Designation: C1845 – 16

Standard Practice for The Separation of Lanthanide Elements from Uranium Matrices Using High Pressure Ion Chromatography (HPIC) for Isotopic Analyses by Inductively Coupled Plasma Mass Spectrometry (ICP-MS)[1]

This standard is issued under the fixed designation C1845; 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 practice provides instructions for the rapid separation of lanthanide elements using high pressure ion chromatography (HPIC) from dissolved uranium materials such as: nuclear fuels, uranium ores, hydrolyzed UF_6, and depleted, natural, or enriched oxides/powders, or metals. When optimized, this technique will produce purified elemental fractions of the lanthanide elements isolated from the bulk uranium matrix allowing for isotopic assay using inductively coupled plasma mass spectrometry (ICP-MS).

1.2 This practice is most applicable for analyte concentrations of nanograms per gram uranium or higher. For ICP-MS detection and measurement of analyte concentrations lower than this, it would be necessary to perform additional precleanup or concentration techniques, or both, which are not addressed in this practice.

1.3 When combined with isotope dilution, this practice can also be used for improved precision assays of the lanthanide elements using the principle of isotope dilution mass spectrometry (IDMS).

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

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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C859 Terminology Relating to Nuclear Materials
C1052 Practice for Bulk Sampling of Liquid Uranium Hexafluoride
C1075 Practices for Sampling Uranium-Ore Concentrate
C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis
C1689 Practice for Subsampling of Uranium Hexafluoride
C1769 Practice for Analysis of Spent Nuclear Fuel to Determine Selected Isotopes and Estimate Fuel Burnup
D1193 Specification for Reagent Water
E105 Practice for Probability Sampling of Materials

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology C859.

4. Summary of Practice

4.1 Solid samples are dissolved according to Practices C1168, C1347, or other appropriate methods. Uranium hexafluoride can be sampled in accordance with Practices C1052 and C1689. The resulting dissolver solution is processed to produce solutions of isolated lanthanide elements for mass spectrometric isotopic analysis. The elements are selectively separated from the dissolver solution and collected using HPIC instrumentation equipped with automated fraction collection. Appropriate aliquots of the unseparated dissolutions

[1] This practice 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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[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.

are taken to provide up to 100 ng/mL of a lanthanide element on the analytical column to be separated from 3.5 mg/mL or less of uranium. In a strong nitric acid matrix, no pre-separation valence adjustments are necessary.

NOTE 1—This practice has been verified to separate 0.7 mg of total uranium from the lanthanide analytes. 20 ng total of each analyte has been shown to have efficient resolution on the column to yield purified elemental samples. If larger uranium and analytes sample sizes are being considered, it is suggested that these be verified by the lab for efficient uranium removal and analyte resolution.

4.2 For the separation HPIC sample aliquots are injected using a 200 µL sample loop and loaded onto a 4 by 250 mm high pressure cation exchange column with sulfonic acid functional groups and an ion exchange capacity of ~80 micro-equivalents/columns. First, complexation and removal of the bulk dissolved uranium matrix is accomplished using a dilute hydrochloric acid eluent which is directed to waste. Next, the lanthanide elements are selectively eluted off of the column by chelation chromatography using a dilute solution of 2-hydroxyisobutyric acid (α-HIBA). Fractions are collected at automated 20 s time intervals to allow for recovery of the separated analytes, producing purified aliquots of each lanthanide element from the bulk uranium matrix of the dissolver solution for isotopic measurements using ICP-MS.

5. Significance and Use

5.1 The measurement of isotopic distributions for the lanthanide series elements is of important to all phases of the nuclear fuels cycle. Examples include the purification of the Nd isotopes from Ce and Sm isotopes for the determination of atom percent fission through the production of ^{148}Nd in irradiated nuclear fuels using Practice C1769, determination of rare earth content and isotopic distribution in Uranium Ore Concentrates (UOC) for source term and production of lanthanide fission products in irradiated nuclear fuels for determination of performance, improvements of depletion codes, and analysis of burnup indicators.[3]

6. Interferences

6.1 High salt content in the sample can potentially influence both the retention times and the resolution of the analytes. The concentration of the nitric acid in the sample matrix does not necessarily influence the retention times and the resolution of the analytes, but it can influence the removal of uranium. 2 M nitric acid has been successful in efficiently removing uranium.

