

## Pre Concentration of Impurities in Gaseous Uranium Hexafluoride and Their Characterisation by Mass Spectrometry

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**Summary:** Distillation is normally used to remove more volatile impurities from uranium hexafluoride. Here this method of distillation was applied to natural uranium hexafluoride samples to pre concentrate those impurities which are less volatile than  $UF_6$ . Mass spectra were obtained from "pre concentrated" samples using a quadrupole mass spectrometer and were compared with those of "original" samples. The mass spectra were found to be complex due to the formation of different  $UF_6$  daughter ions during ionization process which in some cases also interfere with the impurity peaks. After pre concentration process the fluorides of Cr, Ta, Ir, Rb, Tl, Si, Sr and Rh were identified. Many organic impurities were also found in the sample.

### Introduction

Uranium hexafluoride is a volatile compound, which is converted to reactor fuel after enrichment to about 3%. In order that the fuel functions efficiently, the amounts of certain impurities present should be kept within the limits specified by ASTM [1]. Hydrogen fluoride is a major admixture in uranium hexafluoride which has to be removed. This HF reacts with other impurities present to form their fluorides. During the production of  $UF_6$  the non-volatile fluorides remain behind as an ash in fluorination reactor while the volatile impurities volatilise along with uranium hexafluoride [2]. Corrosion of the containers by HF also adds some specific impurities to the material. However, the relatively high volatility of  $UF_6$  makes its purification possible by distillation, but traces of impurities always remain. Oils, used in pumping system for handling  $UF_6$ , contaminate the material and their fluorination also takes place in presence of hydrogen fluoride. As reported in literature different hydrocarbons and partially substituted halohydrocarbons in uranium hexafluoride must not exceed the certified limits [3].

Purification of uranium hexafluoride from more volatile admixtures is carried out by distillation or sublimation. The main purpose of the present work is to show that those impurity fluorides, having higher sublimation or boiling points will remain behind and can be pre concentrated in a uranium hexafluoride sample after the same process of distillation.

The second purpose of carrying out the present work is to compare the mass spectra of  $UF_6$  samples before and after distillation, and to identify and characterise the peaks due to different species of impurities present. The sources of low mass impurities in a gaseous  $UF_6$  sample were established in an earlier work [4], while in the present work, impurities in the higher mass range (above 45 amu) have been considered.

### Results and Discussion

Mass spectra of the two batches of "original" and "pre concentrated" samples were recorded and the results are shown in Table 2. The left most column shows m/e (mass to charge ratio) values for different ionic species. In the second column ions for the respective m/e are reported which have been observed in the spectra. Next four columns show the peak heights in mA (milli amperes) for the "original" and "pre-concentrated" samples of Batch-1 and Batch-2 respectively. All those signals which appear at or above electrometer gain of  $10^{-14}$  amp were considered as peaks. The electrometer gain can be increased further by an order of magnitude but the noise level then makes the signals uncertain. The following conclusions can be drawn by examining the data given in Table 2.

#### *Inorganic Fluorides*

The most common compound of silicon with fluorine is  $SiF_4$ . This tetrafluoride is more volatile

Table 1. Boiling and sublimation points of some volatile fluorides

Compound	Temp. °C	Compound	Temp. °C
BF <sub>3</sub>	-100	UF <sub>6</sub>	56.4
SiF <sub>4</sub>	-95	VOF <sub>3</sub>	110
SF <sub>6</sub>	-64	IrF <sub>5</sub>	227
SF <sub>4</sub>	-40	MoF <sub>5</sub>	227
S <sub>2</sub> F <sub>2</sub>	-38	TaF <sub>5</sub>	229
Si <sub>2</sub> F <sub>6</sub>	-19	WF <sub>5</sub>	237
WF <sub>6</sub>	17	RuF <sub>5</sub>	272
MoF <sub>6</sub>	35	RhF <sub>5</sub>	277
VF <sub>5</sub>	48	CrF <sub>4</sub>	300
IrF <sub>6</sub>	53	VF <sub>4</sub>	327

than uranium hexafluoride (Table 1). Therefore, it is not surprising that its daughter ion peaks at m/e 47 for SiF<sup>+</sup> and at 66 for SiF<sub>2</sub><sup>+</sup> were not seen in the spectrum of pre-concentrated sample. The other peaks, SiF<sub>3</sub><sup>+</sup> at m/e 85 and SiF<sub>4</sub><sup>+</sup> at 104 interfere

with other impurity peaks and hence the effect of pre-concentration is not clear.

