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ECBC-TR-246

DETECTION OF CHEMICAL AGENTS AND RELATED COMPOUNDS IN WATER USING ATTENUATED TOTAL REFLECTANCE – FOURIER TRANSFORM INFRARED (ATR-FTIR) TECHNOLOGY

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August 2002

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave Blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	2002 August	Final; May 2002

4. TITLE AND SUBTITLE

Detection of Chemical Agents and Related Compounds in Water Using Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) Technology

5. FUNDING NUMBERS

PR-2E2E-B-G(ER25)

6. AUTHOR(S)

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7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

DIR, ECBC, ATTN: AMSSB-RRT-CF, APG, MD 21010-5424

8. PERFORMING ORGANIZATION REPORT NUMBER

ECBC-TR-246

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

This report documents the performance of the Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) Technology for the detection of various chemical compounds in water. Three classes of compounds were tested, chemical agent simulants, hydrolysis products, and chemical agents. These compounds were tested at varying concentrations to determine the minimum concentration detectable.

14. SUBJECT TERMS

ATR-FTIR	DMMP	HD	GD
Critical angle	PMPA	GA	GF
Evanescent waves	DEAETh	GB	VX
Total internal refraction	CVAOA	MPA	
Diamond sensing element	EA2192	TDG	

15. NUMBER OF PAGES

24

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. Z39-18
298-102

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PREFACE

The work described in this report was authorized under Project No. 2E2E-B-G(ER25). This work was started and completed in May 2002.

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DETECTION OF CHEMICAL AGENTS AND RELATED COMPOUNDS IN WATER USING ATTENUATED TOTAL REFLECTANCE - FOURIER TRANSFORM INFRARED (ATR-FTIR) TECHNOLOGY

1. INTRODUCTION

"Nations have used toxic chemical agents in the past, and we cannot ignore the possibility that they will use them in the future."
Departments of the Army, Navy, and Air Force Field Manual FM 3-9[1]

Use of chemical and biological weapons in warfare is not new. As early as 1000 BC, the Chinese used arsenic smokes. Solon of Athens put hellebore roots in the drinking water of Kirrha in 600 BC. During World War I, the Germans used chlorine, phosgene, and mustard.[2] During the World War II era, the Japanese had a massive biological warfare program that included contamination of over 1000 wells around Harbin with typhoid bacilli in 1939 and 1940. In Nanking, General Ishii Shiro, head of the Japanese biological warfare effort, laced chocolates with the anthrax bacteria and gave the candy to local children. Chinese POWs were fed a special holiday meal of dumplings injected with either typhoid or paratyphoid, then sent home to spread the infection.[3]

Water supplies can become contaminated for a number of reasons, not all of which are intentional. Today's high technological society lends itself to the expectation of the existence of devices capable of identifying toxins in the water supply. Indeed, the military has an initiative in place to produce a hand-held water-monitoring device capable of detecting toxins in concentrations of parts per billion. As part of this initiative, several potential technologies are being evaluated. This report evaluates the base line performance of the Attenuated Total Reflectance - Fourier Transform Infrared (ATR-FTIR) Technology in its ability to detect chemical agents, stimulants, and hydrolysis products.

2. BACKGROUND

The ATR-FTIR is based on the optical principle of total internal reflection. When a beam of light traverses the surface between mediums, it is divided into two components; a refracted ray and a reflected ray as shown in Figure 1 where θ_1 is the angle of incidence (which is equal to the angle of reflection), and θ_2 is the angle of refraction. If the direction of propagation of the wave is from a more dense medium (i.e., glass) to a less dense medium

[1] *Potential Military Chemical/Biological Agents and Compounds*, p 3, Army Field Manual No. 3-9, Navy Publication No. P-467, Air Force Manual No. 355-7; Headquarters, Departments of the Army, Navy, and Air Force; Washington, DC, 12 December 1990.
[2] Sidell, Frederick, R.; Takafuji, Ernest T.; and Franz, David R., Eds., *Medical Aspects of Chemical and Biological Warfare*, pp 11-16, Office of the Surgeon General at TNN Publications, Washington, DC, 1997.
[3] Harris, Sheldon H.; *Factories of Death: Japanese Biological Warfare, 1932-45, and the American Cover-Up*, p 77, Routiledge, New York, NY, 1994.

(i.e., air) and is perpendicular (θ_1=0) to the interface between the mediums, the refracted ray continues in the same direction, and the refracted ray is reflected back 180° as shown in Figure 2a. If the angle of incidence is not zero, the refracted ray is bent away from a normal toward the surface shown in Figure 2b. In the instance of light propagation from a more dense to a less dense medium, the angle of refraction is greater than the angle of incidence ($\theta_2 > \theta_1$). As the angle of incidence increases, so does the angle of refraction (Figures 2b-2d). At some critical angle, corresponding to a refractive angle of 90°, the refractive component of the beam disappears as shown in Figure 2e. This is the point of total reflection. For any angle of incident greater than the critical angle, the entire beam is reflected as shown in Figures 2f-2g.

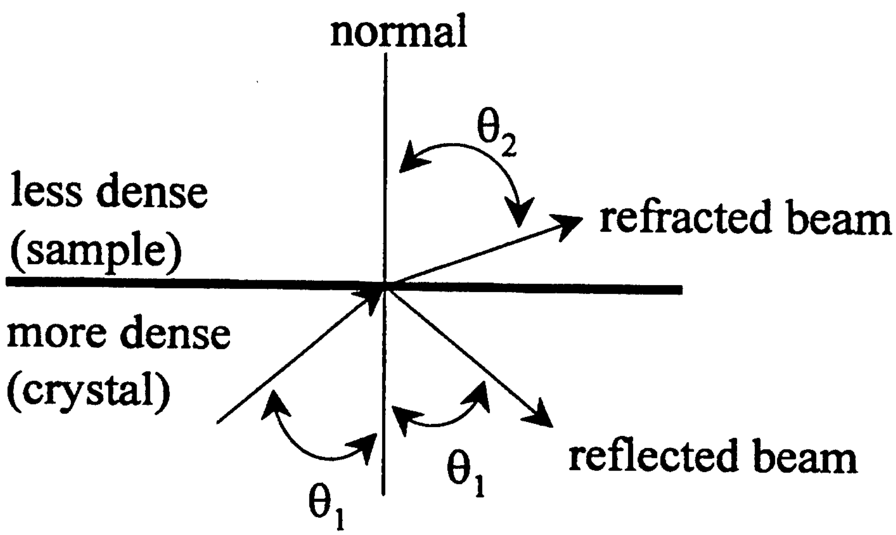


Figure 1. Refraction/Reflection of Beam of Light with Sample

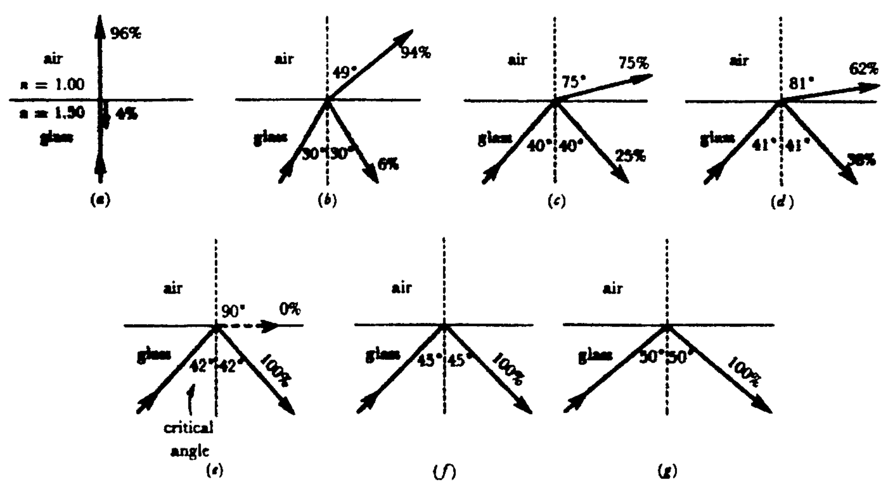


Figure 2.[4] Illustration of Dependence of Angle of Beam

[4]Miller, Franklin, Jr., *College Physics, 3rd ed.,* p 516, Hargrove Brace Jovanovich, Inc., New York, NY, 1972.

