

# THE PURIFICATION OF DINITROGEN TETRAFLUORIDE BY GAS CHROMATOGRAPHY, ITS MASS SPECTRUM, INFRA-RED SPECTRUM AND VAPOR PRESSURE CURVE\*

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## INTRODUCTION

Dinitrogen tetrafluoride ( $N_2F_4$ ) which had been prepared by a method described by COLBURN AND KENNEDY<sup>1</sup> was found to contain nitrous oxide impurity which at times comprised 15 % of a sample. A feasible method of purification was necessary to determine physical properties accurately. Standard methods such as low temperature distillation, vacuum line fractional condensation, and chemical reaction to remove nitrous oxide were attempted, but were found to be either too laborious or ineffective. Therefore, a gas chromatographic method was developed that isolated the compound from crude mixtures. Mass spectrometric analysis showed that it was free of all contaminants.

The removal of nitrous oxide from dinitrogen tetrafluoride by distillation was not practical because difficulty was encountered in reaching equilibrium. Nitrous oxide is usually present in the starting material ( $NF_3$ ) if it is prepared by the electrolysis of ammonium bifluoride<sup>2</sup>. A method was devised in this laboratory which provided nitrogen trifluoride that was in excess of 99 % pure. Filtration at liquid nitrogen temperature through a sintered glass disc purified large quantities rapidly and efficiently. Upon pyrolysis of this material, however, nitrous oxide was still present in the product, along with unreacted  $NF_3$ ,  $CF_4$ ,  $NO$ ,  $SiF_4$  and  $N_2F_2$ . This was found to be due to oxygen which had been condensed into the starting material.

Nitrogen trifluoride, carbon tetrafluoride, and nitric oxide could be removed almost entirely by fractionation of the crude pyrolysis product from a  $-160^\circ$  slush bath (isopentane). Nitrous oxide ( $N_2O$ ), silicon tetrafluoride ( $SiF_4$ ), and dinitrogen difluoride ( $N_2F_2$ ) could not be removed easily from large quantities of material. Nitrous oxide remained as the principal contaminant and  $N_2F_2$  and  $SiF_4$  were present in only low concentrations.

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## EXPERIMENTAL

*Chromatography*

The chromatographic apparatus shown schematically in Fig. 1 was constructed. Solenoid valves were used in place of stopcocks since valve switching could be accomplished much more rapidly. A section of copper refrigeration tubing  $\frac{1}{4}$  in. o.d. and 160 cm long was packed with Burrell silica gel (catalog No. 341-25). This

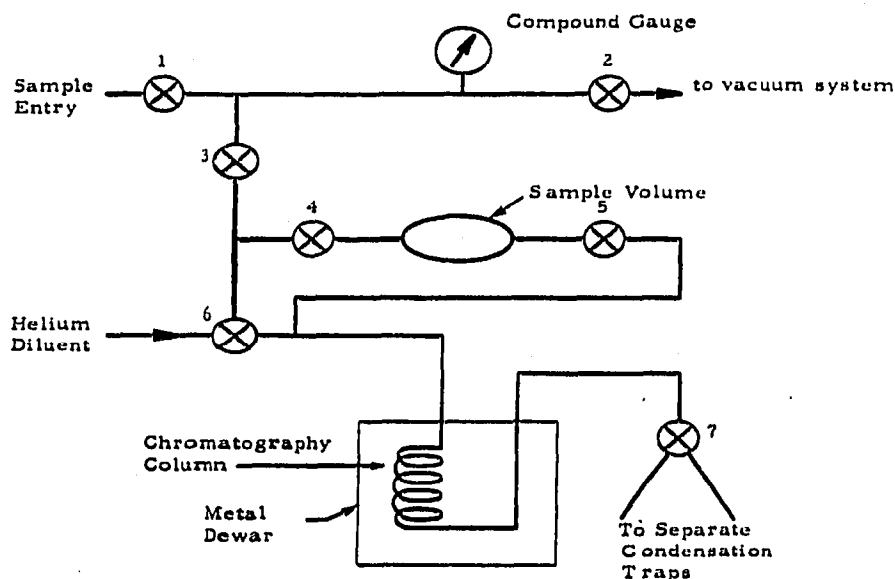


Fig. 1. Schematic diagram of chromatography apparatus. Valves 1, 2, 3, 4, 5 are 2-way electrically operated solenoid valves. Valves 6 and 7 are 3-way electrically operated solenoid valves.

was used as the original column. Helium at an indicated flow rate of 50–60 ml/min on a Kromo-Tog Flowmeter was used as an eluent. A typical chromatogram obtained using this column is shown in Fig. 2. Approximately one liquid ml of pure dinitrogen tetrafluoride/h can be obtained by this method. This is certainly useful on a laboratory size preparative scale.

