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PRODUCTION AND IDENTIFICATION
OF
HELIUM DIFLUORIDE

Final Summary Report
to
Office of Naval Research

ARPA Order 615
Program Code 5910

AN-1530

October 1966



AEROJET-GENERAL NUCLEONICS
SAN RAMON, CALIFORNIA

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PRODUCTION AND IDENTIFICATION OF HELIUM DIFLUORIDE

Final Summary Report

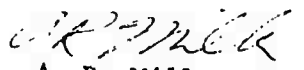
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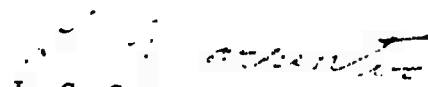
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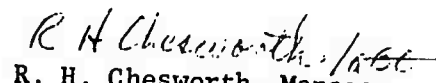
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Program Code 5910


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PRODUCTION AND IDENTIFICATION OF
HELIUM DIFLUORIDE: FINAL REPORT*

SYNOPSIS

An 18-month program to produce and identify the helium difluoride molecule is summarized in this final report. Nine tritiated samples were produced during the program; new IR absorption peaks found in two samples suggest that tritium decay is producing observable changes. It appears too soon to assign these new peaks to helium-compound formation. Experiments during the program indicated it is possible to detect helium-containing compounds in samples containing as little as one-half curie of tritium. This work was performed under Contract Nonr-4795(00), ARPA Order 615, Program Code 5910, with the Office of Naval Research.

The beta decay of tritium in a bifluoride-containing specimen was followed by infrared spectrophotometry for evidence of the conversion of $F-T-F^-$ ions into $F-He-F$ molecules. Difficulties in producing suitable samples consumed so much time that the period available for observation proved too brief to support any valid conclusions; however, AGN will continue observations of the samples under a company-funded program.

The first phase of the program was initially divided into the study of the growth of suitable single crystals and the production of composite pressed disks. Both $NaHF_2$ and KHF_2 were originally considered, but $NaHF_2$ was chosen because water-free NaF , the starting material, can be readily obtained. On the other hand, water-free KF is not commercially available and is difficult to handle without moisture pick-up from the atmosphere.

It was experimentally determined that the optimum method of producing samples was to mix a small amount of polycrystalline $NaHF_2$ with KBr , and cold-press the mixture into transparent pellets. The nine tritiated samples produced under this contract were fully encased to prevent the escape of radioactive material.

It is expected that definitive results will be obtained in six to eight months.

*Published by Aerojet-General Nucleonics

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PRODUCTION AND IDENTIFICATION OF HELIUM DIFLUORIDE:
FINAL REPORT

I. INTRODUCTION

The purpose of this program was to produce and identify the helium difluoride molecule; this final report summarizes activities of Aerojet-General Nucleonics under Contract Nonr-4795(00) with the Office of Naval Research from 1 December 1964 through 31 August 1966.

The beta decay of tritium in a bifluoride-containing specimen was followed by infrared spectrophotometry for evidence of the conversion of $F-T-F^-$ ions into $F-He-F$ molecules. New peaks found in two of the tritiated samples produced during this program suggest that tritium decay is producing observable changes. Difficulties in producing suitable samples consumed so much time that the period available for observation proved too brief to support any valid conclusions; however, AGN will continue observations of the samples under a company-funded program.

The original goal of this program was to fabricate an IR-transparent sample capable of producing a detectable quantity of HeF_2 in several months. The program was based on an article by Pimentel and Spratley, and one by Pimentel, Spratley and Miller. Pimentel and Spratley (Ref. 1) suggested that the helium difluoride molecule might prove to be stable and they defined expected infrared absorption frequencies by analogy with the isoelectronic HF_2^- ion and xenon-fluorine compounds.

Pimentel, Spratley and Miller (Ref. 2) suggested that the beta decay of a tritium atom, held in an appropriate solid lattice, should provide ideal conditions for the formation of HeF_2 . The lattice used in this study contained sodium bifluoride, a material having distinct $F-H-F^-$ ions in which the hydrogen atom is strongly held between the two fluorine atoms. The recoil energy of tritium is so low (an average of 24 kcal/mole) relative to the H-F bond

strength (100 kcal/mole) that the ^3He daughter should not be displaced from the position of the parent ^3H atom. Tritium decay in the TF_2^- ion, then, should convert it to HeF_2 .

The beta particle ejected during decay was not expected to interfere with the IR spectrum since it should come to rest far enough from the parent to eliminate interaction with any helium-fluorine molecule that might form. Furthermore, the ionic bifluoride lattice consists of alternating regions of plus and minus charges which should not be greatly affected by the presence of an additional electron. Regardless of that, it is possible for the beta particle to become trapped in the lattice, forming a defect, such as an F center, that interferes with light. Fortunately, electron defects generally are active in the visible and ultraviolet region (Ref. 3) and so should not appear in the IR spectrum.

The program as scoped fell into two phases: the production of an appropriate solid lattice containing a tritium atom; and observation of beta decay for formation of HeF_2 . It was originally thought that it would be necessary to incorporate 25 curies of tritium into the sample (sufficient to produce ten micromoles of helium in 76 days) if the lower limit of detectability was one micromole as suggested by Pimentel. Experiments performed during this program indicated that much smaller quantities can be detected, however, so that it is possible to detect helium-containing compounds in samples containing as little as one-half curie of tritium.

A tritiated NaHF_2 lattice, observed with an IR spectrophotometer over a period of several months, was expected to show new absorption peaks growing at a rate corresponding to the decay of tritium. The new peak will grow at a linear rate of 0.1% per week for the first few months; the rate is linear because the time from synthesis is much less than the half-life of tritium.

The infrared-active absorption frequencies expected for TF_2^- and $^3\text{HeF}_2$, calculated from the data of Pimentel and Spratley (Ref. 1), on the basis of the measured peaks for $^1\text{HF}_2^-$ are shown in Table 1.

Table 1

THE VIBRATIONAL POTENTIAL FUNCTION AND INFRARED-ACTIVE
FREQUENCIES OF ${}^1\text{HF}_2^-$ (EXPERIMENT), AND TF_2^- AND ${}^3\text{HeF}_2^-$ (PREDICTED)

	Bond Length $\text{\AA}$	Force Constant*			Frequency, cm^{-1}	
		f_r	f_{rr}	f_α	ν_2	ν_3
${}^1\text{HF}_2^-$	1.13	2.31	1.72	0.28	1230	1425
TF_2^-	1.13	2.31	1.72	0.28	730	846
${}^3\text{HeF}_2^-$	1.08	3.47	0.35	0.28	763	1942

* f_r is the bond-stretching force constant (in millidynes/ $\text{\AA}$); f_{rr} is the bond-stretching interaction force constant (in millidynes/ $\text{\AA}$); f_α is the angle bending force constant (in millidyne- $\text{\AA}$ /radian).

ν_2 is the asymmetric-stretching frequency; ν_3 is the bending frequency.

The IR beam in the Perkin Elmer Model 21 is 3 by 10 mm, consequently the sample dimensions along the beam path, necessary to incorporate 25 curies of tritium, was set by the concentration of tritium. For example, a fully tritiated NaHF_2 sample must be 0.85 mm in the beam direction; a sample containing 1% fully tritiated NaHF_2 in an alkali halide diluent must be 85 mm long. The advantage of a short, fully tritiated NaHF_2 lattice is offset by the difficulty of producing a single crystal, polycrystalline NaHF_2 scatters too much of the IR. On the other hand, a small concentration of NaHF_2 dispersed in an alkali halide matrix requires a rather long sample that absorbs too much of the IR beam. A third technique, suspension of the tritiated material in a liquid, was found to be unsuitable after a brief investigation. The first phase of the program therefore was initially divided into the study of the growth of suitable single crystals and the production of composite pressed disks. The major part of this program was consumed in developing techniques for producing an acceptable sample.

Both NaHF_2 and KHF_2 were originally considered, but NaHF_2 was chosen because water-free NaF , the starting material, can be readily obtained. On the other hand, water-free KF is not commercially available (although it could have been made from the elements if necessary) and is difficult to handle without moisture pick-up from the atmosphere.

Although the IR spectrum of NaHF_2 single crystals apparently has not been published, it was expected to resemble the spectrum of KHF_2 (Ref. 4) since the F-H-F distance is the same for both lattices (Ref. 5), and it is the IR absorption of the F-H-F^- ion that was of interest to this program. The F-D-F distance is the same as the F-H-F distance (Ref. 6) suggesting that the F-T-F distance is also the same. In addition, the IR spectra for pressed halide disks containing NaHF_2 and KHF_2 are identical (Ref. 7).

On the other hand, NaHF_2 has a different primitive unit cell than KHF_2 (Ref. 8) and the IR spectra of the two bifluorides in mixed crystals of KBr shown an additional peak for NaHF_2 (Ref. 7). The spectra are also different (Ref. 7) in a Nujol mull. Consequently, several experiments were performed to obtain the IR spectra of NaHF_2 in a perfluorokerosene mull and in a composite KBr pressed disk.

II. REVIEW OF RESULTS

Nine tritiated samples containing quantities of tritium sufficient to indicate the formation of helium-compounds were produced under this contract. The samples were fully encased to prevent the escape of radioactive material, and thus can be safely handled or stored. Two of the samples (Pellet 5 and Pellet 8) will be stored in a dry ice chest to minimize possible decomposition of newly formed helium compounds.

Over the next 6 to 8 months, IR spectra will be obtained from these samples in a continuing effort to discern a helium compound. The examinations will be performed without additional cost to ONR; any encouraging results will be reported through the channels established for this contract.

A. SUMMARY

The program as originally scoped fell into two logical phases: the production of the tritiated samples, and observation of these samples over several months to detect the formation of helium-containing compounds. After familiarization studies and screening tests, it was experimentally determined that the optimum method of producing samples was to mix a small amount of polycrystalline NaHF_2 with KBr , and cold-press the mixture into transparent pellets. The optimum conditions for fabricating rectangular tritiated pellets were found to include:

- Use 1% tritiated NaHF_2
- Mix the NaHF_2 with the KBr for 5 minutes (when using less than 0.5g of material) in a mechanical mixer/grinder (Wig-L-Bug)

- Evacuate the die for 5 minutes
- Apply pressure in the range between 9.7 and 13×10^4 psi

It was originally considered that 25 curies of tritium would be required (in each sample) to be able to detect the formation of helium compounds, but experimental results showed that 0.5 curies of tritium were detectable in a reasonable length of time. The principal characteristics of the nine pellets produced under this program are summarized in Table 2.

Table 2
PRINCIPAL CHARACTERISTICS OF TRITIATED PELLETS

<u>Pellet No.</u>	<u>Tritium Content, curies</u>	<u>Infrared Transmission</u>
1	0.20	Very poor
2	0.20	(Contaminated with window cement)
3	7.14	Very poor
4	0.62	Fair
5	1.3	Good
6	1.6	Fair
7	0.1	Excellent
8	2.0	Good
9	3.0	Very poor

Although the observation time available during the course of this program proved too brief to permit firm conclusions as to the identity of the new peaks observed in two samples, the following results were obtained:

- The use of large single crystals for samples requires the handling of unacceptable quantities of tritium.
- A liquid-nitrogen-cooled TF_2 film can be used with a low-temperature IR cell if the film is 0.1 mm thick.
- The pressed-pellet technique is the best approach to sample production.

- Helium compounds are detectable in 0.5-curie tritium samples.

