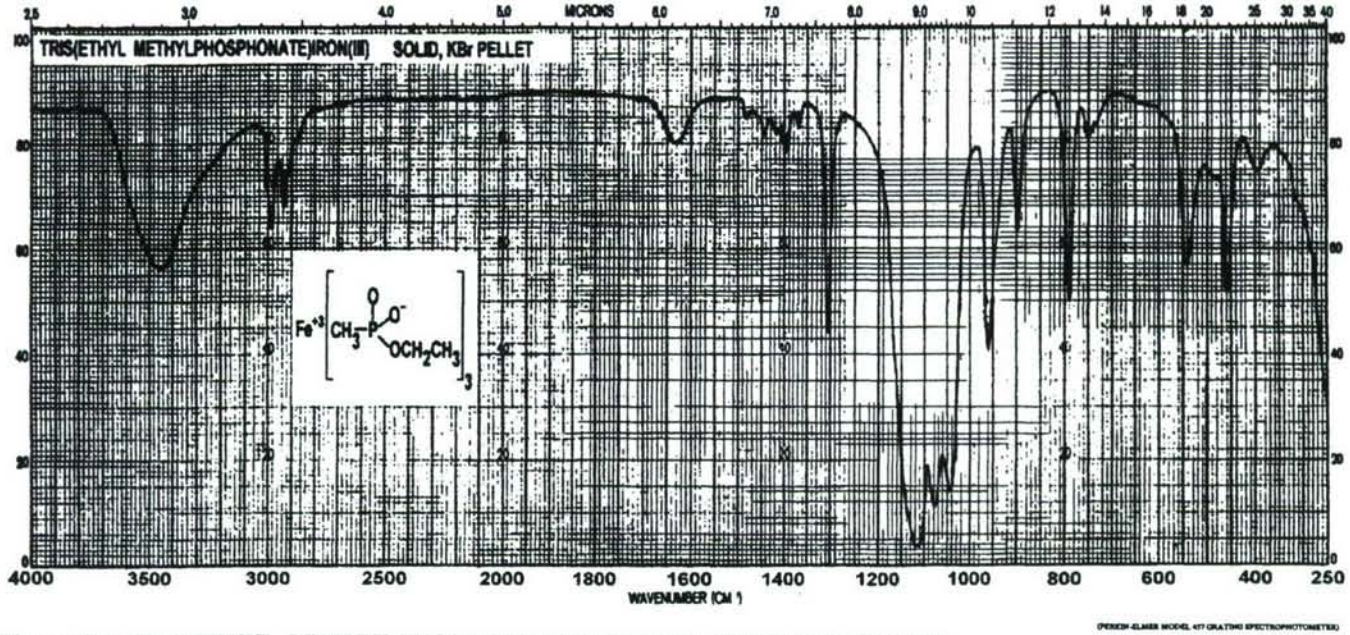


Figure 454 TRIS(ETHYL METHYLPHOSPHONATE)IRON(III), SOLID, KBr PELLET

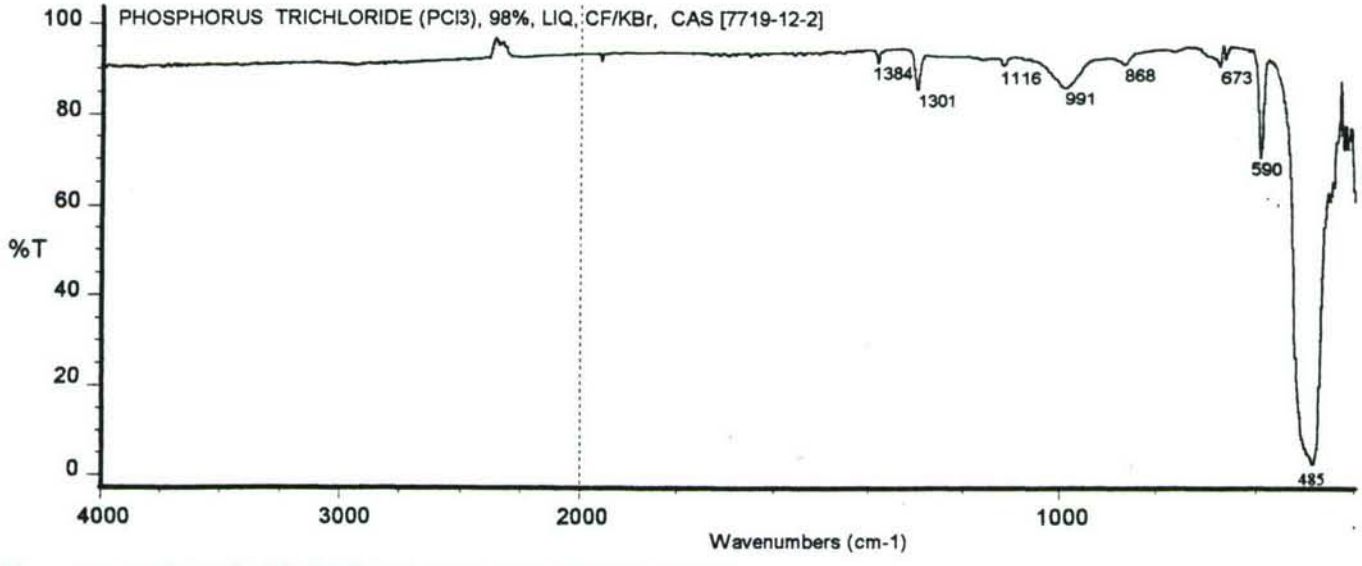


Figure 455 PHOSPHORUS TRICHLORIDE, 98%, LIQUID, CF/KBr

moisture the presence of the P-acid (POOH) moiety is evident by the bands at 2799, 2451, 1650, 1159, 1005 and 937 cm^{-1}. The 2451 cm^{-1} band may also be due to the P-H stretching vibration of a compound such as phosphorous acid (phosphonic acid), $HP{=}O(OH)_2$. After 60 minutes of exposure the PCl_3 band, which was at 485 cm^{-1}, is gone from the spectrum. The product(s) after 5 days of exposure to atmospheric moisture may be a combination of products such as $H\text{-}P{=}O(OH)_2$ and $HO\text{-}P{=}O(OH)_2$. The former compound arising from the hydrolysis of PCl_3,

while the latter compound (phosphoric acid, H_3PO_4) coming from the oxidation of PCl_3 followed by hydrolysis. The hydrolysis and or oxidation/hydrolysis may be summarized as follows:

PCl_3 -HOH→ H-O-PCl_2 → H-P=O$(Cl)_2$ -HOH→ H-P=O(OH)(Cl) -HOH→ H-P=O$(OH)_2$

PCl_3 -[O]→ O=P$(Cl)_3$ -HOH→ HO-P=O$(Cl)_2$ -HOH→ HO-P=O(OH)(Cl) -HOH→ O=P$(OH)_3$.

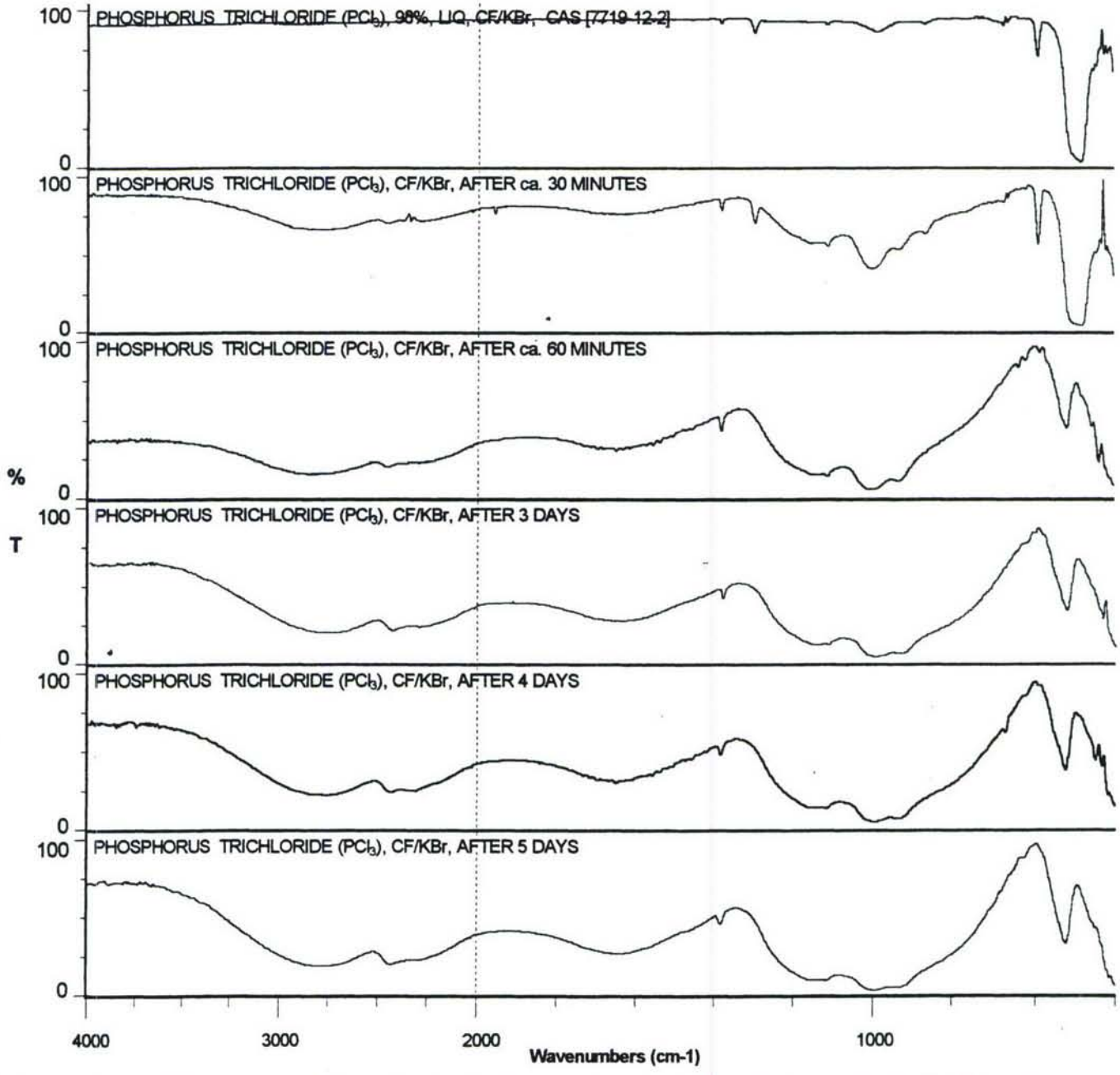


Figure 456 PHOSPHORUS TRICHLORIDE, LIQUID, CF/KBr, AFTER EXPOSURE TO ATMOSPHERIC MOISTURE

3.10.24 Phosphorus Tribromide PBr_3

The infrared spectrum of phosphorus tribromide as a thin liquid film between KBr discs (windows) is reproduced as ***Figure 457***. The band assignments are as follows: 1269 cm^{-1} vw (possible ν P=O from $POBr_3$, which has a literature value[iiiii] of 1261 and a *calculated* value of 1258 cm^{-1}), <400 cm^{-1} s [ν PCl_3, this band occurs just under 400 cm^{-1} (KBr cutoff) having a literature value[iiiii] of 392 cm^{-1}].