6.2 The presence of high concentrations of sulfate, phosphate, oxalate, and halides in the sample matrix will potentially have an effect on the retention times and the resolution of the analytes.

NOTE 2—Using a smaller sample injection loop volume with a higher analyte concentration can reduce the effects of the matrix on the retention times and the resolution of the analytes.

6.3 Temperature can impact the retention times and the resolution of the analytes and, where possible, a thermal compartment should be employed to maintain consistency between sample analyses.

7. Apparatus

7.1 *High pressure ion chromatograph* equipped with a single variable speed gradient pump capable of delivering flow rates of 0.001 to 10 mL/min. The system requires eluent degas capability and a low pressure gradient mixer capable of mixing four independent eluent streams.

7.1.1 Optionally the HPIC may be equipped with a post-column reaction coil using a chromophore for detection via a single or multi-wavelength UV/Vis absorption detector to measure the appropriate wavelength emission.

7.1.2 Using an integrated online detector is useful for initial instrument testing and setup of the parameters for the lanthanide separations and determining initial time intervals for the collection of fractions. Also, with the detector online during fraction collection it could be used as a trigger for the fraction collector. CAUTION: The nature of the post-column chromophore solution may have an impact in post separation analyses.

7.2 *Autosampler* for sample injection equipped with a 10-port injections switching valve is recommended. Alternately, a manual injection setup can be used.

7.3 *Sample loop.* A 200 µL sample loop is considered to be optimal for this practice; however, injection loops can vary from 25 to 1000 µL depending on sample concentrations.

NOTE 3—Matrix effects with regard to peak resolution must be considered when choosing large sample loop volumes.

7.4 *Analytical column.* Standard bore high pressure analytical column (250 × 4 mm I.D.) with sulfonic acid functional groups and an ion exchange capacity of ~80 micro-equivalents/columns. Standard bore is required over micro bore columns to support greater resolution for complex sample matrices.

7.5 *Guard column.* Standard bore guard column (50 × 4 mm I.D.) is required to protect the analytical column from sample contaminates which will degrade the performance of the column.

7.6 *Fraction collector.* Automated fraction collector either as a standalone system that communicates with the HPIC unit or integrated into the instrument.

8. Reagents and Materials

8.1 *Purity of Reagents*—High purity grade acids and reagent grade chemicals shall be used for the preparation of eluent stock solutions. High concentrations of ionic impurities in eluents will degrade column performance over time and adversely affect the separation chemistry resulting in inconsistent retention times or unacceptable overlaps, or both, between the rare earth elemental fractions. It is intended that all acids and reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.

8.2 *Purity of Water*—Type II Reagent Grade Water with a specific resistance of 18.2 MΩ-cm, according to Specification D1193, shall be used in the preparation of all high purity acids, reagents, and eluents.

[3] *Re-evaluation of Spent Nuclear Fuel Assay Data for the Three Mile Island Unit 1 Reactor and Application to Code Validation*, *Annals of Nuclear Energy*, Vol 87, Part 2, January 2016, pp. 267–281.

8.3 *Nitric Acid (HNO_3),* concentrated, ρ ~1.42 g/mL ~70 % (m/m).

8.4 *Nitric Acid (HNO_3), 2.0 M*—Dilute 125 mL concentrated HNO_3 to a final volume of 1000 mL with water.

8.5 *Hydrochloric Acid (HCl),* concentrated, ρ ~1.18 g/mL, ~36 % (m/m).

8.6 *Hydrochloric Acid (HCl), 1.0 M*—Dilute 100 mL concentrated HCl to a final volume of 1000 mL with water.

8.7 *Ammonium Hydroxide,* 28 % NH_3 in H_2O, ≥99.99 % purity.

8.8 *α-Hydroxyisobutyric acid (α-HIBA), 0.4 M, reagent grade, 99 %*—Dissolve 41.6 g α-HIBA in 500 mL water (8.2), buffer to a pH of 4.5 with Ammonium Hydroxide, approximately 18 mL, and bring to a final volume of 1000 mL.

9. Hazards

9.1 Strong acids are used for the preparation of reagents. Wear appropriate personal protective equipment while handling nitric and hydrochloric acids. Lab coat, gloves, and safety glasses with side shields are considered to be the minimum requirement. When handling large volumes of acid, a full face shield should be used.

