Designation: C1842 − 16

Standard Test Method for The Analysis of Boron and Silicon in Uranium Hexfluoride via Fourier-Transform Infrared (FTIR) Spectroscopy[1]

This standard is issued under the fixed designation C1842; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method is suitable for determining boron and silicon impurities as BF_3 and SiF_4 in uranium hexafluoride. This test method is an alternative to those described in Test Methods C761 and C1771.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C761 Test Methods for Chemical, Mass Spectrometric, Spectrochemical, Nuclear, and Radiochemical Analysis of Uranium Hexafluoride

C787 Specification for Uranium Hexafluoride for Enrichment

C859 Terminology Relating to Nuclear Materials

C996 Specification for Uranium Hexafluoride Enriched to Less Than 5 % ^{235}U

C1052 Practice for Bulk Sampling of Liquid Uranium Hexafluoride

C1703 Practice for Sampling of Gaseous Uranium Hexafluoride

C1771 Test Method for Determination of Boron, Silicon, and Technetium in Hydrolyzed Uranium Hexafluoride by Inductively Coupled Plasma—Mass Spectrometer After Removal of Uranium by Solid Phase Extraction

2.2 *Other Documents:*

ANSI N14.1 Nuclear Materials – Uranium Hexfluoride – Packaging for Transport[3]

ISO 7195 Nuclear Energy – Packaging of Uranium Hexafluoride (UF_6) for Transport[4]

3. Terminology

3.1 Except as otherwise defined herein, definitions of terms are as given in Terminology C859.

3.2 *Definitions of Terms Specific to This Standard:*

3.2.1 *detection limit, n*—based on the minimum absorbance obtainable at a given pressure to yield a meaningful result. In accordance with Terminology C859, a low concentration level could be achieved with these methods.

3.2.2 *FTIR, n*—Fourier-transform infrared spectroscopy.

3.2.3 *K, n*—infrared absorbance constant in pressure units [1/Pa], K = OD/Pressure.

3.2.4 *"1S" container, n*—a nickel or Monel container as described in ANSI N14.1.

4. Summary of Test Method

4.1 To perform the Fourier-Transform Infrared (FTIR) spectroscopic analysis of boron and silicon impurities in uranium hexafluoride, a sample must be collected in a "1S" container or equivalent with the methods described in Practices C1052 or C1703.

4.2 The bottle is kept at room temperature. The manifold and the sample cell are maintained at 50°C. In these conditions, UF_6 is mainly in solid phase in the bottle and boron and silicon are present in the gaseous phase of manifold. In this medium, the boron and silicon chemical forms are respectively BF_3 and SiF_4.

4.3 The test method is based on the analysis in the gas phase. The gas phase is analyzed at 50°C by FTIR spectrometry to determine the B and Si concentration in uranium hexafluoride.

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[1] This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

Current edition approved June 1, 2016. Published July 2016. DOI: 10.1520/C1842-16.

[2] For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

[3] Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, http://www.ansi.org.

[4] Available from International Organization for Standardization (ISO), ISO Central Secretariat, BIBC II, Chemin de Blandonnet 8, CP 401, 1214 Vernier, Geneva, Switzerland, http://www.iso.org.

4.4 The manifold and sample cell are filled at the vapor pressure of UF_6 at room temperature (near 12 kPa).

4.5 After a screening, if the spectrum is the UF_6 spectrum, this test method can be used to check the compliance of UF_6 as specified in Specifications C787 and C996.

4.6 The boron and silicon determinations are done on the gaseous phase. The concentration and the limits of detection are in units of µg/g U.

4.7 There are no spectral interferences from uranium hexafluoride's infrared absorbences.

5. Significance and Use

5.1 This test method utilizes FTIR spectroscopy to determine the boron and silicon concentration in uranium hexafluoride.

5.2 These detection limits are low and very effective to check the compliance of UF_6 with Specifications C787 and C996.

6. Hazards

6.1 Uranium hexafluoride is a hazardous material. It is a highly reactive and toxic substance in addition to its radioactive properties. It must be handled as a gas in containers and manifolds using materials of construction that are inert to fluorine-bearing gases, such as nickel, Monel™, copper, or aluminum.

