

PRELIMINARY DATA FROM A SURVEY STUDY OF THE EFFECTS  
OF IONIZING RADIATION ON VOLATILE INORGANIC  
COMPOUNDS OF FLUORINE, OXYGEN, AND NITROGEN

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Introduction

Very little has appeared in the literature concerning the radiation chemistry of covalent inorganic compounds in condensed phase. In the search for new high energy oxidizers, it sounds plausible that ion fragmentation, electron capture, ion-molecule reactions and free radical combination reactions at low temperatures may be utilized.

Conversion of several per cent of low molecular weight materials by non-chain reactions requires radiation doses of the order of 100 megarads. A 3 Mev Van de Graaff with a gold target supplies this dose to a small sample in one hour. The sample can be held at any desired temperature in a Dewar flask. Detection of products, many of them highly reactive, is accomplished by direct distillation at low temperature and very low pressure into a time-of-flight mass spectrometer. With this basically simple technique, a survey of radiolysis of many systems, both pure and binary, is under way. This report describes results obtained thus far.

Experimental<sup>a)</sup>

Horizontal X-ray source. Large doses of 2-3 Mev bremsstrahlung (up to 100 megarad/hr) are generated by directing the 3 Mev electron beam from a Van de Graaff accelerator onto a water-cooled gold target (Figure 1). The vertical electron beam is deflected 90°, producing a horizontal beam, so that sample placement may be facilitated (Figure 2).

Reaction vessel. Samples to be irradiated are condensed into the cooled tip of a 4 mm o.d. thin-walled stainless steel tube. A brass slug, silver-soldered over the end of the tube, acts as a heat sink. A metering valve (Nupro No. SS-4M) connected to the tube with Swagelok fittings and equipped with a Kel-F O-ring seal and a micrometer handle complete the vessel.

Sample size. A standardized sample size of 0.075 mmole of reactant was chosen. In a binary reaction system the total sample comprises 0.15 mmole. These amounts provide a convenient sample for analysis and are considered to be safe in the event of an explosion in the 2 ml reaction vessel.

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a) Further experimental details may be found in Papers Presented, ARPA Propellant Contractors Synthesis Conference, IIT Research Institute, Chicago, April 13-15, 1964.

Cooling provisions. The irradiations are carried out at 77°K by immersing the reaction vessel in liquid nitrogen within a specially constructed vacuum flask (Figure 3) which contains a cooled side arm that is also convenient for accurate placing of the sample tube. A thermocouple and demand system replenishes the liquid nitrogen as necessary.

Dosimetry. Liquid dosimeters are of too large a volume to allow accurate determination of the dose delivered to the small (~50 µl) samples used in this study. A new cadmium dosimeter based on photoactivation has been developed by one of us<sup>a)</sup> and is useful in this study. When cadmium nuclei are irradiated with >1.25 Mev photons, metastable Cd<sup>111m</sup> nuclei are produced which decay with a 49 minute half life and emit 149 and 247 kev photons. A 50 µl volume (430 mg) of cadmium metal which has been irradiated for 5 minutes provides a sufficient activity count for accurate dosimetry.

Analysis. The samples under study are maintained at 77°K before, during and after irradiation. No warming is allowed until the sample tube has been connected to the mass spectrometer and analysis for non-condensable gases is complete. At 77°K the gases observed may include F<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>. When analysis for the non-condensable gases is complete these gases are pumped off through another valve until the pressure reaches ~0.05 mm, at which point analysis for gases which are condensable at 77°K, but which exert a significant vapor pressure at this temperature, is accomplished. Both NF<sub>3</sub> and OF<sub>2</sub> are among the compounds which may be seen at this point. The liquid nitrogen bath is removed when these data have been collected and in its place is substituted a 77-350°K variable cryostat. That sample is now slowly warmed and sequential fractions are distilled into the Bendix time-of-flight mass spectrometer. A rough separation is thus accomplished and the identification of products is made somewhat easier. Excess amounts of all components observed in the product mixture are pumped off at the temperature at which they are observed before the temperature is raised and the next fraction examined. The data thus obtained provide a qualitative indication of the compounds produced in the radiolysis and will serve as a guide for future, larger scale work.

## Results

Irradiations of pure substrates. Irradiation of one-component systems is a desirable prerequisite for the study of multi-component systems. The irradiation of a pure compound provides data which may indicate the identity of active intermediates which may then be considered for use as reactants in mixed systems. In addition, the possibility exists that products will result from such treatment that will be interesting in their own right. Also, it is necessary to obtain as much product identification data as possible in single-component systems in order to simplify the analytical problems encountered when mixtures are irradiated.

The data in Table. 1 are presented in the following manner: the second column lists the temperature of the sample tube from which the products are distilled into the mass spectrometer at ~ 8 x 10<sup>-6</sup> mm; the third

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a) C. D. Wagner, to be reported elsewhere.

column lists the products as identified by the mass spectra obtained at the respective temperatures, and the fourth column lists ions observed but for which no identification could be made.

Irradiations of Binary Mixtures. The low temperature irradiation of binary mixtures is being studied as a unique synthetic method which may produce compounds which have not been previously observed because of their low thermal stabilities. Their synthesis by purely chemical means may be very difficult or perhaps impossible, thus the collection of data describing such structures is a primary aspect of this study. The data below are presented in the same manner as those above (Table 2).

#### DISCUSSION

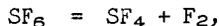
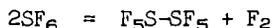
The basic processes which are responsible for reaction on irradiation of these covalent inorganic systems are due almost entirely to excitation and ionization of the molecules by the secondary electrons generated in the sample by Compton scattering. The primary species produced are excited molecule ions, and excited molecules; these species decompose to fragment ions and radicals and react with the bulk substrate and with one another to give the observed products. At present little is known of the reactions of such species at 77°K, and in this study, which is intended merely to indicate areas for promising further research, little emphasis has been placed on the elucidation of possible mechanisms of reactions. Such information can only be gained by considering the yields of the various products in a quantitative manner.

