



Designation: C1109 – 23

# 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 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 standard. No other units of measurement are included in this standard.

1.8 *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.*

<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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1.9 *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  
C1009 Guide for Establishing and Maintaining a Quality Assurance Program for Analytical Laboratories Within the Nuclear Industry

C1220 Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste

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

E177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods

E288 Specification for Laboratory Glass Volumetric Flasks

E438 Specification for Glasses in Laboratory Apparatus

E1154 Specification for Piston or Plunger Operated Volumetric Apparatus and Operator Qualification

## 3. Terminology

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

3.2 *Definitions:*

3.2.1 *atomic emission*—characteristic radiation emitted by an electronically excited atomic species. **D7035**

<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.

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 *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 *bias*—difference between the expectation of the test results and an accepted reference value. **E177**

3.2.4 *calibration blank solution*—calibration solution prepared without the addition of any reference solutions. **D7035**

3.2.5 *calibration curve*—plot of net signal intensity versus elemental concentration using data obtained during calibration.

3.2.6 *calibration reference solution(s)*—solutions containing known concentrations of one or more elements in 1 % nitric acid for instrument calibration.

3.2.7 *critical limit* ( $L_C$ )—minimum significant value of an estimated net signal or concentration, applied as a discriminator against background noise. **(1)**

3.2.8 *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**

3.2.9 *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 % nitric acid.

3.2.10 *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**

3.2.11 *limit of detection* ( $L_D$ )—value for which the false negative error is  $B$  using a given critical limit. **(1)**

3.2.11.1 *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)**<sup>3</sup> for additional guidance.

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

3.2.13 *linearity check solution(s)*—solution(s) of nitric acid with a volume fraction concentration of 1 % 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.

3.2.14 *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.

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

3.2.16 *spectral interference*—an interference caused by the emission from a species other than the analyte of interest. **D7035**

3.2.16.1 *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)**. In this practice, elemental constituents of aqueous leachate solutions are determined simultaneously or sequentially by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

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 material removed from a waste form by aqueous leaching.

4.4 Additional general guidelines are provided in Guide **C1009**, 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 % 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

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

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

6.2 *Glassware*, volumetric flasks complying with the requirements of Specification **E288**, made of borosilicate glass complying with the requirements of Specification **E438**. 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 Specification **E1154**, for pipetting and dispensing of solutions, acids, and so forth.

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

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.

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>4</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 ( $\text{HNO}_3$ ) of sufficiently high purity to permit its use without lessening the accuracy of the determination.

<sup>4</sup> ACS Reagent Chemicals, Specifications and Procedures for Reagents and Standard-Grade Reference Materials, 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.

7.4 *Nitric Acid, Volume Fraction 1 %*—Volumetrically dilute 10 mL of concentrated  $\text{HNO}_3$  (**7.3**) to 1000 mL with water.

NOTE 3—The volume fraction can be up to 5 % provided the same volume fraction is used in all calibration blank, calibration reference, and check solutions.

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 mg/L to 10 000 mg/L.

7.6 *Calibration Blank Solution, 1 %  $\text{HNO}_3$* .

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  $L_D$  for each element. Add sufficient concentrated  $\text{HNO}_3$  to bring the final solution to 1 %  $\text{HNO}_3$ . Prior to preparing the multielement solutions, analyze each stock solution separately to check for strong spectral interference and the presence of impurities (**4**). 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 4—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. 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 5—Step **8.2** may be omitted if none of the samples requires filtration.

8.3 Add sufficient high-purity concentrated  $\text{HNO}_3$  to bring the leachate sample solution to volume in 1 %  $\text{HNO}_3$ . If the leachate is known to be a chloride solution, or  $\text{HNO}_3$  is

undesirable for other experimental reasons, concentrated hydrochloric or other mineral acid may be used instead. The acid conditions of the calibration and check solutions used in the analytical procedure must match those of the leachate sample. It is necessary that quantities of acid and sample be carefully measured during acidification to allow correction of results to account for dilution.

## 9. Analytical Conditions

9.1 *Analytical Lines*—Suggested analytical lines for typical elements are given in **Table 1**. Additional lines for these and other elements of interest, and information about possible interfering lines, can be found in compilations of analytical lines for ICP-AES (**5-13**).

9.2 *Selection of Analytical Conditions*—Select an optimum combination of analytical lines, background correction methods, plasma viewing position, and plasma/spectrometer operating conditions to obtain the following for each element:

- 9.2.1 The lowest attainable  $L_D$ ,
- 9.2.2 The acceptable linear dynamic range,
- 9.2.3 Avoidance or minimization of spectral and non-spectral interference, and
- 9.2.4 Best attainable precision.