7. Apparatus

7.1 *Fourier-Transform Infrared Spectrophotometer,* with a resolution of ±0.5 cm^{-1} or better. The scanning range depends on the equipment being used, but at minimum shall be 600 to 1550 cm^{-1}.

7.2 *A Manifold System,* built with materials of construction inert to fluorine-bearing gases. The manifold system shall be conditioned and passivated with an appropriate fluorinating agent.

7.3 *A Sample Cell,* windows are made of material(s) inert to fluorine-bearing gases, for example, zinc selenide (ZnSe). A cell path length of more than 150 mm was found to be sufficient for the required LOD. The cell is heated at 50°C.

7.4 *A Pressure Gauge,* which can be read to 1 Pa is necessary.

7.5 *Absorbence Data,* or OD optical density, can be determined to 0.001 units.

8. Calibration and Standardization

8.1 *Calibration:*

8.1.1 BF_3 and SiF_4 are calibrated between 15 and 150 Pa. The cell temperature is maintained at 50°C. Different pressures of pure BF_3 or pure SiF_4 are introduced between 15 and 150 Pa. The maximum of absorbance and the scans are recorded. The response of absorbance as a function of pressure is linear. The slope of this line is K. The slope is constant from near zero absorbance to about 0.8 absorbance units.

8.1.2 The K value are measured at 1441 cm^{-1} for BF_3 and 1029 cm^{-1} for SiF_4 (see Fig. 1 and Fig. 2).

8.1.3 The operating experience of each laboratory for precision calculations of impurities are critical to the success of the method. Each laboratory shall determine the "K" values specific to its instrumentation: $K = \Sigma\ OD/\Sigma\ Pressure$.

8.2 *Calibration of Pressure Gauge and FTIR Instrument*—Pressure gauges and the FTIR instruments are very stable over time. Annual calibration is recommended.