Without quantitative yield data one can say little concerning proposed sources of the observed products. It is even difficult without such data to state with certainty which products appear in predominant quantities and whether or not a chain reaction has been found. At this point it appears that the yields are modest and are those which one would expect of non-chain processes with G values of the order of 5-10.

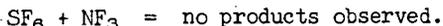
Some of the problems facing the investigator in a study such as this should be mentioned before one proceeds into a discussion of the irradiated systems. Many of the experimental difficulties have been successfully solved: application of a high dose rate of photons to a small sample, adequate cooling of the samples during irradiation, accurate dosimetry on the geometry of small samples, micro separation of the irradiation products, and analysis of micromolar amounts of highly reactive species via time-of-flight mass spectrometry. Aspects which can be improved include a method for mixing reactants in micro quantities at 77°K to be sure that an intimate mixture is obtained and perhaps a mass spectrometric method which would be capable of better identification through higher resolution. The mass spectrometric identification of compounds which are present in the mass spectrometer for a few fleeting seconds in some instances is tenuous. The ambiguity in the identification of ions from their  $m/q$  values alone is also a constant source of difficulty, as in the case of polyoxygen fluorides, where the  $O_4F_2^+$  ion and the  $HO_3SiF_3^+$  ion both possess a  $m/q$  value of 102, and the difference between these masses amounts to only 0.0015 amu.--an unresolvable difference with a TOF mass

spectrometer. Fortunately, most systems lend themselves to TOF mass spectrometry without too much ambiguity. Differences in the volatility of the compounds encountered help to make rational decisions about the identify of the species observed (Table 3).

As the data demonstrate, a large variety of products may be expected in the irradiations of compounds containing the -NF and -OF groups. In most of the irradiations of these fluorine-containing compounds, elemental fluorine,  $F_2$ , is observed as a product. In those cases where no  $F_2$  is found, one may wish to examine the system in order to see if either the starting material(s) or one of the products is likely to be attacked by  $F_2$  at 77°K. Thus, in the case of  $SF_6$ , where one might expect one or both of the following reactions on irradiation,



no product is observed. One hypothesis that might be suggested for this result is that these reactions may proceed in the reverse direction spontaneously at 77°K, the temperature at which the irradiation is performed. A test for this hypothesis would be the successful trapping of the intermediates before the reverse reaction occurs. Using  $NF_3$ , no reaction occurs with  $SF_6$  on irradiation:



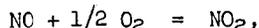
In the presence of  $OF_2$ , however, it is found that products are generated in the irradiation,



thus, it appears that either an irradiation product of  $OF_2$  attacks  $SF_6$  successfully, or some sulfur-containing intermediate has been trapped. In any case, the sulfur-oxygen bond formed resists attack by fluorine and a product is observed.

Similar behavior is exhibited in the case of  $SO_2$ . Alone,  $SO_2$  gives no products on irradiation. In the presence of either  $NF_3$  or  $OF_2$ , however, reaction occurs and all the fluorine which one would normally see from  $NF_3$  or  $OF_2$  alone appears in the products,  $SO_2F_2$ ,  $SF_4O$ , and (possibly)  $SF_4$ . In the case of  $SiF_4$ , no reaction has yet been effected, either alone or with possible trapping agents ( $NF_3$  and  $OF_2$ ).

The nitrogen oxides seem to be fairly regularly interconverted on irradiation. An exception to this is that nitric oxide never appears among the products at 77°K, where we know from experience that it can be observed in a product mixture and quantitatively pumped off. In systems which generate both  $NO$  and  $O_2$ , it is probable that the  $NO$  is lost in the reaction,



which requires little activation energy. In order for us not to see NO in these systems, the above reaction must occur before analysis.

The interesting phenomenon of oxygen hold-up occurs in the irradiation of dinitrogen tetroxide. Whereas no  $O_2$  is observed at 77°K on analysis of a sample of irradiated  $N_2O_4$ , when the temperature is raised to about 175°K,  $O_2$  and NO are evolved. Since we have not observed the trapping of oxygen in the solid  $N_2O_4$  lattice previously, it appears that at 175° a decomposition is occurring; no additional data are yet available concerning the compound(s) which may be the source of this decomposition.

The irradiation of  $CF_3Cl$  in the presence of Xe appears to give a higher product yield than does  $CF_3Cl$  alone. Also, more products are observed, as might be expected from a higher conversion. Xe thus exerts a synergistic effect and may act as an efficient energy transfer agent. Carbon dioxide seems to display a similar effect in the irradiation of  $NF_3$ .

The products from nitrosyl fluoride and nitrosyl chloride show that a great many processes must occur when these systems are irradiated. Although no oxygen is observed among the products, in the case of  $O=NF$  all of the  $O_xF_2$  species normally seen from  $OF_2$  are produced, though  $OF_2$  itself is not seen. If oxygen or  $OF_2$  are products, they must be quantitatively used in secondary reactions. The great variety of N-F compounds and nitrogen oxides produced in these systems add to the confusion, but most striking is the production of apparent dimers (and possibly trimers) of the nitrosyl halides,  $(O=NF)_2$  and  $(O=NCl)_2$ , for which no structure is yet suggested. Many such structures can be written.

The two systems which have been most thoroughly studied in this work are the  $NF_3$  and the  $OF_2$  systems. These materials were both irradiated early in the program and then frequently again both alone and admixed with other reactants. The products of these irradiations, by virtue of the fact that they involve only two elements each, are confined to a small number:

$NF_3$        $N_2$ ,  $F_2$ , cis- $N_2F_2$ , trans- $N_2F_2$ , and  $N_2F_4$

$OF_2$        $O_2$ ,  $F_2$ ,  $O_2F_2$ ,  $O_3F_2$ , and  $O_4F_2(?)$ .

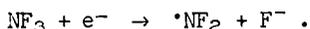
The chemistry involved, however, is complicated. We see in the first case that by some means that all of the fluorine atoms have been stripped from  $NF_3$ , producing  $N_2$ .

