



Designation: C1590 – 21

# Standard Practice for Alternate Actinide Calibration for Inductively Coupled Plasma-Mass Spectrometry<sup>1</sup>

This standard is issued under the fixed designation C1590; 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 practice provides guidance for an alternate linear calibration for the determination of selected actinide isotopes in appropriately prepared aqueous solutions by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). This alternate calibration is mass bias adjusted using thorium-232 ( $^{232}\text{Th}$ ) and uranium-238 ( $^{238}\text{U}$ ) standards. One of the benefits of this standard practice is the ability to calibrate for the analysis of highly radioactive actinides using calibration standards at much lower specific activities. Environmental laboratories may find this standard practice useful if facilities are not available to handle the highly radioactive standards of the individual actinides of interest.

1.2 The instrument response for a series of determinations of known concentration of  $^{232}\text{Th}$  and  $^{238}\text{U}$  defines the mass versus response relationship. For each standard concentration, the slope of the line defined by  $^{232}\text{Th}$  and  $^{238}\text{U}$  is used to derive linear calibration curves for each mass of interest using interference equations. The mass bias corrected calibration curves, although generated from interference equations, are specific to the instrument operating parameters and tuning in effect at the time of data acquisition. Because interference equations are part of the normal ICP-MS manufacturer's software package, this calibration methodology is widely applicable.

1.3 For this standard practice, the actinide atomic mass range that has been studied is from AMU 232 to 244. Guidance for an extended range of AMU 228 to 248 is given in this practice.

1.4 Using this practice, analyte concentrations are reported at each AMU and not by element total (that is,  $^{239}\text{Pu}$  versus plutonium).

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

<sup>1</sup> 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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1.6 *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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.7 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

## 2. Referenced Documents

### 2.1 ASTM Standards:<sup>2</sup>

C859 Terminology Relating to Nuclear Materials

C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis

C1347 Practice for Preparation and Dissolution of Uranium Materials for Analysis

C1411 Practice for The Ion Exchange Separation of Uranium and Plutonium Prior to Isotopic Analysis

C1463 Practices for Dissolving Glass Containing Radioactive and Mixed Waste for Chemical and Radiochemical Analysis

D1193 Specification for Reagent Water

## 3. Terminology

### 3.1 Definitions:

3.1.1 For definitions of terms relating to nuclear materials, refer to Terminology C859.

### 3.2 Abbreviations:

3.2.1 AMU—Atomic Mass Unit

## 4. Summary of Practice

4.1 Calibration for the actinides by ICP-MS can be performed in a variety of ways with varying degrees of data quality. An alternative calibration method has been developed to compensate for instrument mass bias using a generated mass

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

response curve defined by the  $^{232}\text{Th}$  and  $^{238}\text{U}$  data points. The mass response curve defined by  $^{232}\text{Th}$  and  $^{238}\text{U}$  approximates the mass response curve from AMU 232 to 244 as verified experimentally and graphically depicted in Fig. 1. The mass response curve shown reflects the operating parameters and tune of the particular instrument in use at the time of data collection. Different tuning parameters or instrumentation could result in varying degrees of negative, neutral, or positive mass bias. Because the mass response curve defined by  $^{232}\text{Th}$  and  $^{238}\text{U}$  used in this standard practice is determined during each calibration, all potential linear variations in mass bias are compensated for.

4.2 The alternative calibration in this standard practice combines the features of an external linear calibration at each mass of interest with the mass bias correction of a mass/response curve. The correction for mass bias is integrated into the acquisition of the standard data through the use of interference equations which, are part of the normal software package for correction of isobaric interference's in ICP-MS analyses. Multipoint calibration curves are generated at each mass of interest, resulting in more accurate quantification than that of the typical “semi-quantitative” single point calibration based on the mass/response curve alone.

4.3 Sample analyses for blanks and samples are performed using a data acquisition method file without the interference equations that were used to derive the calibration curves. After calibration curves are generated, the calibration files are copied or linked to the analytical acquisition method. The sample responses are acquired at each mass, and concentrations calculated from the mass bias corrected calibration curves. Some ICP-MS vendor supplied control software will permit the linking of separate calibration and acquisition files (that is, one can choose which calibration files to use to quantitate any particular data set regardless of the acquisition file that was used to acquire the data).

4.4 Mixed calibration standard solutions are prepared through dilution of single element stock standards of thorium and known abundance uranium (normally depleted in  $^{235}\text{U}$ )

with dilute nitric acid to develop a calibration series covering the desired concentration range. Standard concentrations are calculated for  $^{232}\text{Th}$  and  $^{238}\text{U}$  for each calibration solution.

4.5 An internal standard is added in a fixed quantity in all standards and samples to correct for both instrument drift and physical sample transport fluctuations. Typically  $^{209}\text{Bi}$  is used but other elements, such as  $^{159}\text{Tb}$ , may also be used.