B. DISCUSSION

The original goal of this program was to form a tritium-containing sample capable of producing a detectable amount of HeF_2^- in a reasonable time. Professor Pimentel originally suggested that ten micromoles would be the minimum amount that would be detectable; however, this was apparently based upon his experience with IR absorption in general rather than with the HF_2^- system. Such an estimate leads to a tritium content of 25 curies.

Experiments performed during this program suggest that with the HF_2^- system only one-half to one curie of tritium will produce a detectable quantity of HeF_2^- in several months.

Samples 3 and 9 (which contain respectively 7.14 and 3.0 curies) do not have sufficient transmission for analysis. They were prepared as part of the experiment to observe any dramatic change. None was observed.

The absorption peak at 960 cm^{-1} found in the 1.3-curie sample (Pellet 5) has been growing in an atypical fashion: although the area of the peak is increasing with time, the peak height is not. The peak seems to be growing sideways, i.e., the resolution is decreasing with time. The sample has been mounted in a permanent IR cell for convenience in observing changes in growth of this peak.

Nothing of interest has been detected from Pellet 4 and 6 (0.62 and 1.6 curies respectively) in 5 months; transmission is only fair, probably because they contain excess NaF and observation has been limited to major peaks.

The 2.0-curie sample (Pellet 8) has very good transmission and has shown a new peak at 1010 cm^{-1} after 2 months; this peak appears to be growing, with respect to time, in the same manner as Pellet 5.

One interesting aspect found during this program is seen in the IR spectra of the tritiated samples: The bending and asymmetric-stretch frequencies for the TF_2^- ion agree with the predicted values in Table 1; this means that the force constants for the TF_2^- ion are the same as those for the $^1\text{HF}_2^-$ ion.

New peaks have been observed in the 2.0- (Pellet 8) and 1.3-curie (Pellet 5) samples after several weeks that were not observed immediately after production; the peaks fall in the predicted region of 750 to 2000 cm^{-1} . Two additional samples (Pellets 4 and 7), which also transmit in the region around 1000 cm^{-1} , show nothing of interest, probably because of their lower tritium content. The fact that these latter two do not show new peaks in this region indicates that the peaks found in Pellets 5 and 8 are not caused by external contamination.

Although the peaks in Pellet 5 and Pellet 8 appear to be growing in a curious manner, it is too soon to draw any conclusions. If new peaks are caused by a helium-containing compound they should continue to grow over the coming months; in six or eight months the picture should be considerably clearer.

III. SAMPLE DEVELOPMENT

Three different techniques are applicable to the incorporation of tritium into a suitable sample: the single-crystal method; the pressed-pellet method; and the liquid-suspension (mull) method. The optimum method would:

- 1) Provide for incorporation of the necessary quantity of tritium
- 2) Produce a sample transparent to IR
- 3) Be amenable to a test program up to a year's duration
- 4) Minimize the possibility of radioactive contamination

All three methods were initially considered; however, the mull technique, which is inherently more hazardous because the sample is liquid, was dropped early in the program. The results of the studies described in the following pages indicated that the pressed-pellet technique offered the best chance for success. In this technique, a small amount of polycrystalline NaHF_2 is mixed with KBr and cold-pressed into a transparent disk; the KBr serves as a support for the dispersion of the polycrystalline bifluoride grains.

Initial studies were performed with normal hydrogen to eliminate the hazards of radioactive contamination until the techniques could be well developed. Since the chemical behavior of normal hydrogen is virtually indistinguishable from that of tritium, its use permits rapid and safe development in techniques and procedures.

Development of the crystal-growing technique (Section A, below) was aborted when it was determined that excessive amounts of tritium would have

to be handled to obtain a 25-curie specimen, and 12 potential vendors refused to bid on the fabrication of a tritiated, encapsulated specimen. Major effort under this phase of the program was then shifted to the production of a composite pressed disk (Section B, below).

A. CRYSTAL-GROWING

A short screening program was performed to compare the formation of crystals at room temperature with the use of rapid quenching from higher temperatures (c.f. Quarterly Reports No. 1 and 2; AN-1410, April 1965 and AN-1437, June 1965). Common laboratory salts (such as copper sulfate, sodium bromate, potassium ferricyanide, and nickel sulfate) were used in aqueous solutions during these tests. The results showed that temperature control was important, and that room-temperature precipitation was superior to the rapid-quench approach.

It was anticipated that the use of tritiated NaHF_2 single crystals might be the optimum approach, although either NaHF_2 or KHF_2 has a suitable lattice for the purpose of this study. Effort initially was concentrated on the NaHF_2 because it is less hygroscopic and thus will provide greater transparency to IR with less effort. The greater solubility of KHF_2 compared to NaHF_2 , and other factors, led to investigation of the growth of single crystals to KHF_2 .

There were two approaches to the production of tritiated single crystals of NaHF_2 : the first approach investigated the reaction of Na_2CO_3 with HF (48% aq.); the second investigated repeated recrystallization of NaHF_2 from tritiated water. The latter approach was also used with KHF_2 .

1. Methods

A common method was used in each of the three investigations with minor differences: the crystals were grown in saturated solutions on a dacron thread suspended in the solution as well as on the sides of the beakers. Paper tissues were then used to remove the moisture from the crystals and X-ray diffraction patterns were obtained.

The dacron threads proved to be suitable substrates for nucleation of the crystals, and also simplified removal of crystals from a solution. Crystals formed on the thread in much the same fashion in

either HF or water solutions; in each case, the crystals apparently form from the surface of the solution down, and grow together if left undisturbed.

Recrystallization involved the selection of the largest crystals on the dacron thread. These selected crystals were then used as seeds in another, saturated mother liquor.

2. Na_2CO_3 Plus HF

Anhydrous Na_2CO_3 was slowly added to boiling 48% HF until saturation was reached. The solution was then allowed to cool slowly and the supernate transferred to a Teflon beaker. Crystals were observed on the sides of the beakers in two or three days. Crystals with sharp edges were observed on the dacron strand at 35-power magnification; after 10 minutes, the microscope slide was noticeably etched and the crystals were less transparent, presumably due to moisture absorbed from the air. The crystals were then transferred to a petri dish and submerged in a halocarbon oil to prevent contact with airborne moisture.

Crystals scraped from the side of a beaker were oven-dried and ground to a fine powder in an alumina mortar. The powder was placed in an X-ray sample cell, covered with Mylar and examined in a Phillips Norelco X-ray Diffractometer. The resulting pattern contained only NaHF_2 and Mylar lines.

3. NaHF_2 Solution

Five pounds of technical grade (the best commercially available) NaHF_2 were obtained. X-ray diffraction analysis of the powder revealed only NaHF_2 lines. Screening studies of the solubility of NaHF_2 in HF (48% aq.) and in distilled water indicated that HF increases the solubility of NaHF_2 ; for example, the solubility of NaHF_2 in water was found to be 4.5 g/100 ml at 26°C , [compared to 4.0 g/100 ml reported by Bradley and Otts (Ref. 9)]; in HF (48% aq.), the solubility was 14.7 g/100 ml.

Crystals of NaHF_2 were grown in six saturated solutions of NaHF_2 in 48% aq. HF and six saturated solutions of NaHF_2 in H_2O . The solutions were prepared by slowly adding technical grade NaHF_2 to the aqueous medium until complete saturation was reached. The solutions were then transferred to 100-ml Teflon beakers and placed in a fume hood. A thin dacron thread, equipped with a Teflon anchor, was added to each solution and the beakers were covered with paper tissue to prevent contamination. The crystals were grown by slow evaporation; the growth of the crystals was frequently observed to determine the best medium.

The results of 20 days of growth confirmed the hypothesis that 48%-aq. HF is a better medium than water for crystal formation. Crystals of NaHF_2 grew readily in all six 48%-aq. HF solutions, whereas only a few crystals were observed in three of the water solutions. (Crystals were not observed in the other water solutions.)

X-ray diffraction patterns were obtained for the NaHF_2 crystals nucleated from both types of solution. The crystals were removed from the mother liquid, dabbed with tissue paper, and ground in an alumina mortar. The resultant powder was placed on a glass slide, covered with Mylar (to reduce water absorption during analysis, although later work showed this step to be unnecessary) and mounted in the Phillips Norelco X-ray Diffractometer. The resulting Cu-K α spectrum of the HF-grown crystals contained the published lines for the NaHF_2 lattice with the same relative intensities. In addition, there were two lines corresponding to d-spacings of 3.42 and 2.197 Å. The first of these is known to be caused by Mylar, but the second was not identified. These results indicate that the crystals grown from aqueous and HF (aq) solutions are essentially pure NaHF_2 and do not contain appreciable amounts of hydrates (i.e., $\text{NaHF}_2 \cdot n\text{H}_2\text{O}$) or extra HF (i.e., $\text{NaHF}_2 \cdot n\text{HF}$).

4. KHF₂ Solutions

Although either the NaHF₂ or the KHF₂ lattice was considered suitable for this study, the former is far less hygroscopic; in consequence, most of the work during the first two quarters of the program dealt with the NaHF₂ lattice. (Since water absorbs IR in the region of interest, its concentration must be minimized.) A rather detailed report (Ref. 10) indicated, however, that the absorption of water by KHF₂ is less serious than anticipated. On the other hand, the solubility of KHF₂ (41 g/100 ml) is much greater than that of NaHF₂ (4 g/100 ml), thus KHF₂ should crystallize more rapidly. Furthermore, more information is available on the growth of KHF₂ crystals than on NaHF₂. Accordingly the growth of KHF₂ single crystals was also investigated.

A saturated solution of KHF₂ in distilled H₂O was prepared, using the same arrangement as for NaHF₂ except that polyethylene containers were used. Very thin plates with areas of several square centimeters grew in a matter of a few hours. Temperature control of the solution is extremely important because KHF₂ has a large positive heat of solution and its solubility has a large temperature dependence. Crystal-growing studies were suspended while attempts were made to locate a controlled-temperature water bath.

It became evident that the single-crystal method was not the best way to produce the desired sample. The incorporation of tritium into a bifluoride lattice by growing a single crystal from a tritiated aqueous solution is hindered by the fact that sodium and potassium bifluoride are very soluble so that large (up to 2500 curie) amounts of tritium would have to be handled to obtain a 25-curie specimen. Furthermore, eleven nuclear firms and Harshaw Chemical Company refused to bid on fabrication of a tritiated, encapsulated specimen. Major effort for the program was therefore shifted to the production of a composite pressed disk.

B. PREPARATION OF NaHF₂

In the pressed-pellet technique, a small quantity of tritiated bifluoride is mixed with diluent and cold-pressed into a disk. Because there is an upper limit on the concentration of bifluoride in this technique (about 4%), the isotopic concentration of tritium must be as high as possible

(ideally, 100%). The method used in this program to achieve fully tritiated NaHF_2 was to react tritium with fluorine and then react the resultant TF with NaF. The procedures were developed using normal material.

This method was appropriate because of the availability of people experienced in the handling of reactive fluorides, and of equipment for handling reactive fluorides. This capability was developed over the past several years during research for the U. S. Air Force.

1. Formation of Anhydrous HF

Desiccation of HF is difficult because of its strong affinity for water. In addition, HF reacts with both sulfuric acid and phosphorous pentachloride to form water (Ref. 11). On the other hand, fluorine and hydrogen can be satisfactorily dried by passage through liquid-nitrogen traps and the desiccated elements can then be reacted to form anhydrous HF.