The mass spectrum of  $NF_3$  shows  $NF_3^+$ ,  $NF_2^+$  and  $NF^+$  as predominant ions with significant yields of  $N^+$  and even  $F^+$  as well;<sup>(4)</sup> the formation of

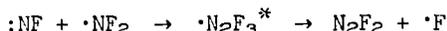
(4) C. H. Colburn and A. J. Kennedy, J. Am. Chem. Soc. 80, 5004 (1958).

the fragment ions is presumably accompanied by formation of  $F_2$  and  $F$ . Similar products may arise from the initial excitation of  $NF_3$  during radiolysis in the condensed phase, but here the detailed course of events may be modified by collisions between excited species and surrounding molecules.

Recombination of ions and electrons should lead to the formation of  $\cdot\text{NF}_2$  and  $:\text{NF}$  radicals. Formation of  $\cdot\text{NF}_2$  radicals and  $\text{F}^-$  ions may occur also by the exothermic process



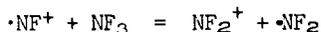
Formation of  $\text{N}_2\text{F}_4$  can clearly occur by recombination of  $\cdot\text{NF}_2$  radicals;  $\text{N}_2\text{F}_2$  may form similarly from  $:\text{NF}$  radicals though the energy release will favor decomposition of the product. The exothermic cross-coupling radical reaction



is also a possibility. A possible route to  $\text{N}_2$  and  $\text{F}_2$  is provided by the related reaction



in which the first step makes available about 4 ev of excitation energy. Still other possibilities are provided by ion-molecule reactions such as



which may be slightly exothermic, and by reactions of  $\text{F}^-$  with any of the positive ions mentioned above.

Similar reasoning can be made to account qualitatively for the products obtained from  $\text{OF}_2$ . The task ahead will be to gain more data concerning these systems, to obtain more concrete evidence for the mechanism of the reactions and to attempt to devise experiments in which some of the intermediate species postulated may be trapped and identified.

#### Conclusion

The technique described and the results obtained serve to indicate that low temperature radiation synthesis is indeed a tool which may prove to be of value in the study of endothermic oxidizing agents of low thermal stability. Although no quantitative product distribution has been measured, and some of the products are still not identified, the guidelines established by a survey study such as this will be of great value in choosing systems worthy of further study. The mass spectrometric analysis scheme for the product mixtures will provide a monitoring system in guiding the separation of larger amounts of the irradiation products. Other techniques, such as gas-liquid chromatography, infrared and U.V. spectroscopy, as well as NMR, will, of course, have to be applied in the characterization of those compounds which we have until now deemed "uncharacterized".

#### Acknowledgment

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Table 1

Compound Irradiated	Temp, °K	Products Identified (In Approximate Order of Abundance)	Ions Observed-Source Unidentified
NF <sub>3</sub>	77 100 134	N <sub>2</sub> , F <sub>2</sub> (see Fig. 4) <u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u> N <sub>2</sub> F <sub>4</sub>	
N <sub>2</sub> F <sub>4</sub>	77 105	N <sub>2</sub> , F <sub>2</sub> , NF <sub>3</sub> <u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u>	
FNO	77 123 161 223 293	N <sub>2</sub> , NO N <sub>2</sub> O, <u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u> O <sub>2</sub> F <sub>2</sub> , O <sub>3</sub> F <sub>2</sub> , O <sub>4</sub> F <sub>2</sub> (?) N <sub>2</sub> F <sub>4</sub> N <sub>2</sub> O <sub>4</sub> , NO <sub>2</sub> F (?)	N <sub>3</sub> F <sup>+</sup> , O <sub>2</sub> <sup>+</sup> (2) N <sub>2</sub> O <sup>+</sup> (2) N <sub>2</sub> F <sup>+</sup> (2) NOF <sup>+</sup> , N <sub>2</sub> O <sub>2</sub> F <sup>+</sup> , N <sub>2</sub> OF <sub>2</sub> <sup>+</sup> N <sub>3</sub> O <sub>2</sub> F <sup>+</sup> , plus those observed at 223
ClNO	77 195 292	N <sub>2</sub> , NO N <sub>2</sub> O <sub>4</sub> , N <sub>2</sub> O, Cl <sub>2</sub>	N <sub>2</sub> OCl <sup>+</sup> , N <sub>2</sub> O <sub>2</sub> Cl <sup>+</sup>
N <sub>2</sub> O	77 244	N <sub>2</sub> , O <sub>2</sub> N <sub>2</sub> O <sub>4</sub>	
NO	77 124 243	N <sub>2</sub> N <sub>2</sub> O N <sub>2</sub> O <sub>4</sub>	
N <sub>2</sub> O <sub>4</sub>	77 176	N <sub>2</sub> (no O <sub>2</sub> ) NO, O <sub>2</sub> , trace N <sub>2</sub> O	

2) This species evolved from a decomposition at this temperature.

(Continued)

Table 1 (Contd)

Compound Irradiated	Temp, °K	Products Identified (In Approximate Order of Abundance)	Ions Observed-Source Unidentified
OF <sub>2</sub>	77	F <sub>2</sub> , O <sub>2</sub>	
	107	COF <sub>2</sub> , <sup>(3)</sup> O <sub>2</sub> , <sup>(2)</sup> F <sub>2</sub> <sup>(2)</sup> OF <sub>2</sub> <sup>(2)</sup>	
	128	O <sub>2</sub> , <sup>(2)</sup> F <sub>2</sub> , <sup>(2)</sup> CO <sub>2</sub> <sup>(3)</sup>	
	176	O <sub>3</sub> F <sub>2</sub> , O <sub>2</sub> F <sub>2</sub> , O <sub>2</sub> , <sup>(2)</sup>	
	219	Cl <sub>2</sub> , <sup>(3)</sup> O <sub>4</sub> F <sub>2</sub> (?) O <sub>2</sub> F <sub>2</sub> , O <sub>3</sub> F <sub>2</sub> (trace), O <sub>2</sub> , <sup>(2)</sup> CClF <sub>3</sub> (trace) <sup>(3)</sup>	
SO <sub>2</sub>		No products observed to 350°.	
SO <sub>2</sub> F <sub>2</sub>	83	O <sub>2</sub> , OF <sub>2</sub>	SO <sub>4</sub> F <sup>+</sup> , SO <sub>2</sub> F <sub>3</sub> <sup>+</sup>
	143	CO <sub>2</sub> (trace) <sup>(3)</sup>	
	253	SOF <sub>4</sub> , SF <sub>6</sub>	
SF <sub>6</sub>		No products observed to 350°.	
SiF <sub>4</sub>		No products observed to 350°.	
CF <sub>3</sub> Cl	77	CF <sub>4</sub>	
	293	C <sub>2</sub> F <sub>6</sub> , CF <sub>2</sub> Cl <sub>2</sub> , Cl <sub>2</sub> , and C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> or C <sub>2</sub> ClF <sub>5</sub> .	
CCl <sub>4</sub>	208	Cl <sub>2</sub>	
	293	C <sub>2</sub> Cl <sub>6</sub> , plus a C <sub>3</sub> species, probably C <sub>3</sub> Cl <sub>8</sub> .	