As shown in Figure 3, light is an electromagnetic wave. This figure shows that the electric and magnetic fields pulsate about the y and z-axes and propagate in the x direction. While in total internal reflection, the direction of propagation never leaves the first medium, the electric and magnetic fields are transmitted into medium 2, creating an evanescent wave as shown in Figure 4. Evanescent waves decay exponentially as they penetrate into the second medium. Depending on the composition of the material in media 2, certain wavelengths of radiation will be absorbed. The absorbed wavelengths are those required to excite electrons in the media to higher energy levels.

In ATF-FTIR, the material of interest rests on a high refractive index crystal through which a beam of IR radiation is transmitted at an angle of incidence greater than the critical angle of the crystal. The beam is reflected off the crystal/sample interface, through the crystal, to reflect again off the bottom surface of the crystal. This beam bounces back and forth through the crystal as shown in Figure 5 until it exits the crystal and enters a detector. The angle of incidence of the IR beam is a critical parameter. Obviously, the angle of incidence must be either equal to or exceed the critical angle or there is no internal reflection. Secondly, since energy is absorbed at each reflection, the greater the number of reflections in the crystal, the more absorption takes place in the sample, increasing the detection capability. This is especially important for dilute liquid samples. Decreasing the angle of incidence increases the number of reflections. Decreasing the angle of incidence also increases the depth of penetration of the evanescent wave, also increasing absorption in the sample. The optimum system will have a high index of refraction crystal; the higher the index of refraction, the smaller the critical angle. Smaller critical angles allow lower angles of incidence, thus increasing the number of reflections in the crystal.

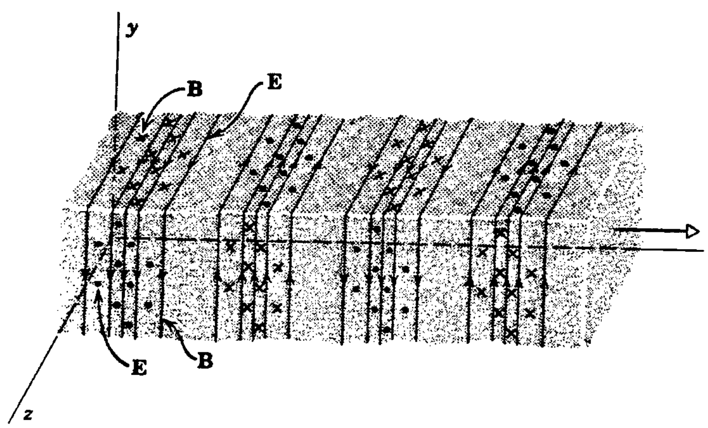


Figure 3.[5] Light as Electromagnetic Wave

[5]Halliday, David, and Resnick, Robert, *Physics: Parts I and II, 2nd ed.*, p 982, John Wiley and Sons, New York, NY, 1966.

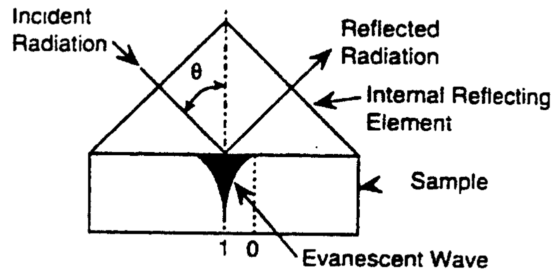


Figure 4.[6] Illustration of Evanescent Wave

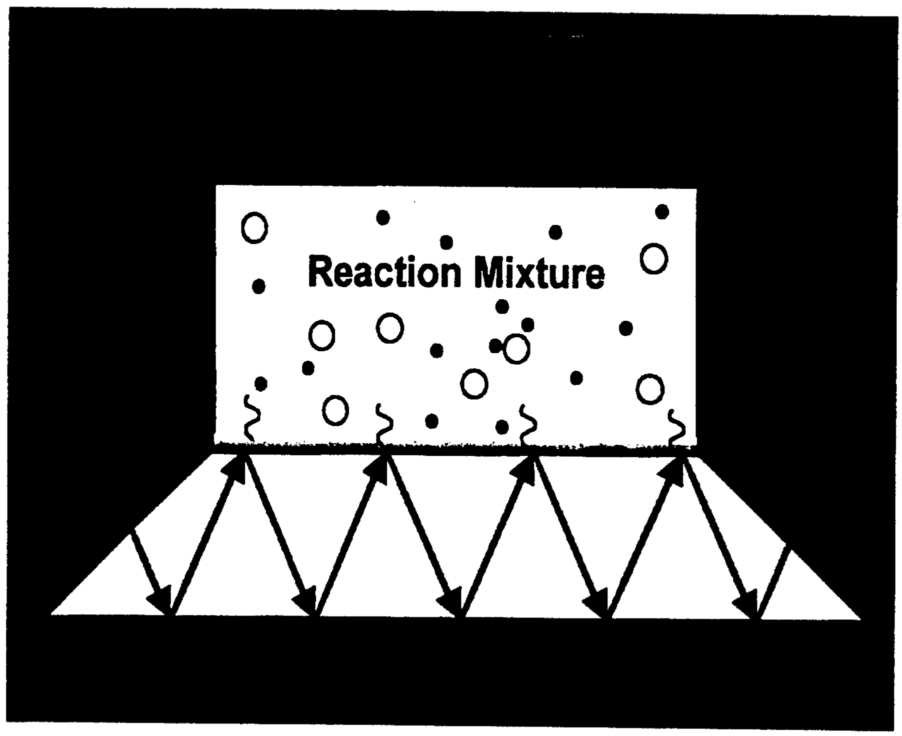


Figure 5. Reaction Mixture

3. INSTRUMENTATION

The system in this study was a ReactIR™ 4000 FTIR by Applied Systems Incorporated (ASI) - a Mettler-Toledo Company (Columbus, OH), using a DuraDisk with a DiComp™ diamond sensing element. A Mercury Cadmium Telluride (MCT) detector was used. ReactIR™ version 2.21 software was used to collect and analyze the data. Figure 6 shows the basic setup.

[6]Taken from Spectra-Tech marketing literature.