An initial separation was performed with the column immersed in a Dewar

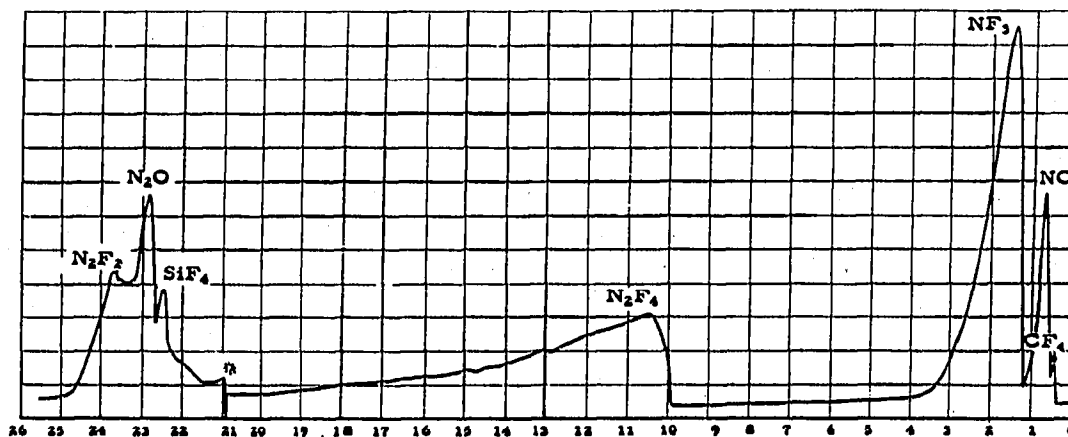


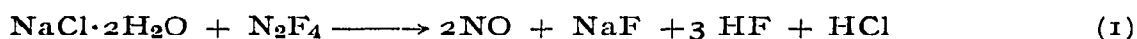
Fig. 2. Typical chromatogram showing  $N_2F_4$  purification. The asterisk indicates peak caused by temporary change in flow rate due to switching valve No. 7.

flask packed with dry ice. Nitrogen trifluoride, nitric oxide, and carbon tetrafluoride were thus taken off using 3-way valve No. 7 and were put into the trapping system reserved for impurities. Dinitrogen tetrafluoride was next eluted and was "cut" by the use of valve No. 7 into the trapping section for pure material. After all the  $N_2F_4$  had been eluted, the column was raised from the Dewar flask and was allowed to come to room temperature. Only then did the other impurities (nitrous oxide, silicon tetrafluoride, and dinitrogen difluoride) elute into the impurity trapping section of the apparatus.

### *Infrared analysis*

The infrared analysis of pure dinitrogen tetrafluoride became complicated when it was found that this material reacted with sodium chloride windows. Material that had been chromatographed and pure was placed into a stainless steel infrared cell that was fitted with freshly polished sodium chloride windows. Spectrum A of Fig. 3 shows the absorptions observed. The presence of nitrosyl chloride (NOCl) is apparent at 5.55 and 5.60  $\mu$ . It seemed unlikely that nitrosyl chloride had been eluted from the chromatographic column without being observed, and a reaction in the sampling cell was suspected. The sample was allowed to stand in the sampling cell for a period and another spectrum was taken. The spectra shown in B and C of Fig. 3 shows the results at 30 and 100 min after original sampling. The nitrosyl chloride intensity increased rapidly until dinitrogen tetrafluoride was no longer observed in spectrum C. Spectrum D is a "blank" run on the sampling cell after all materials had been pumped out. The absorptions show that the windows were seriously attacked.

The mechanism of this reaction may be complex but eqns. (1) through (4) are a possible explanation.



