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# Standard Practice for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy<sup>1</sup>

This standard is issued under the fixed designation C1109; 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 is applicable to the determination of low concentration and trace elements in aqueous leachate solutions produced by the leaching of nuclear waste materials, using inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

1.2 The nuclear waste material may be a simulated (non-radioactive) solid waste form or an actual solid radioactive waste material.

1.3 The leachate may be deionized water or any natural or simulated leachate solution containing less than 1 % total dissolved solids.

~~1.4 The analysis must be conducted with an inductively coupled plasma-atomic emission spectrometer.~~

~~1.5 The values stated in SI units are to be regarded as the standard.~~

~~1.6~~

1.4 This practice should be used by analysts experienced in the use of ICP-AES, the interpretation of spectral and non-spectral interferences, and procedures for their correction.

1.5 No detailed operating instructions are provided because of differences among various makes and models of suitable ICP-AES instruments. Instead, the analyst shall follow the instructions provided by the manufacturer of the particular instrument. This test method does not address comparative accuracy of different devices or the precision between instruments of the same make and model.

1.6 This practice contains notes that are explanatory and are not part of the mandatory requirements of the method.

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

1.8 This standard does not purport to address all of the safety problems, 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:*<sup>2</sup>

C859 [Terminology Relating to Nuclear Materials](#)

C1009 [Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry](#)

C1220 [Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste](#) ~~D1129 Terminology Relating to Water~~

D1193 [Specification for Reagent Water](#)

D7035 [Test Method for Determination of Metals and Metalloids in Airborne Particulate Matter by Inductively Coupled Plasma Atomic Emission Spectrometry \(ICP-AES\)](#)

~~E135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials~~ [Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials](#)

E177 [Practice for Use of the Terms Precision and Bias in ASTM Test Methods](#)

2.2 *ISO and European Standards:*<sup>3</sup>

ISO 1042 [Laboratory Glassware—One-mark Volumetric Flasks](#)

<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. Current edition approved June 1, 2004; 2010. Published July 2004; December 2010. Originally approved in 1988. Last previous edition approved in 1998 as C1109-98; C1109-04. DOI: 10.1520/C1109-104.

<sup>2</sup> 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.

<sup>3</sup> The boldface numbers in parentheses refer to the list of references at the end of this standard.

<sup>3</sup> Available from American National Standards Institute (ANSI), 25 W. 43rd St., 4th Floor, New York, NY 10036, <http://www.ansi.org>.

### 3. Terminology

#### 3.1 Definitions:

3.1.1 *Inductively Coupled Plasma Emission Spectroscopy (ICP-AES)*—refer to Terminology E135

3.1 For definitions of pertinent terms not listed here, see Terminology C859.

3.1.2 *water*—refer to Terminology D1129.

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

##### 3.2 Definitions:

3.2.1 *analytical curve*—the plot of net signal intensity versus elemental concentration using data obtained during calibration.  
*atomic emission*—characteristic radiation emitted by an electronically excited atomic species. **D7035**

3.2.1.1 *Discussion*—In atomic (or optical) emission spectrometry, a very high-temperature environment, such as a plasma, is used to create excited state atoms. For analytical purposes, characteristic emission signals from elements in their excited states are then measured at specific wavelengths.

3.2.2 *calibration*—the process by which the relationship between net signal intensity and elemental concentration is determined for a specific element analysis.  
*background correction*—process of correcting the intensity at an analytical wavelength for the intensity due to the underlying spectral background of a blank. **D7035**

3.2.2.1 *Discussion*—During sample analysis, measurements are made of the background intensity near the peak wavelength of the analytical lines. Correction of the analytical line peak intensity to yield the net line intensity can be made by subtraction of either (a) a single intensity measurement performed on the high or low wavelength side of the analytical line (single-point background correction), or (b) an interpolated background intensity from background measurements acquired on both the high and low wavelength sides of the analytical line (double-point background correction).