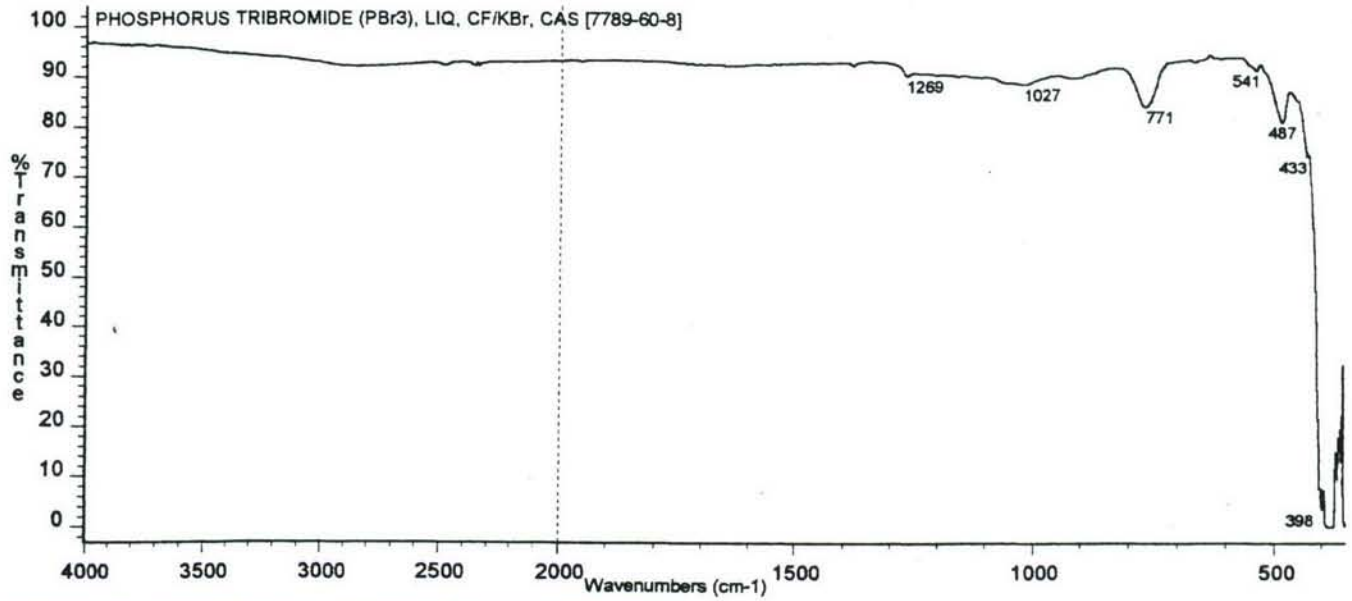


FIGURE 457 PHOSPHORUS TRIBROMIDE, LIQUID, CF/KBr

The effect of atmospheric moisture on a thin liquid film of phosphorus tribromide is illustrated by the infrared spectra presented in ***Figure 458***. The spectra after one day of exposure indicate the formation of a P-acid as indicated by the bands near 2830, 2488, 2300, 1673, 1150 (ν P=O), 1030 and 930 cm^{-1} (POH). The 2488 cm^{-1} band may be due to a P-H stretching vibration from a P-acid such as $H\text{-}P{=}O(OH)_2$. The products formed as a result of the exposure of PBr_3 to atmospheric moisture may be similar to those formed from PCl_3 (***Figure 457***) namely, $H\text{-}P{=}O(OH)_2$ and $HO\text{-}P{=}O(OH)_2$. The former compound produced from the hydrolysis of PBr_3 and the latter compound being produced from the oxidation of PBr_3 to $POBr_3$ followed by hydrolysis.

[iiiii] Corbridge, D.E.C., "The Infrared Spectra of Phosphorus Compounds" in Topics In Phosphorus Chemistry, Volume 6, p. 336, Table XXIV, Grayson, M., and Griffith, E.J., Editors, John Wiley, New York, 1969.
[iiiii] ibid., p. 335, Table XXII.

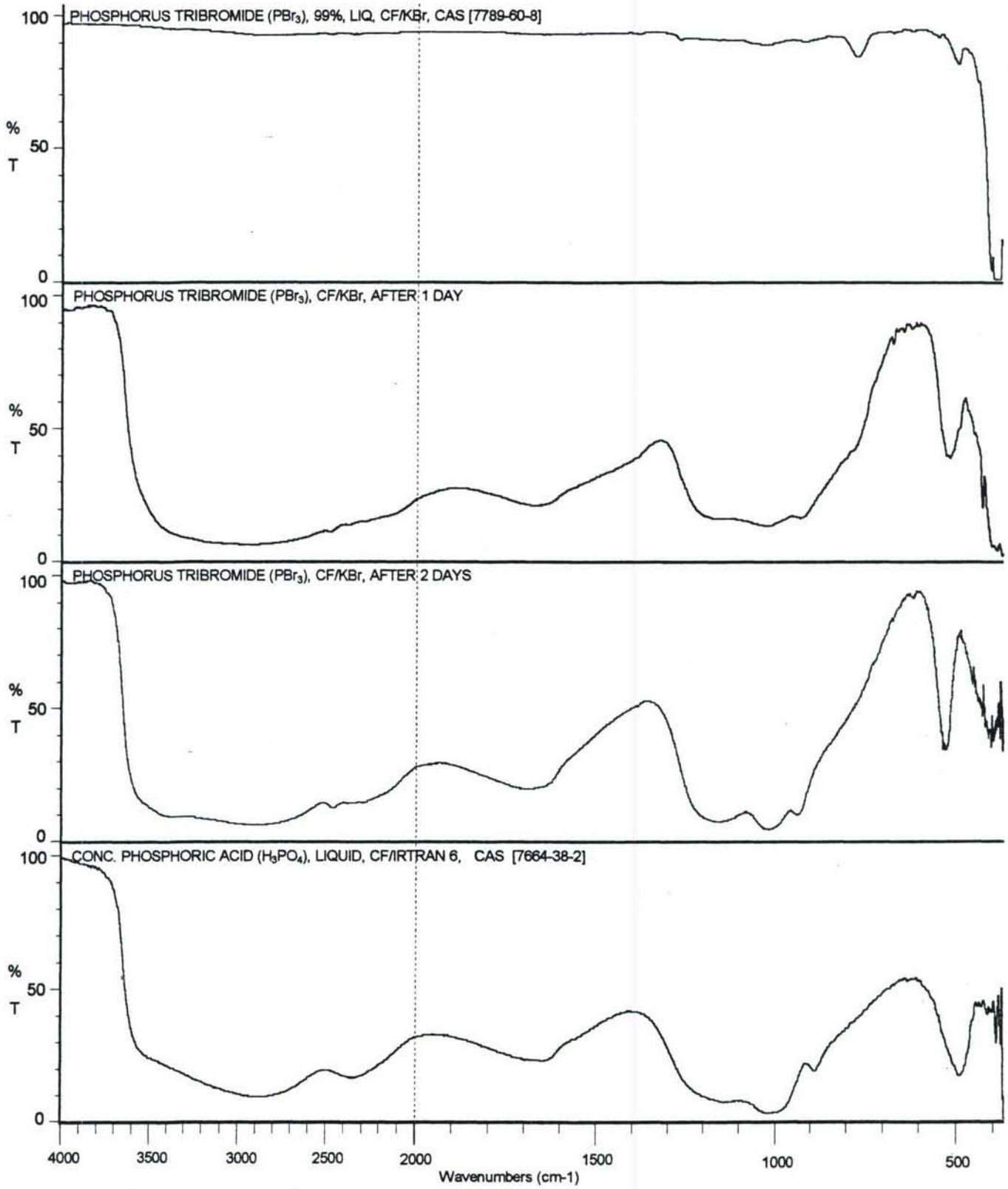


Figure 458 PHOSPHORUS TRIBROMIDE, PBr_3, LIQUID, CF/KBr (THE BOTTOM SPECTRUM IS FOR PHOSPHORIC ACID, H_3PO_4, AS A LIQUID FILM BETWEEN IRTRAN 6 WINDOWS)

3.10.25 Phosphorus Oxychloride (Phosphoryl Chloride) $O=PCl_3$

The infrared spectrum of phosphorus oxychloride (phosphoryl chloride) as a thin liquid film between KBr windows is reproduced as ***Figure 459***. The band assignments are as follows: 2587 cm^{-1} vvw (2 x 1298 = 2596 cm^{-1}), 1384 cm^{-1} vvw (KNO_3 from the KBr windows), 1298 cm^{-1} ms (ν P=O *calculated* value is 1290 cm^{-1}), 589, 581 cm^{-1} s (ν_{as} PCl_3), 484 cm^{-1} m (ν_{sy} PCl_3).