## 5. Significance and Use

5.1 One of the benefits of this standard practice is the ability to calibrate for the analysis of highly radioactive actinides using calibration standards at much lower specific activities (that is,  $^{232}\text{Th}$  and  $^{238}\text{U}$ ). Environmental laboratories may find this standard practice useful if facilities are not available to handle the highly radioactive standards of the individual actinides of interest.

5.2 The degree of actual mass bias is variable and is dependent upon instrument tune parameters. This standard practice uses universal interference equations to derive a mass bias correction that is specific to the instrument parameters and tune used for sample data acquisition and not based on a historical average.

5.3 Mass bias correction uses the instrument software interference equations and does not require additional subsequent off-line calculations.

5.4 The methodology that this standard practice is based on has been used for the determination of  $^{232}\text{Th}$  and  $^{237}\text{Np}$  in enriched uranium solutions and the determination of  $^{241}\text{Am}$  in plutonium and uranium legacy oxides following dissolution and ion extraction chromatography separation.

5.5 Data presented in Section 12 were developed using a quadrupole ICP-MS. This practice can also be applied to high resolution ICP-MS with appropriate validation.

## 6. Interferences

6.1 Isotopes of different elements forming atomic ions with the same nominal mass-to-charge ratio ( $m/z$ ) may cause isobaric interferences in ICP-MS if present in sufficient quantity (that is,  $^{238}\text{U}$  with  $^{238}\text{Pu}$  and  $^{241}\text{Pu}$  with  $^{241}\text{Am}$ ). Because the isotopic abundance of actinides vary widely, it is not practical to apply an interference correction unless the isotopic abundance of the interference is well characterized. In addition, the hydride of an abundant isotope can interfere with the adjacent higher mass (that is,  $^{238}\text{U}^1\text{H}$  on  $^{239}\text{Pu}$ ). For these reasons, it is prudent to implement actinide separation methods utilizing extraction chromatography resins prior to ICP-MS analysis to significantly reduce these interferences.<sup>3</sup>

6.2 Analyte memory can occur when there are large concentration differences between standards and/or samples that are analyzed sequentially. Thorium can exhibit memory within the sample introduction system. A rinse solution containing 0.2 M nitric acid and 0.2 M sulfuric acid has been found to be beneficial in reducing thorium carryover.

<sup>3</sup> Maxwell, S. L., “Rapid Actinide-Separation Methods,” *Journal of Applied Radioactivity Measurements*, Vol 8, No. 4, 1997, pp. 36-44.

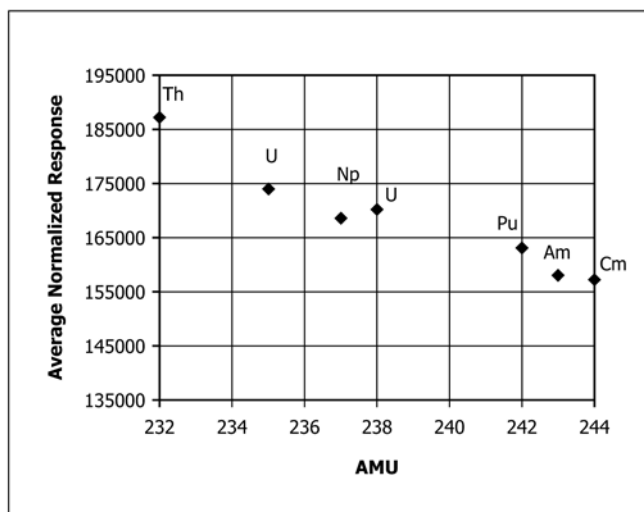


FIG. 1 Atomic Mass Versus Average Normalized Response

## 7. Apparatus

7.1 *ICP-MS*, computer controlled with associated software and peripherals.

7.2 *Autosampler*, optional, with tube racks, disposable plastic sample tubes.

7.3 *Variable Micro and Macro Pipettes*.

## 8. Reagents

8.1 *Argon (Ar) Gas*, high purity  $\geq 99.99\%$ .

8.2 *Deionized Water*, high purity, conforming to Specification **D1193**, Type I.

8.3 *Nitric Acid*, (*Specific Gravity 1.42*), concentrated nitric acid ( $\text{HNO}_3$ ), trace metal grade or better.

8.4 *Sulfuric Acid*, (*Specific Gravity 1.84*), concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ), trace metal grade or better.

8.5 *Bismuth Stock Solution*, (*1000  $\mu\text{g/mL Bi}$* ), matrix nominal 10 %  $\text{HNO}_3$ .

8.6 *Thorium Stock Solution*, (*1000  $\mu\text{g/mL Th}$* ), matrix nominal 2 %  $\text{HNO}_3$ .