3.2.3 *calibration blank*—a 1% (v/v) solution of nitric acid in deionized water.  
*bias*—between the expectation of the test results and an accepted reference value. **E177**

3.2.4 *calibration reference solution(s)*—solutions containing known concentrations of one or more elements in 1% (v/v) nitric acid for instrument calibration.  
*calibration*—the process by which the relationship between net signal intensity and elemental concentration is determined for a specific element analysis.

3.2.5 *detection limits (DL)*—the concentration of the analyte element equivalent to three times the standard deviation of ten replicate measurements of the matrix blank.  
*calibration blank solution*—calibration solution prepared without the addition of any reference solutions. **D7035**

3.2.6 *instrument check solution(s)*—solution(s) containing all the elements to be determined at concentration levels approximating the concentrations in the specimens. These solutions must also contain 1% (v/v) nitric acid.  
*calibration curve*—plot of net signal intensity versus elemental concentration using data obtained during calibration.

3.2.7 *linear dynamic range*—the elemental concentration range over which the analytical curve remains linear to within the precision of the analytical method.  
*calibration reference solution(s)*—solutions containing known concentrations of one or more elements in 1% (v/v) nitric acid for instrument calibration.

3.2.8 *linearity check solution(s)*—solution(s) containing the elements to be determined at concentrations that cover a range that is two to ten times higher and lower than the concentration of these elements in the calibration reference solutions. These solutions also contain 1% (v/v) nitric acid.  
*critical limit ( $L_c$ )*—minimum significant value of an estimated net signal or concentration, applied as a discriminator against background noise. **(1)**

3.2.9 *non-spectral interference*—changes in the apparent net signal intensity from the analyte due to physical or chemical processes that affect the transport of the analyte to the plasma and its vaporization, atomization, or excitation in the plasma.  
*inductively coupled plasma (ICP)*—a high-temperature discharge generated by a flowing conductive gas, normally argon, through a magnetic field induced by a load coil that surrounds the tubes carrying the gas. **D7035**

3.2.10 *off-peak background correction*—during specimen analysis, measurements are made of the background intensity near the peak wavelength of the analytical lines. Correction of the analytical line peak intensity to yield the net line intensity can be made by subtraction of either (a) a single intensity measurement performed on the high or low wavelength side of the analytical line (single-point background correction), or (b) an interpolated background intensity from background measurements acquired on both the high and low wavelength sides of the analytical line (double-point background correction).  
*instrument check solution(s)*—solution(s) containing all the elements to be determined at concentration levels approximating the concentrations in the samples. These solutions must also contain 1% (v/v) nitric acid.

3.2.11 *on-peak spectral interference correction*—adjustments made in observed net intensity of peak of interest to compensate for error introduced by spectral interferences.  
*interelement correction*—a spectral interference correction technique in which emission contributions from interfering elements that emit radiation at the analyte wavelength are subtracted from the apparent analyte emission after measuring the interfering element concentrations at other wavelengths. **D7035**

3.2.12 *sensitivity*—the slope of the linear dynamic range.

3.2.13 *spectral interference*—light emission from spectral sources other than the analyte element that contributes to the apparent net signal intensity of the analyte. Sources of spectral interference include spectral line overlaps, broadened wings of intense

spectral lines, ion-atom recombination continuum emission, molecular band emission, and stray (scattered) light effects.

#### 4. Summary of Practices

4.1 The general principles of emission spectrometric analysis are given in Ref **limit of detection ( $L_D$ )**—value for which the false negative error is  $B$  using a given critical limit. **(1)**

3.2.12.1 *Discussion*—If the analytical standard deviation is constant with respect to concentration, this can be computed as 3.7 times the standard deviation of the analytical results from ten matrix blank samples spiked at approximately the anticipated detection limit; otherwise, see references **(1, 2)** for additional guidance.

3.2.13 *linear dynamic range*—the elemental concentration range over which the calibration curve remains linear to within the precision of the analytical method.