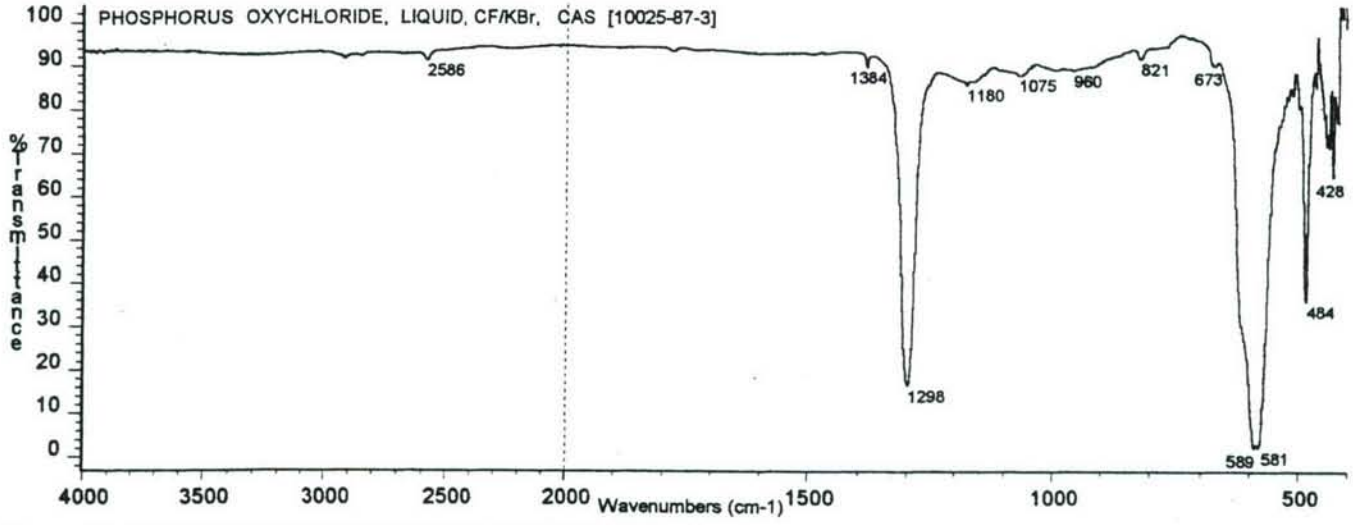
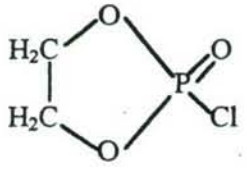


Figure 459 PHOSPHORUS OXYCHLORIDE (PHOSPHORYL CHLORIDE), LIQUID, CF/KBr

3.10.26 Phosphorus Sulfochloride (Thiophosphoryl Chloride) $S=PCl_3$

The infrared spectrum of phosphorus sulfochloride (thiophosphoryl chloride) as a thin liquid film between KBr windows is given as ***Figure 460***. The band assignments are as follows: 1506 cm^{-1} vvw (2x 751 = 1502 cm^{-1}), 1384 cm^{-1} vvw (KNO_3 from KBr windows), 1302 cm^{-1} vw (ν P=O from $POCl_3$?), 965 cm^{-1} vw (534 + 430 = 964 cm^{-1}), 751 cm^{-1} s (ν P=S), 534 cm^{-1} s (ν_{as} PCl_3), 430 cm^{-1} ms (ν_{sy} PCl_3).

3.10.27 2-Chloro-2-Oxo-1,3,2-Dioxaphospholane (2-Chloro-1,3,2-Dioxaphospholane-2-Oxide)



The infrared spectrum of 2-chloro-2-oxo-1,3,2 -dioxaphospholane (2-chloro-1,3,2-dioxaphospholane-2-oxide) as liquid film between KBr discs (windows) is given as ***Figure 461***. The band assignments are as

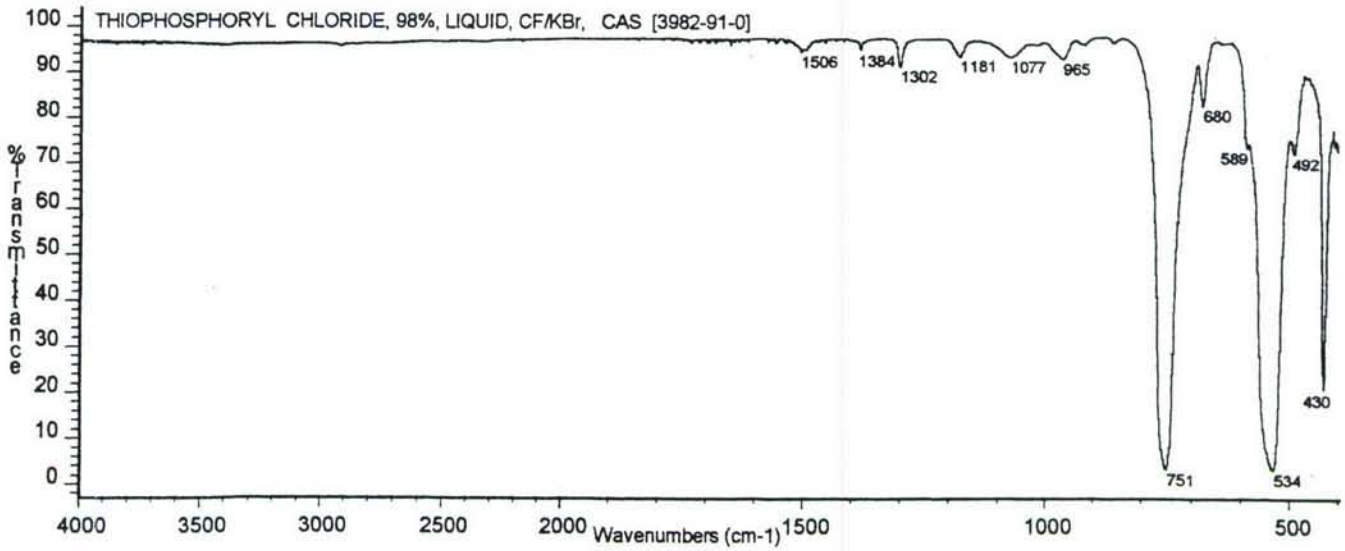


Figure 460 PHOSPHORUS SULFOCHLORIDE (THIOPHOSPHORYL CHLORIDE), 98%, LIQUID, CF/KBr

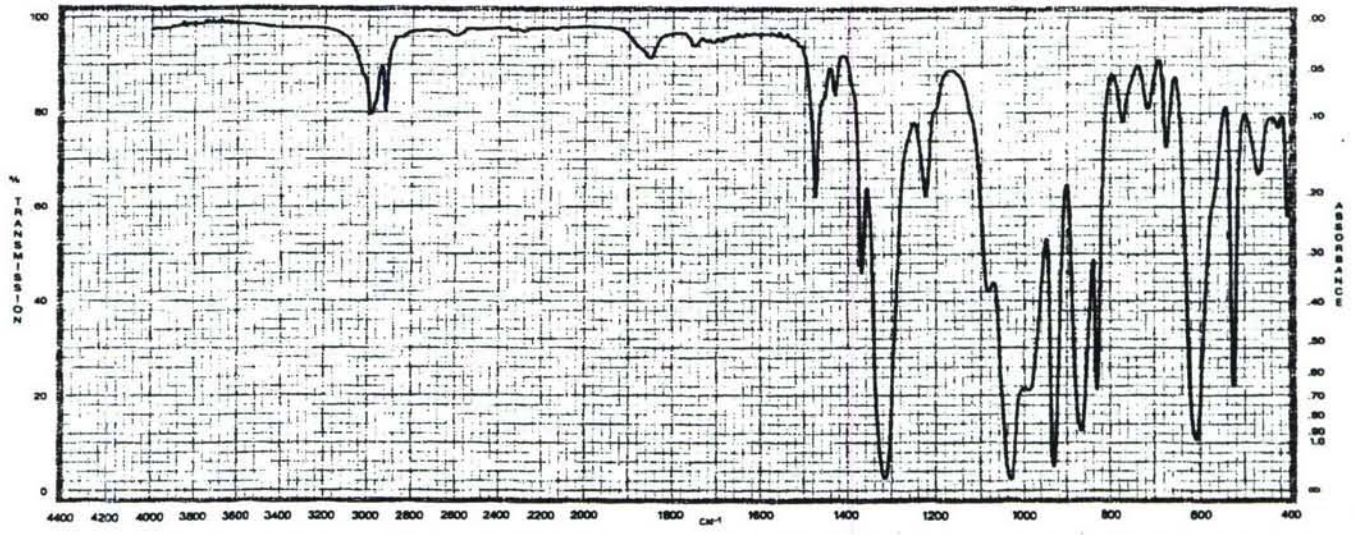


Figure 461 2-CHLORO-2-OXO-1,3,2-DIOXAPHOSPHOLANE (2-CHLORO-1,3,2-DIOXAPHOSPHOLANE-2-OXIDE), 97%, LIQUID, CF/KBr

follows: 2988 cm^{-1} vw (ν_{as} CH_2), 2921 cm^{-1} vw (ν_{sy} CH_2), 1474 cm^{-1} w (δ CH_2), 1313 cm^{-1} s (ν P=O, *calculated* value is 1306 cm^{-1}), 1223 cm^{-1} w (ω, τ CH_2), 1028 cm^{-1} (ν P-O-C), 926 cm^{-1} ms (ν C-C), 604 cm^{-1} ms (CCO), 522 cm^{-1} m (ν P-Cl).

3.11 Inorganic Compounds Containing Phosphorus

3.11.1 Ammomiun Hexafluorophosphate NH_4PF_6

The infrared spectum of ammonium hexafluorophosphate as a solid between KBr discs (windows) is reproduced as ***Figure 462***. The band assignments are as follows: 3326 cm^{-1} ms (ν NH_4^+), 2851 cm^{-1} vw (2 x 1431 = 2862 cm^{-1}), 1431 cm^{-1} ms (δ NH_4^+), 829 cm^{-1} s (ν_{as} PF_6^-), 561 cm^{-1} ms (ν_{sy} PF_6^-).