Chromium forms fluorides of higher boiling or sublimation point than uranium hexafluoride. Peaks of Cr<sup>+</sup>, CrF<sup>+</sup> and CrF<sub>2</sub><sup>+</sup> at m/e 52, 71 and 90 respectively, were observed in the spectrum of pre concentrated samples of the two batches. These peaks are more intense in the batch-1 spectrum owing to higher concentration of chromium.

There are several fluorides of sulphur, like SF<sub>6</sub>, SF<sub>4</sub> and S<sub>2</sub>F<sub>2</sub> which are all more volatile than uranium hexafluoride. In the mass spectrum, there are two peaks due to the sulphur fluorides. Peak at m/e 70 due to SF<sub>2</sub><sup>+</sup>, shows the behavior of a more volatile compound. SF<sup>+</sup> peak at m/e 51 interferes

Table 2. Peak heights in mA for impurity species found in original and pre concentrated samples.

m/e	Ion	BATCH-1		BATCH-2	
		Original	Pre Conc.	Original	Pre Conc.
47	SiF <sup>+</sup>	0.03	-	-	-
50	CF <sub>2</sub> <sup>+</sup>	0.01	0.03	0.03	0.20
51	CHF <sub>2</sub> <sup>+</sup> , SF <sup>+</sup> , UF <sub>1</sub> <sup>+5</sup> , V <sup>+</sup>	0.03	0.01	0.01	0.03
52	Cr <sup>+</sup> (84%)	-	0.10	-	0.03
53	Cr <sup>+</sup> (9%)	-	0.01	-	0.02
65	C <sub>2</sub> H <sub>3</sub> F <sub>2</sub> <sup>+</sup>	0.01	-	0.01	-
66	SiF <sub>2</sub> <sup>+</sup>	0.03	-	-	-
68	Unidentified	-	0.02	-	-
70	SF <sub>2</sub> <sup>+</sup>	0.03	-	-	-
71	CrF <sup>+</sup>	-	0.07	-	0.02
77	C <sub>6</sub> H <sub>5</sub> <sup>+</sup>	-	-	-	0.01
81	Unidentified	0.03	-	-	0.02
85	SiF <sub>3</sub> <sup>+</sup> , Rb <sup>+</sup> (72%), *UF <sup>+3</sup>	0.80	0.10	0.09	0.10
87	Rb <sup>+</sup> (27%)	0.03	0.09	-	0.03
88	Sr <sup>+</sup>	-	0.09	0.07	0.50
90	CrF <sub>2</sub> <sup>+</sup>	-	0.40	-	0.09
93	C <sub>6</sub> H <sub>5</sub> O <sup>+</sup>	0.02	0.02	-	0.03
100	C <sub>2</sub> F <sub>4</sub> <sup>+</sup>	0.04	0.03	0.03	0.05
101	C <sub>2</sub> HF <sub>4</sub> <sup>+</sup>	0.01	-	-	0.02
103	Rh <sup>+</sup>	-	0.08	-	0.02
104	RbF <sup>+</sup> (72%), SiF <sub>4</sub> <sup>+</sup>	0.03	0.07	-	0.08
106	RbF <sup>+</sup> (27%)	-	0.20	-	0.05
107	SrF <sup>+</sup>	0.01	0.30	0.50	3.00
122	RhF <sup>+</sup>	-	0.20	-	0.06
123	RbF <sub>2</sub> <sup>+</sup> (72%)	-	0.03	-	0.01
124	RbF·HF <sup>+</sup>	-	0.02	-	0.01
131	C <sub>6</sub> H <sub>2</sub> F <sub>3</sub> <sup>+</sup>	0.10	0.20	0.07	0.10
143	RbF <sub>2</sub> ·HF <sup>+</sup>	0.02	0.02	-	-
162	RbF <sub>3</sub> ·HF <sup>+</sup>	0.02	0.03	0.03	0.01
169	C <sub>12</sub> H <sub>9</sub> O <sup>+</sup>	0.04	0.10	0.03	0.08
181	Ta <sup>+</sup>	0.04	0.09	0.03	0.09
193	Ir <sup>+</sup> , MoF <sub>5</sub> <sup>+</sup>	0.01	0.03	0.02	0.02
205	Tl <sup>+</sup> (70%)	-	0.02	-	-
219	TaF <sub>2</sub> <sup>+</sup>	-	0.02	0.01	0.03
231	IrF <sub>2</sub> <sup>+</sup>	-	0.07	0.02	0.04
243	TlF <sub>2</sub> <sup>+</sup>	-	0.02	0.01	0.02
281	TlF·2HF·0.5H <sub>2</sub> O <sup>+</sup>	-	0.02	0.01	0.01