3.2.14 *linearity check solution(s)*—solution(s) containing the elements to be determined at concentrations that cover a range that is two to ten times higher and lower than the concentration of these elements in the calibration reference solutions. These solutions also contain 1 % (v/v) nitric acid.

3.2.15 *non-spectral interference*—changes in the apparent net signal intensity from the analyte due to physical or chemical processes that affect the transport of the analyte to the plasma and its vaporization, atomization, or excitation in the plasma.

3.2.16 *sensitivity*—the slope of the linear dynamic range.

3.2.17 *spectral interference*—an interference caused by the emission from a species other than the analyte of interest.

**D7035**

3.2.17.1 *Discussion*—Sources of spectral interference include spectral line overlaps, broadened wings of intense spectral lines, ion-atom recombination continuum emission, molecular band emission, and stray (scattered) light effects.

#### 4. Summary of Practice

4.1 Aqueous leachates are prepared, using Test Method C1220, for analysis using this practice.

4.2 The general principles of emission spectrometric analysis are given in Ref **(3)**.<sup>4</sup> In this practice, elemental constituents of aqueous leachate solutions are determined simultaneously or sequentially by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

4.2.3 *Specimens* 4.3 *Samples* are prepared by filtration if needed to remove particulates and acidification to match calibration reference solutions. Filtration should be the last resort to clarify a solution since leach studies are designed to determine the absolute amount of glass dissolved material removed from a waste form by aqueous leaching.

4.3.4 Additional general guidelines are provided in Guide C1009, Terminology D1129, Specification D1193, Terminology C859, and Terminology E135.

#### 5. Significance and Use

5.1 This practice may be used to determine concentrations of elements leached from nuclear waste materials (glasses, ceramics, cements) using an aqueous leachant. If the nuclear waste material is radioactive, a suitably contained and shielded ICP-AES spectrometer system with a filtered exit-gas system must be used, but no other changes in the practice are required. The leachant may be deionized water or any aqueous solution containing less than 1 % total solids.

5.2 This practice as written is for the analysis of solutions containing 1 % (v/v) nitric acid. It can be modified to specify the use of the same or another mineral acid at the same or higher concentration. In such cases, the only change needed in this practice is to substitute the preferred acid and concentration value whenever 1 % nitric acid appears here. It is important that the acid type and content of the reference and check solutions closely match the leachate solutions to be analyzed.

5.3 This practice can be used to analyze leachates from static leach testing of waste forms using Test Method C1220.

#### 6. Apparatus

6.1

6.1 Ordinary laboratory apparatus are not listed, but are assumed to be present.

6.2 *Glassware*, volumetric flasks complying with the requirements of ISO 1042, made of borosilicate glass complying with the requirements of ISO 3585. Glassware should be cleaned before use by soaking in nitric acid and then rinsing thoroughly with water.

6.3 *Filters*, inert membrane, having pore size of 0.45  $\mu\text{m}$  or smaller.

6.4 *Piston-operated Volumetric Pipettors and Dispensers*, complying with the requirements of ISO 8655, for pipetting and dispensing of solutions, acids, and so forth.

6.5 *Bottles*, tetrafluoroethylene or polyethylene, for storage of calibration and check solutions.

<sup>4</sup> Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.

<sup>4</sup> The **boldface** numbers in parentheses refer to the list of references at the end of this standard.

6.6 Disposable Gloves, impermeable, for protection from corrosive substances. Polyvinyl chloride (PVC) gloves are suitable.

6.7 Inductively Coupled Plasma-Atomic Emission Spectrometer, computer controlled, with a spectral bandpass of 0.05 nm or less, is required to provide the necessary spectral resolution.

**NOTE 1**—The spectrometer may be of the simultaneous multielement or sequential scanning type. The spectrometer may be of the air-path, inert gas-path, or vacuum type, with spectral lines selected appropriately for use with the specific instrument. ~~Either an analog or digital readout system may be used.~~

**NOTE 2**—An autosampler having a flowing rinse is recommended.

## 7. Reagents and Materials

7.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.<sup>5</sup> Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 Purity of Water—Unless otherwise indicated, references to water shall be understood to mean reagent water as defined by Type I of Specification D1193 or water exceeding these specifications.