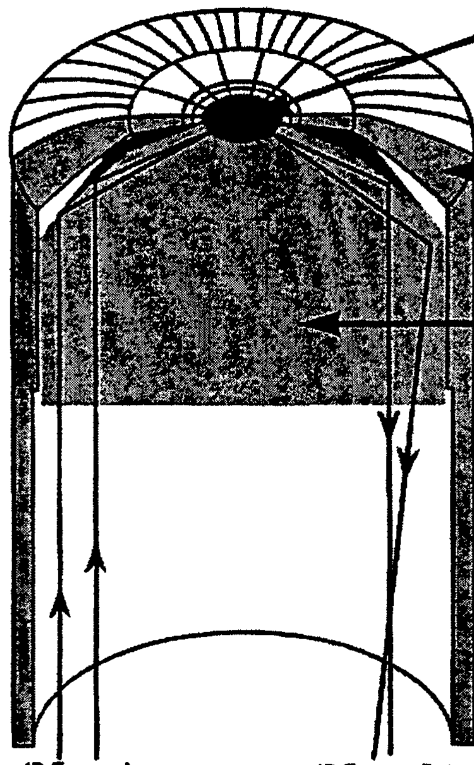


Figure 6. DuraDisk and Energy Pathway

The diamond sensing element sits on a ZnSe support element, all of which is enclosed by a hastelloy housing. Using a pipette, investigators placed the samples, consisting of various concentrations of chemical compounds, on the diamond sensing element. For consistency, eight drops of each sample were used. The IR beam channeled in through the bottom of the DuraDisk is reflected through the diamond crystal where the sample absorbs certain wavelengths of energy, then exits to the detector (Figure 6).

For convenience, absorption is discussed in terms of wave numbers as opposed to either wavelengths or frequencies where the wave number, k, is defined as

$$k = 2\pi/\lambda \tag{1}$$

and λ is the wavelength in centimeters of the absorbed radiation. The ReactIR™ 4000 measures absorptions in the $4000>k>650$ cm^{-1} range and can display any section of wave numbers in that range. Figures 7-9 show representative spectra of absorbance versus wave number for the compounds dimethyl methylphosphonate (DMMP), diethylamino ethylthiol (DEAETh), and dimethylphosphoroamidocyanidate (agent GA). The software labels the wavelength of each peak.

