



Designation: C1220 – 98 (Reapproved 2004)

Standard Test Method for Static Leaching of Monolithic Waste Forms for Disposal of Radioactive Waste¹

This standard is issued under the fixed designation C1220; 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 test method covers the relative chemical durability of simulated and radioactive monolithic waste forms, such as glasses, ceramics, or cermets, in various test solutions at temperatures $<100^{\circ}\text{C}$ under low surface-area-to-volume (S/V) ratio conditions.

1.2 This test method can be used to distinguish differences in the leaching behavior of various simulated or radioactive waste forms under the specific conditions of the test based on analysis of the test solution. Data from this test are used to calculate the normalized elemental mass loss from specimens exposed to aqueous solutions at temperatures $<100^{\circ}\text{C}$.

1.3 Specimen surfaces may be altered during this test. These altered surfaces may be used to study the reaction of monolithic waste forms during static exposure to solutions.

1.4 This test method must be performed in accordance with all applicable quality assurance requirements for acceptance of the data.

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.* For a specific hazard statement, see 7.3.2.

2. Referenced Documents

2.1 ASTM Standards:²

C1109 Practice for Analysis of Aqueous Leachates from Nuclear Waste Materials Using Inductively Coupled Plasma-Atomic Emission Spectroscopy

¹ This test method is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.07 on Waste Materials.

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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.

C1174 Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste

D1125 Test Methods for Electrical Conductivity and Resistivity of Water

D1129 Terminology Relating to Water

D1193 Specification for Reagent Water

D1293 Test Methods for pH of Water

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

2.2 *EPA Document:*³

Test Methods for Evaluating Solid Waste, Physical/Chemical Methods

3. Terminology

3.1 Definitions:

3.1.1 *accumulated dose*—the sum of the absorbed doses received by the system considered regardless of whether it is exposed to radiation in a continuous or discontinuous fashion.

3.1.2 *accuracy*—the closeness of agreement between the accepted reference value and individual results (Practice E177).

3.1.2.1 *Discussion*—In its usage in this test method, *accuracy* includes the effects of precision and bias. The term is applied to measurements wherein a specific standard reference is available such as NIST standard mass and reference solutions traceable to a standards organization. The term “accurate to within” a specified range means that individual measurements on a reference standard are always within the specified range, for example, within 2°C of a certified NIST thermocouple, within 0.5 mg of a NIST standard mass or within 10 % of the value for a reference solution.

3.1.3 *actinide*—any element with atomic number of 89 to 103.

3.1.4 *bias of a measurement process*—a generic concept related to a consistent or systematic difference between a set of

³ SW846A, 3rd Ed., Revision 1, U.S. Environmental Protection Agency, Washington, DC, December 1987.

test results from the process and an accepted reference value of the property being measured (Practice E177).

3.1.5 *chemical durability*—the resistance of a glass, ceramic, or cermet test specimen to the release of its constituents to an aqueous solution under the specific conditions of this test.

3.1.5.1 *Discussion*—The response of glass, ceramics, or cermets under other conditions is outside the scope of this test method.

3.1.6 *closed system*—a system that precludes the transport of matter into or out of the system.

3.1.7 *high-purity water*—ASTM Type I or Type II water with a maximum total matter content of 0.1 g/m³, a minimum electrical resistivity of 16.67 MΩ·cm at 25°C, and no detectable soluble silica (see Specification D1193 and Terminology D1129).

3.1.8 *ion selective electrode (ISE)*—a device for measuring F⁻.

3.1.9 *leachant*—a solution used, or intended for use, in leaching.

3.1.10 *leachate*—the solution resulting from a leach test.

3.1.11 *leaching*—the action of removing soluble constituents from a solid into a solution.

3.1.12 *monolithic specimens*—specimens that are physically one coherent piece, as opposed to powdered specimens that consist of many small pieces of irregular configuration. Monolithic specimens may consist of several individual phases, but they must be bound in a stable coherent configuration.

3.1.13 *nuclear waste forms*—solid materials in which radioactive wastes have been immobilized.

3.1.14 *open system*—a system that permits the transport of matter into or out of the system, e.g., O₂ and/or CO₂ diffusion into or out of the system.

3.1.15 *polytetrafluoroethylene (PTFE)*—a material produced from various monomers that are polymerized into the plastic.

3.1.16 *precision of a measurement process*—a generic concept related to the closeness of agreement between test results obtained under prescribed like conditions from the measurement process being evaluated (Practice E177). In this test method, precision will be measured by either standard deviation or relative standard deviation.

3.2 *Abbreviations:*

3.2.1 *EDX*—energy-dispersive x-ray fluorescence instrument (or analysis).

3.2.2 *ICP*—inductively coupled plasma.

3.2.3 *PFA*—perfluoroalkoxy.

3.2.4 *SEM*—scanning electron microscope (or microscopy).