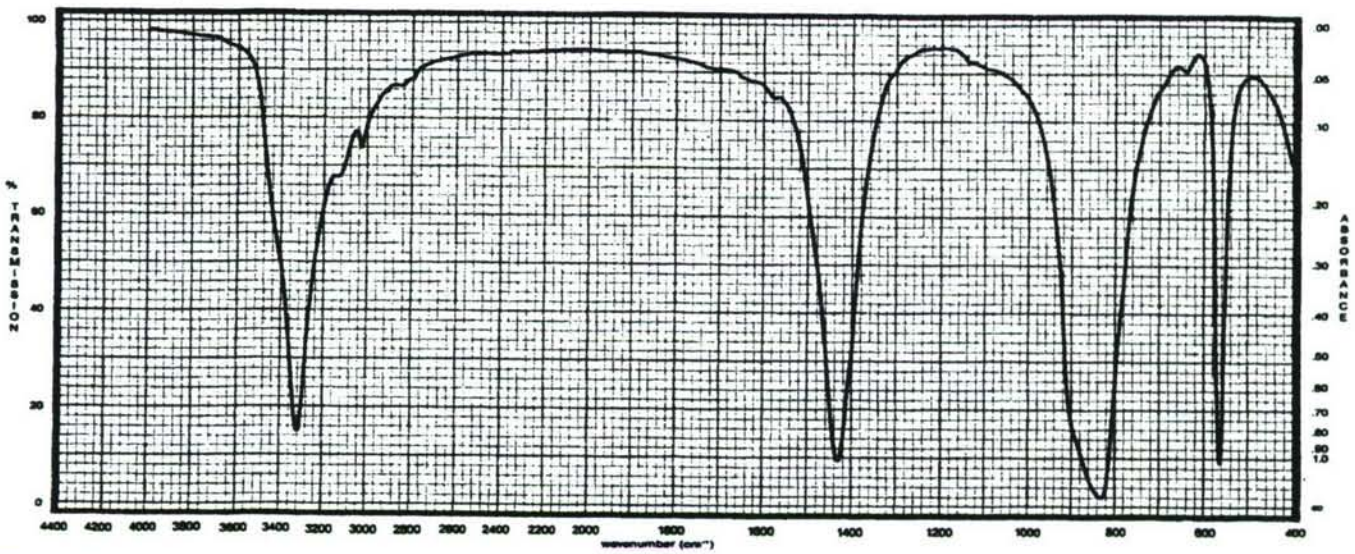


Figure 462 AMMONIUM HEXAFLUOROPHOSPHATE (NH_4PF_6), 99.99%, SOLID BETWEEN KBr DISCS (WINDOWS)

3.11.2 Potassium Hexafluorophosphate KPF_6

The infrared spectrum of potassium hexafluorophosphate as a solid between KBr discs (windows) is presented as ***Figure 463***. The band assignments are as follows: 830 cm^{-1} s (ν_{as} PF_6^-) and 560 cm^{-1} ms (ν_{sy} PF_6^-).

3.11.3 Sodium Hexafluorophosphate $NaPF_6$

The infrared spectrum of sodium hexafluorophosphate as a solid between CsI discs (windows) is reproduced as ***Figure 464***. The upper spectrum shows the sample as received, with water bands visible at 3457, 2037 and 1623 cm^{-1}. The lower spectrum is for the sample after drying overnight. The water bands are now almost gone from the spectrum. The band assignments are as follows: 3457 cm^{-1} ms, 2037 cm^{-1} vw and 1623 cm^{-1} m (H_2O), 843 and 828 cm^{-1} s (ν_{as} PF_6^-), 559 cm^{-1} ms (ν_{sy} PF_6^-).

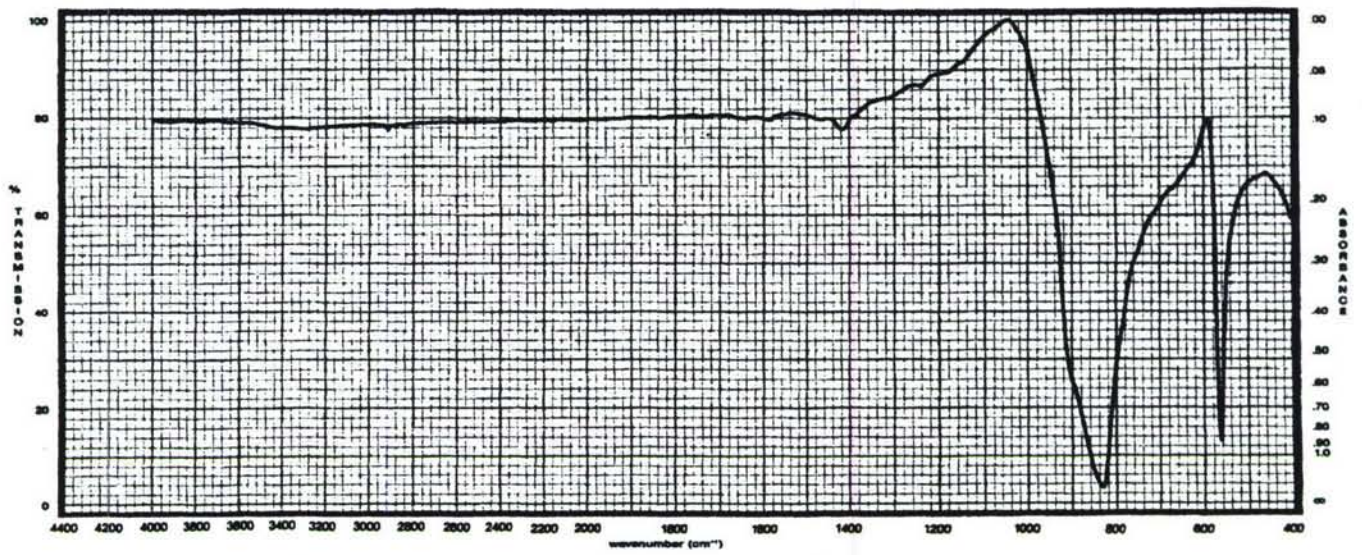


Figure 463 POTASSIUM HEXAFLUOROPHOSPHATE, 98%, SOLID BETWEEN KBr DISCS (WINDOWS)

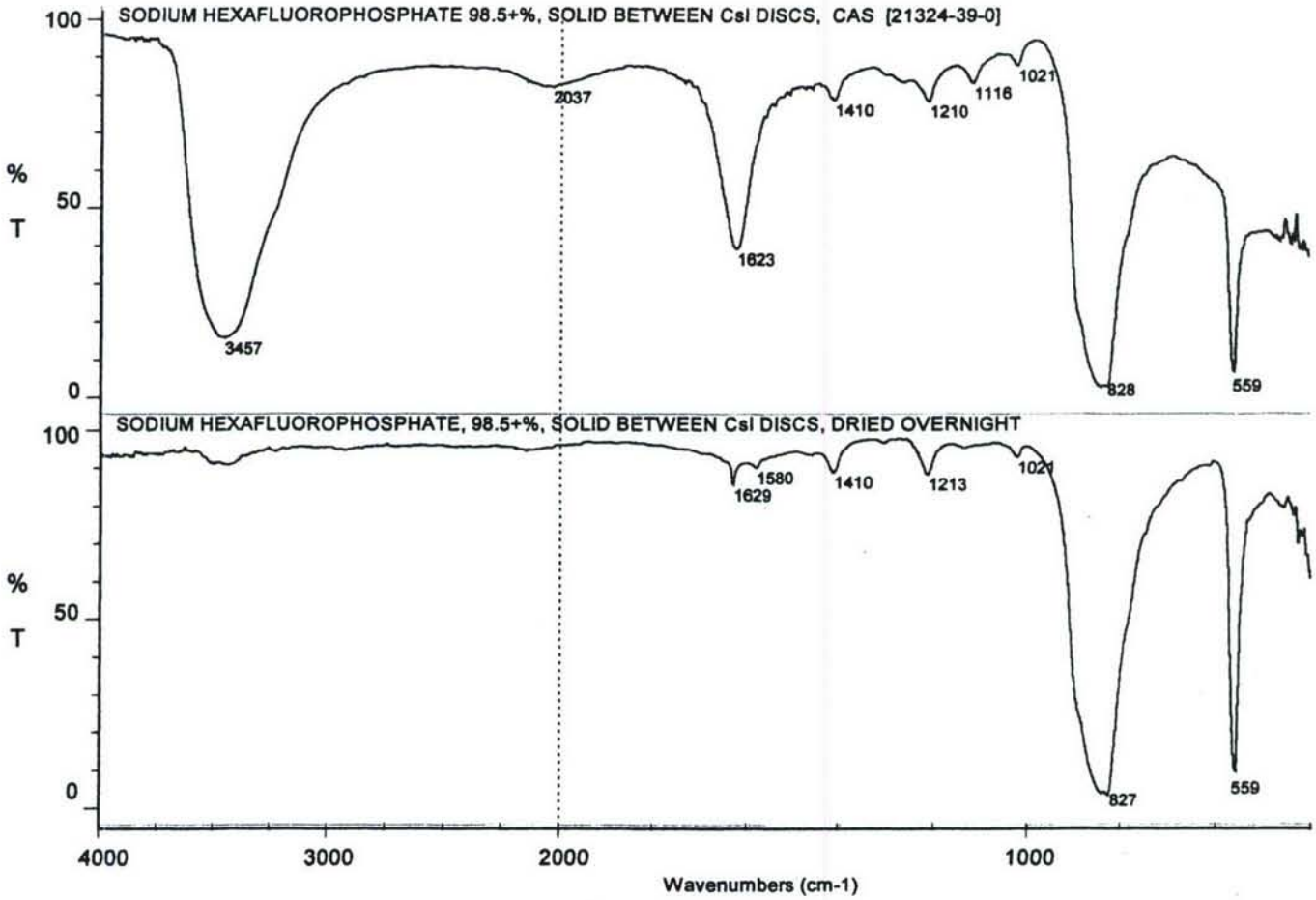


Figure 464 SODIUM HEXAFLUOROPHOSPHATE, 98.5+%, SOLID BETWEEN CsI DISCS (WINDOWS)
***UPPER SPECTRUM*–THE SAMPLE AS RECEIVED**
***LOWER SPECTRUM*–THE SAMPLE AFTER DRYING OVERNIGHT**

3.11.4 Silver Hexafluorophosphate $AgPF_6$

The infrared spectrum of silver hexafluorophosphate as a solid between KBr discs (windows) is given in ***Figure 465***. The band assignments are as follows: 830 cm^{-1} s (ν_{as} PF_6^-), 559 cm^{-1} ms (ν_{sy} PF_6^-).