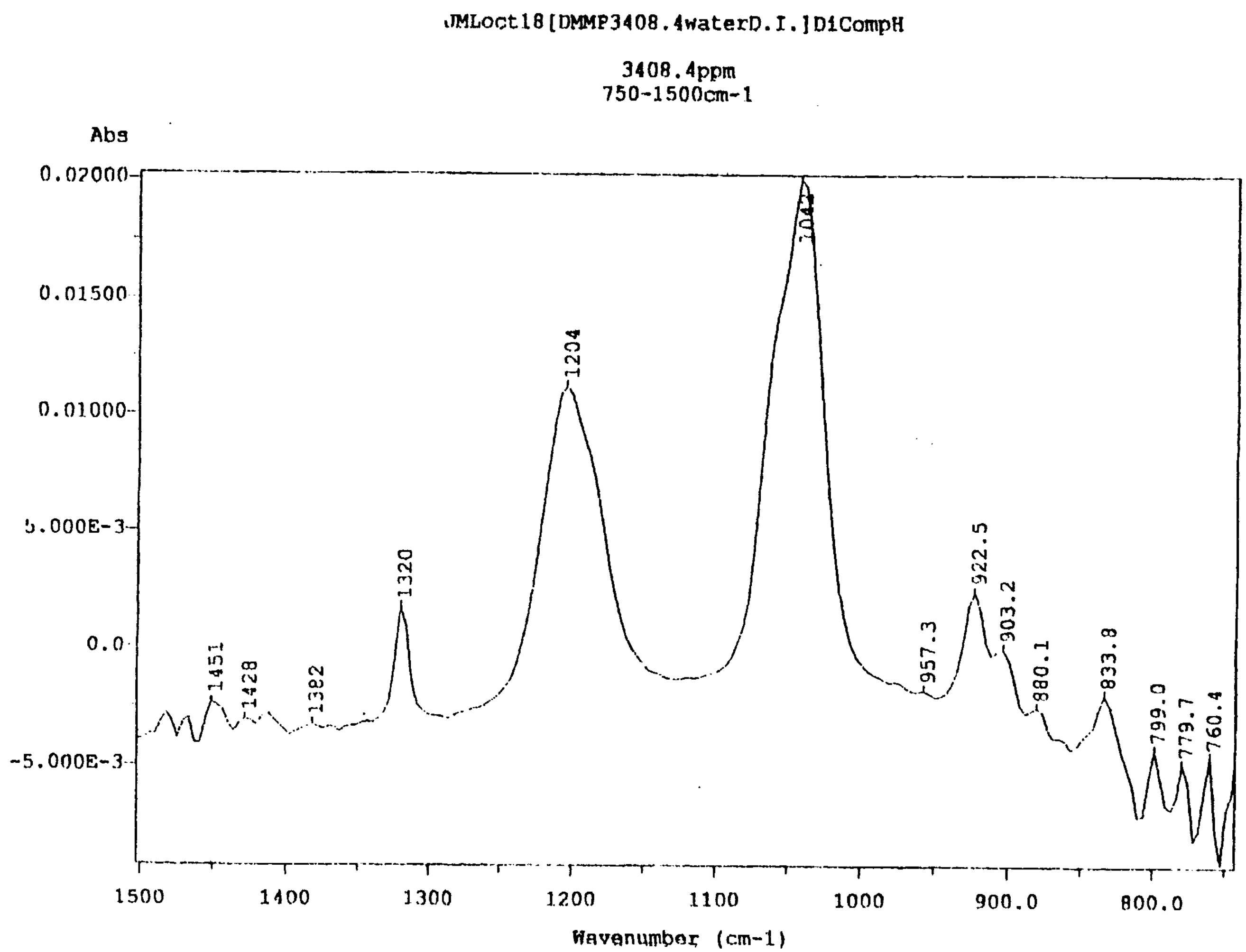


Figure 7. ATR Spectra of 3408 ppm of DMMP in Water - ReactIR™ 4000

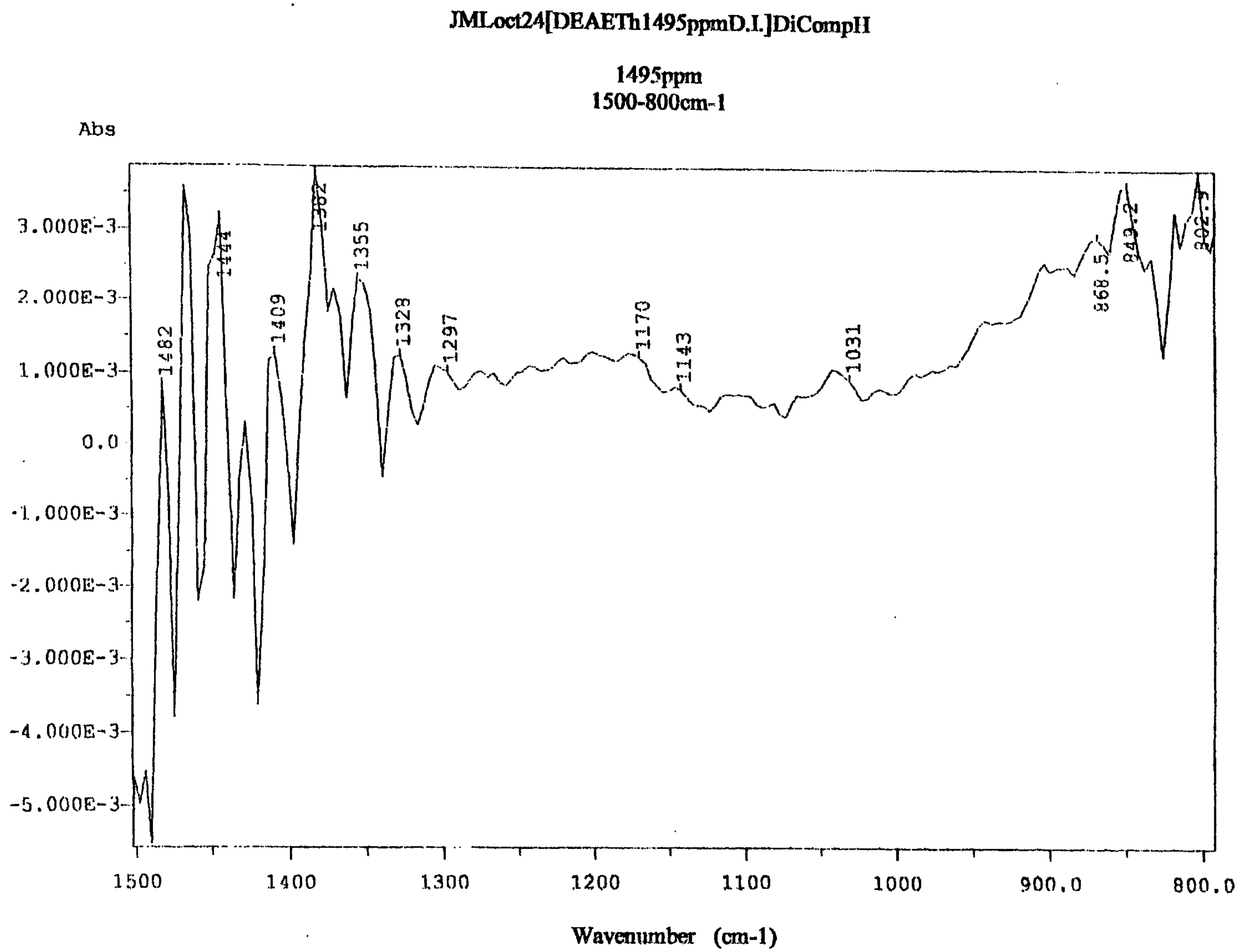


Figure 8. ATR Spectra of 1495 ppm of DEAETh in Water - ReactIR™ 4000

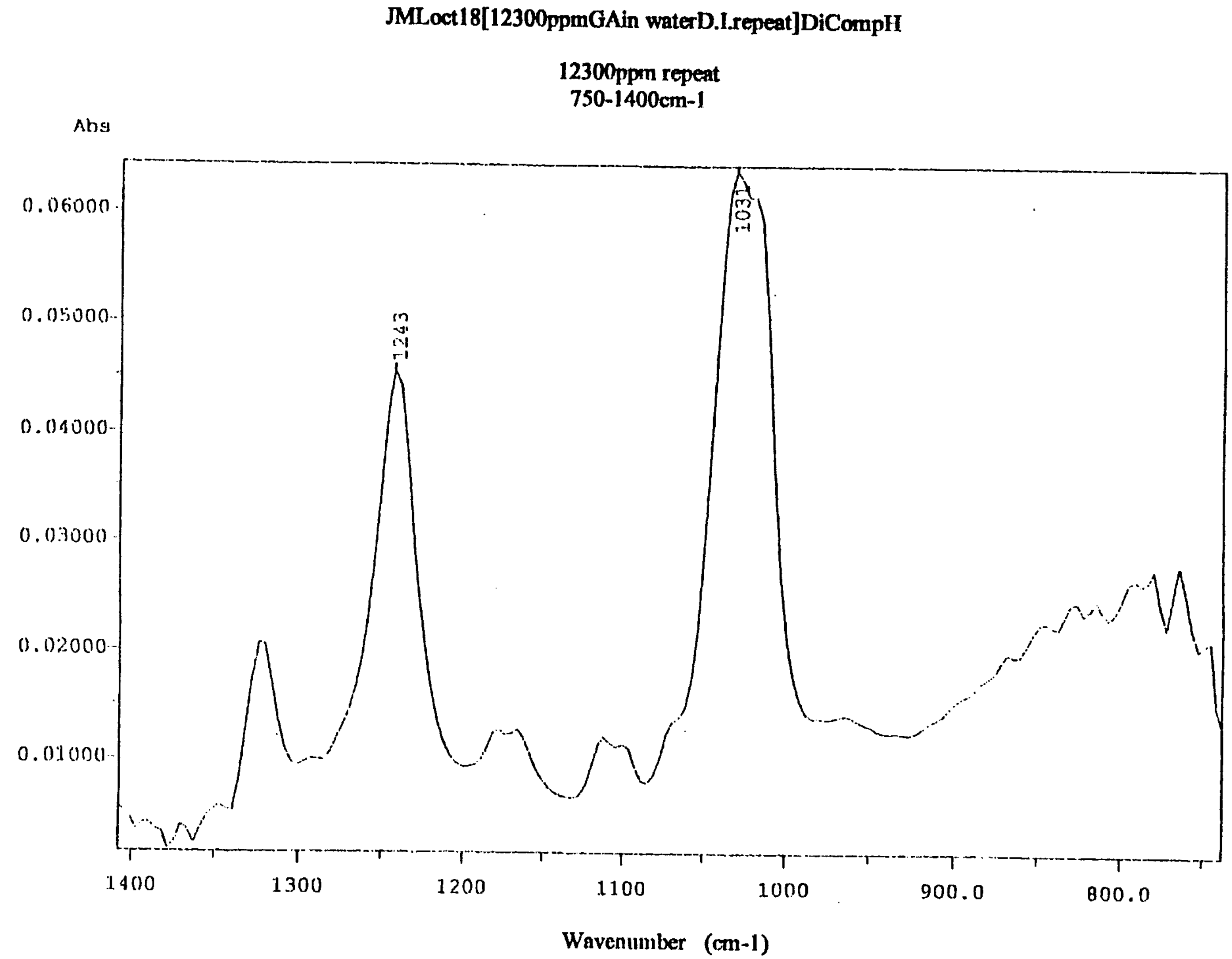
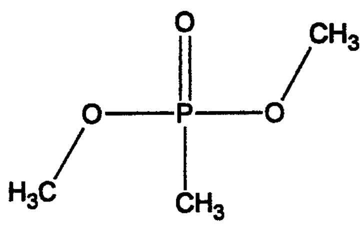


Figure 9. ATR Spectra of 12300 ppm of GA in Water - ReactIR™ 4000

4. CHEMICALS

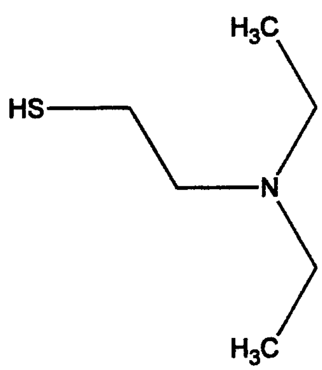
The three classes of chemical compounds tested were: chemical agent simulants, hydrolysis products, and chemical agents. Below, for each class of compounds, is a list of the compound used, along with its symbol, structure, and CAS number. The chemical agent, T, (bis[2(2-chloroethylthio)ethyl]ether) was not tested because of its insolubility in water. The simulant DEAETh was synthesized in the laboratory. Therefore, it has no CAS number.

