



Designation: C1441 – 13

Standard Test Method for The Analysis of Refrigerant 114, Plus Other Carbon- Containing and Fluorine-Containing Compounds in Uranium Hexafluoride via Fourier-Transform Infrared (FTIR) Spectroscopy¹

This standard is issued under the fixed designation C1441; 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 covers determining the concentrations of refrigerant-114, some other carbon-containing and fluorine-containing compounds, hydrocarbons, and partially or completely substituted halohydrocarbons that may be impurities in uranium hexafluoride when looked for specifically. The two options are outlined for this test method. They are designated as Part A and Part B.

1.1.1 To provide instructions for performing Fourier-Transform Infrared (FTIR) spectroscopic analysis for the possible presence of Refrigerant-114 impurity in a gaseous sample of uranium hexafluoride, collected in a “2S” container or equivalent at room temperature. The all gas procedure applies to the analysis of possible Refrigerant-114 impurity in uranium hexafluoride, and to the gas manifold system used for FTIR applications. The pressure and temperatures must be controlled to maintain a gaseous sample. The concentration units are in mole percent. This is Part A.

1.2 The method described in part B is more efficient because there isn't matrix effect. FTIR spectroscopy identifies bonds as C-H, C-F, C-Cl. To quantify HCH compounds, these compounds must be known and the standards available to do the calibration.

After a screening, if the spectrum is the UF₆ spectrum or if the other absorption peaks allow the HCH quantification, this test method can be used to check the compliance of UF₆ as specified in Specifications C787 and C996. The limits of detection are in units of mole percent concentration.

1.3 Part A pertains to Sections 7 – 10 and Part B pertains to Sections 12 – 16.

1.4 These test options are applicable to the determination of hydrocarbons, chlorocarbons, and partially or completely substituted halohydrocarbons contained as impurities in uranium

hexafluoride (UF₆). Gases such as carbon tetrafluoride (CF₄), which absorb infrared radiation in a region where uranium hexafluoride also absorbs infrared radiation, cannot be analyzed in low concentration via these methods due to spectral overlap/interference.

1.5 These test options are quantitative and applicable in the concentration ranges from 0.003 to 0.100 mole percent, depending on the analyte.

1.6 These test methods can also be used for the determination of non-metallic fluorides such as silicon tetrafluoride (SiF₄), phosphorus pentafluoride (PF₅), boron trifluoride (BF₃), and hydrofluoric acid (HF), plus metal-containing fluorides such as molybdenum hexafluoride (MoF₆). The availability of high quality standards for these gases is necessary for quantitative analysis.

1.7 These methods can be extended to other carbon-containing and inorganic gases as long as:

1.7.1 There are not any spectral interferences from uranium hexafluoride's infrared absorbances.

1.7.2 There shall be a known calibration or known “K” (value[s]) for these other gases.

1.8 The values stated in SI units are to be regarded as the standard.

1.9 *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

¹ This test method is under the jurisdiction of ASTM Committee C26 on Methods of Test.

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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.

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 % ²³⁵U

C1052 Practice for Bulk Sampling of Liquid Uranium Hexafluoride

2.2 USEC Document

USEC-651 Uranium Hexafluoride: A Manual of Good Handling Practices³

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 detection limit, *n*—based on the minimum absorbance obtainable at a given pressure to yield a meaningful result in accordance with Eq 2. In accordance with Terminology C859, a low concentration level that can be achieved with these methods is 0.003 mol percent at the 95 % confidence level.

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

3.1.3 *K*, *n*—infrared absorbance constant in pressure units, where:

$$K = \frac{\text{mole percent concentration standard (pressure)}}{\text{absorbance}} \quad (1)$$

3.1.4 “2S” container, *n*—a nickel container with a 1.0 L capacity.

4. Summary of Test Methods

4.1 Part A is based on the collection of an all gas sample of UF₆. The gas sample is then analyzed at room temperature via FTIR to determine the percent Refrigerant-114 in uranium hexafluoride.

4.2 Part B is based on the collection of an all gas sample of UF₆. There are two differences with the Part A:

—the calibration is performed in UF₆.

—the path length used is 5 meters equipped with zinc selenide (ZnSe) optics.

4.3 In Parts A and B, the pressure is kept low enough so that the manifold and sample cell are filled only with gaseous UF₆.

5. Significance and Use

5.1 This test method (Part A) utilizes FTIR spectroscopy to determine the percent Refrigerant-114 impurity in uranium hexafluoride. Refrigerant-114 is an example of an impurity gas in uranium hexafluoride.