The gases were stoichiometrically introduced into a 300-cc Monel container at a pressure of 2 atm and at a rate that kept the container temperature below about 100°C . The resultant HF was examined for purity with an all-Monel gas chromatograph, the column of which is a single, Monel U-tube initially immersed in liquid nitrogen. The sample is injected into the helium carrier and the lower vapor-pressure components condense on the column. Any other component present (e.g., N_2 or H_2) continues on to the thermal-conductivity and electron-capture detectors. The liquid-nitrogen dewar is then removed, allowing the column to warm at a known rate. As the column approaches the normal boiling point of a component, it is released into the carrier and delivered to the detectors. Several gases have been found to elute near their normal boiling points (e.g., OF_2 , NF_3 , FNO_2 and N_2F_4).

The HF produced by reaction of the purified elements showed only the gas-chromatographic peak characteristic of HF. No water could be detected.

2. Formation of NaHF_2

NaHF_2 was successfully prepared by the reaction of HF with NaF. An amount of HF calculated to be sufficient for complete reaction was condensed with liquid nitrogen into a Monel bomb containing 1 g of NaF. The

bomb was closed, removed from the charging apparatus and heated at 100°C for 15 min, reattached to the loading apparatus and connected to an evacuated pressure gauge. It was found to have an immeasurable residual pressure (less than 0.1 atm). When opened, the bomb contained a white sample. The X-ray diffraction pattern of this sample was indistinguishable from that for NaHF_2 . (The X-ray diffraction pattern of the starting material agreed with the published pattern for NaF .) Subsequent experiments showed that complete reaction occurs rapidly at room temperature, obviating the heating step.

3. Formation of Higher-Acid Fluorides

Higher-acid fluorides (e.g., $\text{NaF} \cdot 2\text{HF}$) were undesirable in the final sample because they produce additional IR absorption lines. For example, KH_2F_3 contains H_2F_3^- ions which can be expected to produce absorption lines in addition to the two IR lines of the HF_2^- ion (Ref. 12). Solid KH_2F_3 can be formed by reacting two moles of the HF with one of KF.

Three higher-acid fluorides of NaF are known: $\text{NaF} \cdot 2\text{HF}$, $\text{NaF} \cdot 3\text{HF}$ and $\text{NaF} \cdot 4\text{HF}$ (Ref. 13). Froning, *et al.* (Ref. 14) describe them as semifluorides. The sodium system was chosen in preference to the potassium system because anhydrous NaF is readily obtainable whereas KF is usually hydrated; and the undesirable, higher-acid fluorides are readily converted to the bifluoride because of their high HF partial pressure.

A study of the higher-acid fluorides was then performed by reacting HF with NaHF_2 . The experiments were performed similarly to the NaF-HF experiments: HF/ NaHF_2 molar ratios of 0.1 through 0.7 were obtained by condensing HF into a liquid-nitrogen-cooled vessel containing NaHF_2 . After heating at 100°C for 10 to 15 min the vessel was attached to an evacuated vacuum gauge and the interconnecting valve was opened. In all cases the pressure gauge indicated 0.33 atm. (The vapor pressure of HF at 20°C is 1.1 atm.) Even after removal of some of the HF by alternate evacuation and back-filling with helium, the pressure over the sample was still 0.33 atm. These results are, of course, consistent with the presence of a two-phase system.

The resultant samples were slushy at low HF/ NaHF_2 ratios and very fluid (like water) at higher ratios. When the samples were removed

from the vessel, they immediately lost HF, increased in viscosity and then became solid. Some of the slushy material was cooled with liquid nitrogen for observation with an X-ray diffractometer; the resultant spectrum showed only the NaHF_2 lines.

Apparently, the HF partial pressure over the two-phase mixture of NaHF_2 and the next higher fluoride is so high at room temperature that HF is readily lost, leaving only the NaHF_2 phase. This phase, having an HF partial pressure at room temperature of about 10^{-5} atm, is stable at room temperature.

4. The HF Partial Pressure Over the NaF- NaHF_2 Two-Phase Region

It is essential that the partial pressure of HF (TF) over the tritiated sample be low enough to prevent the escape of tritium and the resultant health hazards. The HF partial pressure over NaHF_2 at any temperature can have any value over a range of several orders of magnitude according to the stoichiometry. Because NaHF_2 does not sublime congruently, the HF partial pressure over any NaHF_2 single phase will be a value between that for the NaF- NaHF_2 two-phase region and the $\text{NaHF}_2\text{-NaF} \cdot 2\text{HF}$ two-phase region. Furthermore, knowledge of the expected rate of tritium loss was a necessary part of the application for amendment to AGN's radioactive-handling license. Consequently, a study was initiated to determine this pressure as a function of temperature.

The HF partial pressure on the HF-rich side of NaHF_2 (at room temperature) was found to be 0.33 atm. The HF partial pressure on the NaF-rich side has been measured by Froning, et al (Ref. 14) who report values obtained between 147° and 269°C . Although the results are in fair agreement, the experimental range is too wide for confident extrapolation to room temperature; however, extrapolation gives a value of 10^{-5} atm, a value readily measurable by the Knudsen-cell technique (Ref. 16).

A room-temperature Knudsen-cell experiment was performed with a platinum cell. The orifice size and vaporization time were selected to give a 10-mg weight loss for an HF partial pressure of 10^{-5} atm, yet the experimentally determined weight loss was less than 0.1 mg, a factor of 1/100 of the extrapolated literature value.

Additional Knudsen-effusion experiments were performed to determine the reason for the low experimental room-temperature value compared to the value extrapolated from References 14 and 15. The experimental value could be low because of:

- 1) A low sublimation coefficient,
- 2) A previously unrecognized phase transition,
- 3) The data in the literature are wrong, or
- 4) An error in the AGN room-temperature experiment.

The additional experiments were performed at temperatures ranging from 127° to 198°C.

Three lids with different orifices as well as one without an orifice were used; the apparatus is shown in Figure 1. The NaHF_2 sample previously heated to drive off a few percent of the HF (to ensure the presence of some NaF) was placed in a platinum crucible. The crucible was then placed in a copper outer crucible and one of the three platinum lids was placed on the inner crucible. The outer crucible was then attached to a vacuum system by means of an O-ring fitting.

When the residual pressure fell below 10^{-5} torr, an isothermal water bath was raised around the crucible assembly. At the conclusion of the run, the bath was lowered and the crucible assembly was cooled with a room-temperature bath. The sample chamber was then brought to atmospheric pressure with helium and removed for weighing.

Temperatures and heating times were corrected by performing a series of calibration experiments in which a thermocouple was placed into the platinum cell containing NaF powder. (The NaF powder was the residue from the series of effusion runs.) Loss of sample by effusion through the opening between the lid and crucible was determined by using a lid without an orifice in performing experiments.

Apparent pressures calculated from Knudsen's formula are shown in Figure 2. The apparent increase in HF partial pressure with decreasing orifice size suggests that the sublimation coefficient (the free-surface sublimation rate divided by the equilibrium sublimation rate) is smaller than unity.