8.7 *Uranium Stock Solution*, (*1000  $\mu\text{g/mL U}$* ), matrix nominal 2 %  $\text{HNO}_3$ .

8.8 *Radioisotope Standards* ( $^{241}\text{Am}$ ,  $^{242}\text{Pu}$ ,  $^{244}\text{Cm}$ , etc.) can be purchased<sup>4</sup> to verify calibration curves if laboratory and ICP-MS have proper engineering and procedural controls to safely handle radiological material.

<sup>4</sup>Eckert and Ziegler Isotope Products, 24937 Avenue Tibbits, Valencia, CA 91355, www.ezag.com.

## 9. Hazards

9.1 Personnel using this procedure shall be knowledgeable of the safety precautions necessary for normal chemical, radiological handling protocol and instrumental operation of ICP-MS.

9.2 Nitric and sulfuric acids are strong oxidizers, avoid contact with flammable, powdered, or combustible materials. Avoid contact with skin, eyes and clothing. Do not breathe or ingest vapors.

9.3 Actinide bearing materials are radioactive and toxic. Adequate laboratory facilities and ventilation hoods along with safe handling techniques must be used. A detailed discussion of all safety precautions needed is beyond the scope of this standard practice. Follow site and facility specific radiation protection and chemical hygiene protocol.

## 10. Procedure

10.1 *Calibration Standard Preparation*—Because the focus of this practice is on mass bias correction and not on any particular calibration concentration range or sample matrix, minimal instruction is given for the preparation of calibration standards.

10.1.1 *Mixed Calibration Standard* solutions are prepared through the quantitative dilution of single element bench stock standards of thorium and known abundance uranium (normally depleted in  $^{235}\text{U}$ ) with an internal standard (such as  $^{209}\text{Bi}$  or  $^{159}\text{Tb}$ ) in nominal 1 % nitric acid or other acid concentration appropriate to match sample matrix. A final concentration of 10  $\mu\text{g/mL}$  for each element is recommended.

**TABLE 1 Universal Interference Equations Used to Perform Calibration Mass Bias Correction**

Mass Bias Corrected Calibration Response	Calibration Interference Equation
Corrected (228) =	Response (228) $\times$ 0 – (238) $\times$ 0.6667 + (232) $\times$ 1.6667
Corrected (229) =	Response (229) $\times$ 0 – (238) $\times$ 0.5 + (232) $\times$ 1.5
Corrected (230) =	Response (230) $\times$ 0 – (238) $\times$ 0.3333 + (232) $\times$ 1.3333
Corrected (231) =	Response (231) $\times$ 0 – (238) $\times$ 0.1667 + (232) $\times$ 1.1667
Corrected (232) =	Response (232) $\times$ 1
Corrected (233) =	Response (233) $\times$ 0 + (238) $\times$ 0.1667 + (232) $\times$ 0.8333
Corrected (234) =	Response (234) $\times$ 0 + (238) $\times$ 0.3333 + (232) $\times$ 0.6667
Corrected (235) =	Response (235) $\times$ 0 + (238) $\times$ 0.5 + (232) $\times$ 0.5
Corrected (236) =	Response (236) $\times$ 0 + (238) $\times$ 0.6667 + (232) $\times$ 0.3333
Corrected (237) =	Response (237) $\times$ 0 + (238) $\times$ 0.8333 + (232) $\times$ 0.1667
Corrected (238) =	Response (238) $\times$ 1
Corrected (239) =	Response (239) $\times$ 0 + (238) $\times$ 1.1667 – (232) $\times$ 0.1667
Corrected (240) =	Response (240) $\times$ 0 + (238) $\times$ 1.3333 – (232) $\times$ 0.3333
Corrected (241) =	Response (241) $\times$ 0 + (238) $\times$ 1.5 – (232) $\times$ 0.5
Corrected (242) =	Response (242) $\times$ 0 + (238) $\times$ 1.6667 – (232) $\times$ 0.6667
Corrected (243) =	Response (243) $\times$ 0 + (238) $\times$ 1.8333 – (232) $\times$ 0.8333
Corrected (244) =	Response (244) $\times$ 0 + (238) $\times$ 2 – (232) $\times$ 1
Corrected (245) =	Response (245) $\times$ 0 + (238) $\times$ 2.1667 – (232) $\times$ 1.1667
Corrected (246) =	Response (246) $\times$ 0 + (238) $\times$ 2.3333 – (232) $\times$ 1.3333
Corrected (247) =	Response (247) $\times$ 0 + (238) $\times$ 2.5 – (232) $\times$ 1.5
Corrected (248) =	Response (248) $\times$ 0 + (238) $\times$ 2.6667 – (232) $\times$ 1.6667

10.1.2 *Calibration Blank* consists of the same acid matrix as the standard solutions with the same concentration of internal standard.