If water were adsorbed on the sodium chloride windows used, the dihydrate shown in eqn. (1) may be present. The formation of NOCl might then be accomplished as shown in eqns. (2) and (3). Hydrogen chloride and hydrogen fluoride were present in the spectrum shown in C as evidenced by the absorption at 3.4  $\mu$  and by bands at 2.65 and 2.8 to 2.9  $\mu^3$ . Nitrogen dioxide was also present as shown by an absorption at 6.15  $\mu$  in spectrum C.

### *Mass spectrum*

Mass spectrometric analysis of the first impurity section ( $NF_3$ , NO,  $CF_4$ ), and also the second section ( $N_2O$ ,  $SiF_4$ ,  $N_2F_2$ ), showed only these materials present. An analysis

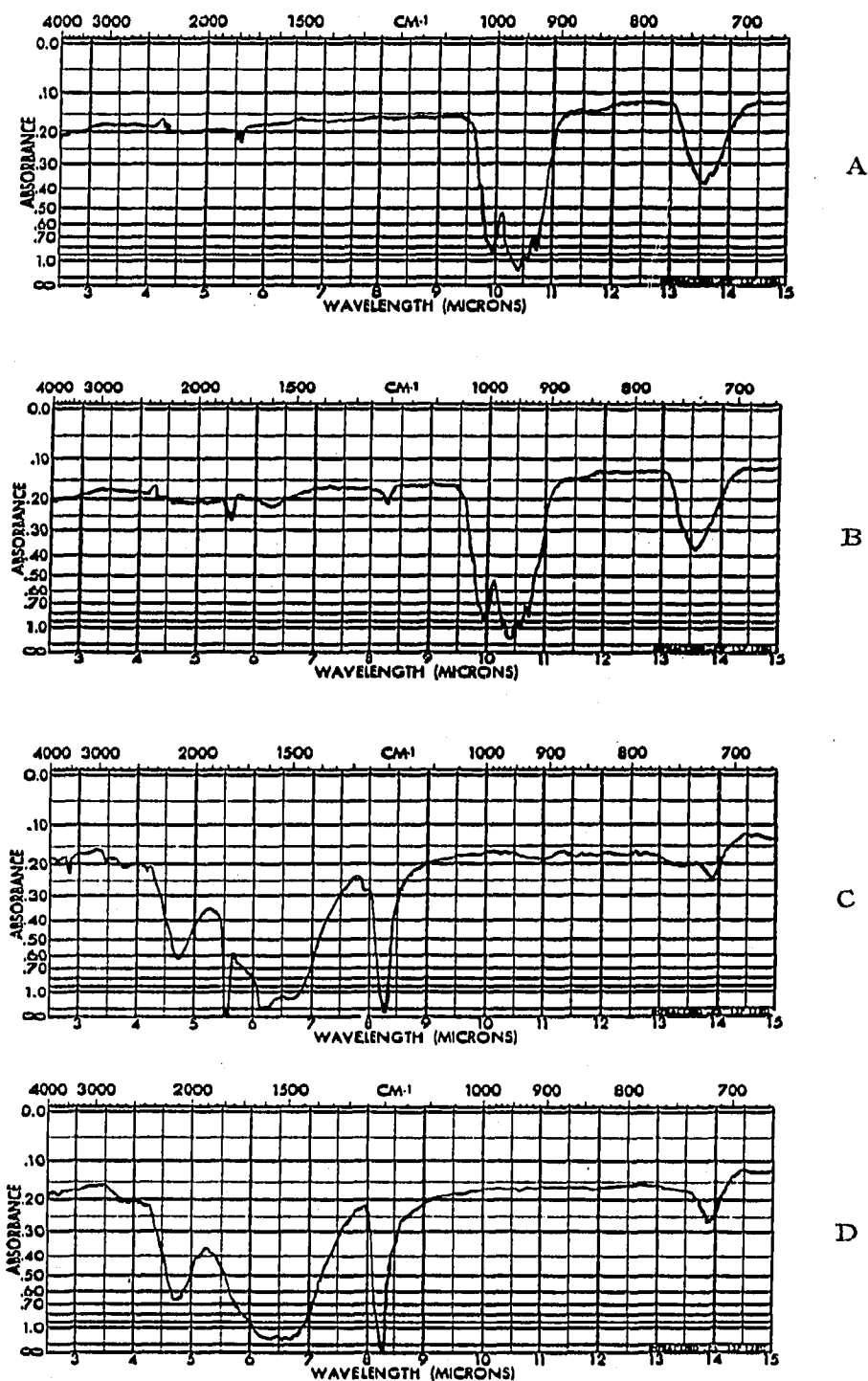


Fig. 3. Infrared spectra. A. Run 10 min after sampling; B. Run 30 min after sampling; C. Run 100 min after sampling; D. Cell blank after running sample.