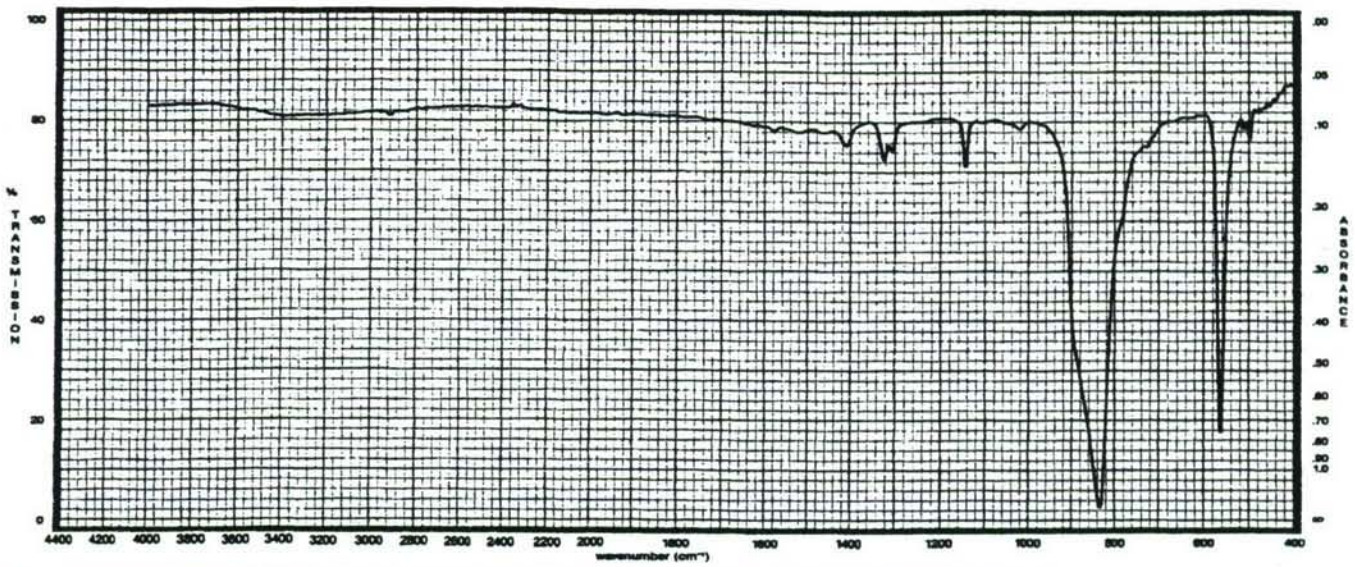


Figure 465 SILVER HEXAFLUOROPHOSPHATE, 98%, SOLID BETWEEN CsI DISCS (DRIED)

3.11.5 Tetrabutylammonium Hexafluorophosphate $(H_9C_4)_4NPF_6$

The infrared spectrum of tetrabutylammonium hexafluorophosphate as a solid between CsI discs (windows) is presented as ***Figure 466***. The band assignments are as follows: 2965 cm^{-1} m, 2936 cm^{-1} w, 2879

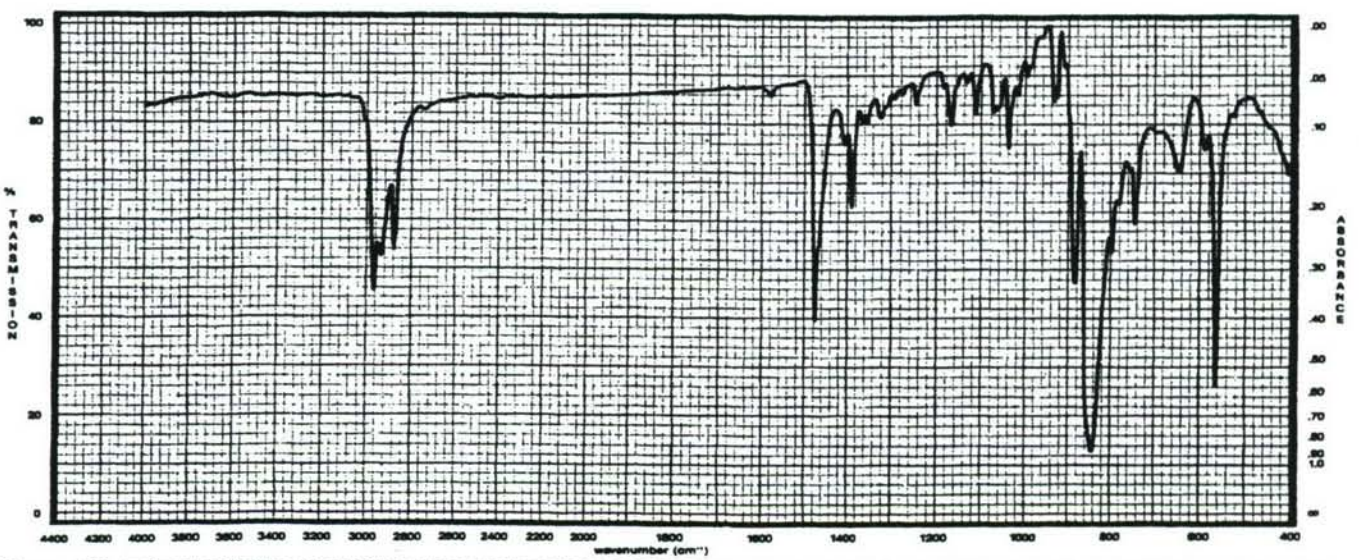


Figure 466 TETRABUTYLAMMONIUM HEXAFLUOROPHOSPHATE, 98%, SOLID BETWEEN CsI DISCS (WINDOWS)

cm^{-1} (ν CH_3 and ν CH_2), 1473 cm^{-1} m (δ CH_2 and δ_{as} CH_3), 1386 cm^{-1} w (δ_{sy} CH_3), 839 cm^{-1} s (ν_{as} PF_6^-), 739 cm^{-1} vw (CH_2 rock), 557 cm^{-1} ms (ν_{sy} PF_6^-).

3.11.6 Aluminum Phosphate $AlPO_4$

The infrared spectrum of aluminum phosphate as a solid between CsI windows is given as ***Figure 467***. The band assignments are as follows: ca 3400 cm^{-1} m and 1624 cm^{-1} w (H_2O), 1135 cm^{-1} s (ν PO_4^{-3}).[kkkkk]

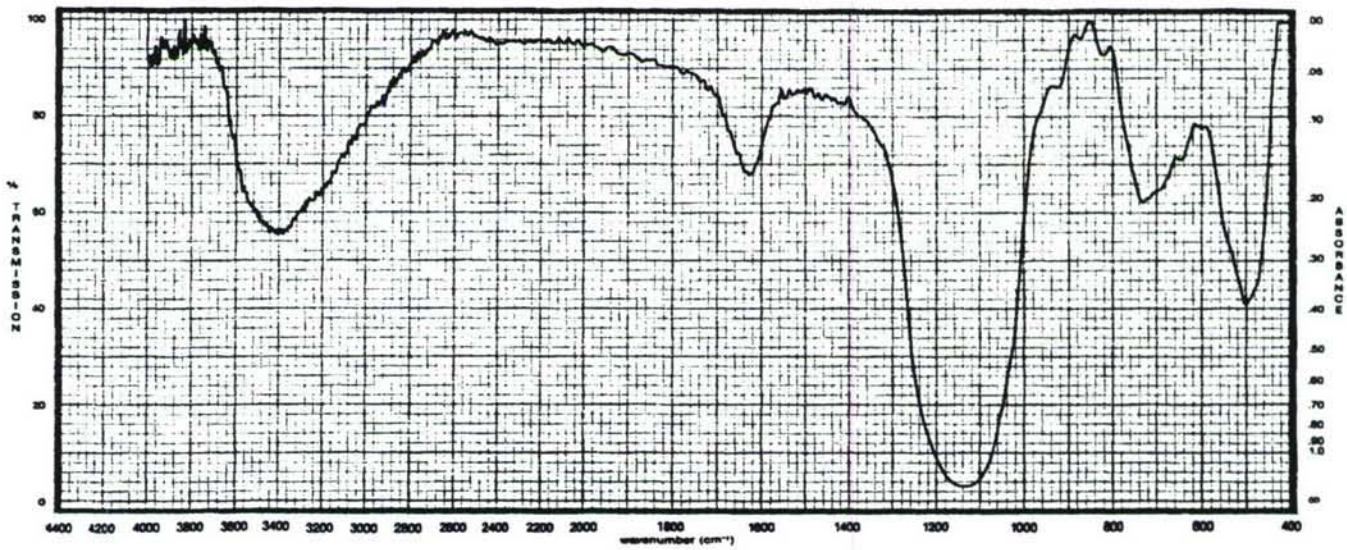


Figure 467 ALUMINUM PHOSPHATE, SOLID BETWEEN CsI DISCS (WINDOWS)

3.11.7 Sodium Phosphate, Tribasic Dodecahydrate $Na_3PO_4 \cdot 12H_2O$

The infrared spectrum of tribasic sodium phosphate dodecahydrate as a solid between KBr windows is presented as ***Figure 468***. The band assignments are as follows: ca 3200 cm^{-1} ms broad, ca 2360 cm^{-1} w and 1654 cm^{-1} w (H_2O), 1012 cm^{-1} s (ν PO_4^{-3}), ca 560 cm^{-1} w (PO_4^{-3} deformation).

3.11.8 Sodium Phosphate, Monobasic Monohydrate $NaH_2PO_4 \cdot H_2O$ $(HO)_2P(O)(ONa) \cdot H_2O$

The infrared spectrum of monobasic sodium phosphate monohydrate as a solid between CsI discs (windows) is presented as ***Figure 469***. The band assignments are as follows: 3527 cm^{-1} m and 3448 cm^{-1} w

[kkkkk] The PO_4^{-3} ion absorbs strongly at 1100-1000 cm^{-1}. Colthup, N.B., Daly, L.H., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", p. 345, Sec. Ed., Academic Press, N.Y., 1975.

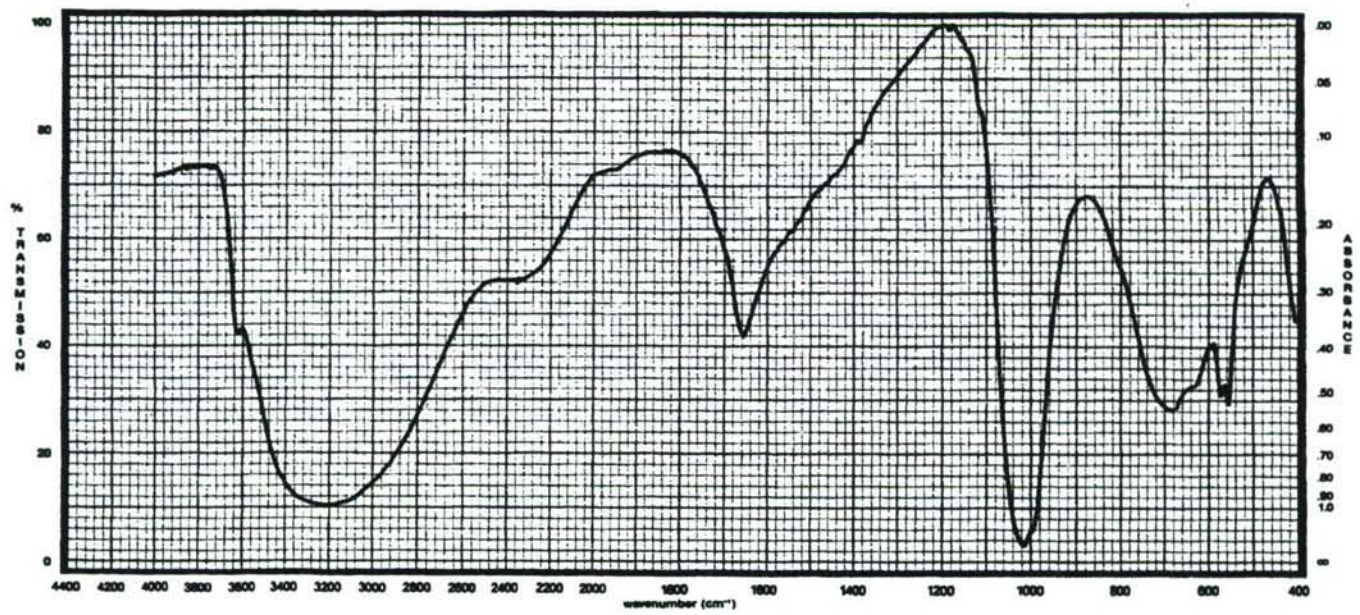


Figure 468 SODIUM PHOSPHATE, TIBASIC, DODECAHYDRATE, 98⁺%, SOLID BETWEEN KBr DISCS (WINDOWS)