7.3 Nitric Acid (specific gravity 1.42)—Concentrated nitric acid (HNO<sub>3</sub>).

7.4 Nitric Acid, High-Purity—Nitric acid of higher purity than reagent grade, specially prepared to be low in metallic contaminants. The acid may be prepared by sub-boiling distillation ~~(2(4))~~, or purchased from commercial sources.

7.5 Stock Solutions—May be purchased or prepared from metals or metal salts of known purity. Stock solutions should contain known concentrations of the element of interest ranging from 100 to 10 000 mg/L.

7.6 Calibration Blank Solution, 1 % (v/v) HNO<sub>3</sub>.

7.7 Calibration Reference Solutions, Instrument Check Solutions, and Linearity Check Solutions:

7.7.1 Prepare single-element or multielement calibration reference solutions by combining appropriate volumes of the stock solutions in acid-rinsed volumetric flasks. To establish the calibration slope accurately, provide at least one solution with element concentration that is a minimum of 100 times the ~~detection limit~~<sub>D</sub> for each element. Add sufficient nitric acid to bring the final solution to 1 % HNO<sub>3</sub>. Prior to preparing the multielement solutions, analyze each stock solution separately to check for strong spectral interference and the presence of impurities ~~(35)~~. Take care when preparing the multielement solutions to verify that the components are compatible and stable (they do not interact to cause precipitation) and that none of the elements present exhibit mutual spectral interference. Transfer the calibration reference solutions to acid-leached FEP TFE-fluorocarbon or polyethylene bottles for storage. Calibration reference solutions must be verified initially using a quality control sample and monitored periodically for stability.

**NOTE 1**—Solutions in polyethylene bottles are subject to transpiration losses that may affect the assigned concentration values.

~~7.6.2 Prepare the instrument check solution(s) and linearity check solutions in a similar manner.~~

~~7.6.3 Fresh solutions should be prepared as needed with the realization that concentrations can change with age. 3—Solutions in polyethylene bottles are subject to transpiration losses that may affect the assigned concentration values.~~

~~7.7.2 Prepare the instrument check solution(s) and linearity check solutions in a similar manner.~~

7.7.3 Fresh solutions should be prepared as needed with the realization that concentrations can change over time. The recommended maximum shelf life for calibration reference solutions, instrument check solutions, and linearity check solutions is one month.

## 8. Specimen Preparation

8.1 Filter the leachate through a clean, inert membrane filter having pore size of 0.45 μm or smaller, using an inert filter support (avoid the use of fritted glass supports). Examine the filtered leachate to verify the absence of visible solids or suspended colloids. Compare the analyses of filtered and unfiltered aliquots of the original leachate solution to determine whether the filter membrane contributes to the blank level of the filtered solution. The deposit on the filter may be analyzed separately if required.

8.2 Add sufficient high-purity concentrated nitric acid to bring the leachate sample solution to volume 1% HNO<sub>3</sub> Sample Preparation

8.1 If necessary to remove solids or suspended colloids, filter the leachate through a clean filter, using an inert filter support (avoid the use of fritted glass supports). Examine the filtered leachate to verify the absence of visible solids or suspended colloids. The deposit on the filter may be analyzed separately if required.

8.2 Prepare filtered and unfiltered aliquots of a calibration blank solution, and compare the results of these aliquots to determine whether the filter membrane contributes to the blank level of the filtered solution.

**NOTE 4**—Step 8.2 may be omitted if none of the samples requires filtration.

8.3 Add sufficient high-purity concentrated nitric acid to bring the leachate sample solution to volume 1 % HNO<sub>3</sub>. ~~If the leachate is known to be a chloride solution, or nitric acid is undesirable for other experimental reasons, concentrated hydrochloric or other~~

<sup>5</sup> Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmacopeial Convention, Inc. (USPC), Rockville, MD.