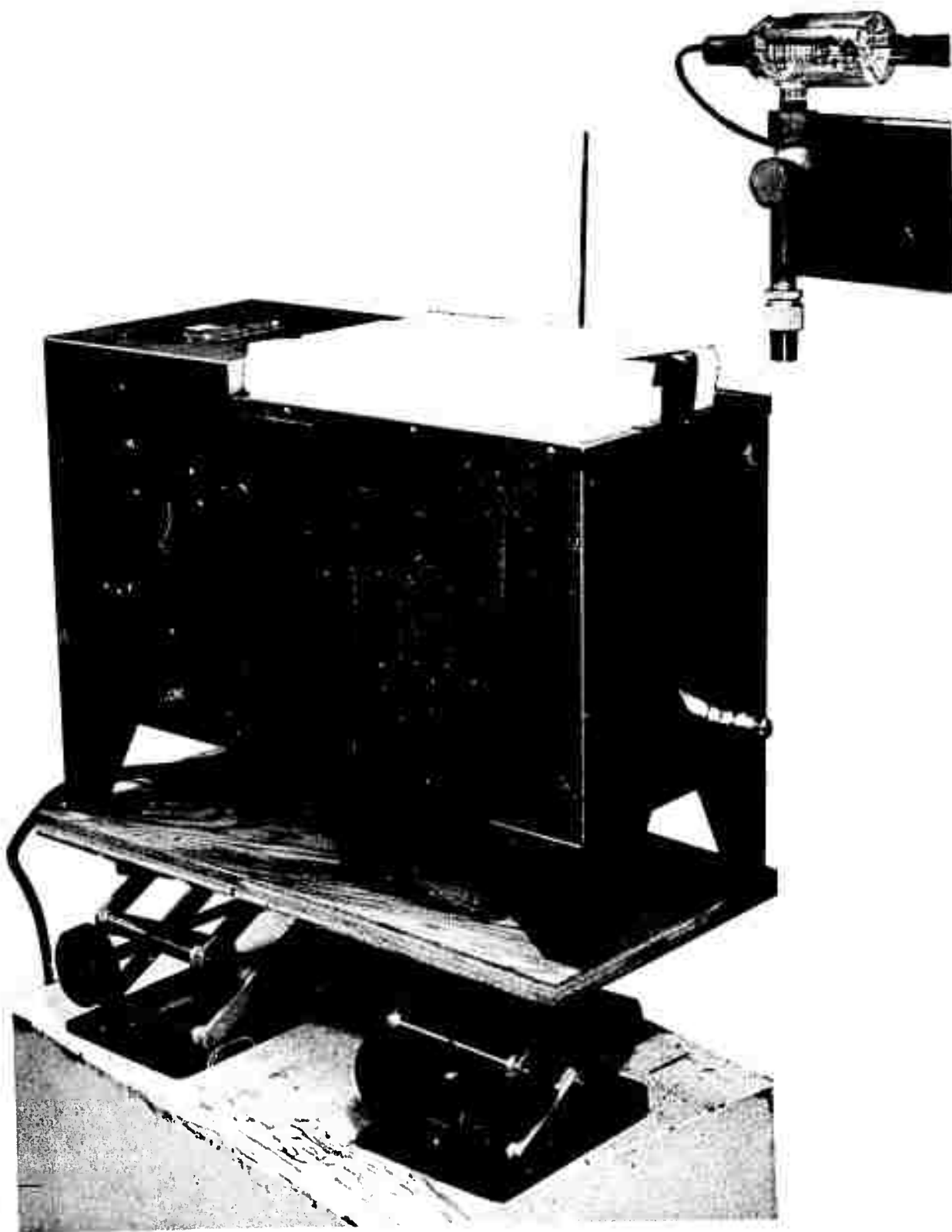


FIGURE 1. KNUDSEN - EFFUSION APPARATUS

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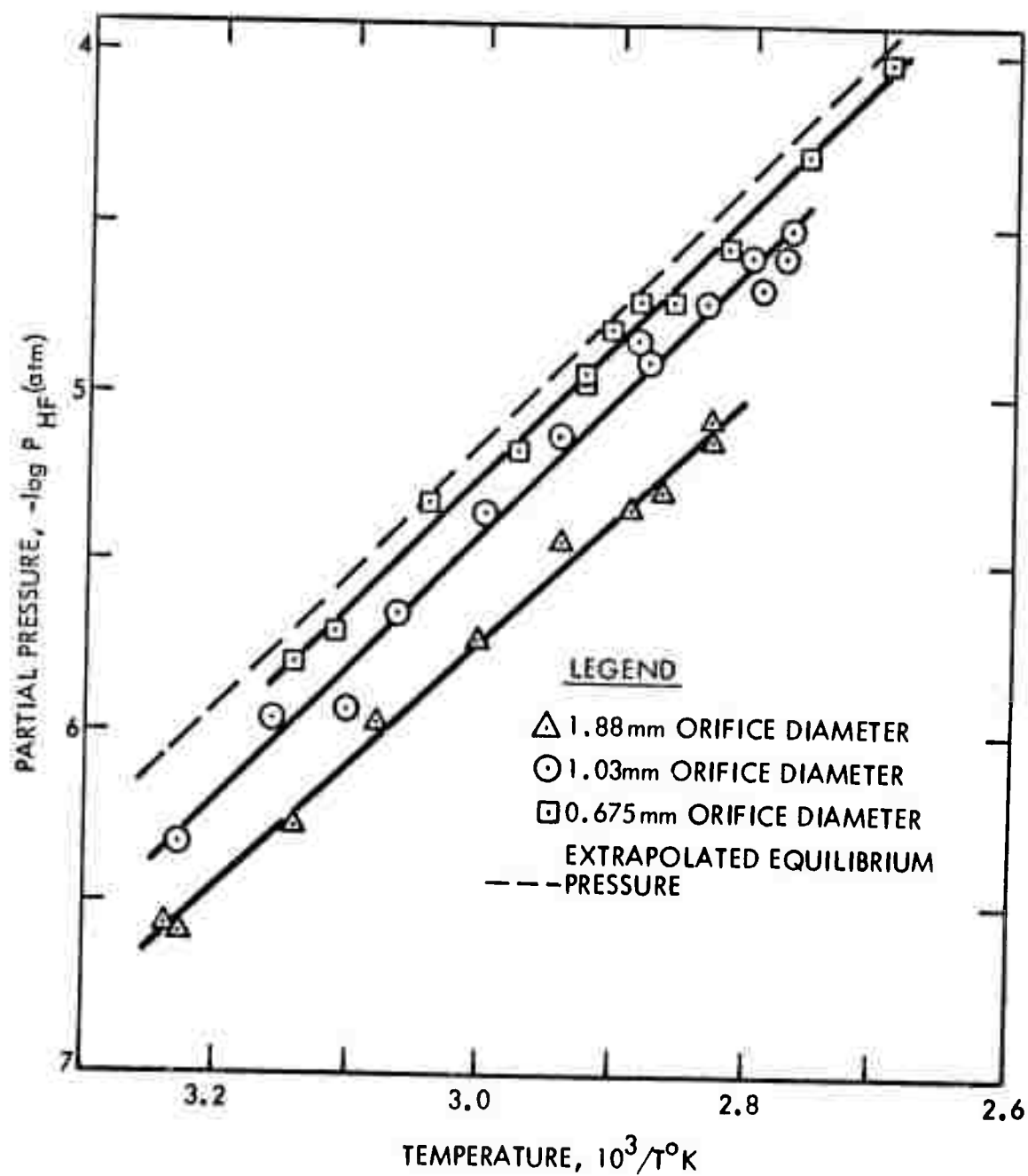


FIGURE 2. THE HF PARTIAL PRESSURE AS A FUNCTION OF TEMPERATURE OVER THE NaHF_2 - NaF TWO-PHASE REGION

The use of Motzfeldt's relation (Ref. 17) suggests that the equilibrium HF partial pressure is lower by a factor of 15 than the value obtained by extrapolation of the data in References 14 and 15, and that the sublimation coefficient is approximately 0.05. The maximum credible TF-loss rate from the final sample was then calculated to be an acceptable 8×10^{-12} microcuries/cc in a vacuum. The rate in air will, of course, be much smaller.

C. PRESSED-PELLET TECHNIQUE

The first three pellets were pressed from sodium bifluoride without the use of a diluent. The samples which had thicknesses of 0.9, 1.1, and 2.9 mm were translucent to visible light and opaque to IR. Two additional samples, prepared by mixing 0.5 mole % NaHF_2 with KBr, were transparent to visible light. The thicker one (5.3 mm) was opaque to IR, but the thinner one (1.2 mm) transmitted about 65% of the IR beam, giving a spectrum similar to that reported by Ketelaar, Haas, and van der Elksen (Ref. 7).

Two pellets containing only KBr were prepared in evaluating the pressing technique. The pellets were of high quality; their IR spectra showed only a trace of water; they transmitted nearly 100% of the IR beam.

An evacuable, Perkin-Elmer KBr die was initially used for pellet fabrication. This die produces pellets 13 mm in diameter and any thickness up to 25 mm. A pressure of 50,000 psi for 1 minute was initially used.

A rectangular (2.5 x 16 mm) evacuable die (Fig. 3) was also obtained for the pellet work. This die has two advantages over the circular die used previously: 1) the shape of sample it produces more nearly approaches the shape of the IR beam, reducing the quantity of tritium needed, and, 2) after the sample has been pressed, the central laminar layer of the die can be removed (with the sample still ensconced) covered with windows and mounted directly in the IR beam.

At the conclusion of the pellet-pressing step, the middle section of the pellet-pressing die is removed with the sample firmly attached and placed into the IR spectrometer for analysis. The two sample holders originally received are 4 mm thick, limiting the final sample to 3 mm in the beam-path direction. Thicker sample holders which allow production of samples of 10 mm beam-path length were obtained locally.

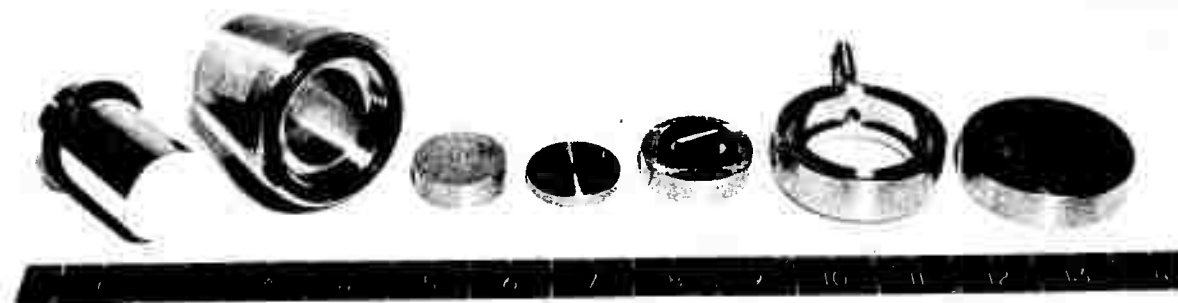


FIGURE 3. EVACUABLE DIE USED FOR PRESSURE KBr SAMPLES

It then became apparent that the combination of NaHF_2 as a potential tritium carrier and KBr as a matrix diluent offered the best possibility for success. The second choice, AgCl , was dropped from further consideration as a matrix when exothermic reactions were found to occur during power-grinding; NaHF_2 -KBr samples were then used exclusively.

IR observations on the final samples were made in the region 650 to 2000 cm^{-1} . Initially, the only absorption lines will be those caused by the asymmetric stretch and bending modes at 846 and 730 cm^{-1} for the TF_2^- ion. The total observation period of several months is so short relative to the half-life of tritium that these absorptions of the TF_2^- ion will not appear to change. Absorption caused by formation of any helium compound will increase by 0.11% per week. Since the TF_2^- peaks are always present, it is important that they be well resolved so that they do not obscure too much of the IR scan.

The parameters which affect the infrared spectrum of a KBr-NaHF_2 pressed pellet were studied so that samples of maximum transmission and resolution could be produced. These parameters include:

- 1) Particle sizes of KBr and NaHF_2 ,
- 2) Homogeneity of KBr and NaHF_2 mixtures,
- 3) Magnitude and duration of applied pellet-pressing pressure,
- 4) Concentration of NaHF_2 in KBr,
- 5) Thickness of pellet in the IR beam path, and
- 6) Amount of moisture present in the pressed pellet.

The study showed the optimum conditions for pellet-pressing include:

- 1) Mechanical-grinding time (includes consideration for homogeneity) -- 10 to 15 minutes,
- 2) Pellet-forming pressure -- 80,000 to 100,000 psi
- 3) Duration of applied pressure -- 1 to 10 minutes
- 4) Evacuation period of pellet die -- 3 to 10 minutes
- 5) Concentration -- < 4%

1. Mechanical Grinding

To facilitate the grinding and mixing of the NaHF_2 -KBr powders, grinding was performed in an agate vial with agate ball pestles mounted on a mechanical grinder (Wig-L-Bug, Crescent Dental Manufacturing Company). Samples containing Infrared Quality KBr (Harshaw Chemical Company) and 0.0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0 and 10% NaHF_2 (both technical grade and material synthesized as described earlier) were studied to determine the optimum grinding time. Grinding times were investigated through the range from 1 to 25 minutes.

The optimum grinding time was 10 to 15 minutes for a 1.5g sample for all concentrations of NaHF_2 in KBr. Within this range, optically clear KBr pellets and translucent-to-opaque NaHF_2 -KBr pellets were prepared. For grinding times less than 10 minutes, individual grains of NaHF_2 were observable in the pellet, and one minute of grinding produced optically clear disks except for an irregular dispersion of NaHF_2 grains through the pellet. Pellet flaking, the predominant symptom of excessive grinding, was observed for grinding times longer than 20 minutes for 0.5g samples.

2. Optimization of Pressure and Grinding Time

The optimum conditions for pressing NaHF_2 -KBr disks with acceptable IR-transmission properties were determined experimentally. This phase of the program was performed in a helium-pressurized glove-box to minimize moisture absorption by the KBr and to simulate work with tritium (the next phase of the program). Anhydrous $\text{Mg}(\text{ClO}_4)_2$ was used as the desiccant in the glove-box. Fogging of the samples, which occurred with technical-

grade NaHF_2 , did not occur when AGN-synthesized NaHF_2 was used. The period of die evacuation (prior to pressure application) was investigated over the range from 1 to 30 minutes. The best samples were produced in the 3- to 10-minute range. The absorption peak at 1640 cm^{-1} (attributed to H_2O) was never completely removed by the die-evacuation step but was reduced to an acceptable level.

The isostatic pressure used to form the disks was varied from 40,000 to 100,000 psi over periods ranging from 1 to 10 minutes. Although the duration of pressure application was not critical, the applied pressure was subject to limitations. At pressures below 80,000 psi, the pellet-rejection rate was fairly high; the major problem here was opaque pellet centers, apparently caused by improper leveling of the powder in the pellet press and inadequate pressing pressure. This opacity problem was minimized at pressures above 80,000 psi.

3. Optimization of Tritium Concentration and Sample Lengths

Because relatively large amounts of tritium must be incorporated into the sample, both sample length (in the IR-beam-path direction) and tritium concentration must be maximized. The effects of these parameters on sample resolution and transmittance were therefore studied. The results showed that resolution decreases with increasing NaHF_2 concentration but is unaffected by sample length; as expected, transmittance decreases with increasing path length.

Stacking several thin pellets (each about 1 mm thick) gave equal or better IR absorption spectra than a single pellet of equivalent thickness.

D. LOW-TEMPERATURE-CELL STUDIES

Since the pressed disk technique presents certain problems, an alternate technique involving the use of a low-temperature IR cell to observe a liquid-nitrogen-cooled tritium fluoride film was investigated. This method had been developed almost to the operational stage under an AGC-sponsored IR&D program; it was estimated that the experimental apparatus could be completed with about two man-weeks of effort. The problem to be solved was the construction of a vacuum-tight internal sample cell. In previous experiments

(under the IR&D program), the inner cell had leaked TF into the evacuated area between the inner and outer cells. For the current work, the Teflon gaskets originally used to seal the AgCl windows were replaced by epoxy* cement developed for use in liquid nitrogen.

The low-temperature IR cell was made operational with a 0.4-mm-thick natural-HF film maintained between silver chloride crystals and functioned for 72 hr at -196°C under about 1 micron of pressure. (An equivalent TF film would have contained 120 curies.) The 0.4-mm HF film proved too thick to transmit IR.

