



# Standard Test Method for Isotopic Analysis of Uranium Hexafluoride by Single- Standard Gas Source Mass Spectrometer Method<sup>1</sup>

This standard is issued under the fixed designation C 1344; 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 ( $\epsilon$ ) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This test method covers the isotopic analysis of uranium hexafluoride ( $\text{UF}_6$ ) and may be used for the entire range of  $^{235}\text{U}$  isotopic compositions for which standards are available.

1.2 This test method is applicable to the determination of the isotopic relationship between two  $\text{UF}_6$  samples. If the abundance of a specific isotope of one sample (the standard) is known, its abundance in the other can be determined. This test method is flexible in that the number of times a given material is admitted to the ion source may be adjusted to the minimum required for a specified precision level.

1.3 The sensitivity with which differences between two materials can be detected depends on the measuring system used, but ratio-measuring devices can generally read ratio-of-mol ratio differences as small as 0.0001.

1.4 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.5 *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.* Specific hazards statements are given in Section 7.

## 2. Referenced Documents

### 2.1 ASTM Standards:

C 787 Specification for Uranium Hexafluoride for Enrichment<sup>2</sup>

C 996 Specification for Uranium Hexafluoride Enriched to Less Than 5 %  $^{235}\text{U}$ <sup>2</sup>

### 2.2 Other Document:

USEC-651, *Uranium Hexafluoride: A Manual of Good Handling Practices*<sup>3</sup>

## 3. Terminology

### 3.1 Definitions of Terms Specific to This Standard:

3.1.1 *drop through, n*—a measurement of the amount of the  $^{238}\text{UF}_5^+$  ion beam that can be passed through the  $^{235}\text{UF}_5^+$  collector slit and measured on the  $^{235}\text{UF}_5^+$  collector, stated as a percentage of the total  $^{238}\text{UF}_5^+$  signal.

3.1.2 *memory corrections, n*—corrections applied to the sample analysis results for memory effects.

3.1.3 *memory effect, n*—the inability of the mass spectrometer to omit completely the isotopic composition of the sample analyzed previously from attributing to the results of further samples analyzed.

3.1.4 *normal isotopic abundance material, n*— $\text{UF}_6$  having a value of 0.711 weight percent (wt %)  $^{235}\text{U}$ .

3.1.5 *ratio-of-mol-ratios, n*—the mol ratio ( $^{235}\text{U}/^{238}\text{U}$ ) of the sample divided by the mol ratio of the standard, or the inverse condition of the mol ratio of the standard divided by the mol ratio of the sample.

## 4. Summary of Test Method

4.1 *Test Method*—The unknown sample and a standard with an isotopic composition close to that of the sample are introduced in sequence into the Neir mass spectrometer.  $\text{UF}_5^+$  ions of the isotopes are focused through a mass-resolving collector slit and onto a faraday cup collector. Measurements are made of  $^{235}\text{UF}_5^+$  to the total of the other  $\text{UF}_5^+$  isotopes. With the known composition of the standard, calculation of the  $^{235}\text{U}$  composition of the sample can be determined.

## 5. Significance and Use

5.1 Uranium hexafluoride is a basic material used to prepare nuclear reactor fuel. To be suitable for this purpose, the material must meet the criteria for isotopic composition. This test method is designed to determine whether the material meets the requirements described in Specifications C 787 and C 996.

### 5.2 ASTM Committee C-26 Safeguards Statement:

5.2.1 The material (uranium hexafluoride) to which this test method applies is subject to the nuclear safeguards regulations governing its possession and use. The analytical procedure in

<sup>1</sup> 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.

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<sup>2</sup> *Annual Book of ASTM Standards*, Vol 12.01.

<sup>3</sup> Available from U.S. Enrichment Corporation, 6903 Rockledge Dr., Bethesda, MD 20817.

this test method has been designated as technically acceptable for generating safeguards accountability data.

5.2.2 When used in conjunction with appropriate certified reference materials (CRMs), this procedure can demonstrate traceability to the national measurement base. However, adherence to this procedure does not automatically guarantee regulatory acceptance of the regulatory safeguards measurements. It remains the sole responsibility of the user of this test method to ensure that its application to safeguards has the approval of the proper regulatory authorities.

## 6. Apparatus

6.1 *Neir Mass Spectrometer*, with the following features and capabilities:

6.1.1 A single-focusing spectrometer, with a 127-mm minimum deflection radius, is satisfactory when equipped and focused as follows:

6.1.1.1 The sample inlet system must have two sample holders, to which  $UF_6$  containers can be attached, and the necessary valves to evacuate the sample lines through which the sample and standard are introduced. The sample inlet system should be nickel or Monel for use with corrosive gases, and should have minimum volume.

