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.