- 2) This species evolved from a decomposition at this temperature.
- 3) From the action of the sample on the Kel-F grease on the O-ring seal.

Table 2

Compound Irradiated	Temp, °K	Products Identified (In Approximate Order of Abundance)	Ions Observed-Source Unidentified
NF <sub>3</sub> & O <sub>2</sub>	77	N <sub>2</sub> , (2)	NO <sup>+</sup> , N <sub>2</sub> O <sup>+</sup> , NO <sub>2</sub> <sup>+</sup> , N <sub>2</sub> F <sup>+</sup> , OF <sup>+</sup>
	100	F <sub>2</sub> (2)	
	143	F <sub>2</sub> , (2) O <sub>2</sub> , (2) FNO N <sub>2</sub> O, <u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u> , NO <sub>2</sub> F (?)	
	211	Cl <sub>2</sub> , (3) OF <sub>2</sub> , (2) O <sub>3</sub> F <sub>2</sub> OF <sub>2</sub> , (2) O <sub>2</sub> (2)	
	253	N <sub>2</sub> O <sub>4</sub>	
NF <sub>3</sub> & OF <sub>2</sub>	77	N <sub>2</sub> , O <sub>2</sub> , F <sub>2</sub> ,	NO <sup>+</sup>
	108	<u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u> , COF <sub>2</sub> (3)	
	116	CO <sub>2</sub> , (3) N <sub>2</sub> O	
	211	O <sub>2</sub> F <sub>2</sub>	
	253	N <sub>2</sub> O <sub>4</sub>	
NF <sub>3</sub> & N <sub>2</sub> O	77	N <sub>2</sub> , O <sub>2</sub> , F <sub>2</sub>	
	110	<u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u> ,	
	179	FNO, Cl <sub>2</sub> , (3) NO <sub>2</sub> F (?)	
	253	N <sub>2</sub> O <sub>4</sub>	
NF <sub>3</sub> & NO	77	N <sub>2</sub>	N <sub>2</sub> <sup>+</sup> , NF <sup>+</sup>
	83		
	98	<u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u> (large amounts)	
	113	N <sub>2</sub> F <sub>4</sub> (large amounts) N <sub>2</sub> O	
	193	N <sub>2</sub> O <sub>4</sub> , FNO	
NF <sub>3</sub> & N <sub>2</sub> O <sub>4</sub>	77	N <sub>2</sub> , F <sub>2</sub> , trace O <sub>2</sub>	O <sub>2</sub> <sup>+</sup> , N <sub>2</sub> <sup>+</sup> , NF <sub>2</sub> <sup>+</sup>
	111	<u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u>	
	148	N <sub>2</sub> F <sub>4</sub> , N <sub>2</sub> O, FNO NFO <sub>2</sub> (?)	
	204	N <sub>2</sub> O <sub>4</sub>	

2) This species evolved from a decomposition at this temperature.

3) From the action of the sample on the Kel-F grease on the O-ring seal.

(Continued)

Table 2 (Cont'd)

Mixture Irradiated	Temp, °K	Products Identified (In Approximate Order of Abundance)	Ions Observed—Source Unidentified
NF <sub>3</sub> + SO <sub>2</sub>	77	N <sub>2</sub> , F <sub>2</sub>	
	99	<u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u>	
	123	N <sub>2</sub> F <sub>4</sub> , SO <sub>2</sub> F <sub>2</sub> , SF <sub>4</sub> (trace), CO <sub>2</sub> (3)	
	169	SO <sub>2</sub> F <sub>4</sub> (?)	
NF <sub>3</sub> + SF <sub>6</sub>		No products other than those of NF <sub>3</sub> alone observed up to 350°.	
NF <sub>3</sub> + SiF <sub>4</sub>		(Same as above)	
NF <sub>3</sub> + CCl <sub>4</sub>	77	N <sub>2</sub> , CF <sub>4</sub>	
	128	N <sub>2</sub> F <sub>4</sub> , <u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u> , CCl <sub>2</sub> F <sub>2</sub>	
	173	Cl <sub>2</sub> , NF <sub>2</sub> CCl <sub>3</sub> (?) →	NCl <sup>+</sup> , NF <sub>2</sub> CCl <sup>+</sup> , NFCCL <sub>2</sub> <sup>+</sup> ,
	195	CCl <sub>3</sub> F	
	293	C <sub>2</sub> Cl <sub>6</sub>	
NF <sub>3</sub> + C <sub>2</sub> H <sub>2</sub>	77	N <sub>2</sub>	
	89	<u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u>	
	156	CHF=CHF	
	186	C <sub>6</sub> H <sub>6</sub> , NF <sub>2</sub> CH=CHF (?) →	NF <sub>2</sub> <sup>+</sup> , CHF <sup>+</sup> , CHNF <sup>+</sup> , C <sub>2</sub> NF <sub>2</sub> <sup>+</sup> , C <sub>2</sub> NF <sub>2</sub> H <sup>+</sup> , C <sub>2</sub> NF <sub>2</sub> H <sub>2</sub> <sup>+</sup>
NF <sub>3</sub> + CO <sub>2</sub>		Increased yields of normal NF <sub>3</sub> irradiation products as well as some COF <sub>2</sub>	
NF <sub>3</sub> +F <sub>2</sub> C=CH <sub>2</sub>	77	N <sub>2</sub> , CF <sub>4</sub>	
	130	N <sub>2</sub> F <sub>4</sub> , <u>cis-N<sub>2</sub>F<sub>2</sub></u> , (traces) <u>trans-N<sub>2</sub>F<sub>2</sub></u> (traces)	
	293	CF <sub>3</sub> CH <sub>2</sub> F, F <sub>2</sub> NCH <sub>2</sub> CF <sub>3</sub> (?) →	NF <sub>2</sub> <sup>+</sup> , CF <sub>3</sub> <sup>+</sup> , C <sub>2</sub> NF <sub>2</sub> <sup>+</sup> , C <sub>2</sub> NF <sub>2</sub> H <sup>+</sup> , (weak intensities)