A new cell was assembled with a 0.1-mm-thick HF film, corresponding to a 40-curie sample. The film was lost as a result of difficulties during transport of the apparatus in the IR laboratory; however, the limited observations made with the film indicated IR translucency, and it appears likely a 0.1-mm HF film will transmit. No further activity is contemplated in this area, but the technique apparently is satisfactory and usable.

* 65 wt% Shell Epon 128 and 35 wt% General Mills Versamid 125.

IV. EQUIPMENT STUDIES

A. DETERMINATION OF IR SENSITIVITY

The work scope for this program specified fabrication of an IR sample containing 25 curies of tritium. This quantity of tritium will produce 10 micromoles of helium in 76 days, originally thought to correspond with the lower limit of detectability (estimated by Professor Pimentel to be 10 micromoles) by IR absorption spectroscopy. Because IR-transparent samples containing more than a few curies of tritium could not be produced, the lower limit of detectability was investigated in the hope that the value estimated by Pimentel was unduly conservative. The $^1\text{HF}_2^-$ ion was chosen for this experiment because it can be studied easily and the results can be applied to the $^3\text{HF}_2^-$ ion and the HeF_2 molecule.

Samples containing from 0.08 to 0.8 micromoles of natural NaHF_2 (corresponding to 1.2 to 12 millicuries in fully tritiated samples) were fabricated. The IR absorption spectra of selected samples (Figures 4 through 6, p 33 et seq.) indicate that the 0.2-micromole NaHF_2 sample represents the lower limit of detectability for the $^1\text{HF}_2^-$ ion. Although this value corresponds to a 3-millicurie level, the IR-absorption sensitivity for mass-one hydrogen is approximately twice that for mass-three hydrogen*, and, consequently, the lower limit of detectability for the $^3\text{HF}_2^-$ ion (and, it is believed, for the HeF_2 molecule as well) should be 0.4 micromoles. Thus a 0.0-curie sample can, in principle, produce a detectable spectrum in three months. (A 3-curie sample could, in principle, produce a detectable spectrum in three to four weeks.)

The actual relationship is complex; see Section III.B.

B. WINDOW-CEMENT STUDY

ACN's radioactive-material license requires double containment of radioactive samples. The TF partial pressure over the tritiated sodium bifluoride/potassium bifluoride samples will be low enough to satisfy the MPC requirements of 2×10^{-5} microcuries/cc so that the sample lattice can be considered a primary container. Secondary containment was accomplished by affixing IR-transparent windows to both sides of the sample holder immediately after the sample was removed from the press.

A study was made to find a suitable cement and curing-time/temperature combination for attaching the windows to the metal sample holder. The best combination was found to be 65/35 wt% mixture of Shell Epon 828 and General Mills Versamid 125 cured at room temperature.

V. TRITIUM STUDIES

A. INITIAL TRITIUM WORK

During the initial work with tritium, leaks were found in the tritium cylinders received from the vendor (ORNL). The purity of the gas in the cylinders (specified at 99% pure tritium) was experimentally determined. The gas was exposed to fluorine and then to NaF in the usual manner. After exposure to fluorine it was apparent that appreciable portions (later found to be O_2 and N_2) were unreactive to fluorine. Also the appearance of the NaF exposed to the gaseous mixture was atypical. Two methods were used to determine the tritium concentration in the cylinder.

The concentration of tritium in the original gas was determined by P-V-T measurements on the product TF (the most expeditious method then available). A quantity of gas from the tritium cylinder was allowed to react with an equal amount of F_2 (as determined by P-V-T relations). The resultant TF was condensed with liquid nitrogen while the remaining residual gas (if any) was pumped out. (Because of the small quantities involved, relatively large amounts of non-condensable impurities, such as air, would not be detectable on the Bourdon gauge.) The pressure of the gas when warmed to room temperature was less than the vapor pressure; i.e., there was no liquid phase present. This measured pressure when used with the known volume of the system and the HF-association factor (1.1) given by Long, et al, (Ref. 18) yielded the total number of moles. The calculation showed that only about one-fifteenth of the cylinder gas was tritium, rather than the 99% stated by the vendor.

The second method placed an upper limit on the concentration of tritium in the gas cylinder. The experiment to synthesize NaTF_2 was repeated, but with 15 times the quantity of gas removed from the tritium cylinder for the first method. The quantity of F_2 was also increased by the same factor to assure complete reaction with the tritium in the apparatus. The resultant TF was condensed with liquid nitrogen and the residual non-condensables were pumped off. The TF was reacted with sufficient NaF to give stoichiometric NaTF_2 if the gas in the original tritium cylinder contained only one-fifteenth tritium. The reaction produced a crusty solid.

From earlier experiments with natural HF and NaF, it was known that an excess of HF would produce a slushy NaHF_2 . The crusty appearance of the resultant sample indicated that the gas in the cylinder was at least one-fifteenth tritium. The results of the TF pressure measurements, though less accurate, also placed a lower limit of one-fifteenth on the tritium content of the cylinder.

B. FORMATION OF TRITIATED SAMPLES

The optimum conditions for fabrication of rectangular tritiated pellets (2.5 by 16 mm cross section for this program) were determined to be:

- 1) Concentration of tritiated NaHF_2 -- 1 wt%
- 2) Mixing period (Wig-L-Bug) -- 5 minutes for < 0.5 g of material
- 3) Die-evacuation period -- 5 minutes
- 4) Applied pressure -- 9.7×10^4 to 1.3×10^5 psi

The tritium concentration is controlled by varying the thickness of the pellet.

The first two pellets were produced before the discovery of the low tritium content in the gas cylinder. After pressing, the first tritiated sample was opaque to visible light; additional pressing did not improve transmittance. From earlier work with natural material, it was known that a sample opaque to visible light would not transmit IR. A second pellet pressed in the same manner was transparent to visible light.

At this point it was decided to produce a sample with less than the desirable IR transmission, but with sufficient tritium for detection of

any helium-containing molecule in a reasonable time. Therefore a pellet subsequently found to contain 7 curies was fabricated. This pellet, which was translucent to visible light, was opaque to IR radiation even below 1000 cm^{-1} . The low tritium content of the cylinder was discovered and 200 additional curies were received without cost to the contract.

The second shipment of tritium cylinders was examined more closely; the contents were analyzed to determine the hydrogen isotopic composition and the concentration of impurities other than protium or deuterium. A CEC Model 21-611 mass spectrometer was modified to permit direct injection of a sample into the diatron section to increase the sensitivity. Known mixtures of gases suspected to be contaminants in the tritium were analyzed separately to determine relative sensitivities of the modified equipment. This calibration was necessary because the observed response is a function of both the electron-capture cross section of, and the detector sensitivity for, the species of interest. Results of the mass-spectrometric analysis (Table 3) indicated that the tritium content of the sample was 82.4%, with less than 1% mass-one hydrogen. Argon (11%) was the principal impurity.

Table 3

TRITIUM-SAMPLE ANALYSIS BY MASS SPECTROMETRY

<u>Gas</u>	<u>Mass</u>	<u>Composition, Mole %</u>
Hydrogen	2	0.4
Helium	4	0.6
Oxygen	32	0.5
Nitrogen	28	2.0
Argon	40	11.0
Water	18	2.0
Miscellaneous	--	1.1
Tritium	6	82.4

The concentration of mass-one hydrogen (protium) was of greatest concern since other impurities (totaling 17%), such as Ar or N, are readily removable during the bifluoride-forming step. The results of the mass-spectrometer study indicated insufficient protium content to interfere with the experiment.

A cursory examination of the mass-spectrometric results revealed apparent disagreement with the IR results. IR spectrograms of tritiated samples show absorption peaks for the TF_2^- ion at 730 and 846 cm^{-1} (asymmetric stretch and bending vibrations, respectively), and for the HF_2^- ion at 1230 cm^{-1} (the bending mode; the 1425 cm^{-1} stretching mode peak is not visible because of poor transmission in this region). The bending absorptions are about the same magnitude, suggesting that the tritium-to-protium ratio is about 1, but this is not a valid conclusion because absorption intensities are a complex function of the mass (Ref. 19); simply stated, the lower-mass isotope will absorb more than the higher-mass isotope.

There is also the possibility that water originally absorbed in the KBr matrix can exchange with the TF_2^- ions to increase the magnitude of the observed HF_2^- absorption peaks. In this event, however, a T_2O molecule must be formed to replace every H_2O molecule that was exchanged with a TF_2^- ion.



The existence of absorption peaks attributable to T_2O would indicate the extent of absorbed-water contribution. A special pellet (Number 7), containing 0.1 curie of tritium, was fabricated in an effort to detect the T_2O molecule. The transmission of this pellet is excellent, indicating peaks at 970 and 2160 cm^{-1} , corresponding, respectively, to the asymmetric stretch and bending frequencies; however, the absorptions are not sufficient to satisfactorily account for a 1:1 tritium-to-protium ratio. The $\text{H}_2\text{O}/\text{T}_2\text{O}$ exchange is estimated to contribute from 2 to 5% of the observed HF_2^- peak.

Since helium-containing molecules are detectable in a reasonable time by observing samples containing considerably less than 25 curies, three additional samples (Pellets 4 through 6) containing 0.62, 1.3 and 1.6 curies of tritium were fabricated. Such samples have a considerably greater range of transmission and, consequently, a higher probability of indicating helium-compound formation than samples containing larger quantities of tritium in the form of NaTF_2 . Of course, any product absorptions will be correspondingly weaker for a given time.

During the last few months of the program, three additional samples (Pellets 7 through 9) containing 0.1, 2.0 and 3.0 curies were fabricated. The composition of the tritium carrier was chosen to be fully tritiated stoichiometric NaHF_2 . In earlier samples, relatively less HF was added so that a two-phase mixture of a few percent NaF in NaHF_2 was obtained. This ensured low enough HF partial pressure for safe handling, but the excess NaF reduces IR-transmission. Stoichiometric sodium bifluoride was used in an effort to obtain the best possible sample. This process does not increase health hazards, because the tritiated NaHF_2 is exposed to vacuum after preparation long enough to shift the composition to the NaF-rich side of the NaHF_2 single phase. The composition then has an HF partial pressure characteristic of the NaF- NaHF_2 two-phase region, yet is still single phase. In addition, the method of sealing the sample with cemented windows was demonstrably effective in retaining the tritium for safe handling and observation.