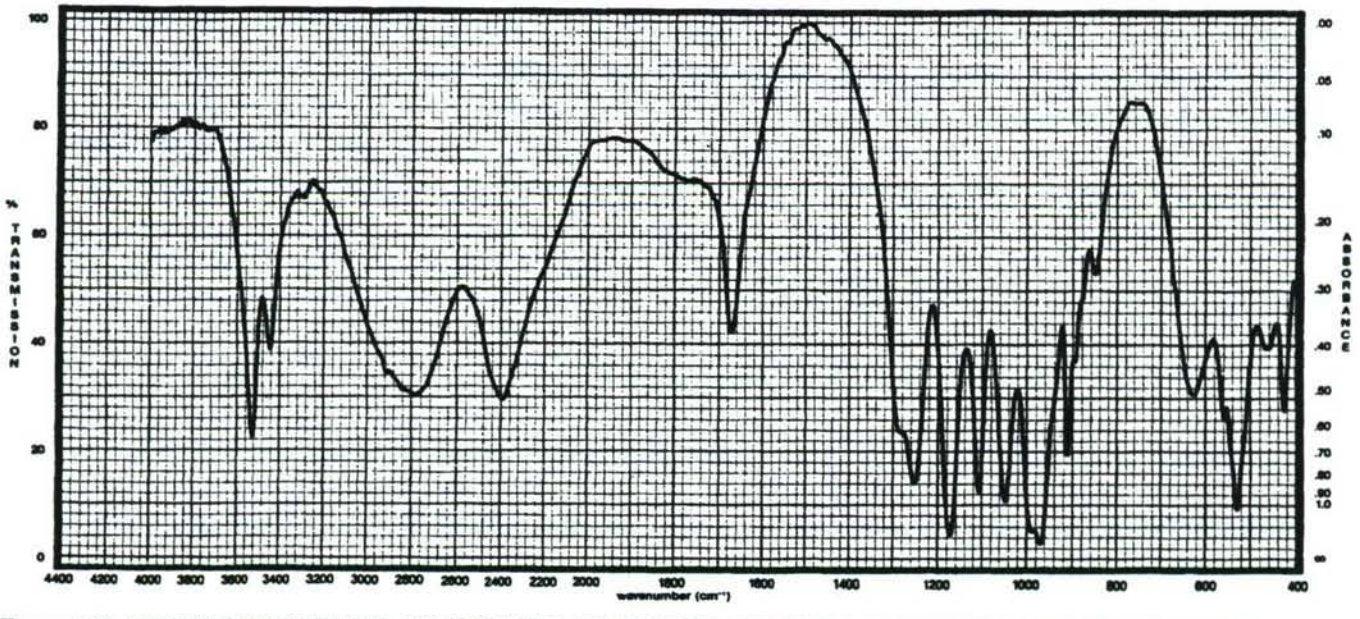


Figure 469 SODIUM PHOSPHATE, MONOBASIC, MONOHYDRATE, SOLID BETWEEN CsI DISCS (WINDOWS)

(H_2O), 2770 and 2398 cm^{-1} m broad (POH), ca 1770 vvw (POH), 1671 m cm^{-1} (H_2O), 1250 cm^{-1} ms, 1170 cm^{-1} s (ν_{as} PO_2^-), 1104, 1044 cm^{-1} m (ν_{sy} PO_2^-), 985 cm^{-1} sh and 967 cm^{-1} s, 908 cm^{-1} m (ν P-OH), 523 s (PO_2^- deformation).

3.11.9 Sodium Phosphate, Monobasic NaH_2PO_4 $(HO)_2PO(ONa)$

The infrared spectrum of monobasic sodium phosphate as a solid between KBr discs (windows) is reproduced as ***Figure 470.*** The band assignments are as follows: ca 2800, 2400 and 1640 cm^{-1} w, broad (POH), 1291 cm^{-1} ms (ν_{as} PO_2^-), 1059 cm^{-1} s (ν_{sy} PO_2^-), 990 and 934 cm^{-1} s (ν P-OH), 531 cm^{-1} s (PO_2^- deformation).

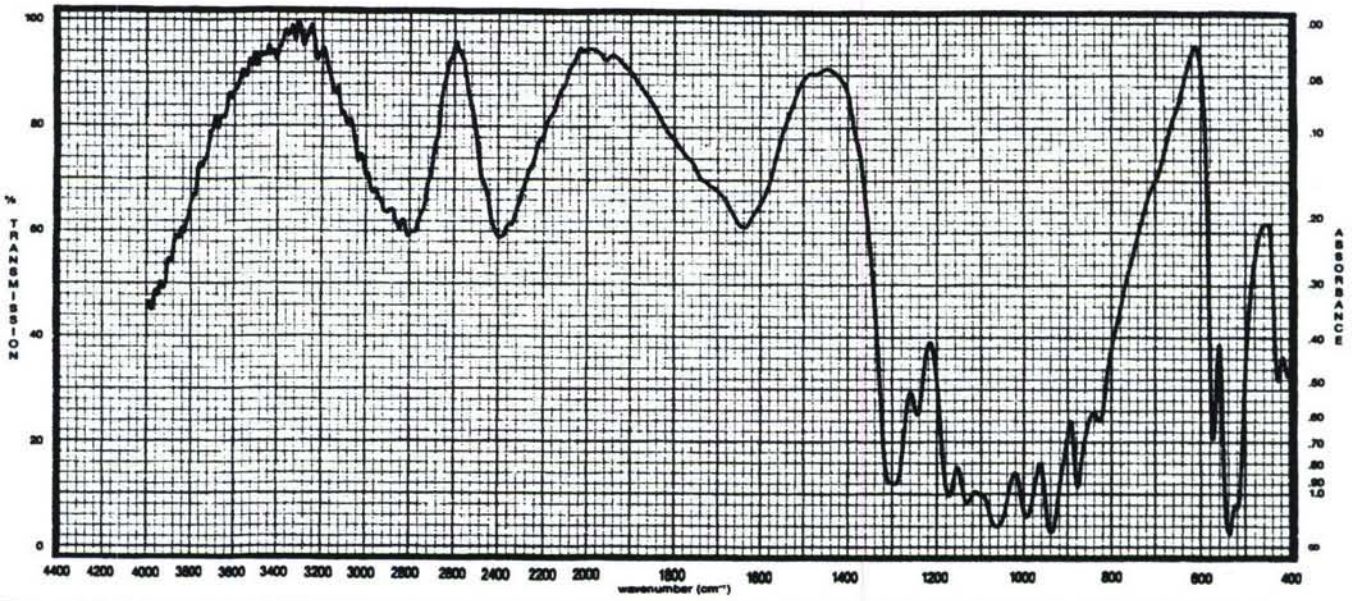


Figure 470 SODIUM PHOSPHATE, MONOBASIC (NaH_2PO_4), 99.999%, SOLID BETWEEN KBr DISCS (WINDOWS)

3.11.10 Potassium Phosphate, Monobasic, Anhydrous KH_2PO_4 $(HO)_2PO(OK)$

The infrared spectrum of anhydrous monobasic potassium phosphate as a solid between KBr discs (windows) is presented as ***Figure 471.*** The band assignments are as follows: 2719 and 2400 cm^{-1} w, 1650 cm^{-1} ms (POH), 1301 cm^{-1} s (ν_{as} PO_2^-), 1104 cm^{-1} s (ν_{sy} PO_2^-), 915 cm^{-1} s (ν P-OH), 541 cm^{-1} s (PO_2^- deformation).

3.11.11 Ammonium Dihydrogen Phosphate $NH_4H_2PO_4$ $(HO)_2PO(ONH_4)$

The infrared spectrum of ammonium dihydrogen phosphate (monobasic ammonium phosphate) as a solid between KBr discs (windows) is given as ***Figure 472.*** The band assignments are as follows: 3240 cm^{-1} s (ν NH_4^+), ca 2720 cm^{-1} sh, 2390 cm^{-1} w and 1680 cm^{-1} ms broad (POH), 1447 and 1408 cm^{-1} s (δ NH_4^+), 1288 cm^{-1} s (ν_{as} PO_2^-), 1105 cm^{-1} s (ν_{sy} PO_2^-), 923 cm^{-1} (ν P-OH), 550 cm^{-1} ms (PO_2^- deformation).