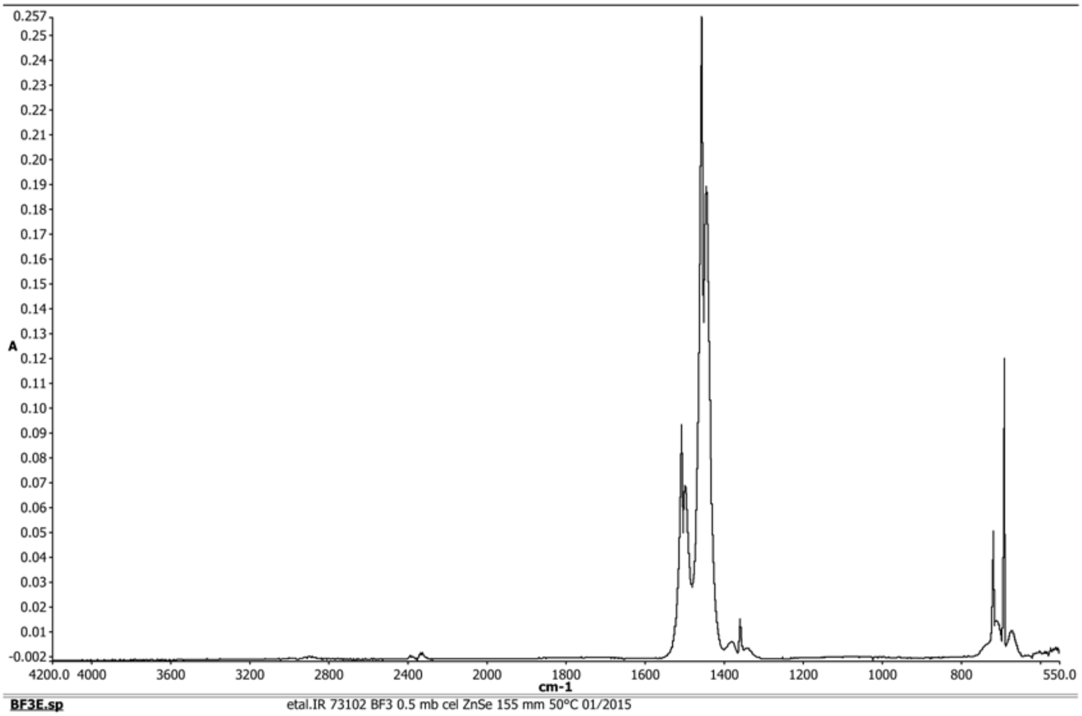

FIG. 1 BF_3 Spectrum in Pure Medium

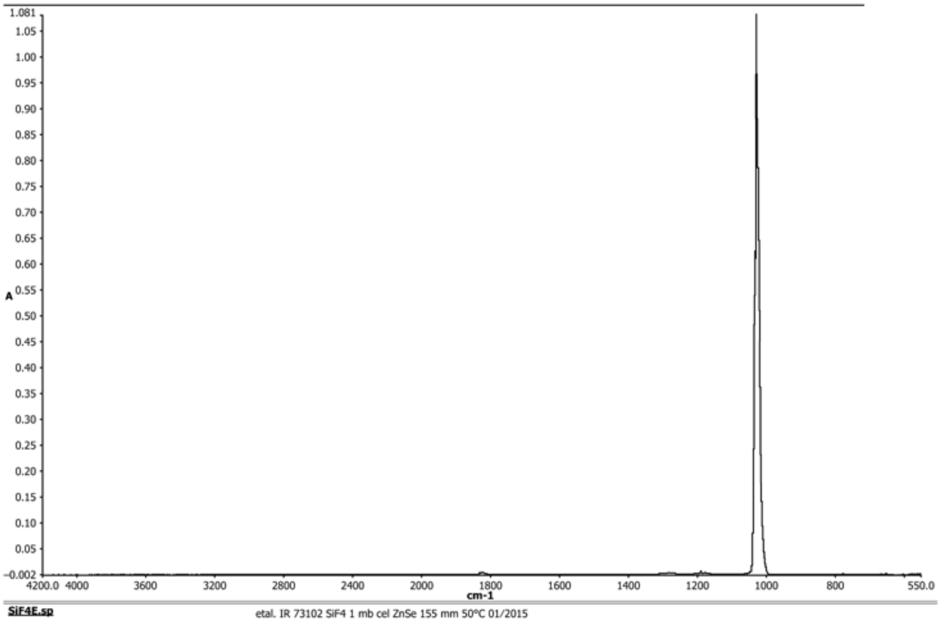

FIG. 2 SiF_4 Spectrum in Pure Medium

8.3 *Calibration Checks*—The calibration of the gauge should be checked before analyzing a UF_6 standard. After the check of the gauge calibration, 10 kPa of UF_6 standard are introduced and the maximum of absorbance at 625 cm^{-1} is recorded. These calibration checks should be performed each day that the instrument is used. If the difference on the OD is above 1 %, the pressure gauge should be recalibrated. If the wavelength difference is greather than 0.5 cm^{-1} , then the FTIR instrument should be recalibrated

9. Procedure

9.1 *Acquire a Sample Scan:*

9.1.1 Weigh the empty bottle (M1).

9.1.2 Withdraw a sample in a 1S bottle with the process defined in Practices C1052 or C1703.

9.1.3 Weigh the bottle to determine the UF_6 mass in the bottle (M2).

9.1.4 Evacuate manifold system until readout on gauge displays a value of less than 10 Pa.

9.1.5 Verify the digital manometer for zero and full scale readings.

9.1.6 Obtain an infrared background spectrum on the FTIR to check that the manifold is clean.

9.1.7 Connect the sample 1S bottle on the manifold and control the tightness.

9.1.8 Open the bottle valve on the manifold. Wait until the pressure is stabilized and close the valve. Record the sample pressure (P).