9.2 Hydrochloric acid (HCl) vapors are very corrosive. All dilutions of HCl solutions should be made in a fume hood to avoid inhalation of vapors.

9.3 Ammonium hydroxide is corrosive. Wear appropriate personal protective equipment when handling and perform work within a chemical fume hood to avoid inhalation of vapors.

10. Sampling, Test Specimens, and Test Units

10.1 Sampling of UOC in a processing environment is performed according to Practices C1075 and liquid uranium hexafluoride by Practice C1052. All others should follow Practice E105.

10.2 Test specimens are obtained through acid dissolution according to Practices C1347, C1168, or other appropriate methods. The dissolution of uranium-plutonium mixed oxides is covered in Practice C1168.

NOTE 4—Many uranium-containing materials such as high-purity metals and oxides dissolve readily in various inorganic acids. Nitric acid dissolutions are preferred for this practice; however, small quantities of HCl, HF, or H_2SO_4 will not affect the HPIC separation.

NOTE 5—Samples prepared using fusion techniques have not been tested.

10.3 *Preparation of Dissolved Samples and Blanks:*

10.3.1 Using 2 M HNO_3 dilute an appropriate aliquot of each sample such that the total uranium concentration is 3.5 mg/mL or less and to provide up to 100 ng/mL of a lanthanide element to be loaded onto the analytical column.

10.3.2 Subsample a 1 mL aliquot of each dilution into a 5 mL vial (preferentially made out of a perfluoroalkoxy (PFA) material).

10.3.3 Fume the aliquots to dryness on a hotplate at a medium heat.

10.3.4 Once dry, add 0.5 mL of 2 M HNO_3 and repeat the dry down process.

10.3.5 Add 1 mL of 2 M HNO_3 to the hot vial, cap, and allow the sample to cool.

NOTE 6—Preferably perform the dry down steps in a trace clean environment or in a HEPA-filtered enclosure to minimize external sources of elemental contamination.

10.3.6 Transfer the sample to the appropriate autosampler vial and label accordingly.

10.4 *Blanks:*

10.4.1 Prepare method blanks that were taken through the dissolution protocol with the samples by following steps 10.3.1 through 10.3.6 above.

10.4.2 Prepare instrument blanks by adding 1 mL of 2 M HNO_3 to the appropriate autosampler vial and label.

11. Preparation of Apparatus

11.1 After extended use or noticeable degradation of column performance, or both, the guard and analytical columns shall be cleaned. It is recommended that they be cleaned separately following the manufacturer's recommendation so that contaminants on the guard column do not elute onto the analytical column.

NOTE 7—If the column is unused for any significant length of time low molarity HCl (10~50 mM) is a suitable storage solution that does not require changing any of the eluents. For long term storage, follow the column manufacturer's instructions.

11.2 If the columns are to be used after long-term storage, prepare them for use following manufacturer's instructions.

11.3 Minimize void volumes in the sample flow path per manufacturer's recommendations and ensure that all tubing connections are tightened to manufacturer's recommendations and are leak free.

11.4 Configure the instrument with a 200 µL sample loop for optimum sample loading and a flow rate of 1.0 mL/min.

NOTE 8—For optimum separation performance refer for manufacturer's manual for ideal column pressure and adjust the eluent flow rate accordingly.

11.5 Verify that all modules of the HPIC system are active and respond to the control computer per manufacturer's instructions.

11.6 Program the gradient pumping profile into the instrument control software as shown in Table 1.

11.7 Check that there are adequate volumes for the eluents listed in Table 1.

NOTE 9—Shelf-life of the 0.4 M α-HIBA eluent is 14 days. Proper buffering of the solution to a pH of 4.5 is important to separation performance.

TABLE 1 Gradient Profile

Time (min)	DI Water (%)	1M HCl (%)	0.4 M HIBA (%)
0.00	0	100	0
0.10	90	0	10
8.00	90	0	10
28.00	35	0	65
35.00	0	0	0

11.8 Prime the system pump heads, autosampler syringe and sample injection loop following the manufacturer's instructions.

11.9 Pre-rinse the analytical and guard columns by pumping the system with 1 M HCl for 5 min followed by 0.01 M HCl for 5 min.

11.10 Follow the first pre-rinse of the columns by pumping the system with 2 M HNO_3 for 5 min followed by 0.02 M HNO_3 for 5 min.