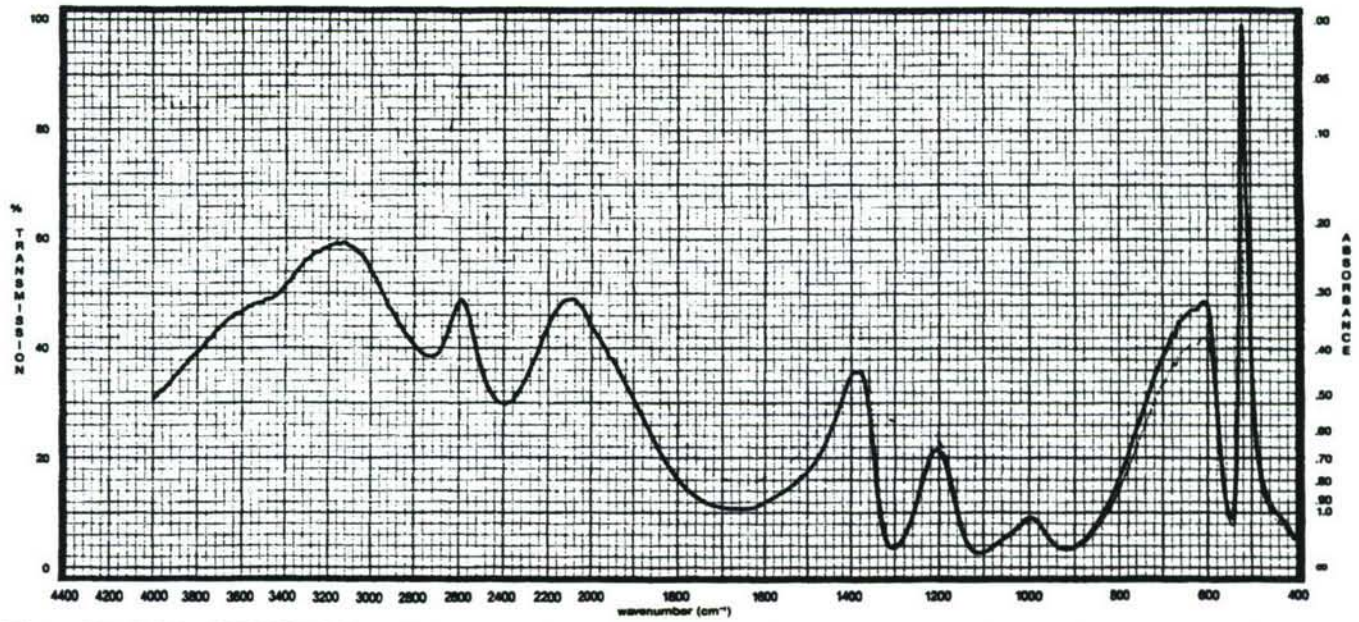


Figure 471 POTASSIUM PHOSPHATE, MONOBASIC, ANHYDROUS (KH_2PO_4), 99.999%, SOLID BETWEEN KBr DISCS (WINDOWS)

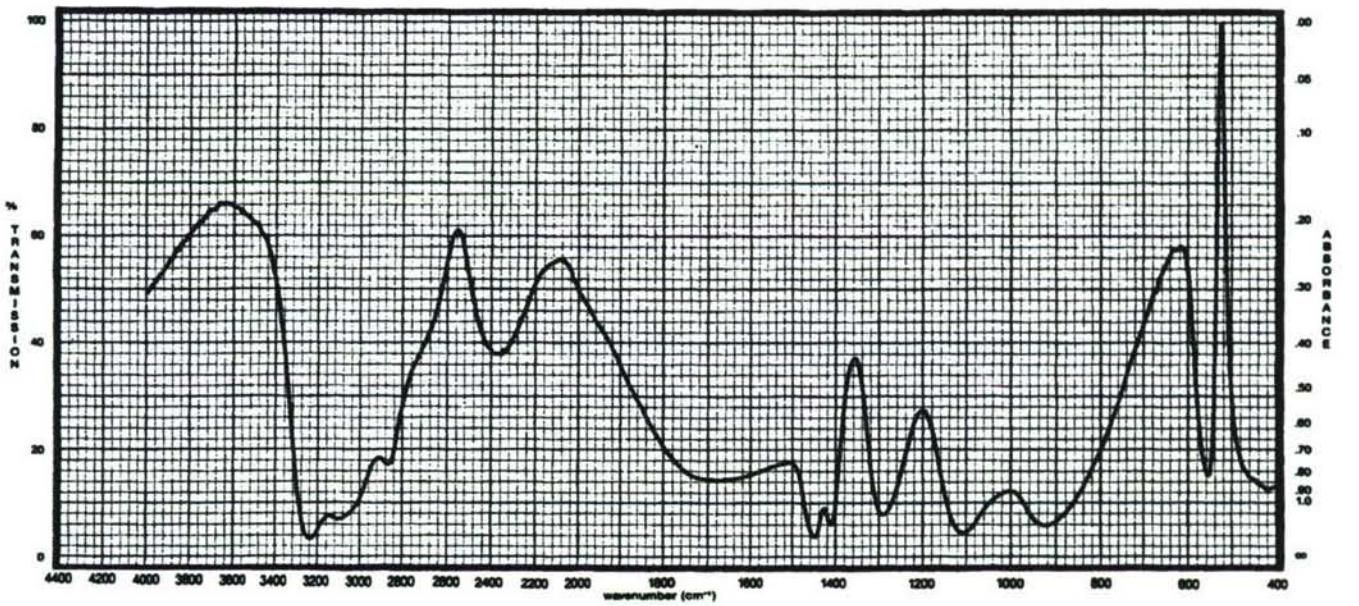


Figure 472 AMMONIUM DIHYDROGEN PHOSPHATE ($NH_4H_2PO_4$), 99.999%, SOLID BETWEEN KBr DISCS (WINDOWS)

3.11.12 Calcium Phosphate, Dibasic, Anhydrous $CaHPO_4$ $HO\text{-}P(O_3)^{-2}\ Ca^{+2}$

The infrared spectrum of anhydrous dibasic calcium phosphate as a solid between KBr discs (windows) is presented as ***Figure 473***. The band assignments are as follows: ca 2800, ca 2390 and 1635 cm^{-1} w,

broad (POH), 1132 and 1068 cm^{-1} s (ν_{as} PO_3^{-2}), 994 cm^{-1} ms (ν_{sy} PO_3^{-2}), 892 cm^{-1} ms (ν P-OH),, 580 and 531 cm^{-1} s (PO_3^{-2}).

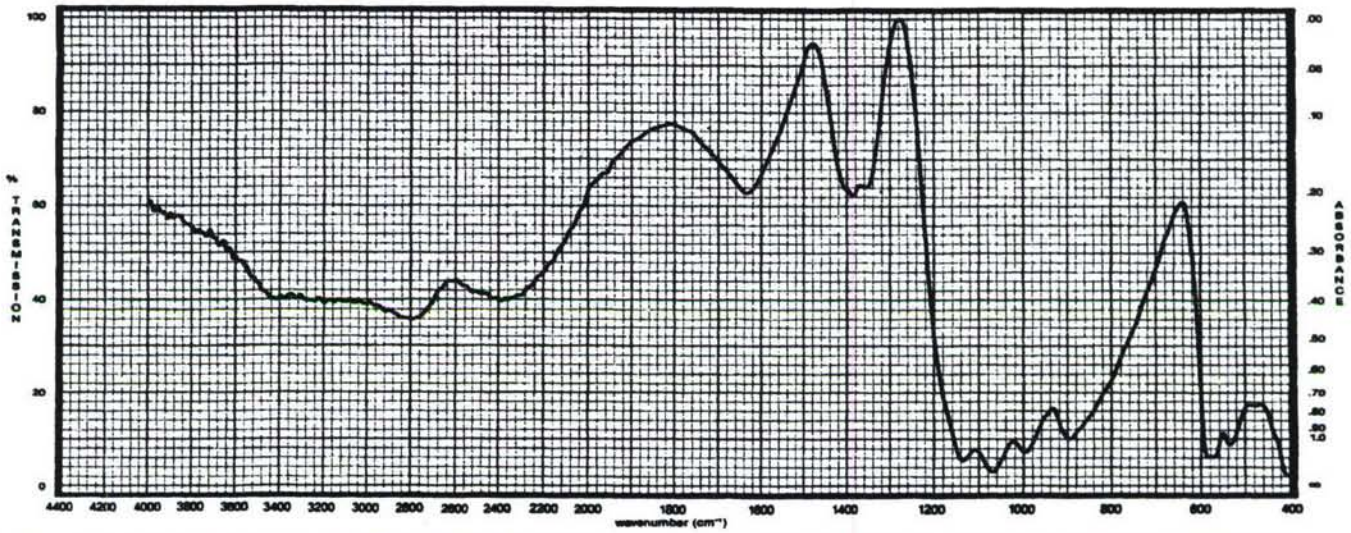


Figure 473 CALCIUM PHOSPHATE, DIBASIC, ANHYDROUS ($CaHPO_4$), SOLID BETWEEN KBr DISCS (WINDOWS)

3.11.13 Sodium Phosphate, Dibasic, Heptahydrate $Na_2HPO_4 \cdot 7H_2O$ $HO\text{-}P(O_3)^{-2}(Na^+)_2 \cdot 7H_2O$

The infrared spectrum of dibasic sodium phosphate heptahydrate is given as ***Figure 474***. The band assignments are as follows: 3443, 3376, 3125, 3088 cm^{-1} ms (H_2O), ca 2850 cm^{-1} sh, ca 2400 cm^{-1} and 1715 cm^{-1} w (POH), 1122 and 1069 cm^{-1} s (ν_{as} PO_3^{-2}), 994 cm^{-1} m and 954 cm^{-1} ms (ν_{sy} PO_3^{-2}), 865 cm^{-1} ms and 822 cm^{-1} (ν P-OH), m 563 and 538 cm^{-1} ms (PO_3^{-2} deformation).

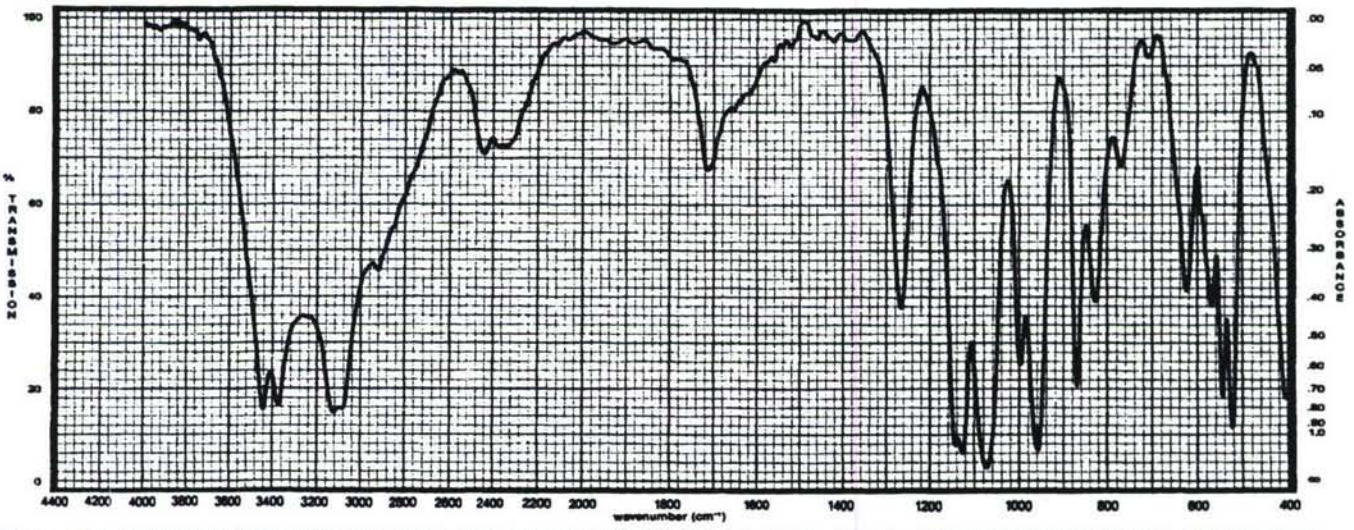


Figure 474 SODIUM PHOSPHATE, DIBASIC, HEPTAHYDRATE ($Na_2HPO_4 \cdot 7H_2O$), SOLID BETWEEN KBr WINDOWS

3.11.14 Potassium Phosphate, Dibasic, Anhydrous K_2HPO_4 $HO\text{-}P(O_3)^{-2}\,(K^+)_2$

The infrared spectrum of anhydrous dibasic potassium phosphate as a solid between KBr discs (windows) is reproduced as ***Figure 475***. The band assignments are as follows: 2917, 2492 and ca 1945 cm^{-1} w, broad (POH), 1123 and 1086 cm^{-1} s ($\nu_{as}\ PO_3^{-2}$), 978 cm^{-1} ms and 951 cm^{-1} sh ($\nu_{sy}\ PO_3^{-2}$), 849 cm^{-1} ms (ν P-OH), 542 cm^{-1} ms and 514 cm^{-1} m (PO_3^{-2} deformation).