10.1.3 *Reagent Blank* consists of the same acid and chemical matrix as the samples (if different from the calibration blank) with the same concentration of internal standard. Consideration should be given to processing the reagent blank through any sample prep evolutions such as digestion or ion extraction chromatography separation.

#### 10.2 *Sample Preparation:*

10.2.1 Prior to analysis, digest/dissolve samples as needed using methods appropriate to the sample matrix such as Practices [C1168](#), [C1347](#), [C1463](#), or other laboratory specific procedures.

10.2.2 Use actinide separation procedures when necessary to reduce matrix and isobaric interferences between overlapping isotopes of interest in the digest solutions; such as Practice [C1411](#), Maxwell's "Rapid Actinide-Separation Methods,"<sup>3</sup> or other laboratory specific procedures.

10.2.3 Dilute sample into appropriate acid matrix (1 to 2 % HNO<sub>3</sub> typical) with the same concentration of internal standard as in the calibration standards. Dilution of samples should be consistent with the span of calibration standards.

#### 10.3 *ICP-MS Instrumental Analysis:*

10.3.1 Set up the ICP-MS for the analysis using the parameters given in the manufacturer's operating manual. Following plasma initiation, allow the instrument to reach thermal equilibrium (generally at least 30 min). Optimize the ICP-MS using routine tuning protocol for elemental analysis or tune specific to the mass range of interest. Limit oxide formation through instrument tuning. Oxides are typically monitored using the % ratio of CeO/Ce, usually ≤1 %.

#### 10.4 *Actinide Calibration w/Mass Bias Correction:*

10.4.1 Actinide calibration with mass bias correction is performed through the use of external linear calibration standards consisting of <sup>232</sup>Th and <sup>238</sup>U with an internal standard (such as <sup>209</sup>Bi and <sup>159</sup>Tb). Multi-point calibration curves are

**TABLE 2 SRS <sup>237</sup>Np Spike Recovery From HEU Solutions**

Date	1 U g/L	2 Np-237 Spk Known' mg	3 Np-237 Smpl w/Spk. mg/mL	4 Np-237 Smpl Avg. µg/mL	5 Np-237 Spk % Rec.
01/24/00	10.2	3.044	3.047	0.069	97.9
01/24/00	9.0	3.044	2.959	0.065	95.1
06/22/00	7.7	3.044	2.928	0.092	93.1
10/05/00	2.2	3.044	4.483	1.188	108.3
10/05/00	4.5	3.044	3.472	0.173	108.4
10/05/00	4.3	3.044	3.383	0.171	105.5
10/05/00	9.3	3.044	3.722	0.369	110.1
02/15/01	2.3	3.044	4.489	1.485	98.7
02/15/01	6.4	3.044	3.403	0.188	105.6
02/15/01	6.1	3.044	3.294	0.155	103.1
02/15/01	9.4	3.044	3.403	0.220	104.6
06/19/01	9.4	3.044	3.285	0.173	102.2
09/13/01	5.5	3.061	2.909	0.031	94.0
09/13/01	5.5	3.061	2.946	0.012	95.8
09/13/01	8.0	3.061	3.176	0.117	99.9
09/26/01	7.9	3.061	3.139	0.122	98.6
10/15/01	5.3	3.061	3.064	0.006	99.9
10/15/01	5.3	3.061	2.864	0.006	93.4
01/04/02	5.2	3.061	3.079	0.091	97.6
01/04/02	5.3	3.061	4.544	1.367	103.8
02/19/02	9.8	3.061	3.200	0.137	100.0
02/25/02	5.5	3.061	4.498	1.383	101.8
02/25/02	5.3	3.061	3.250	0.107	102.7
04/03/02	5.9	3.061	3.269	0.091	103.8
04/03/02	5.9	3.061	3.217	0.105	101.7
04/09/02	NA	3.061	3.090	0.000	100.9
04/09/02	5.5	3.061	4.605	1.322	107.2
04/09/02	NA	3.061	3.255	0.000	106.3
04/09/02	5.3	3.061	3.445	0.084	109.8
04/16/02	4.5	3.061	4.776	1.483	107.6
05/10/02	8.4	3.061	3.063	0.131	95.8
05/30/02	7.3	3.061	2.755	0.161	84.7
05/30/02	5.6	3.061	3.910	1.161	89.8
06/11/02	4.9	3.061	3.236	0.051	104.1
07/01/02	6.2	3.061	3.443	0.143	107.8
07/18/02	4.8	3.061	3.316	0.222	101.1
09/03/02	6.5	3.061	3.248	0.242	98.2
n					37
Avg.					101.0
Std. Dev.					5.8
Bias					1.0