6.1.1.2 A single adjustable leak, operated by an automatic leak control mechanism for admitting the sample into the spectrometer ion source, is preferred.

6.1.1.3 The pumping system of the spectrometer analyzer tube must maintain a pressure below  $5 \times 10^{-8}$  torr with sample flowing into the ion source.

6.1.1.4 Focus the instrument for resolution consistent with precision requirements. A high-current ion beam of  $5 \times 10^{-10}$  to  $1 \times 10^{-9}$  amps is necessary, with a signal-to-noise ratio greater than 3000 in the low-current amplifier system.

6.1.1.5 A dual collector must be used, so that ions from one isotope are passed through a resolving slit and focused on a low-current collector, and ions from all other isotopes are focused on a high-current collector. The preferred method of maintaining the low-current ion beam within the collector slit is by an automatic beam positioner circuit. A resolving slit with adjustable width features enhances the measurement of all isotopes but is not mandatory for isotopic measurements.

6.1.1.6 The amplified high- and low-current signals are fed into a multimeter or other device capable of ratioing high- and low-current signals. If a multimeter is used, the multimeter must have a minimum of 5.5 digits of resolution, a means of ratioing the high- and low-current signals, and interactive communication capability with the controller.

6.1.1.7 The memory effect of the spectrometer must be consistent with the precision required since a high memory level is usually more variable than a low one. Memory values of 2 to 3 % are typical, but up to 10 % memory can be tolerated. The memory characteristics of a spectrometer must be established from periodic measurement of the effect. Current memory values usually will apply until the ion source is replaced, repairs are made on the sample inlet system, or the instrument is refocused so the flow rate of  $UF_6$  is altered significantly.

6.1.1.8 The computer control of the mass spectrometer must allow the operator to monitor parameters of the spectrometer

and check other operating conditions. The development of an interactive program allows input of sample information, performs necessary calculations, makes memory corrections, and records data. Flexibility of the interactive program allows pausing of the instrument for adjustment or restart capability, or both. Suggested methods of analysis checks include the standard deviation (SD) on individual data points, linearity of the data set, and a check of source pressure differences between the standard and sample that can be monitored by the computer program. Manifold valve actuation, conditioning time, and pump-out time are features of the computer control program.

## 7. Hazards

7.1 Since  $UF_6$  is radioactive, toxic, and highly reactive, especially with reducing substances and moisture (see USEC-651), appropriate facilities and practices for analysis must be provided.

## 8. Procedure

### 8.1 *Calibration of Isotopic Standards:*

8.1.1 One working standard is required for the analysis of a sample at any specific concentration of any isotope. Two working standards are required to determine memory corrections. Memory can be measured more precisely with a large difference between two working standards, but the adverse effect of introducing wide concentration ranges into the mass spectrometer must be considered. Ideally, the values obtained from the high- and low-memory standards should symmetrically bracket those of the sample to be corrected. Working standards approximately 5 % apart (having a ratio of ratios of 1.05) are suitable for most applications.

8.1.2 A reasonable limit for the relative  $e$  between the unknown sample and the working standard to which it is compared is 2.5 %. A series of working standards prepared at 5 % intervals and used for sample comparisons thus enables this 2.5 % limit.

8.1.3 Prepare a working standard, and standardize against an oxide blend of CRM standards that is within 0.02 % of the value of the working standard.

### 8.2 *Sample Preparation:*

8.2.1 Attach tubes containing the appropriate working standard,  $S$ , and the sample,  $X$ , to the spectrometer inlet system, and prepare the materials for introduction into the ion source, as follows:

8.2.1.1 If adequate sample and working standard are available, open all valves between the sample and working standard containers and the pumping system, except the valves on the sample and working standard containers. If the amount of sample or working standard is limited, proceed to 8.2.2.

8.2.1.2 Open the valve on the sample container, and then close it quickly to vent gases to the pumping system.

8.2.1.3 After the pumping system has evacuated the vented gases, repeat the steps given in 8.2.1.2 a second time.

8.2.1.4 Repeat the steps given in 8.2.1.2 and 8.2.1.3 for the working standard.

8.2.2 Use the following alternative method of sample purification if the amount of the sample or working standard is limited:

8.2.2.1 Operate the appropriate valves to remove air entrapped in the connectors and to determine that there are no leaks into the inlet system.

8.2.2.2 Freeze the UF<sub>6</sub> by immersing the container in a mixture of water and ice.

8.2.2.3 Open the valve on the container to permit the evacuation of volatile impurities from the container, and then close the container valve.