3) From the action of the sample on the Kel-F grease on the O-ring seal.

(Continued)

Table 2 (Cont'd)

Mixture Irradiated	Temp, °K	Products Identified (In Approximate Order of Abundance)	Ions Observed-Source Unidentified
OF <sub>2</sub> + N <sub>2</sub>	77	O <sub>2</sub> , F <sub>2</sub> , NF <sub>3</sub>	
	107	<u>cis-N<sub>2</sub>F<sub>2</sub></u> , <u>trans-N<sub>2</sub>F<sub>2</sub></u> N <sub>2</sub> , (2) O <sub>2</sub> , (2) OF <sub>2</sub> (2)	
	128	N <sub>2</sub> O, CO <sub>2</sub> , N <sub>2</sub> , (2) O <sub>2</sub> , (2) OF <sub>2</sub> , (2) NO <sub>2</sub> F (?)	
	191	N <sub>2</sub> O <sub>4</sub>	
OF <sub>2</sub> + O <sub>2</sub>	77	(No F <sub>2</sub> observed)	
	93	O <sub>3</sub>	
	133	SiF <sub>4</sub> , (4)	
	173	CO <sub>2</sub> , (3) COF <sub>2</sub> , (3) O <sub>2</sub> , (2) F <sub>2</sub> (2)	
	192	O <sub>3</sub> F <sub>2</sub> , O <sub>2</sub> F <sub>2</sub> , O <sub>2</sub> , (2) F <sub>2</sub> (2)	
OF <sub>2</sub> + N <sub>2</sub> O	77	F <sub>2</sub> , N <sub>2</sub> , O <sub>2</sub>	
	132	COF <sub>2</sub> , (3) FNO, NO <sub>2</sub> F (?)	
	199	N <sub>2</sub> O <sub>4</sub>	
OF <sub>2</sub> + NO(s)	77	O <sub>2</sub> , N <sub>2</sub> , F <sub>2</sub> , OF <sub>2</sub> , NF <sub>3</sub>	
	158	N <sub>2</sub> O, COF <sub>2</sub> , (3) SiF <sub>4</sub> , (4) FNO, NO <sub>2</sub> F (?)	
	193	N <sub>2</sub> O <sub>4</sub>	
OF <sub>2</sub> + N <sub>2</sub> O <sub>4</sub>	77	O <sub>2</sub> , F <sub>2</sub>	
	151	O <sub>2</sub> , (2) CO <sub>2</sub> , (3) COF <sub>2</sub> , (3) NO <sub>2</sub> F (?)	
	193	O <sub>2</sub> F <sub>2</sub> , FNO, O <sub>2</sub> (2)	

2) This species evolved from a decomposition at this temperature.

3) From the action of the sample on the Kel-F grease on the O-ring seal.

4) Impurity.

5) Mixture exploded before irradiation. Products were analyzed in the usual manner.

(Continued)

Table 2 (Cont'd)

Mixture Irradiated	Temp, °K	Products Identified (In Approximate Order of Abundance)	Ions Observed-Source Unidentified
OF <sub>2</sub> + SO <sub>2</sub>	77	O <sub>2</sub> F, F <sub>2</sub> , SF <sub>2</sub> (?) →	SF <sub>2</sub> <sup>+</sup> , SF <sup>+</sup> , S <sup>+</sup> (weak intensities)
	110	SO <sub>2</sub> F <sub>2</sub> , SF <sub>4</sub> , SOF <sub>4</sub> , SF <sub>6</sub>	
	143	CO <sub>2</sub> <sup>(3)</sup> (trace)	
OF <sub>2</sub> + SF <sub>6</sub>	77	O <sub>2</sub> , F <sub>2</sub>	
	137	O <sub>2</sub> F <sub>2</sub> , CO <sub>2</sub> , (3) O <sub>2</sub> , (2) F <sub>2</sub> , (2) OF <sub>2</sub> (2)	
	161	SOF <sub>4</sub>	
OF <sub>2</sub> + SiF <sub>4</sub>		No products other than those of OF <sub>2</sub> alone observed up to 350°.	
OF <sub>2</sub> + CCl <sub>4</sub>		Poor data - ambiguity exists in distinguishing OF from <sup>35</sup> Cl.	
OF <sub>2</sub> + CO <sub>2</sub>	77	F <sub>2</sub> , trace O <sub>2</sub>	
	103	O <sub>2</sub> (2) (large amount)	
	120	COF <sub>2</sub> (3)	
	133	O <sub>2</sub> , (2) OF <sub>2</sub> (2)	
	181	O <sub>2</sub> F <sub>2</sub> , C <sub>3</sub> F <sub>2</sub>	
	220	O <sub>2</sub> , (2) OF <sub>2</sub> , (2) CO <sub>2</sub> (2)	CO <sub>4</sub> F <sub>4</sub> <sup>+</sup> , CO <sub>4</sub> F <sub>3</sub> <sup>+</sup> , CO <sub>2</sub> F <sub>3</sub> <sup>+</sup> , C <sub>2</sub> CF <sub>3</sub> <sup>+</sup> , C <sub>2</sub> O <sub>2</sub> F <sub>2</sub> <sup>+</sup> , COF <sub>3</sub> <sup>+</sup> , CO <sub>2</sub> F <sub>2</sub> <sup>+</sup> , C <sub>2</sub> O <sub>3</sub> <sup>+</sup> , CO <sub>2</sub> F <sup>+</sup>
CF <sub>3</sub> Cl + Xe	77	CF <sub>4</sub>	
	112	Cl <sub>2</sub> , C <sub>2</sub> F <sub>6</sub> , CF <sub>2</sub> Cl <sub>2</sub>	
	183	C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub> , C <sub>2</sub> Cl <sub>2</sub> F <sub>4</sub> , CCl <sub>3</sub> F, XeF <sub>2</sub> (?) →	Xe (?) -132; XeF (?) -151; XeF <sub>2</sub> (?) -170
Cl <sub>2</sub> + Xe		No products observed up to 350°.	