with  $\text{CHF}_2^+$ ,  $\text{UF}_1^{+5}$  and  $\text{V}^+$  peaks.  $\text{SF}^+$  peak is not seen in the batch-2 sample indicating the absence of sulphur. Hence the increase in signal intensity at  $m/e$  51 supports the presence of less volatile  $\text{CHF}_2^+$  and  $\text{V}^+$ . Since no other peaks of vanadium fluorides were seen in the spectra, the peak at  $m/e$  51 is most probably due to  $\text{CHF}_2^+$  and  $\text{UF}_1^{+5}$ .

In the pre concentrated sample of batch-1, there is an unidentified peak at  $m/e$  68. It cannot be boron trifluoride because it is more volatile than uranium hexafluoride and the signal should diminish after pre concentration. The presence of Mo cannot be ascertained because of interference from  $\text{UF}_3^{+3}$  at the main isotope peak of Mo at  $m/e$  98.

The boiling points of rubidium fluorides are higher than uranium hexafluoride [5]. So the peaks due to the rubidium fluoride should enhance by the pre concentration process. At  $m/e$  85,  $\text{Rb}^+$  and  $\text{SiF}_3$  interfere with  $^{235}\text{UF}_1^{+3}$ . The peak intensity is 0.8 mA, while the intensity of corresponding  $^{238}\text{U}$  peak is 0.6 mA. This shows the spectral interference at  $m/e$  85 as shown in figure 2. Further the drop of intensity at  $m/e$  85 after pre concentration process shows the presence of  $\text{SiF}_3^+$ . The minor isotope of Rb can be seen at  $m/e$  87. The peak of  $\text{RbF}^+$  at  $m/e$  104 is enhanced by pre concentration process although it is interfered by  $\text{SiF}_4^+$ . It indicates that

the base peak of  $\text{SiF}_4$  in the spectrum is due to  $\text{SiF}_3^+$  and not  $\text{SiF}_4^+$ . Rubidium forms acid compound,  $\text{RbF}\cdot\text{HF}$ , by reacting with anhydrous hydrogen fluoride [6]. The peaks at  $m/e$  124, 143 and 162 are probably due to the acid compounds of rubidium.

Strontium may be present in uranium hexafluoride in  $\text{SrF}_2$  form which has a higher boiling point than uranium hexafluoride [5]. Strontium concentration level seems to be higher in the batch-2 samples. The peaks due to  $\text{Sr}^+$  and  $\text{SrF}^+$  appear at  $m/e$  88 and 107 respectively. Both the peaks are enhanced by preconcentration.

The peaks at  $m/e$  103 and 122 have been identified as due to  $\text{Rh}^+$  and  $\text{RhF}^+$ . The behaviour of the peak intensities confirms the lesser volatility of rhodium fluorides than  $\text{UF}_6$ . Similarly peaks for tantalum appear at  $m/e$  181 for  $\text{Ta}^+$  and at  $m/e$  219 for  $\text{TaF}_2^+$ . Both these peaks are enhanced by pre concentration, because of higher boiling point of tantalum fluoride.