9.3 Follow the spectrometer manufacturer's recommendation wherever possible in establishing operating conditions. For simultaneous multielement systems, the optimum plasma viewing position and set of operating conditions is usually a compromise (**14**). The combination of conditions selected must be used in all subsequent ICP operations, including determination of  $L_D$ , calibrations, sample analyses, and performance checks. Systematic use of an appropriate method such as reference to an atom-to-ion emission intensity ratio (**4**) to ensure reproducible conditions is recommended.

9.4 Perform at least ten consecutive measurements of a matrix blank and calculate  $L_D$  as described in 3.2.11.1.

9.5 Perform experiments to determine the linear dynamic range for each element of interest. Use  $L_D$  and the linear dynamic range as a guide in the preparation of calibration reference solutions and linearity check solutions.

9.6 Estimate the standard deviation for use in establishing control limits for each element through repetitive analysis of the instrument check solution(s). For a particular element, these control limits are the known elemental concentration plus or minus a multiple of the standard deviation, based on the required confidence limit. For example, a multiple of two times the standard deviation would provide a confidence limit of 95 %. Different control limits may be used for individual samples, or sets of samples, as required by the laboratory. It is recommended that at least ten independent analyses, distributed randomly with respect to time and laboratory operating conditions, be used to estimate the standard deviation.

## 10. Calibration

### 10.1 Calibration of the Spectrometer System:

10.1.1 Follow the spectrometer manufacturer's instructions for forming and stabilizing the plasma. Allow sufficient time for plasma stabilization before making measurements.

10.1.2 Calibrate the spectrometer system using the calibration blank and the appropriate calibration reference solutions, following the same procedure as for sample analysis (see **Section 11**). Obtain separate intensity measurements at the analytical line peak position while introducing the calibration blank and the calibration reference solution. Subtract the analytical line peak intensity determined during analysis of the calibration blank from that of the calibration reference solution analysis to determine the net intensity related to concentration. Then check the accuracy of the calibration by analyzing the instrument check solution(s). The values obtained must fall within the previously determined control limits (see **9.6**) or the instrument must be recalibrated. Finally, check calibration linearity by analyzing the linearity check solutions. The values obtained must be accurate to within 5 % of the known solution concentration for all elements. It is not necessary to check for calibration linearity every time the spectrometer is calibrated provided that the analysis conditions have not been altered.

**TABLE 1 Suggested Analytical Wavelengths of Typical Elements for ICP-AES<sup>A</sup>**

Element	Suggested Wavelength, nm	Estimated Detection Limit, mg/L	Alternative Wavelength, nm	Estimated Detection Limit, mg/L
Aluminum	308.22	0.04	237.32	0.03
Americium	283.23	0.01	292.06	>0.01
Arsenic	193.70	0.05	189.04	0.01 <sup>B</sup>
Barium	493.41	0.002	455.40	0.001
Beryllium	234.86	0.0003	313.04	0.0003
Boron	249.77	0.005	249.68	0.005
Cadmium	214.44	0.002	...	...
Calcium	317.93	0.01	393.37	0.0002
Cerium	418.66	0.05	413.76	0.05
Chromium	267.72	0.007	205.55	0.006
Dysprosium	353.17	0.01	205.50	...
Gadolinium	342.25	0.01	...	...
Iron	259.94	0.006	273.96	0.02
Lanthanum	408.67	0.01	379.48	0.01
Lead	217.00	0.09	220.35	0.04
Lithium	670.78	0.002	...	...
Magnesium	279.55	0.0001	279.08	0.03
Manganese	257.61	0.001	294.92	0.008
Molybdenum	202.03	0.008	203.84	0.01
Neodymium	406.11	0.1	401.22	0.05
Neptunium	382.91	0.09	456.04	0.13
Nickel	231.60	0.02	221.65	0.01 <sup>B</sup>
Phosphorus	214.91	0.08	178.29	...
Plutonium	300.06	0.03	297.25	0.03
Potassium	766.49	0.04	...	...
Rhodium	343.49	0.06	233.48	0.04
Ruthenium	240.27	0.03	...	...
Samarium	442.43	0.05	...	...
Selenium	203.99	0.1	196.03	0.08 <sup>B</sup>
Silicon	288.16	0.03	212.41	0.02
Sodium	589.00	0.03	330.24	1.9
Strontium	421.55	0.0008	407.77	0.0004
Sulfur	180.73	<sup>B</sup>	...	...
Technetium	254.32	0.002	261.00	0.002
Tellurium	214.28	0.04	214.72	0.2
Thorium	401.91	0.08	...	...
Titanium	337.28	0.007	334.94	0.004
Uranium	385.96	0.25	367.01	0.3
Vanadium	292.40	0.008	...	...
Zinc	213.86	0.002	206.20	0.006
Zirconium	343.82	0.008	339.20	0.008

<sup>A</sup> See Refs (**5-13**) for a more complete list. Check those references also to identify any possible interfering spectral lines from components such as rare earths, actinides, or high-concentration components.

<sup>B</sup> Vacuum spectrometer.