2) This species evolved from a decomposition at this temperature.

3) From the action of the sample on the Kcl-F grease on the O-ring seal.

Table 3  
Emergence order of compounds observed in mass spectrometer  
( $P=3 \times 10^{-6}$  mm) and their respective approximate distillation  
temperatures.

Compound	Temp, °K	Compound	Temp, °K
N <sub>2</sub>	77	N <sub>2</sub> F <sub>4</sub>	130
O <sub>2</sub>	77	FN=O	150
F <sub>2</sub>	77	SO <sub>2</sub>	150
NF <sub>3</sub>	77	SF <sub>6</sub>	160
NO	77	Cl-N=O	200
OF <sub>2</sub>	77	N <sub>2</sub> O <sub>4</sub>	200
CF <sub>4</sub>	77	CCl <sub>4</sub>	210
C <sub>2</sub> H <sub>4</sub>	90		
N <sub>2</sub> F <sub>2</sub>	100		
Xe	100		
CH <sub>2</sub> CF <sub>2</sub>	100		
SO <sub>2</sub> F <sub>2</sub>	105		
SiF <sub>4</sub>	110		
CF <sub>3</sub> Cl	110		
COF <sub>2</sub>	120		
N <sub>2</sub> O	125		
C <sub>2</sub> H <sub>2</sub>	125		
CO <sub>2</sub>	125		
SiF <sub>4</sub>	125		

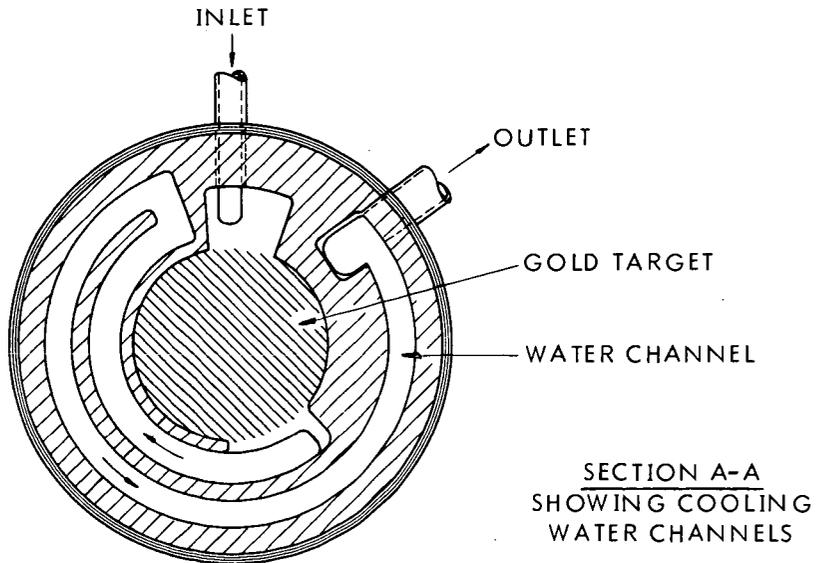
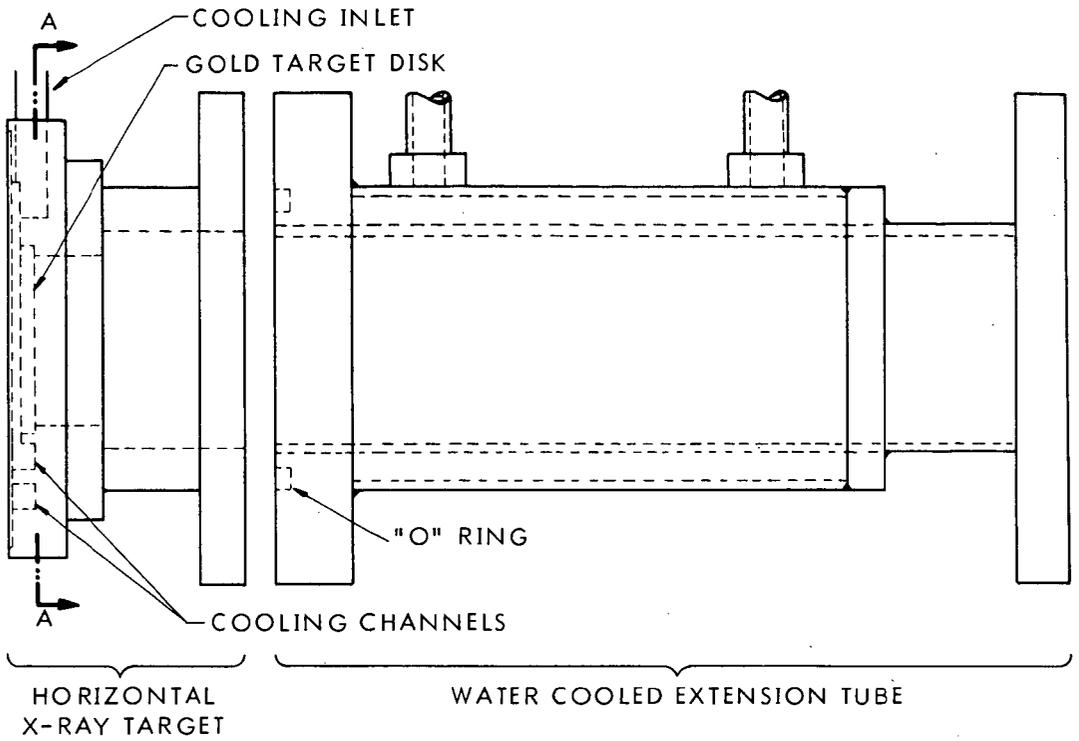