8.2.2.4 Remove the coolant from around the container, allowing the UF<sub>6</sub> to return to room temperature.

### 8.3 Instrument Preparation:

8.3.1 Prepare the instrument for analysis as follows:

8.3.1.1 Operate the appropriate valves to admit the working standard into the ion source.

8.3.1.2 With the beam positioner in the manual mode, adjust the mass spectrometer high-voltage or magnet current to focus the <sup>235</sup>UF<sub>5</sub><sup>+</sup> ion beam through the collector slit to the low-current collector, while the other UF<sub>5</sub><sup>+</sup> ions are collected on the high-current collector. This *peaking up* is complete when the current to the low-current collector is maximized. Place the beam positioner in the automatic mode.

8.3.1.3 Zero both amplifiers as frequently as needed. Some must be zeroed daily; others may require zeroing only once per week.

8.3.1.4 Adjust the variable leak until the flow of UF<sub>6</sub> into the ion source produces a current of approximately 10<sup>-9</sup> amps to the high-current collector. Place the leak control in the automatic position. If the analyzer pressure is not within 2 × 10<sup>-8</sup> torr of that observed when the working standard is admitted as in 8.3.1.1, further purify the UF<sub>6</sub> having the higher pressure.

8.3.1.5 Terminate the flow of the working standard, and evacuate the ion source.

8.3.2 The shortest sequence for the analytical determination is X, S, X, where X and S represent introductions of the sample and standard, respectively. Follow each introduction by evacuation of the ion source before the next introduction. The timing of the introductions and evacuations depends on the instruments being used but is typically approximately 2 min for sample introduction followed by a 30-s evacuation. The number of introductions per analytical sequence depends on the precision required. To minimize errors caused by drift in the spectrometer, always begin and end the sequence with the same material in the spectrometer source. A five-introduction sequence (X,S, X, S, X) is most commonly used. An extra preliminary or equilibration introduction, during which no data are recorded, precedes the determination to make the sample-standard interaction more uniform and to improve the validity of the memory correction. During each introduction of UF<sub>6</sub> into the ion source, conduct the following functions either manually or automatically:

8.3.2.1 Regulate the ion intensity to within 2 % of the desired level by adjusting the variable leak. This regulation may be conducted manually or by an automatic leak control circuit.

8.3.2.2 Adjust the magnet current or high voltage to obtain a maximum low-current collector signal, and maintain at this value for the entire sample introduction period; or repeatedly

sweep across this maximum to obtain a series of scans of the peak maxima during the period.

8.3.2.3 With the instrument peaked up, obtain a reading with the electrometers for the two collectors connected to a multimeter placed in the ratio circuit position. This reading is proportional to the ratio of the number of ions striking the low-current collector over the number of ions striking the high-current collector.

8.3.3 Average all of the readings for the standard. Also average all of the readings for the sample. The two values, R<sub>X</sub> and R<sub>S</sub>, are calculated for each analytical sequence.

8.3.4 Repeat the sequence, as needed, to obtain the desired analytical precision.

8.3.5 To correct for memory effects, intersperse memory sequences with sample sequences, using two memory standards that bracket the sample's isotopic composition and that differ in isotopic composition by approximately 10 %. Designate the results of R<sub>A</sub> and R<sub>B</sub> for memory standards A and B, respectively. Usually, less than 5 % of the total number of determinations needs and to be made on memory standards. Schedule memory measurements more frequently for maximum precision and plot on a time scale. Interpolate the memory factor from this plot at the time a sample is analyzed.

## 9. Calculation

9.1 *Percent Drop Through*—A convenient method for determining ion beam resolution is to measure the “drop through” of the <sup>238</sup>UF<sub>5</sub><sup>+</sup> ion peak. Adjust the high voltage to bring the <sup>238</sup>UF<sub>5</sub> peak onto the low-current collector, and then observe the amount signal remaining on the high-current collector. With normal isotopic abundance material, the drop through should be a minimum value of 93 %. Starting with the instrument in the normal operating position, measure the voltage generated on the high-current collector. Adjust the high voltage to move the <sup>238</sup>UF<sub>5</sub> onto the low-current collector, and observe the drop in voltage on the high-current collector.

$$PDT = \frac{SHCV - HCVAR}{SHCV} \times 100 \% \quad (1)$$

where:

PDT = percent drop through,  
SHCV = starting high-current voltage, and  
HCVAR = high-current voltage after repositioning.