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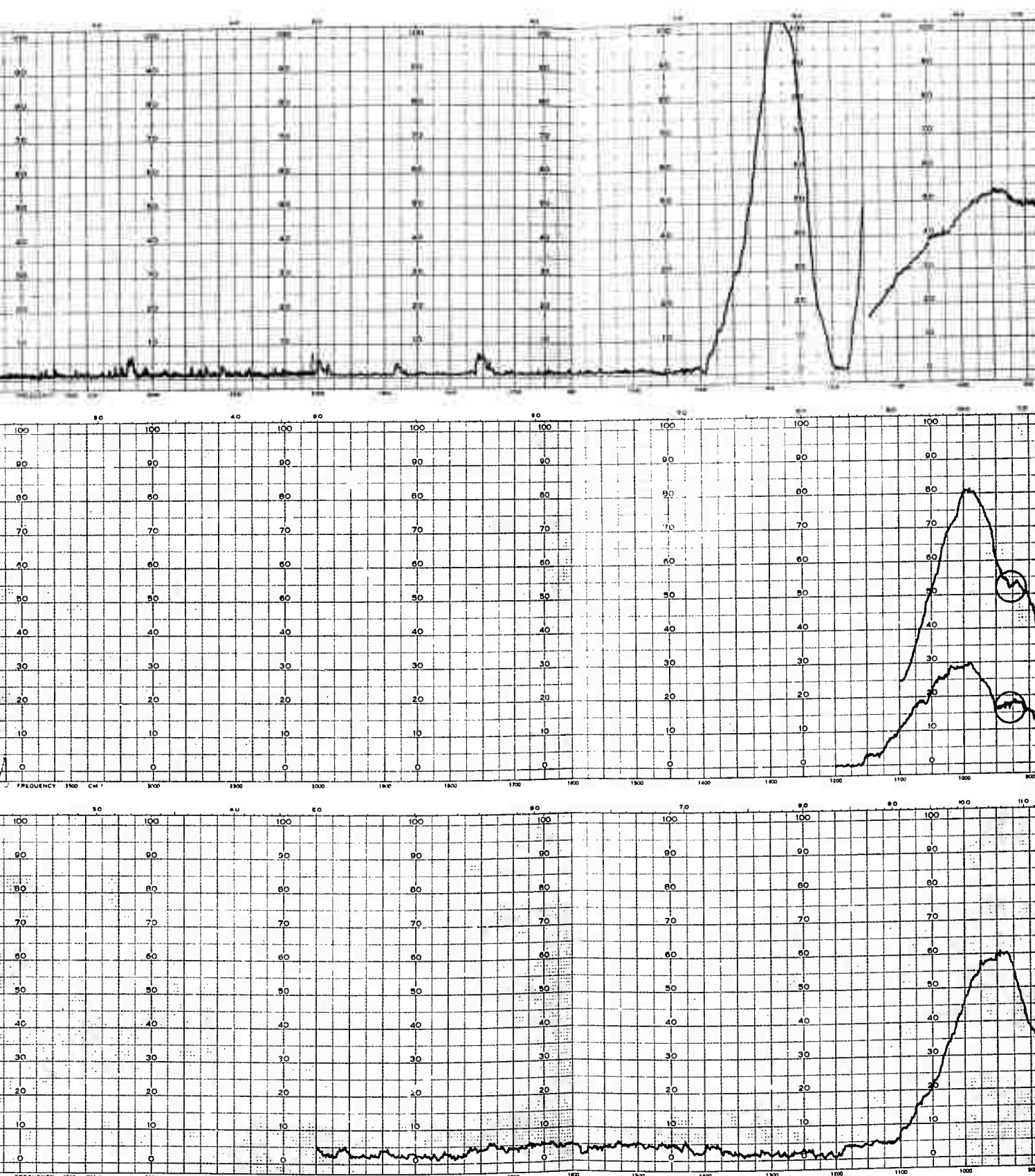
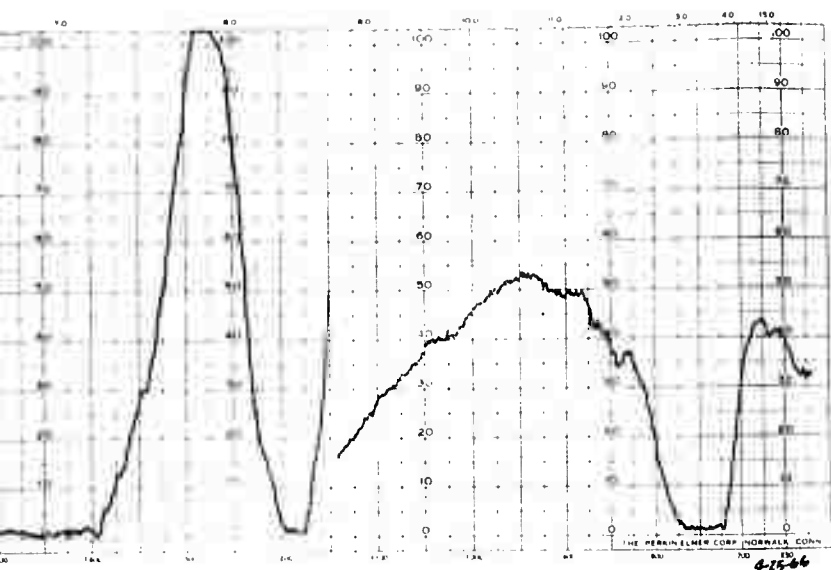
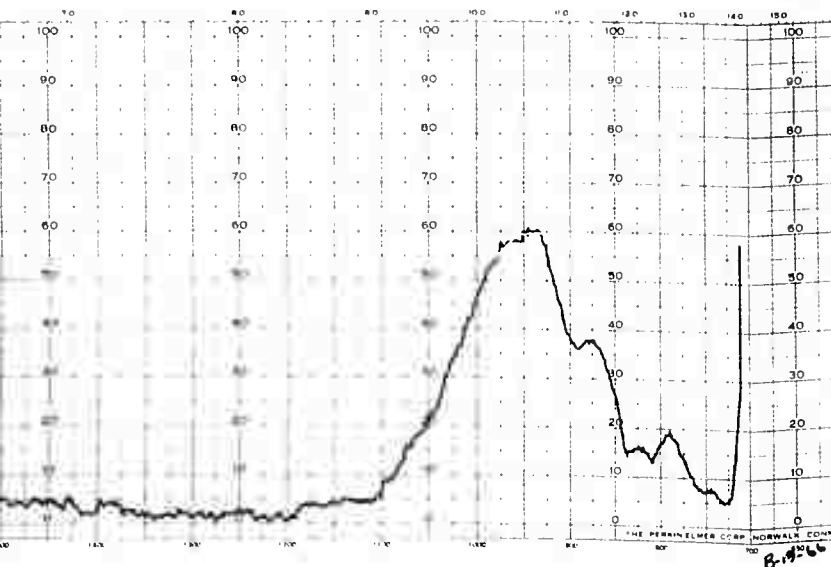
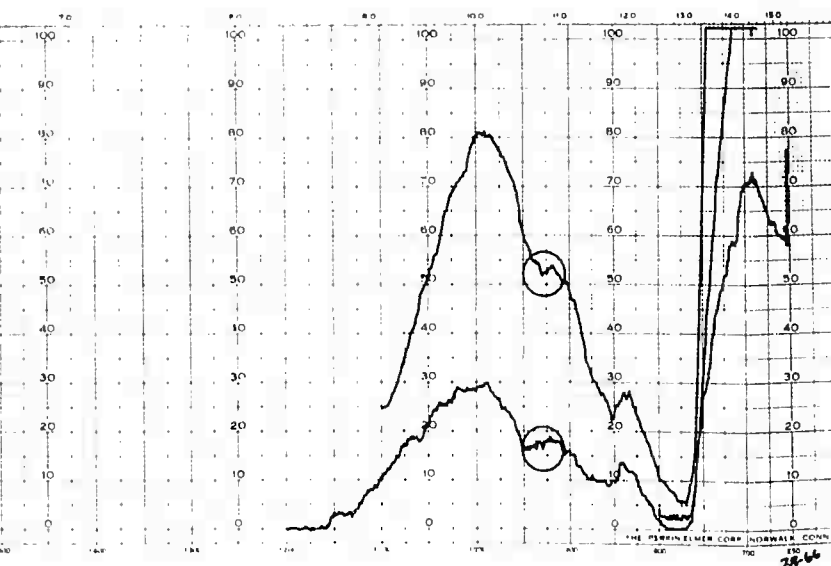


FIGURE 4: PELLET 4 (0.62 curies): INFRARED SPECTRA
(From top to bottom, 25 April, 8 July and 19 August 1966)

A



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ories): INFRARED SPECTRA
8 July and 19 August 1966)

B

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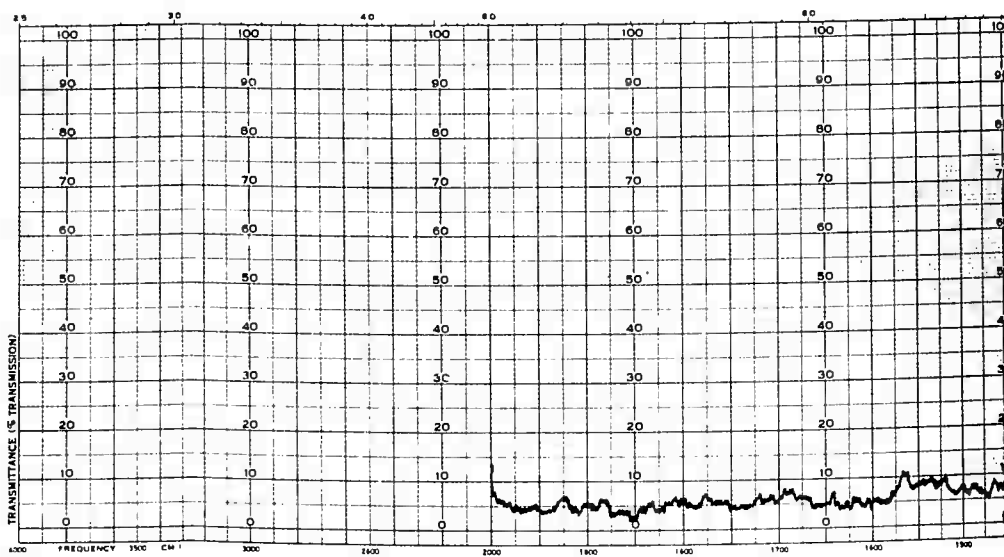
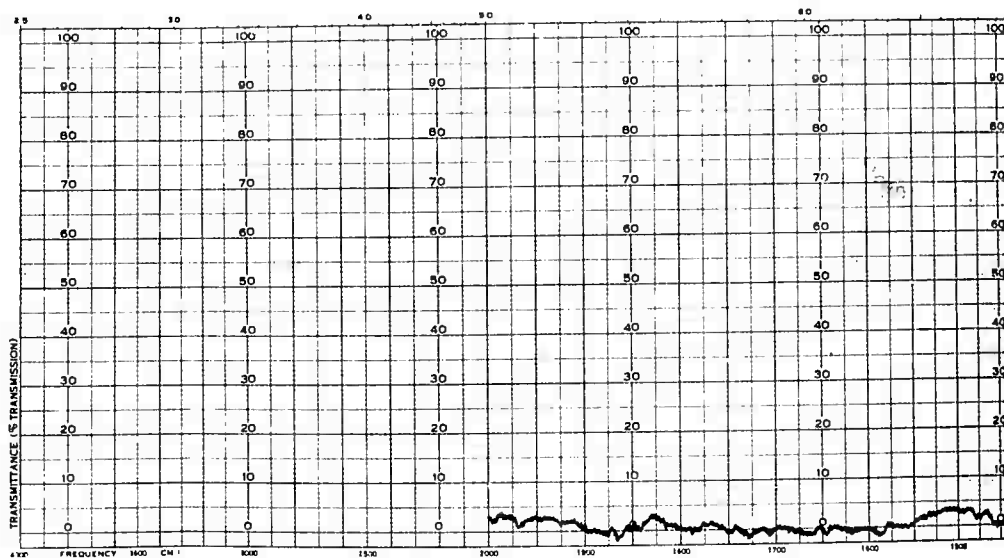
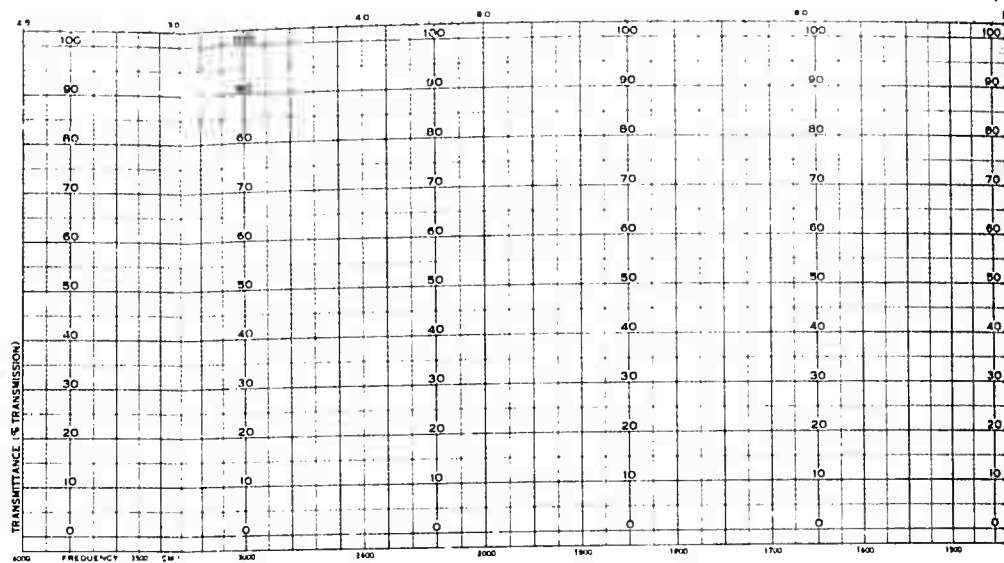