Figure 1. HORIZONTAL X-RAY TARGET WITH WATER COOLED EXTENSION TUBE

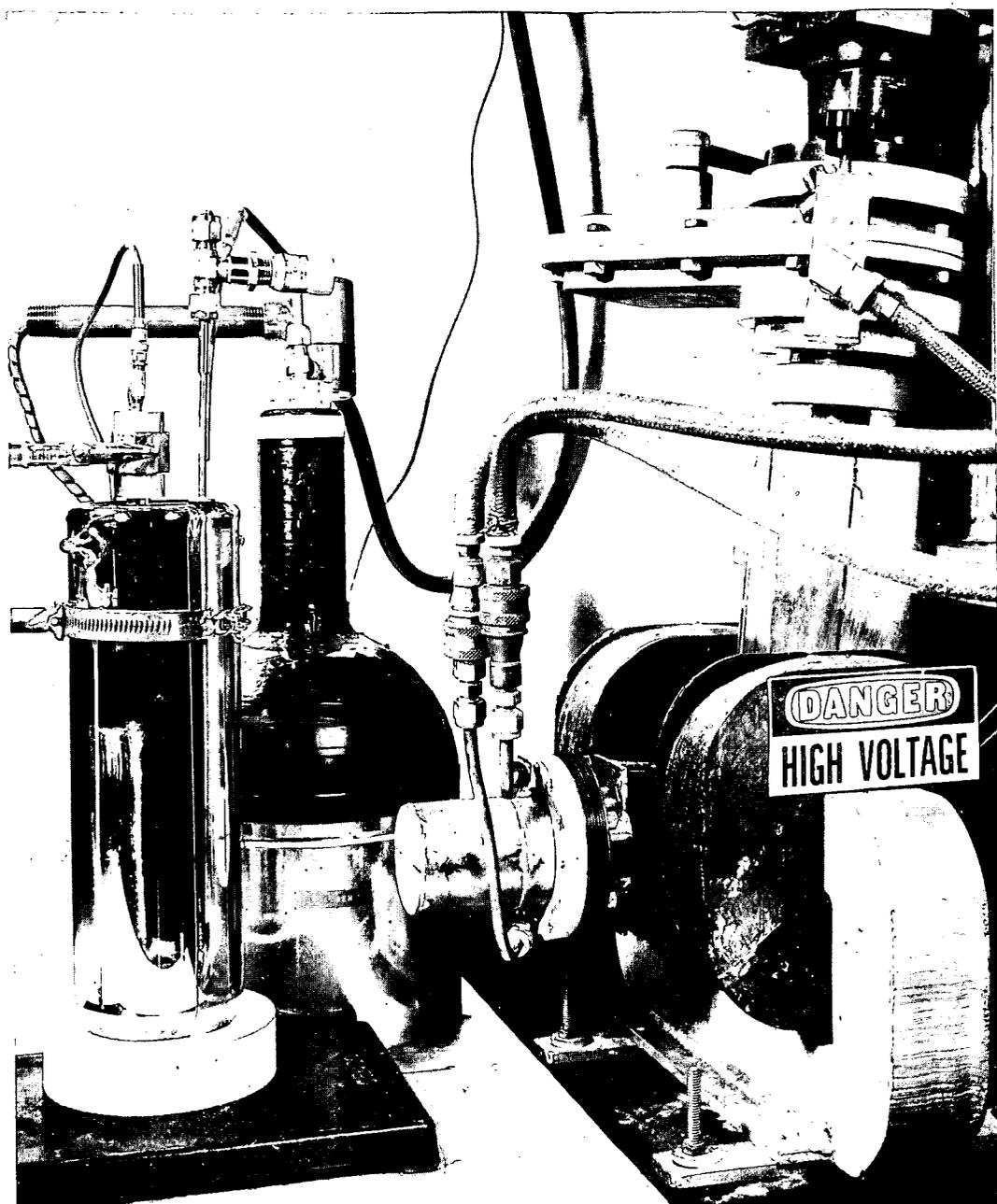


Figure 2. APPARATUS FOR IRRADIATION WITH HIGH ENERGY PHOTONS

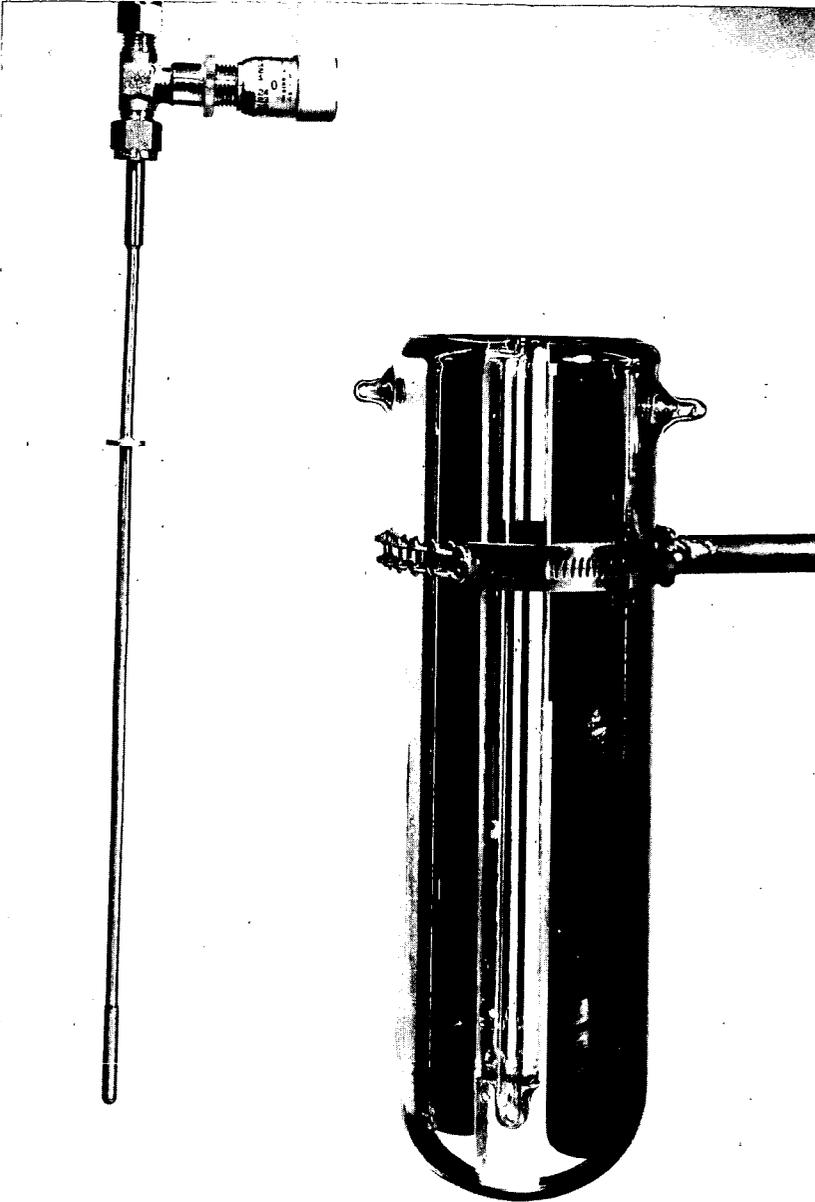