4.1 Chemical Agent Simulants.



DMMP
Dimethyl methylphosphonate

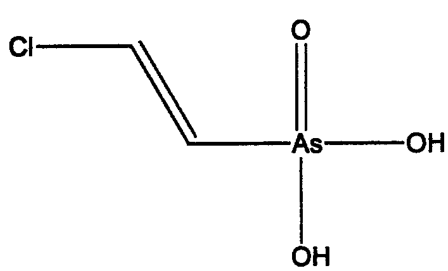
CAS # 756-79-6



DEAETh
Diethylamino ethylthiol

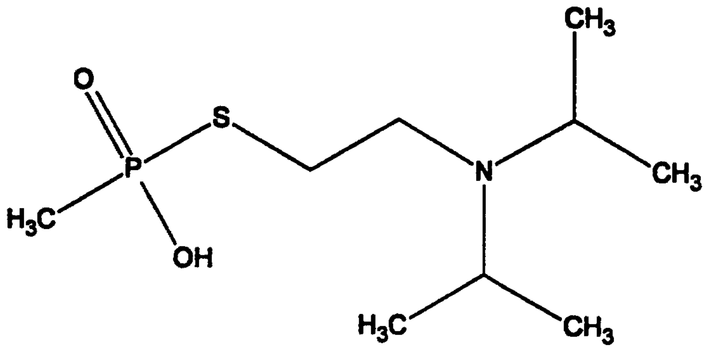
CAS # NONE

4.2 Hydrolysis Products.

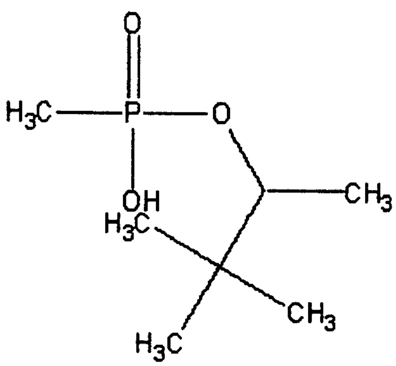


CVAOA
2-Chlorovinylarsonic acid

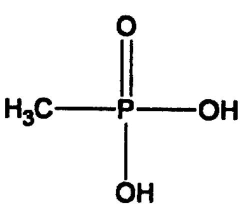
CAS # 64038-44-4



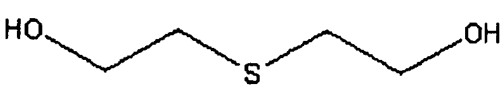
EA2192 (Note: This is a hydrolysis product of VX) CAS # 73207-98-4
S-2(diisopropylaminoethyl)methylphosphonic acid



PMPA CAS # 616-52-4
Pinacolyl methylphosphonic acid

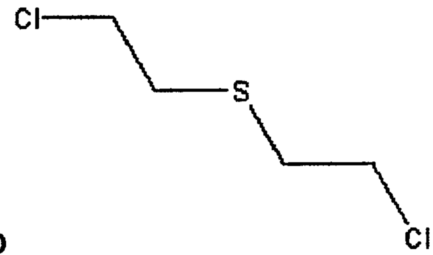


MPA CAS # 993-13-5
Methyl phosphonic acid



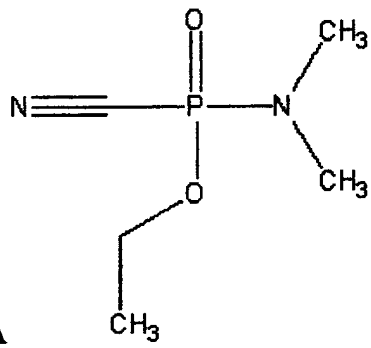
TDG CAS # 111-48-8
Thiodiglycol

4.3 Chemical Agents.



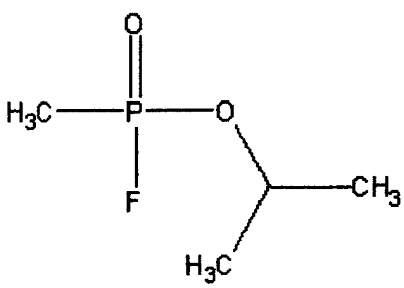
HD
Bis-(2-chloroethyl) sulfide

CAS # 505-60-2



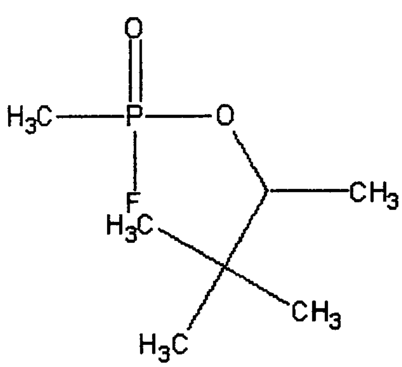
GA
Ethyl N,N-dimethylphosphoroamidocyanidate

CAS # 77-81-6



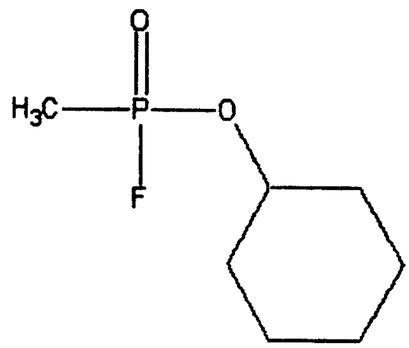
GB
Isopropyl methylphosphonofluoridate

CAS # 107-44-8

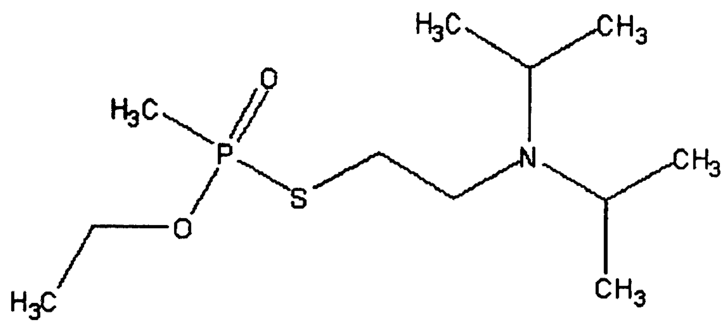


GD
Pinacolyl methyl phosphonofluoridate

CAS # 96-64-0



GF CAS # 329-99-7
Cyclohexyl methylphosphonofluoridate



VX CAS # 50782-69-9
O-ethyl-S-(2-diisopropylaminoethyl)methyl phosphonothiolate

5. RESULTS

5.1 Uncoated Diamond Sensing Element.

Several concentrations of each compound were run on a DuraDisk uncoated diamond sensing element and recorded in data files similar to those represented in Figures 7-9. The peak height for the absorption peaks was measured. For each prominent peak that appeared consistently for all concentrations of a given compound, a graph was made of peak height versus concentration expressed in parts per million (ppm). Figures 10-11 show summary charts for the chemical simulant compounds. Figures 12-16 show the agent hydrolysis compounds, and Figures 17-21 show the results for chemical agents. HD is barely soluble (<1%) in water. Data was not obtainable for a concentration of 1000 ppm. The minimum detectable concentrations for each compound are given in Table 1.