6. Hazards

6.1 Uranium hexafluoride is considered to be 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 nickel containers and well-conditioned nickel manifolds to ensure safety. Suitable handling procedures are described in USEC-651.

7. Apparatus (Part A)

7.1 Fourier-Transform Infrared Spectrophotometer, or dispersive infrared spectrophotometer set up to collect data in the range 4000 to 400 cm⁻¹ with ± 2 cm⁻¹ resolution or better.

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. (See Annex A2.)

7.3 A Nickel Sample Cell equipped with silver chloride windows. The pathlength used in these experiments is 10 cm (0.1m).

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

7.5 Absorbance Data, can be determined to 0.001 units.

8. Calibration (Part A)

8.1 The infrared spectrophotometer is calibration checked daily with a traceable standard of Refrigerant-114. The response of the instrument and the sensitivity of the pressure manometers can be evaluated based on the mole percent concentration Refrigerant-114 calculated. See Table 1 for absorbance maxima and corresponding “K” values.

8.2 The operating experience of each laboratory for precision calculations of the mole percent concentrations of uranium hexafluoride and impurities are critical to the success of the method. Total pressure should be maintained at 100 mm HgA (13.3 kPa) or less. Each laboratory shall determine the “K” values specific to its instrumentation.

8.3 The “K” values used for calibrations are good well beyond the 60 to 75 mm HgA (8 to 10 kPa) in a typical all gas sample.

8.4 The “K” values require that the mole percent concentration of a traceable standard, pressure, and absorbance of a pure gas are known. 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.

9. Procedure (Part A)

9.1 Collecting the Sample—An all gas sample is collected from the apparatus described in Test Method C761. See Annex A1 or Fig. 1 in Test Method C761. The isotope abundance sample tube is replaced by a “2S” container. The valve on the inverted liquid uranium hexafluoride container is closed when the pressure on the manometer reads 75 mm HgA (10 kPa). A

TABLE 1 Typical Infrared Active Gas Molecules, Their Approximate Infrared Frequencies in cm⁻¹, and Their Infrared Absorbance Constants (K) in mm Part A, Determined at Room Temperature (25°C=77°F=298K)

Infrared Active Gas Molecule	Approximate Infrared Frequency in cm ⁻¹	K in kPa
Uranium Hexafluoride = UF ₆	625	11
Uranium Hexafluoride = UF ₆	676	1.6
Refrigerant-114 = C ₂ F ₄ Cl ₂	922	93.2
Refrigerant-114 = C ₂ F ₄ Cl ₂	1052	70.1
Refrigerant-114 = C ₂ F ₄ Cl ₂	1185	48.4
Refrigerant-114a = C ₂ F ₄ Cl ₂	1231	32.1

³ Available from USEC Inc., 6903 Rockledge Drive, Bethesda, MD 20817.

total of three samples are obtained in this manner. If three sample containers (“2S” or equivalent) are not available, three gas charges from one sample can be substituted. However, if the full pressure in the sample container is less than 50 mm HgA (6.7 kPa), the three gas charges from one sample option is not recommended.

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

9.2 Acquire Background Scan (Refer to Annex A2):

NOTE 2—The vacuum manometer Valve C must be open in order for pressure in mm to be read.

9.2.1 Ensure that the cold trap inlet valve (L) and crossover valves (MX1 and MX2) are closed.

9.2.2 Ensure that the chem trap outlet (R), chem trap inlet (Y), sample cell inlet (A), vacuum pump inlet (P), and sample port (S1, S2, or S3) valves are open.

9.2.3 Ensure that all other valves other than Valve C are closed.

9.2.4 Evacuate manifold system until readout on thermocouple gage (T2) displays a value of less than 10 μm .

9.2.5 Verify the digital manometer for zero and full scale readings, if not adjust accordingly.

9.2.6 Obtain an infrared background spectrum on the FTIR.

9.3 Acquire Initial Sample Scan:

9.3.1 Close chem trap inlet valve (Y).

9.3.2 Open the sample container valve and charge the manifold with the full contents of the sample container.

NOTE 3—If the total pressure of the sample is in excess of 13 kPa, a resample is desirable.

9.3.3 Close the sample container valve.

9.3.4 Obtain the infrared spectrum of the gases in the sample charge.

9.4 Interpret Spectrum:

9.4.1 Record the absorbance maxima for the three Refrigerant-114 bands cited in Table 1, if any are present. The absorbance maximum at 1052 cm^{-1} typically experiences the least amount of overlap.