on the  $N_2F_4$  fraction showed that it was pure material. It is a water clear liquid when observed at about  $-160^\circ$  but a white solid when condensed at liquid nitrogen temperature ( $-196^\circ$ ).

Two samples of dinitrogen tetrafluoride which were shown to be pure by infrared analysis (except for the NOCl absorption) were analyzed in a Bendix Time-of-Flight mass spectrometer. The samples used had not been in contact with sodium chloride. Table I gives the results of two analyses.

TABLE I  
MASS SPECTRUM OF  $N_2F_4$

<i>m/e</i>	Ion	Peak height		Relative intensity	
		Sample L-315-31	Sample L-315-31a	Sample L-315-31	Sample L-315-31a
14	$N^+$	128.8	352.8	9.4	11.5
19	$F^+$	60.0	168.0	4.4	5.45
28	$N-N^+$	192.0	503.0	14.1	16.4
33	$N-F^+$	555.2	1370.0	40.8	44.5
47	$N-N-F^+$	206.0	524.0	15.2	17.0
52	$N \begin{smallmatrix} \text{F}^+ \\ \text{F} \end{smallmatrix}$	1360.0	3076.0	100.0	100.0
66	$N-N \begin{smallmatrix} \text{F}^+ \\ \text{F} \end{smallmatrix}$	128.0	312.0	9.4	10.1
71	$NF_3^+$	—	—	—	—
85	$F-N-N \begin{smallmatrix} \text{F} \\ \text{F} \end{smallmatrix}$	202.0	504.0	14.9	16.4
104	$F \begin{smallmatrix} \text{F} \\ \text{F} \end{smallmatrix} N-N \begin{smallmatrix} \text{F}^+ \\ \text{F} \end{smallmatrix}$	40.0	108.0	2.9	3.5

The 100% peak of an impure  $N_2F_4$  sample has been reported<sup>1</sup> to be at mass 33. Our analysis, however, shows that mass 52 is the strongest. This discrepancy may possibly be due to the difference in instruments or to impurities. Another difference was that our material showed peaks at 47, 66, 85, and 104. These were not reported in the work done by COLBURN AND KENNEDY<sup>1</sup>. Since silicon tetrafluoride also exhibits mass peaks at these same points, it was believed that our material might possibly have contained  $SiF_4$  contaminant. A sample of silicon tetrafluoride was analyzed by mass spectroscopy and the results are shown in Table II. In the polyisotopic pattern for  $SiF_4$ , *m/e*'s 85, 86, and 87 were observed using a high resolution response, but only *m/e* 85 and 87 were observed when repeated under the same conditions at which the  $N_2F_3$  samples were run.

Mass 87 was not observed in the  $N_2F_4$  spectrum. Assuming *m/e* 85 in the  $N_2F_4$  spectrum to be completely due to  $SiF_4$ , then *m/e* 87 should be observed, and the ratio of *m/e* 104 to *m/e* 85 should agree with the  $SiF_4$  spectrum. The observed ratios in the two cases are given below.

Ratio <i>m/e</i> 104 to <i>m/e</i> 85	
$N_2F_4$	$SiF_4$
20.6	2.89

There is the possibility that  $\text{SiF}_4$  could be a contaminant in the  $\text{N}_2\text{F}_4$  samples analyzed, since mass 87 for  $\text{SiF}_4$  was used as the analytical peak, and the possibility of error is great with this peak. Even if  $m/e$  85 in the  $\text{N}_2\text{F}_4$  samples were due to  $\text{SiF}_4$  (from the ratio