9.1.9 Obtain the infrared spectrum. The spectrum will be the result of ten scans.

9.2 *Interpret Spectrum:*

9.2.1 Record the absorbance maxima (OD BF_3 and OD SiF_4) and the infrared spectrum (see Fig. 3).

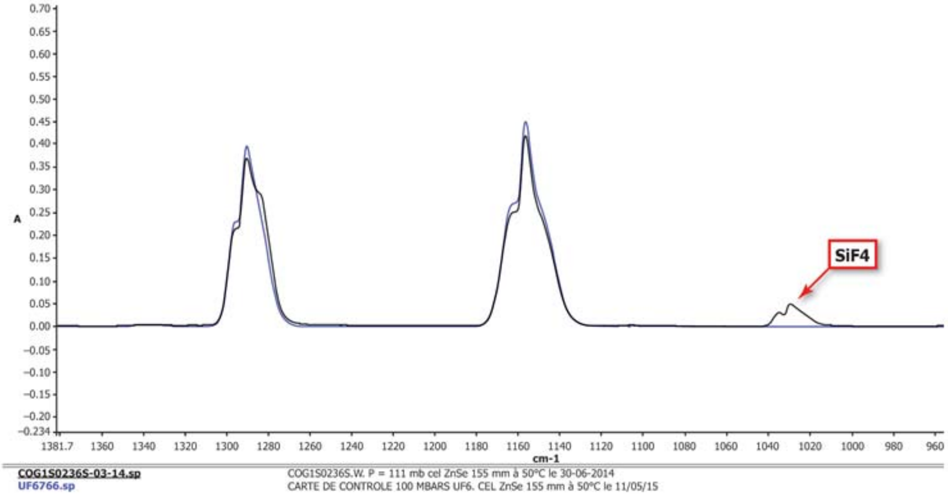

FIG. 3 SiF_4 Spectrum in UF_6 Medium

9.3 *Representativity of the Sample:*

9.3.1 The representativity of the sample is validated by the following process. Control the concentration of UF_6 in the gas phase. If the UF_6 concentration is above 80 %, the sample is validated and the boron and silicon concentration could be determined. If the UF_6 concentration is under 80 %, a resampling is necessary.

9.3.2 To determine the concentration of UF_6 in the gas phase, perform a UF_6 calibration introducing a pressure of pure UF_6 (PUF_6) and record the UF_6 absorbance ($ODUF_6$) to calculate KUF_6 ($KUF_6 = ODUF_6 / PUF_6$). Record the UF_6 absorbance on the infrared spectrum of the sample and calculate the UF_6 pressure with the K value. To calculate the concentration of UF_6 in the gas phase, divide the UF_6 pressure by the sample pressure ($\%UF_6 = PUF_6 / Psample$).

9.4 *Evacuation of the Manifold System:*

9.4.1 Open the cold trap.

9.4.2 Continue the total evacuation until the pressure gauge reads below 10 Pa.

NOTE 1—The manifold system must be passivated with an appropriate fluorinating agent to generate high quality analytical results.

10. Calculation of Boron and Silicon Concentration in UF_6

10.1 *Calculation of K Value:*

10.1.1 The calculation for K is as follows:

$$\text{Ideal Gas Law } PV = nRT$$

where:

P = pressure,
V = volume,
n = moles,
R = gas constant, and
T = absolute temperature

and

$$\text{Beer's Law } OD = \varepsilon \ell C$$

where:

OD = absorbance,
ε = extinction coefficient,
ℓ = cell pathlength, and
C = concentration.

$$C = n/V = P/RT \text{ and } C = OD/\varepsilon\ell$$

$$P/RT = OD/\varepsilon\ell$$

$$K' = \varepsilon\ell/RT = OD/P$$

$$\text{mole } \% = OD/PK'$$

$$K = 1/K'$$

$$\textbf{mole \% } = (\textbf{OD} \times \textbf{K})/\textbf{P and K} = (\textbf{mole \%} \times \textbf{P})/\textbf{OD}$$

10.1.2 Use of a known standard gas (for example, BF_3 and SiF_4) enables the mole % to be known. The actual gas pressure that produces the absorbance maximum peak (at 1441 wavenumbers or 1029 wavenumbers, respectively) provides three of the numbers. With the other three numbers known, K can be calculated.