9.4.2 Record the absorbance maximum for Refrigerant-114a from Table 1, if any is present.

9.4.3 Record the absorbance maximum for uranium hexafluoride at 676 cm^{-1} .

9.4.4 Record the pressure (in mm) from the readout of the digital manometer (C). (If the pressure exceeds 13 kPa resampling is necessary due to the possibility of freeze-out of the UF_6 .)

9.4.5 Monitor the absorbance of uranium hexafluoride at 625 cm^{-1} of the full pressure gas charge.

9.4.5.1 If the absorbance at full pressure exceeds 0.8 units partial evacuation of the manifold is necessary in accordance with the action steps in 9.5.

9.4.5.2 If the absorbance at full pressure is less than 0.8 units, a resample is desirable.

9.5 Partial Evacuation of the Manifold System:

9.5.1 Close the chem trap outlet valve (R).

9.5.2 Open the chem trap inlet valve (Y).

9.5.3 Close the chem trap inlet valve (Y) when the pressure on the digital manometer is no longer decreasing.

9.5.4 Allow a minimum of 30 s residency time in the chem trap (E).

9.5.5 Open the chem trap outlet valve (R) to vent any remaining gases to the always energized vacuum pump (W).

9.5.6 Close the chem trap outlet valve (R) when the readout on the thermocouple gage (T2) is less than 1 Pa.

9.5.7 Repeat step 9.5.1 – 9.5.6, until the pressure on the digital manometer reads 0.1 kPa.

9.6 Scanning the Sample for Uranium Hexafluoride at 625 cm^{-1} :

9.6.1 Scan the sample for uranium hexafluoride at a pressure that results in an infrared peak less than 0.80 absorbance units.

9.6.2 Record the magnitude of the absorbance maximum for the uranium hexafluoride peak at 625 cm^{-1} .

9.6.3 Record the pressure (in mm) from the readout of the digital manometer for the uranium hexafluoride peak at 625 cm^{-1} .

NOTE 4—If the pressure required to obtain an absorbance less than 0.8 units at 625 cm^{-1} is less than 0.40 mm HgA, the values obtained at 676 cm^{-1} are likely to be more reliable.

9.7 Total Evacuation of the Manifold System:

9.7.1 Repeat the action steps in 9.5 until the pressure on the digital manometer reads 0.20 mm HgA or less.

9.7.2 Open the cold trap inlet valve (L) and at least one of the crossover valves (MX1 or MX2).

9.7.3 Continue the total evacuation until the thermocouple gauge (T2) reads below 1 Pa and the digital manometer reads 0 Pa.

9.7.4 Rezero the digital manometer if the readout stabilizes for 2 min at a reading other than 0 Pa.

9.8 Replicate Experiments:

9.8.1 Proceed to Section 10 if the three gas changes from one sample was used in 9.1.

9.8.2 Repeat action steps 9.3 – 9.7.4 twice more, using a fresh replicate sample from the three “2S” containers received.

10. Calculations of Mole Percent Concentrations (Part A)

10.1 Calculate the average mole percent concentrations of Refrigerant-114 and Refrigerant-114a based on their respective absorbances, the “K” values, and the total pressure in the manifold as indicated in Eq 2:

NOTE 5—If the uranium hexafluoride concentration is high, based on the data obtained from the measurements at 625 cm^{-1} , the uranium hexafluoride band at 1157 cm^{-1} may interfere with the Refrigerant-114 band at 1185 cm^{-1} . The Refrigerant-114 concentration may be biased high should this result be included with the data obtained at 922 cm^{-1} and 1052 cm^{-1} .

$$\text{mole percent concentration} = \frac{(\text{absorbance})(K)}{\text{total pressure}} \quad (2)$$

10.2 Calculate mole percent concentration for uranium hexafluoride based on the absorbance at 625 or 676 cm^{-1} , the appropriate “K” value, and the total pressure in the manifold as indicated in Eq 2.

10.3 Determination of the mean mole percent concentrations of Refrigerant-114 and UF₆ plus the percent concentration Refrigerant-114 in UF₆.

10.3.1 Calculate the mean mole percent concentrations of both Refrigerant-114 and Refrigerant-114a in accordance with 10.1 if any is present, using each of the indicated absorbance frequencies listed in Table 1. This result is based on the three gas charges from one sample or three replicate samples.

10.3.2 Sum the mean mole percent concentrations of Refrigerant-114 and Refrigerant-114A and record as total Refrigerant-114.

10.3.3 Calculate the mean mole percent concentration of uranium hexafluoride in accordance with 10.2. This result is based on the three gas charges from one sample or three replicate samples.