$\text{IrF}_5$  and  $\text{IrF}_6$  may be present in uranium hexafluoride as admixtures (Table 1).  $\text{IrF}_5$  is less volatile while  $\text{IrF}_6$  is more volatile than  $\text{UF}_6$ . Two peaks at  $m/e$  193 for  $\text{Ir}^+$  and at 231 for  $\text{IrF}_2^+$  were seen in the spectra. Although  $\text{MoF}_6$  is found in  $\text{UF}_6$  sample (Table1) but in our sample we can not see

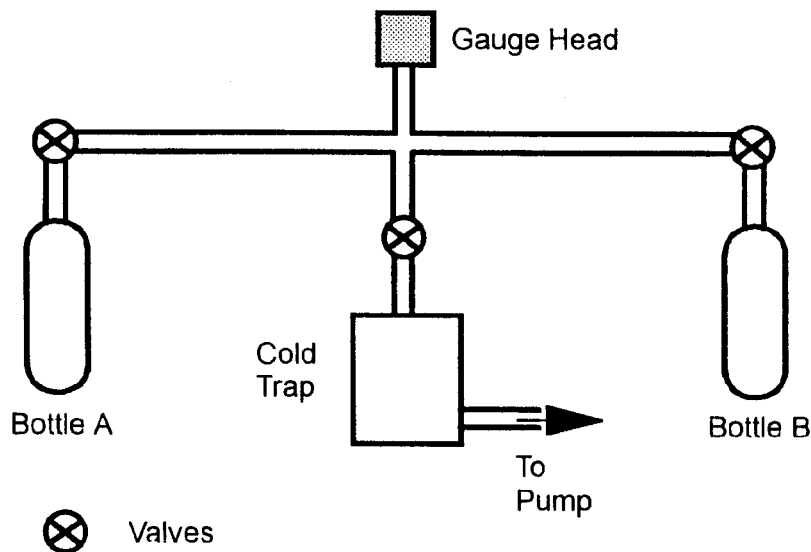


Fig. 1. Monel manifold used for  $\text{UF}_6$  distillation.

uranium hexafluoride was transferred from a main storage container in bottle, labeled "A". From this, a 40 g sample, named as "original sample" was collected in a sample bottle. Distillation was carried out on the remaining material in bottle "A".

First, degassing of distillation assembly along with the UF<sub>6</sub> collection bottle "B" was performed by heating at 70° C and evacuation to 10<sup>-3</sup> mbar. Keeping bottle "A" at room temperature, any HF present was removed to a trap bottle cooled to liquid nitrogen temperature. While keeping bottle "A" at room temperature and bottle "B" at liquid nitrogen temperature, about 2 kg uranium hexafluoride from "A" was allowed to transfer to bottle "B". After stopping the transfer, bottle "A" was heated to 70° C to homogenise the remaining material. The bottle was allowed to cool down to room temperature and then further 0.4 kg material was transferred to bottle "B". The remaining material in bottle "A" was assumed to be rich in less volatile impurities. From this about 40 g material was collected in a second sample bottle and was named as "pre concentrated sample". Same process was repeated on a second bulk of natural uranium hexafluoride to obtain two more samples, "original" and "pre concentrated".

### Conclusions

Although the work presented here is of qualitative nature, it can be concluded from the results obtained that the impurities present in a UF<sub>6</sub> sample and having higher boiling or sublimation points than uranium hexafluoride can be pre concentrated by distillation process. Peaks for the fluorides of Cr, Ir, Rb, Rh, S, Si, Sr, Ta and Tl have been identified and the intensities of those due to less

volatile compounds than uranium hexafluoride, are found to be enhanced after pre concentration. Fluorine compounds of silicon and sulphur are more volatile than UF<sub>6</sub>, resulting in the diminution of peaks of their fluorides in the mass spectrum of pre concentrated samples. Rubidium polyfluoride and their acid compounds have also been identified. Hydrocarbons may contaminate uranium hexafluoride during gas handling and also during experiments. A number of hydrocarbon and fluorohydrocarbon peaks observed in the mass spectra of UF<sub>6</sub> samples, were characterised.

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