11.11 The final pre-rinse of the columns is with 0.4 M α-HIBA for 5 min followed by deionized water whose purity is defined in 8.2 for 10 min to equilibrate the column.

NOTE 10—See Appendix X1 for further details on tested instrument parameters using Chromeleon 6.8 software.

12. Calibration and Standardization

12.1 The HPIC instrument shall be verified for stability and resolution for the lanthanides of interest using a commercial rare earth standard traceable to a national standards body such as NIST. A diluted stock of the standard using 2 M HNO_3 to approximate concentrations of the unknowns will be used as the laboratory control.

NOTE 11—If available the employment of isotopically enriched lanthanide standards can facilitate screening, allowing for efficient calculation of separation factors between analytes.

12.2 Using the procedure below separate a series of a laboratory controls and 2 M nitric acid blanks to ensure the separation is repeatable and there is no carryover from separation to separation. The series will be separated in the order of BLANK – CONTROL – BLANK – CONTROL – BLANK.

12.3 Using the ICP-MS which has been properly tuned and mass calibrated, perform full lanthanide mass scans of the collected fractions for each of the separated controls to evaluate for final elution times for each of the lanthanide elements and the best fractions to use for maximum ICP-MS response and minimum isobaric overlaps. This evaluation will determine the start and end times for the collection of lanthanide fractions using the procedure section of this practice.

12.4 Ensure the blank fractions for instrument backgrounds are within the acceptable limits set by the laboratory.

12.5 If it is determined that adjustments have to be made to the separation protocol based on the evaluation of the controls and blanks it must be completed and verified prior to the separation of the samples.

13. Procedure

13.1 *HPIC Separations:*

13.1.1 Set the start and end collection window using the elution times evaluated in 12.3. During collection fractions are collected continuously using 20 s time intervals.

NOTE 12—The start time for fraction collections should be set at least 1 min before the start of the elution of the first lanthanide peak and 1 min beyond the elution of the last. The initial column elution prior to the start of fraction collections is directed to waste.

13.1.2 Each sample, control, or method blank in the HPIC separation batch should be preceded by a 2 M HNO_3 blank uncollected column rinse followed by a fraction collected instrument blank so that the predetermined analyte fractions can be verified for potential contaminants.

13.1.3 All samples, controls, and blanks in the run batch are injected in series into the HPIC following manufacturer's instructions.

13.2 *Fraction Collection:*

13.2.1 Initially the column eluent is directed to waste as the bulk of the uranium matrix is complexed with the HCl eluent.

13.2.2 As an injected sample elutes automated fractions are collected in 20 s intervals according to the programmed start and end times in 13.1.1. Alternatively fractions can be automatically collected using an integrated UV wavelength detector with post-column reaction with a chromophore if the system is so equipped.

NOTE 13—The lanthanides will elute in the order Lu-Ce. Elution times may vary depending on the HPIC system. For Gd, Eu, Sm, Nd, and Ce, the elution times using the above gradient protocol and a flow rate of 1 mL/min using a standard bore 4 mm system have been tested to be 18, 18.7, 20, 22.3, and 25 min respectively using the parameters listed in Appendix X1. The elution times will be resin and column manufacturer specific, evaluate the analyte elution times for the HPIC column as described in 12.1 through 12.5.

13.3 The collected fractions containing each of the purified lanthanide elements of interest, as determined in 12.3, are ready for isotopic analysis using ICP-MS.

13.4 Each fraction is verified for purity by performing an ICP-MS survey scan across the mass region of interest to evaluate for isobaric overlaps prior to isotopic analysis.

NOTE 14—It is recommended that fractions to either side of the target fraction be saved until this evaluation is completed as drift in elution times may necessitate using those fractions for optimal isotopic analysis.

13.5 When all separations are complete, rinse the column for 10 min with 0.4 M HIBA, followed by 10 min 1 M HCl followed by a further 10 min of 0.01 M HCl.

NOTE 15—If the column will not be used for an extended period of time prepare it for long term storage per manufacturer's instructions.

14. Precision and Bias

14.1 This is not a test method, and no data are generated by this practice, so a precision and bias statement is not required.

15. Keywords

15.1 fission; ICP-MS; inductively coupled plasma; ion chromatography; ion exchange; lanthanides; isotopic analysis; rare earth elements; separation; uranium