10.3.4 Calculate the percent concentration of total Refrigerant-114 in uranium hexafluoride in accordance with Eq 3:

Percent total REFRIGERANT – 114 in UF₆

$$= \left(\frac{\text{mole \% total REFRIGERANT} - 114}{\text{mole \% UF}_6} \right) * 100 \quad (3)$$

NOTE 6—Sample Result Criteria—If the mole percent concentration of uranium hexafluoride in Part A is less than 50 %, a resample is desirable.

11. Precision and Bias (Part A)

11.1 Data—Data are presented for five standards of Refrigerant-114 in nitrogen purchased from a commercial source. The NIST traceable standards were 50.0 ppm (0.00500 mole percent) ± 1%, 100.0 ppm (0.0100 mole percent) ± 1%, 150.0 ppm (0.0150 mole percent) ± 1%, 200.0 ppm (0.0200 mole percent) ± 1%, and 500.0 ppm (0.0500 mole percent) ± 1% where the ± quantities are at the 95% confidence level for the reference values. In addition, a blank gas containing only nitrogen and two “unknown” mixtures of Refrigerant-114 in nitrogen were also analyzed. Each of the five standards was analyzed by one analyst over a five day period using one FTIR instrument. The eight gas samples were analyzed six times each for a grand total of 48 experiments. The data were used to quantify precision and bias.

11.2 Due to difficulties in movement and ownership of nuclear materials, interlaboratory testing is not practical. Therefore reproducibility results were not obtained.

11.3 Precision—Table 2 summarizes the statistical results for estimation of precision. The standard deviation, which is an indication of the precision, is given for each standard and unknown sample. The relative standard deviation has been determined to be 27.2% (averaged over the five standards and two unknowns).

11.4 Table 2 also summarizes the statistical results for bias estimation. The relative difference of the mean result on each standard from its reference value, averaged over the five standards, is 6.5% indicating an average recovery of 93.5% on the standards. This difference is an indication of bias. Standard gas mixtures of Refrigerant-114 in nitrogen with NIST certification or equivalent are suitable for establishing the bias of the method.

12. Principle (Part B)

12.1 There are two main differences with Part A:

- 12.1.1 the calibration is performed in UF₆
- 12.1.2 the pathlength of the IR cell used is 5 m equipped with zinc selenide (ZnSe) optics

13. Reagents and Bottles (Part B)

13.1 The reagents are nitrogen used to rinse the fittings, liquid nitrogen to freeze the gases.

13.2 The standards are a bottle of high purity UF₆ and a bottle of refrigerant with > 99 % purity.

13.3 Bottles and manifold are built with materials of construction inert to fluorine-bearing gases.

14. Calibration (Part B)

14.1 The calibration is performed at room temperature.

14.2 The manifold system is passivated with an appropriate fluorinating agent, for example, ClF₃, then the manifold is pumped overnight to ensure high quality.

14.3 A reference is created at 1 mol %. Four bottles are connected on the manifold: a UF₆ bottle, a refrigerant bottle, an

TABLE 2 Approximate True Refrigerant-114 Concentration (ppm)^A

	50.0 ppm	100 ppm	150 ppm	200 ppm	500 ppm	Unknown No. 1	Unknown No. 2	Average
Values	0.00563 0.00780 0.00400 0.00480 0.00480 0.00380	0.00977 0.00112 0.0137 0.0156 0.0144 0.00527	0.0191 0.0201 0.0229 0.0136 0.0133 0.0186	0.0225 0.0196 0.0253 0.0189 0.0176 0.0226	0.0562 0.0492 0.0632 0.0485 0.0512 0.0459	0.0262 0.0155 0.0271 0.0298 0.0274 0.0348	0.0320 0.0205 0.0225 0.0343 0.0395 0.0154	...
Mean	0.00514	0.01166	0.019	0.0211	0.0524	0.0268	0.0274	...
St. Dev.	0.00146	0.00379	0.00379	0.00286	0.00633	0.00635	0.00928	0.00512
Bias	0.00014	0.00166	0.00294	0.00108	0.00237	^B	^B	^B
% RSD ^C	28.4 %	32.5 %	21.1 %	13.6 %	12.1 %	23.7 %	33.8 %	27.2 %
% Bias ^D	2.8 %	16.6 %	19.6 %	5.4 %	4.7 %	^B	^B	6.5 %

^AData collected under the experimental conditions defined in Section 9. All results for the blank were zero and are not displayed in the table.

^BThese are unknown production samples; bias cannot be determined on them.

^C%RSD = relative standard deviation (percent) = 100* (Std. Dev./Mean).

^DT% Difference = relative difference (percent) = 100* [(Mean – Reference Value)/Reference Value].