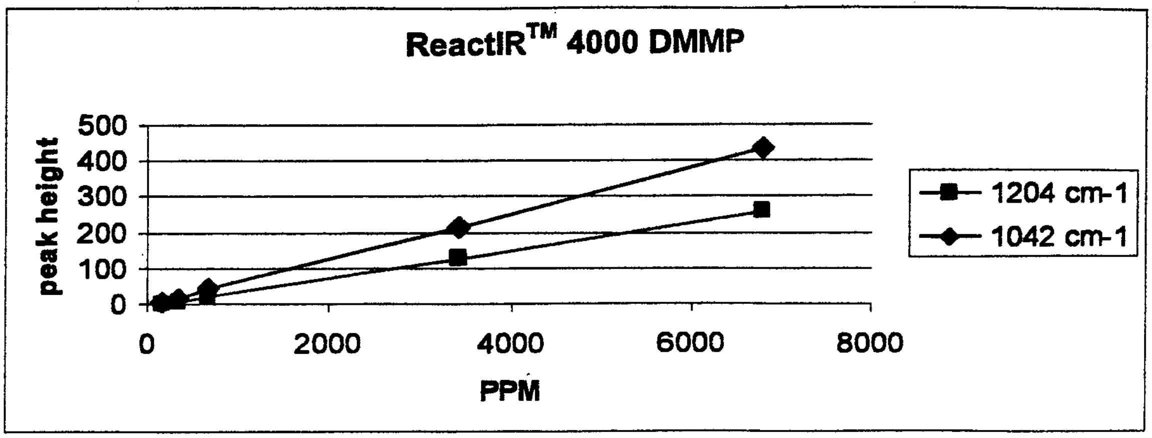


Figure 10. ReactIR™ 4000 DMMP

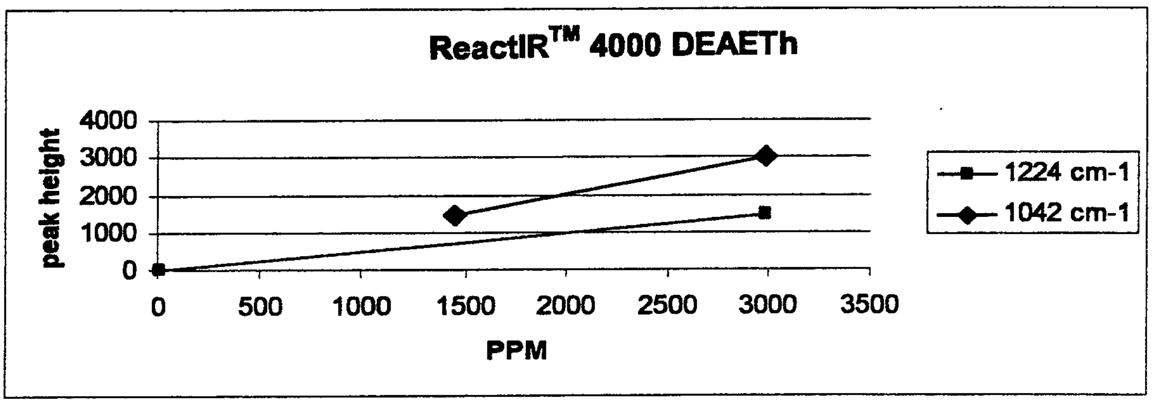


Figure 11. ReactIR™ 4000 DEAETh

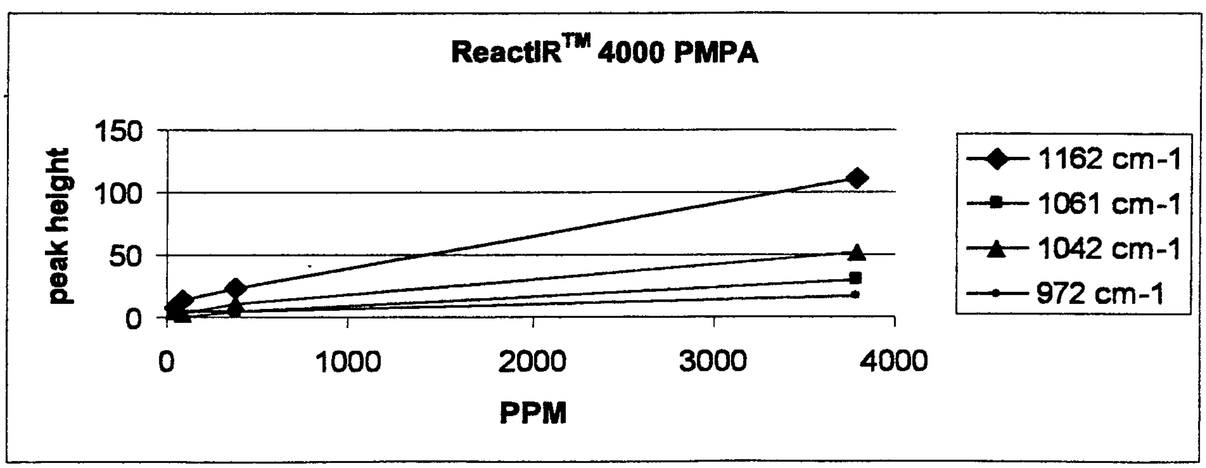


Figure 12. ReactIR™ 4000 PMPA

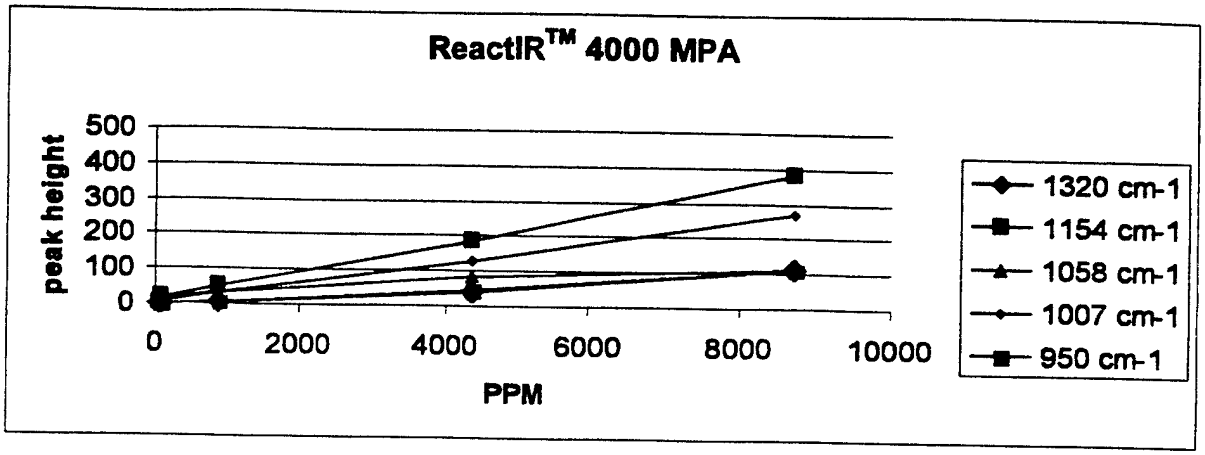


Figure 13. ReactIR™ 4000 MPA

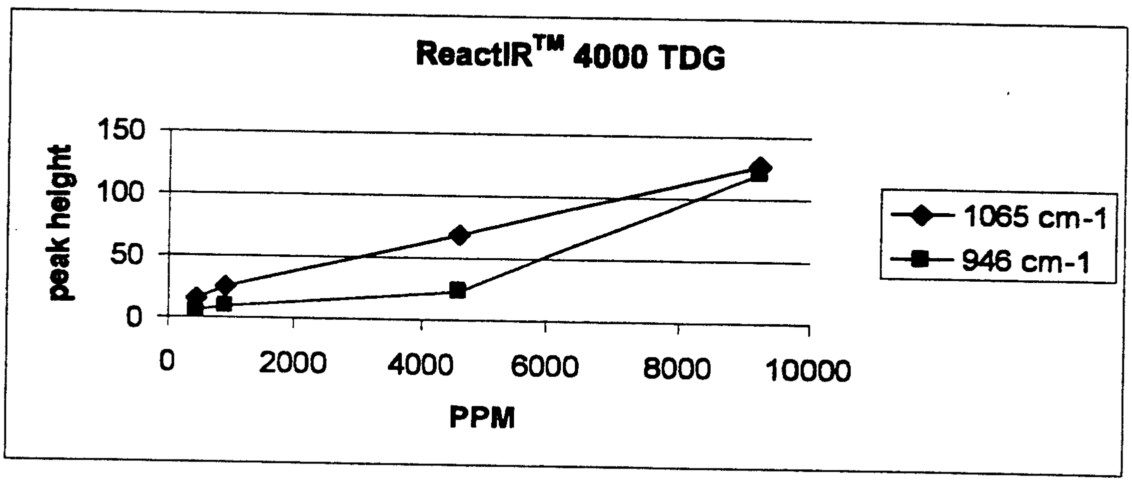


Figure 14. ReactIR™ 4000 TDG

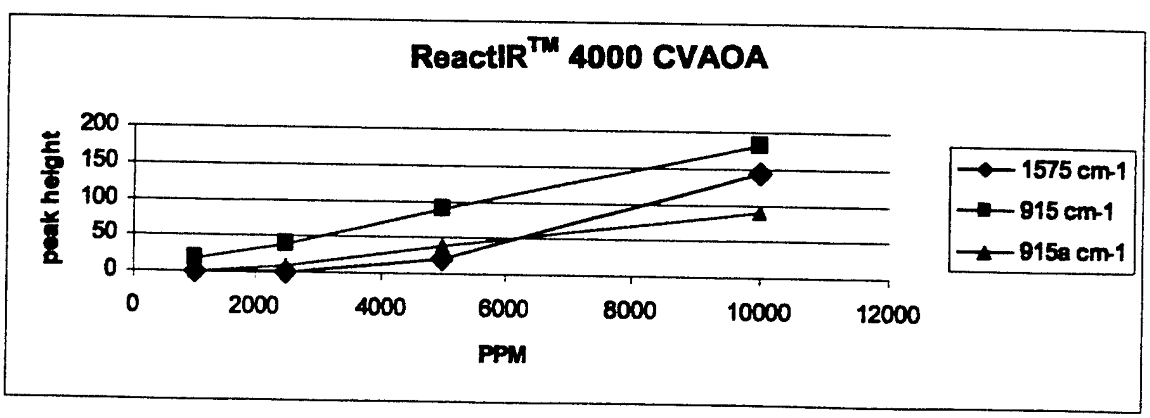


Figure 15. ReactIR™ 4000 CVAOA

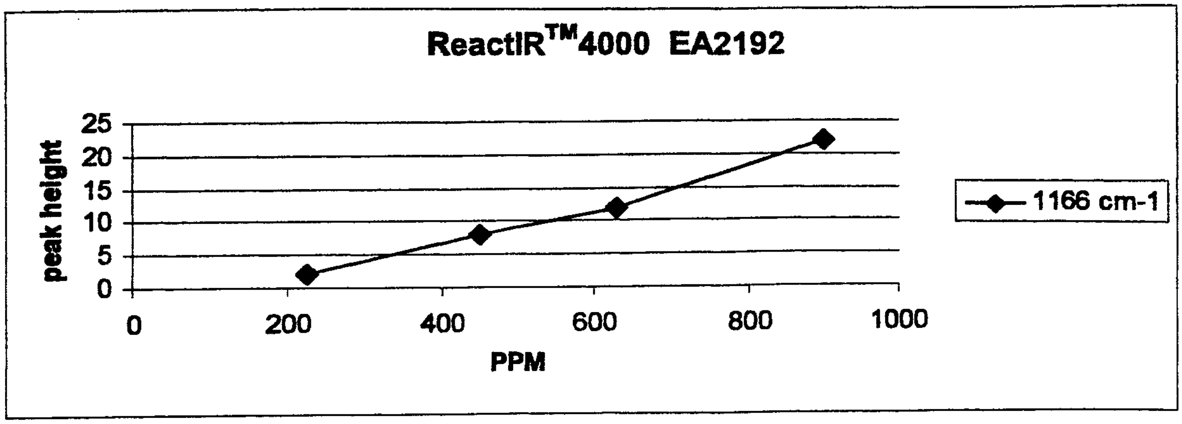


Figure 16. ReactIR™4000 EA2192

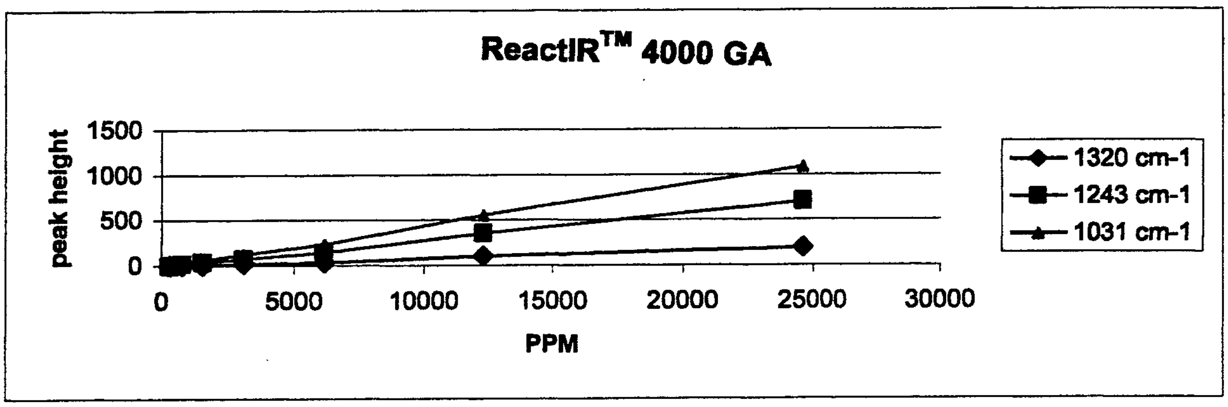


Figure 17. ReactIR™4000 GA

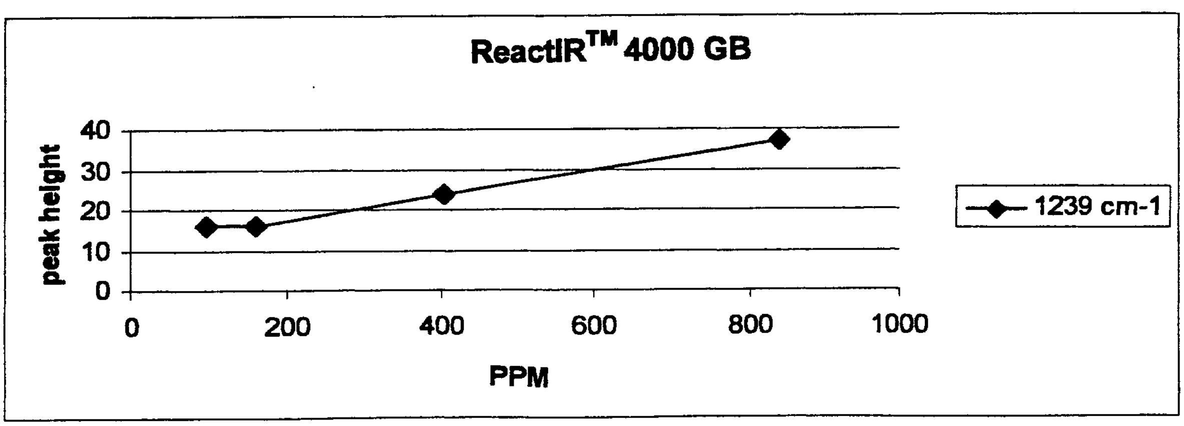


Figure 18. ReactIR™4000 GB

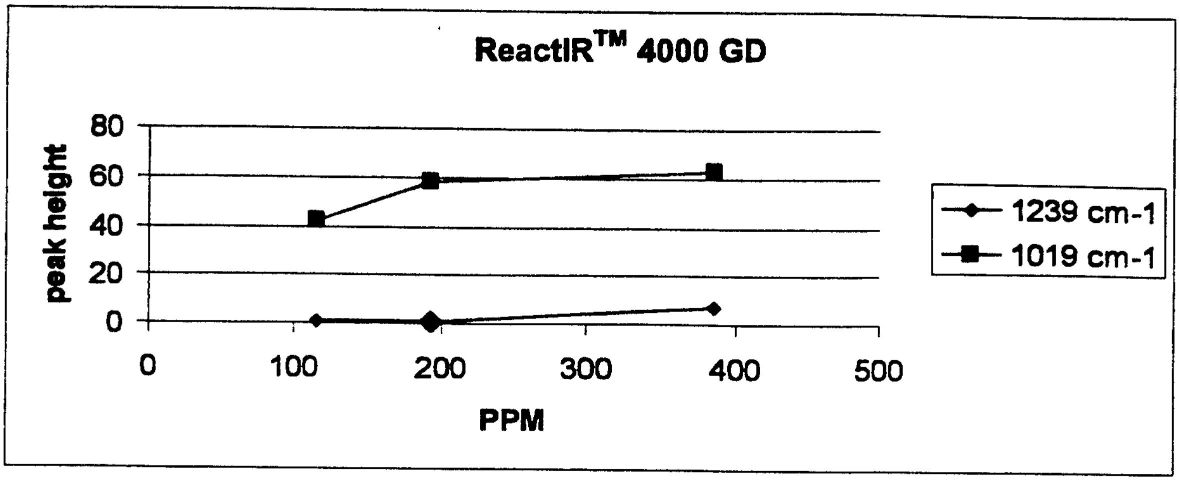


Figure 19. ReactIR™ 4000 GD

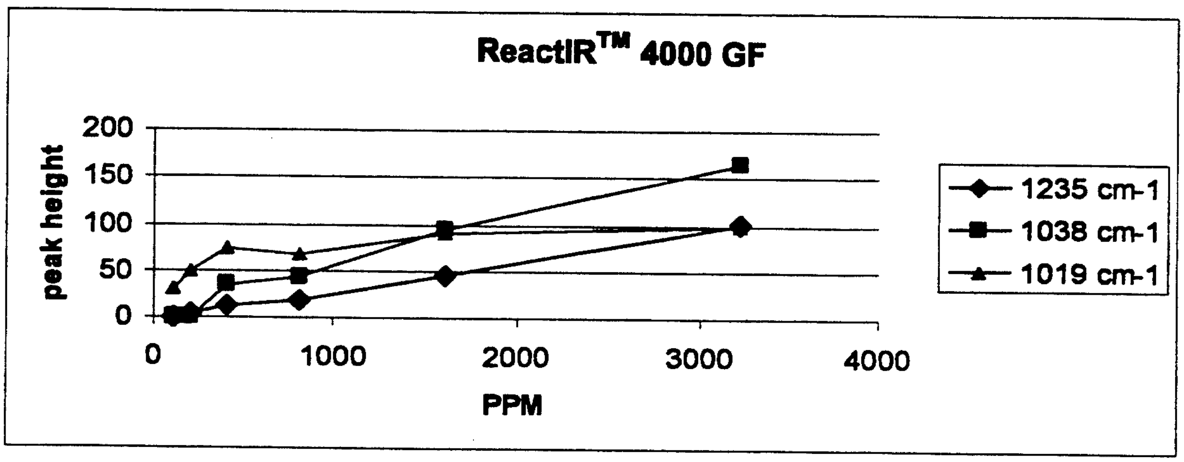


Figure 20. ReactIR™ 4000 GF

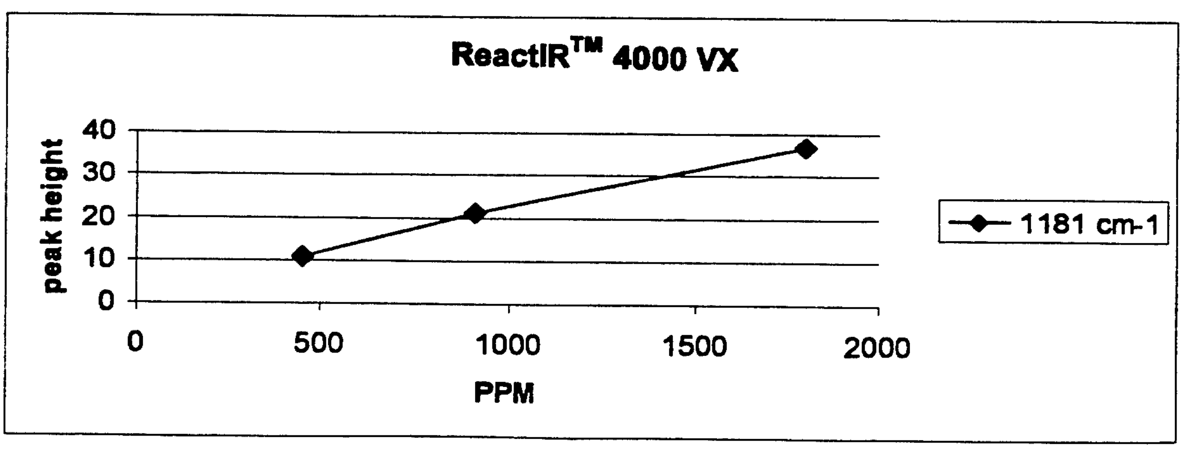


Figure 21. ReactIR™ 4000 VX