FIGURE 5: PELLET 5 (1.3 curies)
(From top to bottom, 25 April, 6)

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A

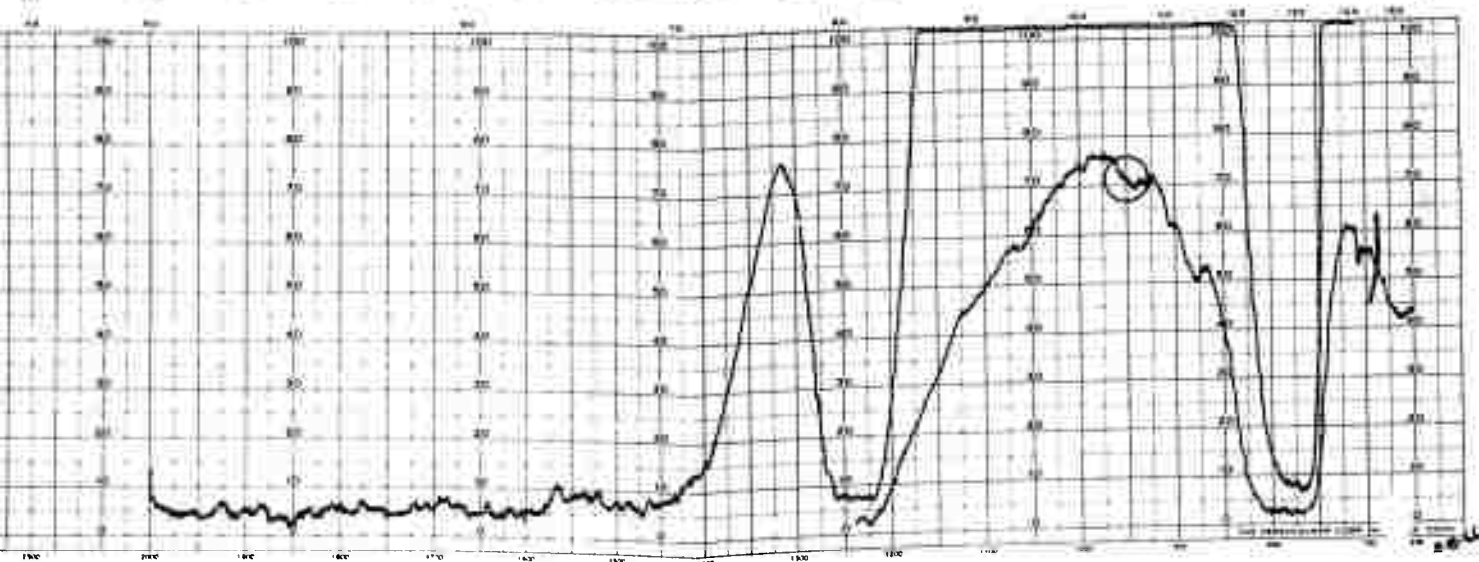
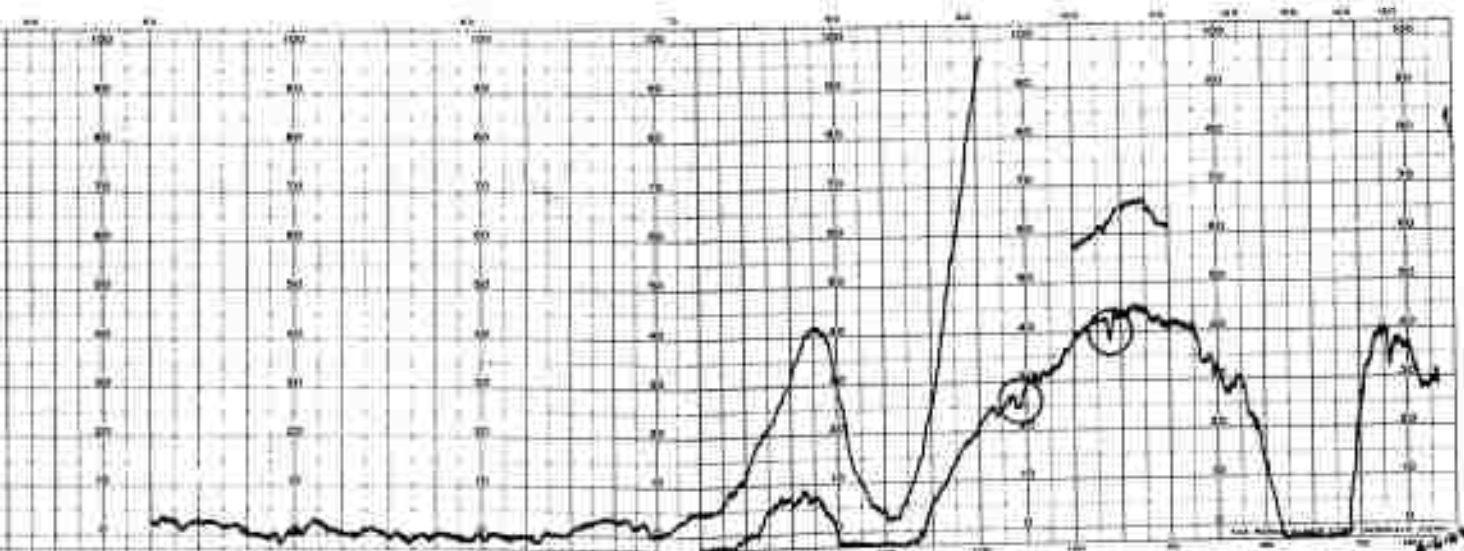
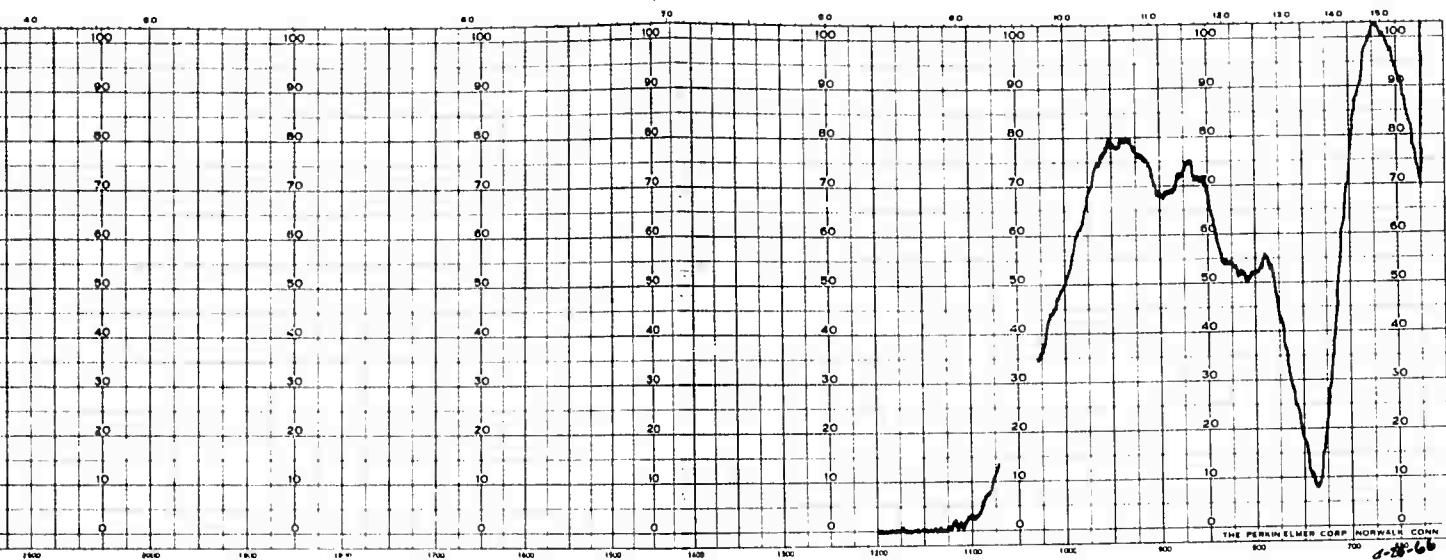


FIGURE 5: PELLET 5 (1.3 curies): INFRARED SPECTRA
(From top to bottom, 25 April, 6 June and 8 August 1966)