10.2 *Calculation of Concentration in UF_6:*

10.2.1 Calculate the partial pressure of BF_3 (PBF_3) and SiF_4 ($PSiF_4$).

$$PBF_3 = ODBF_3/K\,BF_3;\ PSiF_4 = OD\,SiF_4/K\,SiF_4$$

10.2.2 Calculate the mass of UF_6 (MUF6) by the difference of bottle mass empty (M1) and after the sampling (M2).

$$MUF6 = M2 - M1$$

10.2.3 Multiply the mass of UF_6 by 0.6761 to calculate the mass of uranium (MU).

$$MU = MUF_6 \times 0.6761$$

10.2.4 Divide the mass of UF_6 by the volumetric mass of UF_6 to obtain the volume of UF_6 (VUF_6).

$$VUF_6 = MUF_6 \times 5.09$$

10.2.5 Subtract the UF_6 volume from the volume bottle (VB) to calculate the free volume (VFB).

$$VFB = VB - VUF6$$

10.2.6 Add the free volume of the bottle, the manifold volume (VM) and the cell volume (VC) to have the volume (V).

$$V = VFB + VM + VC$$

10.2.7 With the partial pressure and the total volume calculate the number of moles of BF_3 and SiF_4.

$$nBF_3 = PBF_3 \times V/RT\ ;\ nSiF_4 = PSiF_4 \times V/RT\ ;$$

10.2.8 Multiply the number of moles by the molar mass of B or Si to obtain the mass of B (MB) and the mass of Si (MSi).

$$MB = nBF_3 \times 10.81;\ MSi = nSiF_4 \times 28.086$$

10.2.9 Divide the mass of B and Si by the U mass to have the quantity of impurities in µg B/g U and µg Si/g U.

$$[B] = MB/MU\ ;[Si] = MSi/MU$$

10.2.10 See results for B and Si in Table 1 and Table 2.

10.2.11 The units used are Pa for pressure, kg for mass, m^3 for volume, and Kelvin for temperature.

11. Precision and Bias

11.1 Within the different stages of the nuclear fuel cycle many challenges lead to the inability to perform interlaboratory studies for precision and bias. These challenges may include variability of matrices of material tested, lack of suitable reference or calibration materials, limited laboratories performing testing, shipment of materials to be tested, and regulatory constraints. Because of this each individual laboratory utilizing

TABLE 1 Result of Boron Concentration in UF_6

Analysis pressure (kPa)	12
BF_3 pressure (Pa)	0,16
Mass of UF_6 (g)	400
Volume of UF_6 (mL)	78,43
Bottle volume (mL)	150
Empty volume in the bottle (mL)	71,57
Total volume (mL)	2021,57
Mol number of BF_3	1,30.10-7
Mass of BF_3 (µg)	1,41
Mass of U (g)	270,44
B concentration (µg/gU)	0,0052

TABLE 2 Result of Silicon Concentration in UF_6

Analysis pressure (kPa)	10,3
SiF_4 pressure (Pa)	0,0006
Mass of UF_6 (g)	400
Volume of UF_6 (mL)	78,43
Bottle volume (mL)	150
Empty volume in the bottle (mL)	71,56
Total volume (mL)	2021,57
Mol number of SiF_4	4,89.10-8
Mass of SiF_4 (µg)	1,37
Mass of U (g)	270,44
B concentration (µg/gU)	0,0051

this test method should develop their own precision and bias as part of their quality assurance program.

11.2 *Precision:*

11.2.1 The precision has been determined to be about 1 % (average over ten measures).

11.2.2 The precision is determined by the following equation:

$$P = \frac{ts}{\bar{x}\sqrt{n}} * 100$$

where:

t = student coefficient at 95 % confidence,
s = standard deviation,
x = average of measurements, and
n = number of measurements.

11.2.3 The precision has been determined after ten measurements at 100 Pa: (*1*) the BF_3 precision (P) is 0.7 % in the range of 0 to 150 Pa (cf Table 3), (*2*) the SiF_4 precision (P) is 0.4 % in the range of 0 to 150 Pa (cf Table 4).

11.3 *Limit of Quantification:*

11.3.1 Perform ten measurements with the empty cell to record the blank measure. Fig. 4 shows the background. Record the max and min values of OD (cf Table 5 and Table 6) and calculate the blank OD (OD max – OD min).

11.3.2 The limit of quantification (LOQ) is determined by the following equation:

$$\mathrm{LOQ} = \frac{10\ \sigma\ \mathrm{Blank}}{\mathrm{K}}$$

TABLE 3 Precision of BF_3 (100 Pa)

Analysis BF_3	Blank OD
1	0,28303
2	0,28284
3	0,28779
4	0,28812
5	0,28689
6	0,28638
7	0,28596
8	0,28586
9	0,28123
10	0,28139
Average	0,2849
Standard Deviation	0,00259
Precision	0,66 %

TABLE 4 Precision of SiF_4 (at 100 Pa)

Analysis SiF_4	OD
1	0,99716
2	1,00679
3	1,00832
4	1,01802
5	1,00531
6	1,0084
7	1,01029
8	1,011295
9	1,01423
10	1,00521
Average	1,0085
Standard Deviation	0,0056
Precision	0,40 %

where:

10 σ Blank = 10 × standard deviation of blank, and
K = infrared absorbance constant in pressure units [1/Pa], K = OD/Pressure.

