



Designation: C 1109 – 98

# Standard Test Method 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 C 1109; 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 test method is applicable to the determination of low concentration and trace elements in aqueous leachate solutions produced by the leaching of nuclear waste materials.

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 *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:

C 1009 Guide for Establishing a Quality Assurance Program for Analytical Chemistry Laboratories Within the Nuclear Industry<sup>2</sup>

C 1220 Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Wastes<sup>2</sup>

D 1129 Terminology Relating to Water<sup>3</sup>

D 1193 Specification for Reagent Water<sup>3</sup>

E 135 Terminology Relating to Analytical Chemistry for Metals, Ores, and Related Materials<sup>4</sup>

## 3. Terminology

### 3.1 Definitions:

3.1.1 *deemission spectroscopy*—refer to Terminology E 135.

3.1.2 *water*—refer to Terminology D 1129.

3.2 *Definitions of Terms Specific to This Standard:*

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

3.2.2 *calibration*—the process by which the relationship between net signal intensity and elemental concentration is determined for a specific element analysis.

3.2.3 *calibration blank*—a 1 % (v/v) solution of nitric acid in deionized water.

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.

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.

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.

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.

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.

3.2.9 *nonspectral 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.

3.2.10 *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)

<sup>1</sup> This test method is under the jurisdiction of ASTM Committee C-26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.05 on Methods of Test.

Current edition approved July 10, 1998. Published October 1998. Originally published as C 1109 – 88. Last previous edition C 1109 – 93.

<sup>2</sup> *Annual Book of ASTM Standards*, Vol 12.01.

<sup>3</sup> *Annual Book of ASTM Standards*, Vol 11.01.

<sup>4</sup> *Annual Book of ASTM Standards*, Vol 03.05.

an interpolated background intensity from background measurements acquired on both the high and low wavelength sides of the analytical line (double-point background correction).

3.2.11 *on-peak spectral interference correction*—adjustments made in observed net intensity of peak of interest to compensate for error introduced by spectral interferences.

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

3.2.13 *specific 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 Test Method

4.1 The general principles of emission spectrometric analysis are given in Ref (1).<sup>5</sup> In this test method, elemental constituents of aqueous leachate solutions are determined simultaneously or sequentially by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

4.2 Specimens 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.

4.3 Additional general guidelines are provided in Guide C 1009, Terminology D 1129, Specification D 1193, and Terminology E 135.

#### 5. Significance and Use

5.1 This test method 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 test method are required. The leachant may be deionized water or any aqueous solution containing less than 1 % total solids.

5.2 This test method 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 test method 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 test method can be used to analyze leachates from static leach testing of waste forms using C 1220.

#### 6. Apparatus

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

#### 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>6</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 D 1193 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), 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 Reference Solutions, Instrument Check Solutions, and Linearity Check Solutions:*

7.6.1 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 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 (3). 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.

<sup>5</sup> The **boldface** numbers in parentheses refer to the list of references at the end of this standard.

<sup>6</sup> "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

7.6.3 Fresh solutions should be prepared as needed with the realization that concentrations can change with age.

## 8. Specimen Preparation

8.1 Filter the leachate through a clean, inert membrane filter having pore size of 0.45  $\mu\text{m}$  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 %  $\text{HNO}_3$ . If the leachate is known to be a chloride solution, or nitric acid 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 specimen.

## 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 (4-12).

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 detection limit,

9.2.2 The acceptable linear dynamic range,

9.2.3 Avoidance or minimization of spectral and nonspectral 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 (13). The combination of conditions selected must be used in all subsequent ICP operations, including determination of detection limits, calibrations, specimen analyses, and performance checks. Systematic use of an appropriate method such as reference to an atom-to-ion emission intensity ratio (3) to ensure reproducible conditions is recommended.

9.4 Determine the detection limit and the upper limit for linear calibration for each element. Use these analytical limits as a guide in the preparation of the calibration reference solutions and linearity check solutions. Determine three sigma 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 and minus three standard deviations. At least ten independent analyses, distributed randomly with respect to time and laboratory operating conditions, are recommended for estimation of the standard deviations.

**TABLE 1 1Suggested 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
Phosphorus	214.91	0.08	178.29	<sup>B</sup>
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 (4-12) 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.

## 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 specimen 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 ( $3\sigma$ ) or the instrument must be recalibrated. Finally, check calibration