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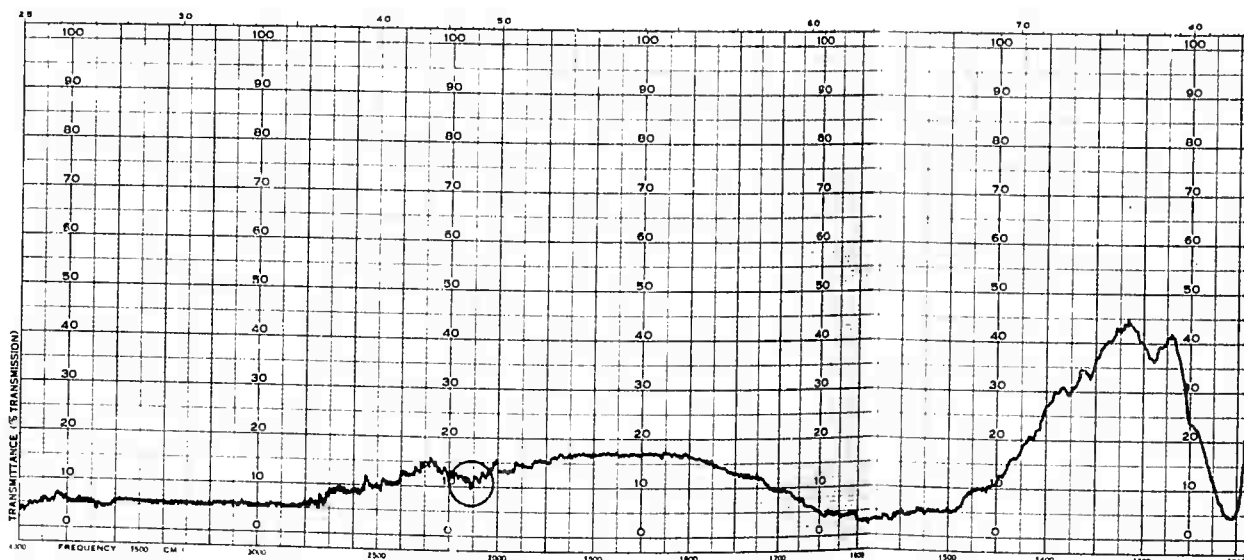
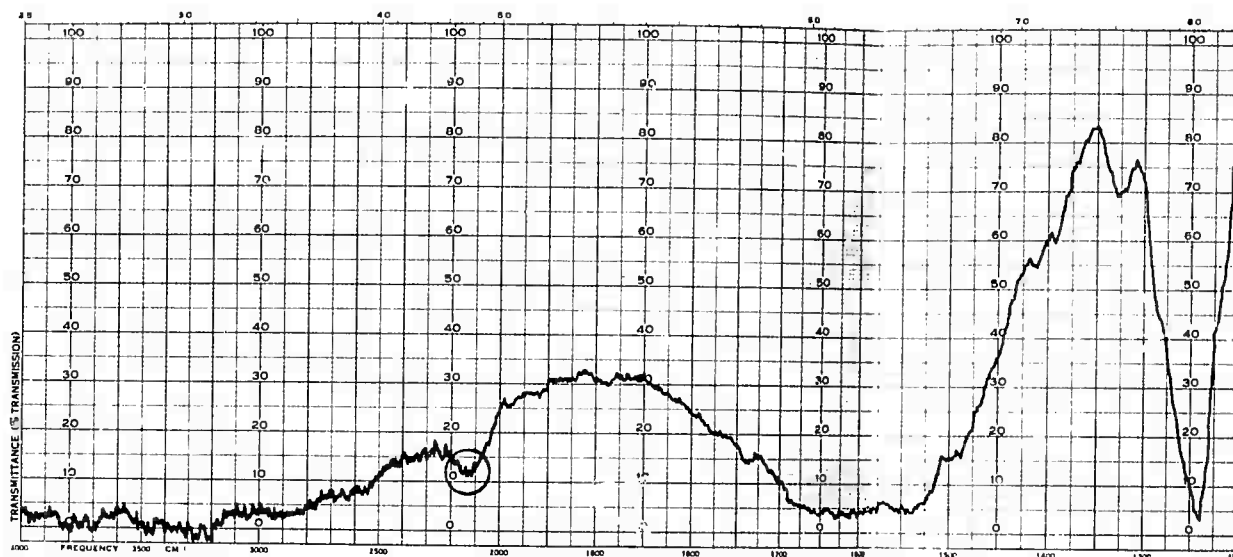
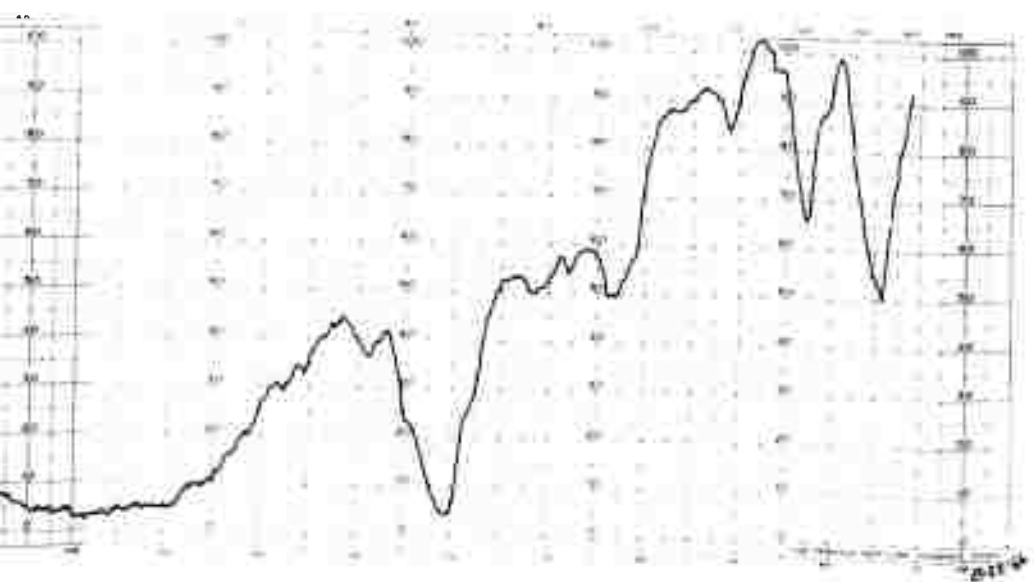
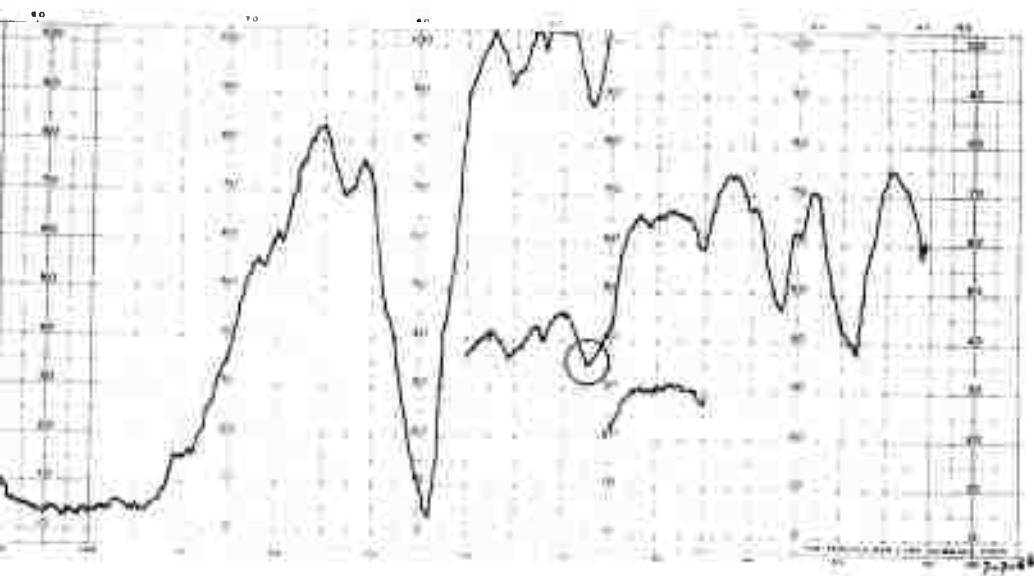


FIGURE 6: PELLET 7 (0.1 curies) : INFRARED SPECTRA
(Top, 7 July 1966, and bottom, 22 August 1966)

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NET 7 (0.1 curies): INFRARED SPECTRA
, and bottom, 22 August 1966)

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FIGURE 7 : PELLET 8 (2.0 curies) : INFRAR
(From top to bottom, 11 July, 2 August and

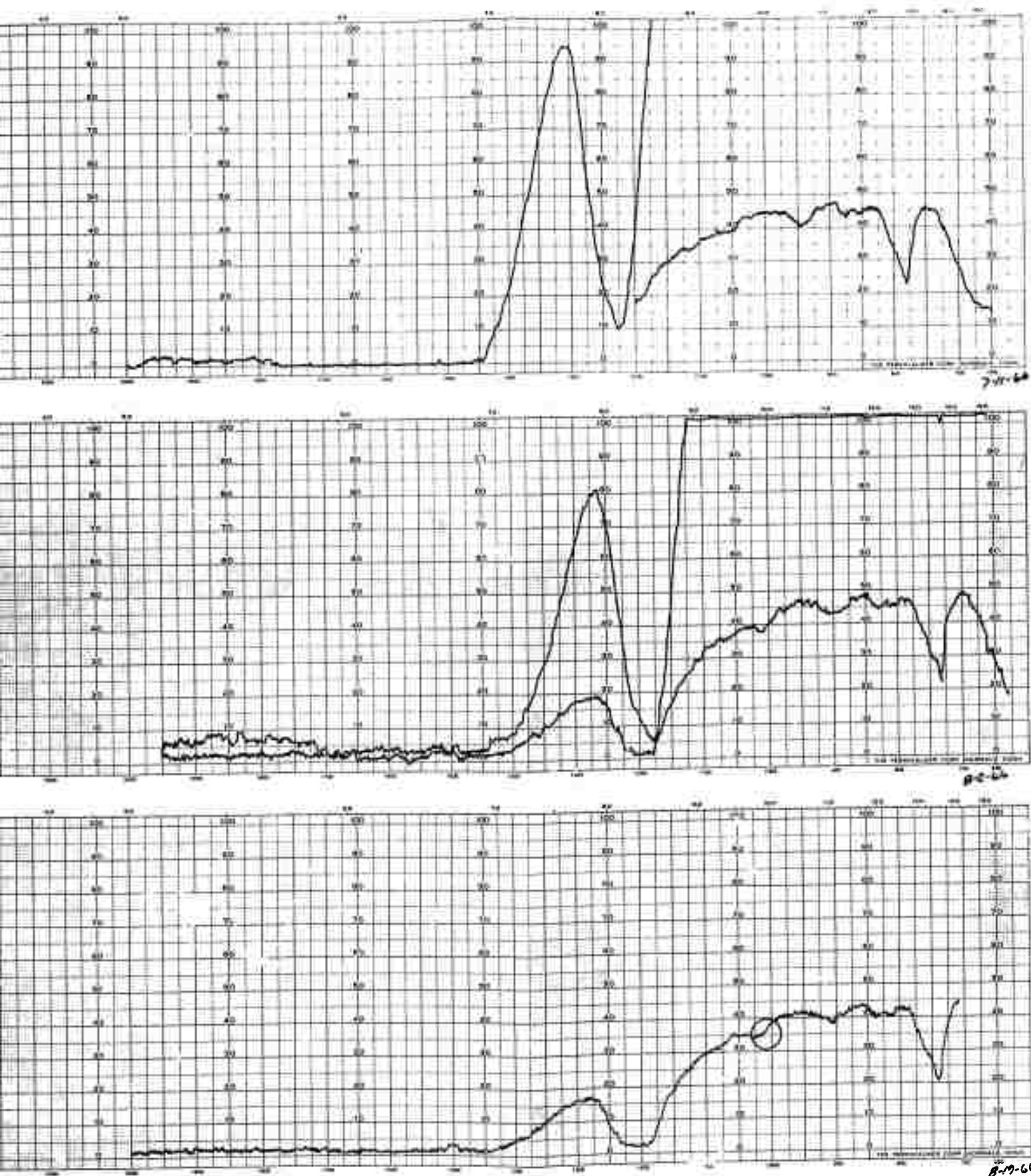


FIGURE 7 : PELLET 8 (2.0 curies) : INFRARED SPECTRA
(From top to bottom, 11 July, 2 August and 19 August 1966)

8

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13 ABSTRACT - An 18-month program to produce and identify the helium difluoride molecule is summarized in this final report. Nine tritiated samples were produced during the program; new IR absorption peaks found in two samples suggest that tritium decay is producing observable changes. It appears too soon to assign these new peaks to helium-compound formation. Experiments during the program indicated it is possible to detect helium-containing compounds in samples containing as little as one-half curie of tritium.

The beta decay tritium in a bifluoride-containing specimen was followed by infrared spectrophotometry for evidence of the conversion of $F-T-F^-$ ions into $F-He-F$ molecules.

It was experimentally determined that the optimum method of producing samples was to mix a small amount of polycrystalline $NaHF_2$ with KBr , and cold-press the mixture into transparent pellets. The nine tritiated samples produced under this contract were fully encased to prevent the escape of radioactive material.

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