11.3.3 The limits of quantification are reported in Table 7.

11.4 *Correction of Impurities in the Solid Phase:*

11.4.1 At equilibrium, the amount of impurity in the solid phase depends on the vapor pressure of the compounds, the free volume (volume occupied by the gas phase inside the bottle) and the temperature.

11.4.2 For example, in Table 8, the repartition of BF_3 between the solid and gas phases is presented at four temperatures for a free volume of 92 % of the total volume. The alpha coefficient corresponds to the ratio of BF_3 concentration in the gas phase divided by concentration in the solid phase.

$$\alpha = BF_3 \text{in the gas phase (ppm/U)} / BF_3 \text{in the solid phase (ppm/U)}$$

11.4.3 Alpha can be calculated theoretically, using the ratio of vapor pressures of BF_3 and UF_6. It can also be measured experimentally.

11.4.4 When the free volume decreases, the proportion of BF_3 in the solid phase increases. It reaches a maximum for the minimum permissible volume in a 1S bottle, as seen in Table 9.

11.4.5 Having quantified the amount of impurity in the gas phase using Section 10, it is the responsibility of the user to make the correction for the impurity in the solid phase. Table 10 presents the typical correction of SiF_4 and BF_3. For SiF_4, the correction is limited and SiF_4 in the gas phase represents more than 94 % of the total.

11.4.6 If the bottle has been filled during sampling with liquid UF_6 and cooled down to room temperature to solidify UF_6, the question of when we reach the thermodynamic equilibrium can be raised due to low diffusion coefficient in solid UF_6. However, since there is little difference for SiF_4 or BF_3 repartition between the UF_6 triple point temperature (64°C) and room temperature (as seen in Table 10), the importance of time between solidification and analysis is small.

12. Keywords

12.1 boron; fluoride compounds; Fourier-transform infrared spectroscopy; silicon; uranium hexafluoride