Figure 3. SPECIAL DEWAR FOR HOLDING SAMPLE DURING IRRADIATION AT  $-196^{\circ}$

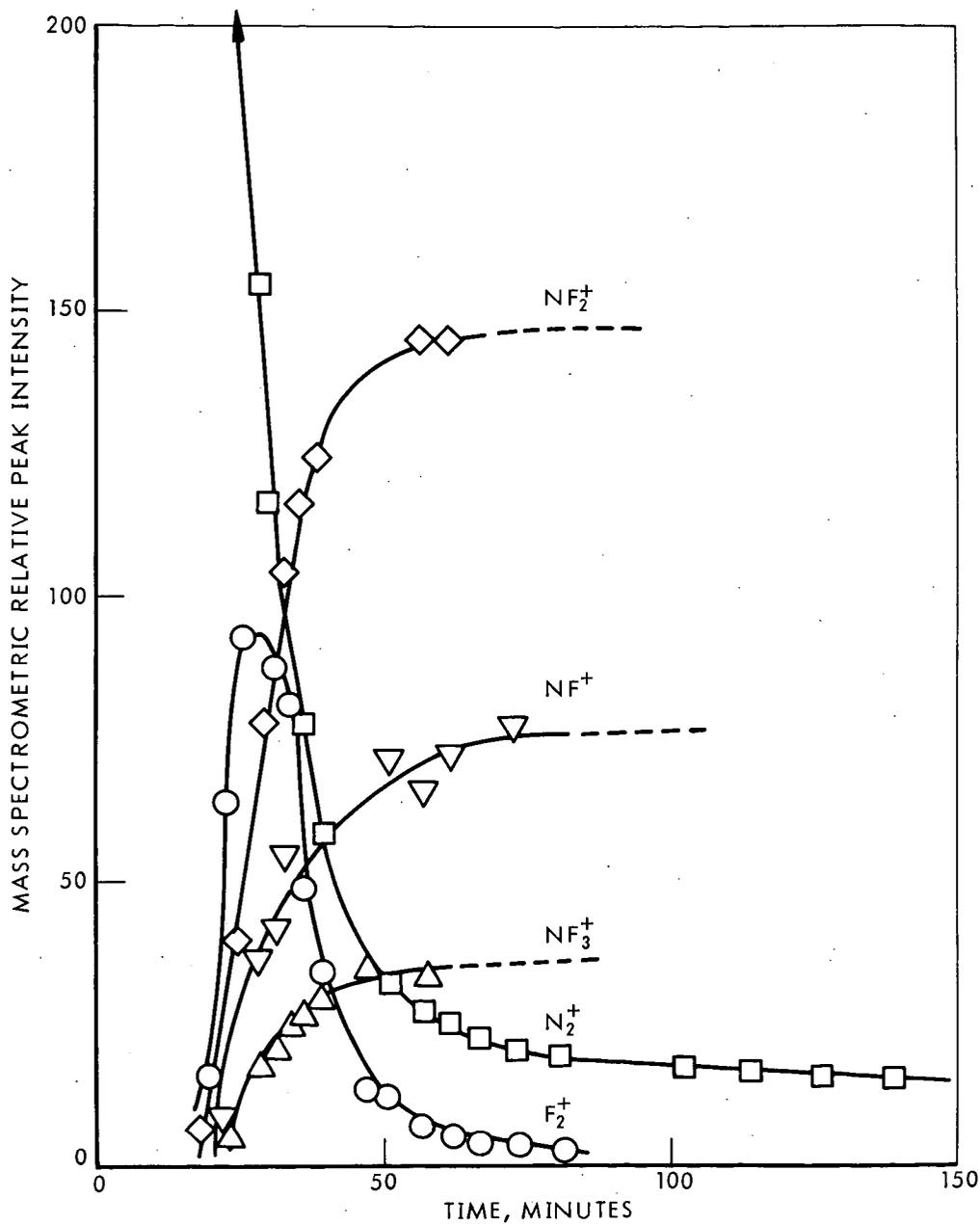


Figure 4. NF<sub>3</sub> IRRADIATION PRODUCT ANALYSIS:  
TIME vs PEAK INTENSITY AT -196°