TABLE II  
MASS SPECTRUM OF  $\text{SiF}_4$

<i>m/e</i>	<i>Ion</i>	<i>Peak height</i>	<i>Relative intensity</i>
19	$\text{F}^+$	22	3.19
28	$\text{Si}^+$	55.9	8.08
47	$\text{SiF}^+$	35.2	5.08
66	$\text{SiF}_2^+$	7.0	1.01
85	$\text{SiF}_3^+$	692.0	100.0
86	$^{20}\text{SiF}_3^+$	*—	—
87	$^{30}\text{SiF}_3^+$	45.0	6.5
104	$\text{SiF}_4$	20.0	2.9

\* Shoulder, could not get a quantitative estimate.

of 104/85 in the spectrum of  $\text{SiF}_4$ ), this would not account for the entire 104 peak. This must therefore be due to  $\text{N}_2\text{F}_4$ .

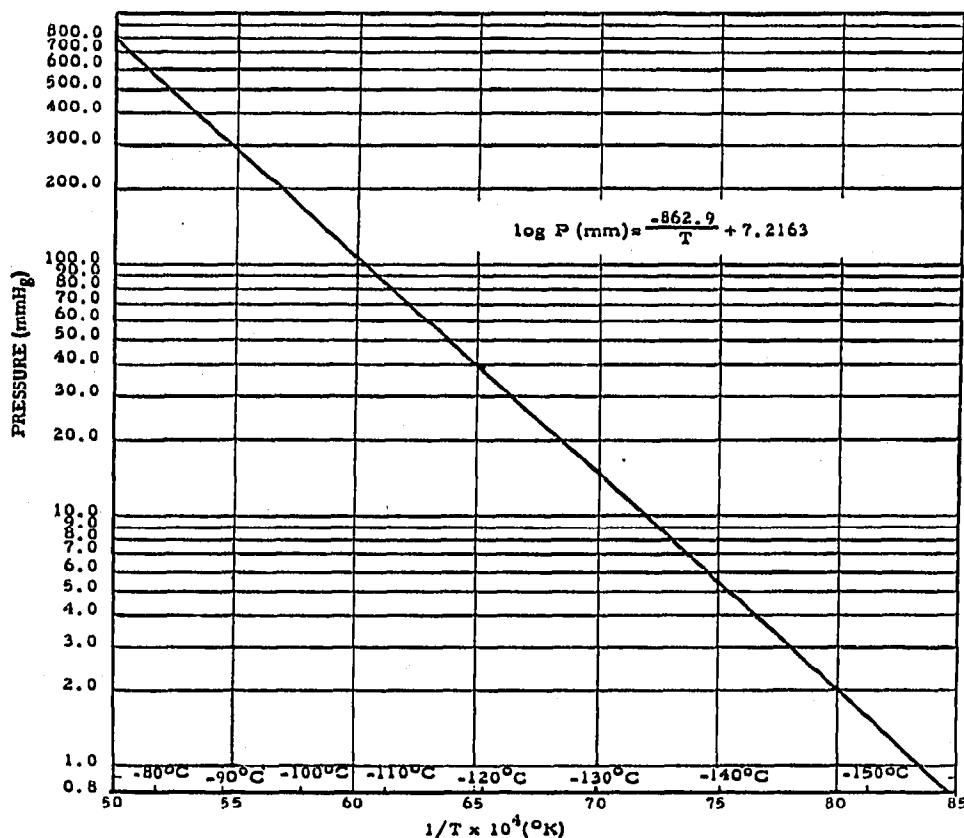


Fig. 4. Vapor pressure of dinitrogen tetrafluoride as a function of temperature.

*Vapor pressure*

The vapor pressure of dinitrogen tetrafluoride was measured at various temperatures and can be expressed by eqn. (5):

$$\log P \text{ (mm)} = \frac{-862.9}{T} + 7.2163 \quad (5)$$

All vapor pressure work was conducted in a passivated metal vacuum apparatus to eliminate any possibility of silicon tetrafluoride formation. A plot of the vapor pressure as a function of temperature is shown in Fig. 4. Using these data the boiling point was calculated to be  $-74.1^{\circ}$ .

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## SUMMARY

The isolation of spectroscopically pure dinitrogen tetrafluoride by a gas chromatographic method is discussed. The infrared spectrum and vapor pressure of this material were then determined and are reported.

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