Table 1. Uncoated Diamond Sensing Element

Compound Tested	Lowest Limit of Detection (ppm)
Chemical Simulants	
DMMP	170.4
DEAETh	1450
Hydrolysis Products	
PMPA	48
MPA	43
TDG	461.5
CVAOA	2000
EA2192	225
Chemical Agents	
GA	307
GB	201
GD	100
GF	150
VX	454
HD	1000

5.2 Coated Diamond Sensing Elements.

Work is currently underway to coat the crystal of the diamond sensing element with a ferrocene type coating to improve its detection capability. The objective of the coating is to draw the chemical compound out of solution to the area of the diamond sensing element where it will make better physical contact with the element. Doing this should put the element in range of the evanescent component of the IR beam through either a ligand or anion exchange between the analyte in the dilute chemical solution and either an anion or ligand in the coating. Table 2 summarizes the work to date on diamond sensing elements with crystals coated with $DEC^{+}NO_3^{-}$ (1,1',3,3,-tetrakis(2-methyl-2-nonyl)ferrocenium nitrate), a polyalkylated ferrocenium salt.

Table 2. Coated (DEC+NO_3-) Diamond Sensing Element

Compound Tested	Lowest Limit of Detection (ppm)
Chemical Simulants	
PMPA	30
MPA	13
EA2192	110
Chemical Agents	
GB	77

6. SUMMARY

To date, off the shelf, unmodified Attenuated Total Reflectance - Fourier Transform Infrared Technology has been successfully used to detect chemical agent and hydrolysis products in solutions as dilute as 100s ppm. Preliminary studies using DEC+NO_3-coating on the crystal of the diamond sensing element has cut the lower detection limit in half for some compounds. With additional work, we believe a coating that will reduce the lower limit of detection down to the parts per billion range can be developed.

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