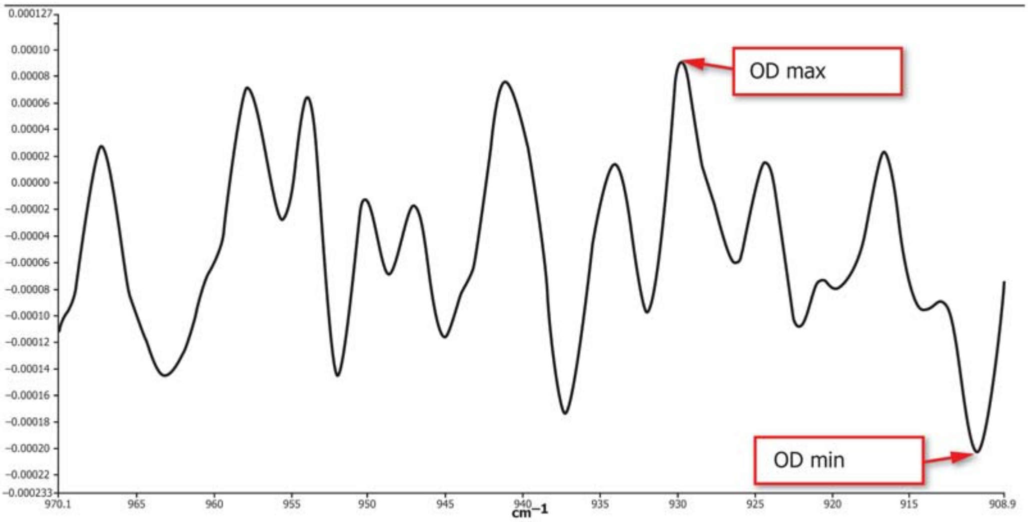

FIG. 4 Infrared Background Spectrum

TABLE 5 BF_3 Results at 1447 cm^{-1}

Blank Spectrum Number	Max OD	Min OD	Blank OD		
1	7,00E-05	-1,50E-04	2,20E-04	Slope =	3,66E-01
2	1,00E-05	-1,90E-04	2,00E-04	Blank Average =	2,20E-04
3	1,00E-05	-1,80E-04	1,90E-04		
4	1,00E-04	-1,10E-04	2,10E-04	LDQ Pa =	9,00E-02
5	1,30E-04	-8,00E-05	2,10E-04		
6	1,40E-04	-4,00E-05	1,80E-04	Standard Deviation =	3,30E-05
7	2,10E-04	-2,00E-05	2,30E-04		
8	2,30E-04	0,00E+00	2,30E-04		
9	1,70E-04	-1,30E-04	3,00E-04		
10	1,40E-04	-9,00E-04	2,30E-04		

TABLE 6 Blank Results for SiF_4

Blank Spectrum Number	Max OD	Min OD	Blank OD		
1	1,30E-04	-3,40E-04	4,70E-04	Slope =	1,10E+00
2	3,00E-05	-5,70E-04	6,00E-04	Blank Average =	5,10E-04
3	6,00E-05	-5,60E-04	6,20E-04		
4	3,00E-05	-5,90E-04	6,20E-04	LDQ Pa =	7,50E-04
5	-1,00E-05	-4,20E-04	4,10E-04		
6	4,10E-04	-3,00E-05	4,40E-04	Standard Deviation =	8,26E-05
7	5,00E-04	0,00E+00	5,00E-04		
8	5,30E-04	-3,00E-05	5,60E-04		
9	2,80E-04	-1,70E-04	4,50E-04		
10	3,30E-04	-1,00E-04	4,30E-04		

TABLE 7 Limits of Quantification

Gas	Wavelength cm^{-1}	LOQ Pa	LOQ µg	Element	LOQ µg/gU (sample with 300 g of UF_6)
BF_3	1447	0.09	0.8 µg	Boron	0.004 µg B/g U
SiF_4	1029	0.08	1.9 µg	Silicon	0.009 µg Si/g U

TABLE 8 Experimental and Calculated Repartition of BF$_3$ in a 1 L Bottle Containing 400 g UF$_6$ (8 % Occupied Volume with Solid UF$_6$)[A]

T (°C)	Alpha Theoretical	Alpha Experimental	Alpha Selected	mU gas (g)	mU solid (g)	amount BF$_3$ gas phase / amount BF$_3$ solid phase	% of BF$_3$ in gas phase
50	319		1211	8,6	261,80	39,8	98
15	1400	5315	5315	1	269,40	19,7	95
-25	14200		5,39E+04	0,041	270,36	8,2	89
-75	2,30E+07	5,20E+07	5,20E+07	1,20E-04	270,40	23,1	96

[A] Theoretical alpha values (column 1) have been obtained using Henry Law. Experimental values (column 2) have been obtained by mixing known values of BF$_3$ and UF$_6$ and determining the amount present in the gas phase. Selected alpha values (column 3) are either experimental values when they exist, or, theoretical value corrected by the ratio of experimental/theoretical values at a different temperature. The selected alpha values are therefore approximated and this leads to approximate results at -25°C.

TABLE 9 Experimental and Calculated Repartition of BF$_3$ in a 1S (0.15 L) Bottle Containing 440 g UF$_6$ (60 % Occupied Volume with Solid UF$_6$)

T (°C)	Alpha Theoretical	Alpha Experimental	Alpha Selected	mU gas (g)	mU solid (g)	amount BF$_3$ gas phase / amount BF$_3$ solid phase	% of BF$_3$ in gas phase
50	319		1211	0,56	296,88	2,3	70
15	1400	5315	5315	0,06	297,38	1,1	**52**
-25	14200		5,39E+04	3,00E-03	297,44	0,5	35
-75	2,30E+07	5,20E+07	5,20E+07	7,00E+07	297,44	1,2	55

TABLE 10 % of SiF$_4$ and BF$_3$ in the Gas Phase

	SiF$_4$		BF$_3$	
	T = 64°C	T = 20°C	T = 64°C	T = 20°C
% of volume occupied by solid UF$_6$				
22 %	99,8	99,2	92,2	91,6
45 %	99,5	98,3	80	81,5
61 %	99,1	97,1	71	72
75 %	98,8	95,8	62	64
85 %	98,3	94,4	54	57

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