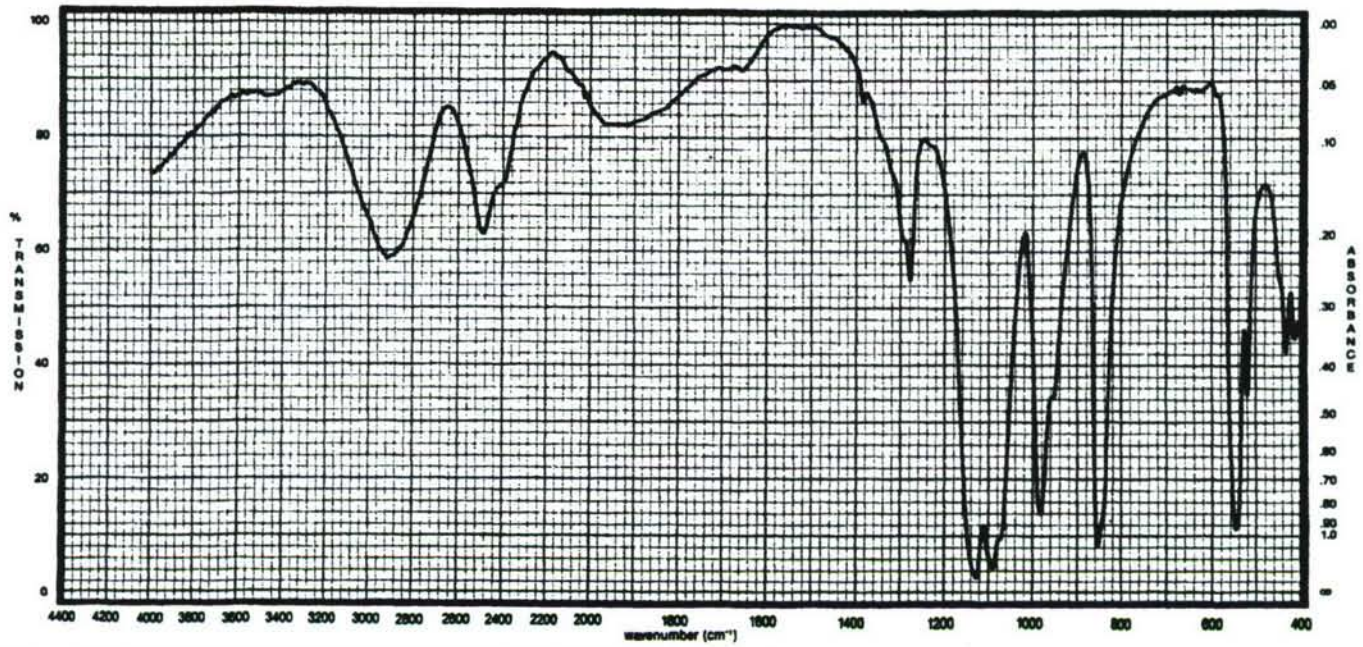


Figure 475 POTASSIUM PHOSPHATE, DIBASIC, ANHYDROUS (K_2HPO_4), SOLID BETWEEN KBr DISCS (WINDOWS)

3.11.15 Sodium Hypophosphite Hydrate $NaH_2PO_2 \cdot xH_2O$ $H_2PO_2^-\,Na^+$

The infrared spectrum of sodium hypophosphite hydrate as a solid between CsI discs (windows) is given in ***Figure 476***. The band assignments are as follows: ca 3320 cm^{-1} w and 1667 cm^{-1} vw (H_2O), 2379 cm^{-1} sh, 2350 cm^{-1} w, 2318 cm^{-1} m and 2280 cm^{-1} vw ($\nu\ PH_2$), 1231 cm^{-1} ms, 1194 cm^{-1} s, 1058 cm^{-1} ms ($\nu_{as}\ PO_2^-$), 1090 cm^{-1} m and 1058 cm^{-1} ms ($\nu\ PO_2^-$), 816 and 808 cm^{-1} ms (PH_2 rocking), 472 cm^{-1} m (PO_2^- deformation).[IIII]

[IIII] In most hypophosphites, at least two, usually sharp, bands occur in the region 2400-2280 cm^{-1}, corresponding to the stretching modes of the PH_2 group. A strong band occurs in the 830-800 cm^{-1} region. This band is often split and is due to PH_2 rocking. Hypophosphites show several strong bands between 1300 and 1000 cm^{-1} assignable to the stretching vibrations of the PO_2^- group. Colthup, N.B., Daly, L.H., and Wiberley, S.E., "Introduction to Infrared and Raman Spectroscopy", p. 311, Sec. Ed., Academic Press, N.Y., 1975.

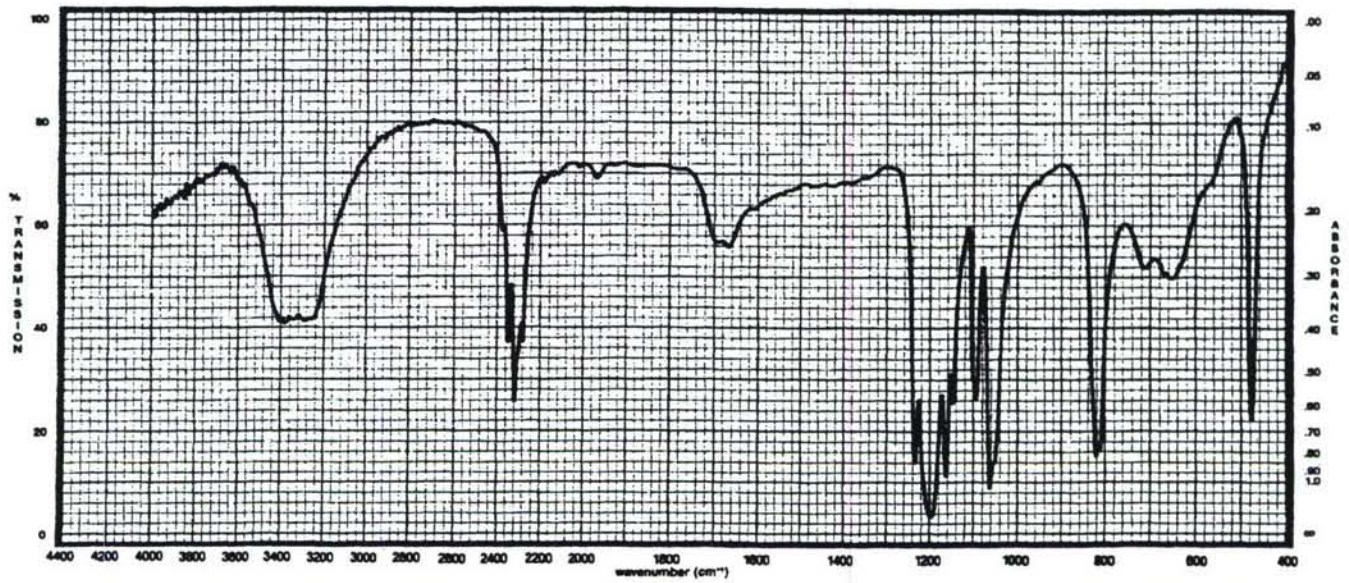


FIGURE 476 SODIUM HYPOPHOSPHITE HYDRATE ($NaH_2PO_2 \cdot xH_2O$), SOLID BETWEEN CsI DISCS (WINDOWS)

4. CONCLUSIONS

Infrared spectra have been determined for various classes of organophosphorus compounds including phosphines, phosphites, phosphonites, phosphinites, phosphoric acid, phosphonic acid, phosphinic acids, phosphine oxides, phosphonic halides, phosphonates, phosphinic halides, phosphinates, phosphates, P-N containing compounds, P=S and P-S containing compounds, P=Se containing compounds, Pyro (P-O-P) compounds and inorganic compounds containing phosphorus.

Infrared spectra were determined over a period of time on the exposure of many of these compounds to atmospheric moisture. The spectra of the resultant compounds were discussed and possible hydrolysis schemes presented. In some cases oxidation followed by hydrolysis was also observed and discussed.

A number of different windows materials, including KBr, NaCl, CsI, CsBr, KRS-5 and CdTe were used to contain the individual compounds for presentation to the infrared spectrometer. KBr would appear to be the window material of choice to 400 cm^{-1}. NaCl has a higher cutoff range (ca 650 cm^{-1}) and thus the presence of such groups as P-Cl, P-Br, P-S would not be able to be ascertained since their characteristic frequencies are below the NaCl cutoff. CsI when exposed to moisture apparently forms cesium sulfate (Cs_2SO_4), as evidenced

by the formation of bands near 1090 and 612 cm^{-1}. Cesium iodide and cesium bromide have transmission limits of 200 and 250 cm^{-1} respectively. KRS-5 (mixture of thallium bromide and thallium iodide) has a transmission limit of about 250 cm^{-1}, but is soft, toxic and more expensive than KBr or NaCl. Cadmium telluride (CdTe) is a dark, brittle and expensive material.

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