9.2 Calculate the memory factor as follows:

$$M = \frac{(R - 1)}{(R_0 - 1)} \quad (2)$$

where:

M = memory factor,  
R = ratio-of-mol ratios for isotopes of interest, calculated from known mol ratios of the two memory standards, and  
R<sub>0</sub> = observed ratio-of-mol ratios, in this case R<sub>A</sub>/R<sub>B</sub> from the results obtained in 8.3.7.

9.3 Calculate the observed ratio of the mol ratios, R<sub>0</sub>, for the isotopes of interest from the following equations:

9.3.1 For isotopes for which adequate standards are available,

$$R_0 = \frac{R_X}{R_S} \quad (3)$$

where:  
 $z$  = wt %  $^{235}\text{U}$  in the standard.

where:  
 $R_X$  = ratio of isotope of interest to all other isotopes in the sample, as measured in 8.3.4,

and

$R_S$  = ratio isotope of interest to all other isotopes in the standard, as measured in 8.3.4.

9.4 The observed ratios,  $R_0$ , are corrected for memory as follows:

$$R_c = MR_0 - (M - 1) \quad (4)$$

where:  
 $R_c$  = corrected ratio of ratios.

9.5 For samples having a  $^{235}\text{U}$  content of approximately 5 % or less:

9.5.1 Calculate the weight percent  $^{235}\text{U}$  ( $U_5$ ) in the sample from:

$$U_5 = \frac{100R_cH}{(100 + R_cH)} \quad (5)$$

where:  
 $R_c$  = corrected ratio-of-mol-ratios obtained from  $^{235}\text{U}$  peak comparisons, and  
 $H$  = weight ratio of  $^{235}\text{U}$  to all remaining isotopes of the standard.

$$H = \frac{100z}{(100 - z)} \quad (6)$$

## 10. Precision and Bias

10.1 *Data*—Data are presented for standard values of wt %  $^{235}\text{U}$  of 0.14400, 0.71109, and 4.4610 enrichment from CRMs. (CRMs are used to provide traceability determination for the bias statement of 10.3.) Determinations were made using two different instruments for each standard value. Analysis of the standards was conducted over a two-month period by four different analysts, with the positional order of the standards reversed for one-half of the determinations. The data for this test method are given in Table 1 for each standard source.

10.2 *Precision*—Table 2 summarizes the data of Table 1, giving means and SDs for all instruments as well as those for each standard value. Statistical tests were performed at the 0.05 level of significance to compare instrument means and variances for all standard values. No significant differences were found except for an unexplained instrument variation for the high standard value. The instrument variation may have resulted from memory problems or high-voltage drift, or both. The percent relative standard deviation (% RSD) indicates that precision is influenced by the concentration of the material analyzed.

10.3 *Bias*—The data in Table 2 show no significant bias.

## 11. Keywords

11.1 single-standard gas source mass spectrometer; uranium hexafluoride

**TABLE 1 Standard Values Data**

Standard Value 0.14400		Standard Value 0.71109		Standard Value 4.4610	
Instrument A	Instrument B	Instrument C	Instrument D	Instrument E	Instrument F
0.14412	0.14402	0.71115	0.71111	4.46094	4.46150
0.14405	0.14400	0.71119	0.71108	4.46058	4.46118
0.14397	0.14402	0.71117	0.71102	4.45979	4.46175
0.14392	0.14397	0.71103	0.71115	4.46116	4.46153
0.14411	0.14397	0.71109	0.71102	4.46126	4.46130
0.14396	0.14394	0.71104	0.71095	4.46070	4.46130
0.14399	0.14406	0.71103	0.71098	4.46032	4.46079
0.14405	0.14413	0.71117	0.71116	4.46117	4.46105
0.14401	0.14399	0.71103	0.71106	4.46150	4.46113
0.14407	0.14400	0.71111	0.71114	4.46091	4.46125
0.14402	0.14398	0.71112	0.71106	4.46154	4.46102
0.14403	0.14402	0.71104	0.71111	4.46133	4.46089



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### TABLE 2 Bias Data

Comparison	Standard Value 0.14400		Standard Value 0.71109		Standard Value 4.4610	
	Instrument A	Instrument B	Instrument C	Instrument D	Instrument E	Instrument F
Number of runs	12	12	12	12	12	12
Mean	0.14403	0.14401	0.71110	0.71107	4.46093	4.46122
SD ( $\times 10^{-5}$ )	5.98	4.93	6.24	6.77	51.56	27.66
Grand mean	0.14402		0.71109		4.46108	
SD ( $\times 10^{-5}$ )	5.43		6.52		43.10	
%RSD	0.037		0.009		0.010	

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