3.2.5 *TEM*—transmission electron microscope (or microscopy).

3.2.6 *XRD*—x-ray diffractometer (or diffraction).

4. Summary of Test Method

4.1 Specimens of known volume and geometric surface area are immersed in the reference leachants without agitation for defined time periods at defined temperatures. The S/V ratio is held constant within 0.5 of 10.0 m⁻¹. Three reference temperatures, 40°, 70°, and 90°C, and a number of specific time periods are identified in a series of test matrices established to

meet objectives that include evaluation of waste forms for comparative purposes. In the test method, three reference leachants are used: high-purity water and two solutions (silicate/bicarbonate and brine) that approximate fluids that the waste form may encounter in a geologic repository. In addition to the reference leachants, others may be used. The test is for application to simulated waste forms and to radioactive specimens.

4.1.1 PTFE test vessels and PTFE specimen supports are used, provided the integrated dose to a PTFE component from all radiation (alpha, beta, or gamma) does not exceed 10⁴ rad (100 Gy), which has been shown to not damage PTFE.⁴ If the integrated dose to the test vessel and specimen support exceeds 10⁴ rad, 304L stainless steel or fused silica vessels and specimen supports are to be used (in such tests involving brine leachants, fused silica vessels and components must be used because of the corrosion of stainless steel by the brine) (see Note 1).

NOTE 1—These modifications to the test method are required when using highly radioactive waste forms.

4.2 Separate specimen and leachant volumes are required for each data point. The test results are based on leachate analyses in all cases and include examination of the leached specimen surface after long-duration tests.

5. Significance and Use

5.1 This test method is intended principally to distinguish differences in the leaching behavior of candidate monolithic, inorganic, radioactive waste forms under low S/V ratio conditions. The test method can be used to produce altered solid specimens to study the reaction of monolithic waste forms during static exposure to solutions. Data from this test may form part of the larger body of data that is necessary in the logical approach to long-term prediction of waste form behavior, as described in Practice C1174. In particular, solution concentrations and characterization and altered surfaces may be used in the testing of geochemical modelling codes. This test method excludes study of powdered or organic materials. This test method can be used as either a “characterization” or “accelerated” test under the protocol of Practice C1174, mentioned above.

5.2 The total absorbed dose for each PTFE test vessel may not exceed 10⁴ rad (100 Gy) during the lifetime of the vessel. Hence, a record of the absorbed dose each vessel receives must be maintained.

5.2.1 More radiation-resistant materials are used when testing in radiation fields where the accumulated absorbed dose exceeds 10⁴ rad (see Note 1).

5.3 Both aerated and deaerated solutions may be used in this test method. However, when testing highly radioactive specimens, tests with deaerated solutions are mandatory to minimize radiolysis effects of nitrogen (see Note 1). Control of the oxygen fugacity is not part of this test method. Such control and measurement may be required for specific uses of leaching

⁴ Strachan, D. M., “Effect of Gamma Irradiation on Simulated Waste Glass Leaching and on the Leach Vessel,” *Journal of the American Ceramic Society*, 66[9], C-158 -C-160, 1983.

data but are beyond the scope of this test method. Preparation of deaerated leachants is covered in 7.2.2.

5.4 The use of PTFE test vessels may result in some F⁻ release from the vessel to the solution. For PTFE vessels that meet the qualification requirements of this test method (see 6.4), the amount of release at low radiation levels, <10⁴ rad, is not significant. Fluoride, at the concentrations encountered in tests where the radiation dose is limited to less than 10⁴ rad and qualified PTFE is used, has not been demonstrated to have an effect on leaching behavior.⁴ The primary reason for limiting the integrated dose to PTFE vessels and specimen supports to 10⁴ rad and requiring that the PTFE vessels be qualified is to ensure that excessive fluoride releases do not occur (see Note 1). In order to monitor fluoride releases, which could have an influence on test results, analysis for F⁻ concentration is a test requirement.

6. Apparatus and Analytical Requirements

6.1 Fig. 1 illustrates the basic features of the test equipment. The specimen is held near the centroid of the leach volume, for example with a monofilament or by use of a coarsely woven support screen. The specimen surface-area-to-leachant-volume (S/V) ratio must be within 0.5 of 10.0 m⁻¹.

6.2 *Test Vessel Material*—The choice of material for construction of the test vessels will depend on the radiation field. When testing is performed in fields that yield an absorbed dose of less than 10⁴ rad, use PTFE PFA vessels that have been qualified (see 6.4).

6.2.1 For fields where the absorbed dose exceeds 10⁴ rad, use fused silica or 304L stainless steel. If the vessel dose exceeds 10⁴ rad and the brine leachant is employed, fused silica vessels are to be used (because of the corrosion of stainless steel by the brine). Use of the same vessel material throughout the test matrix will allow an evaluation of the contribution to the leachate by the vessel, for example, silicon from fused silica. (See Note 1.)

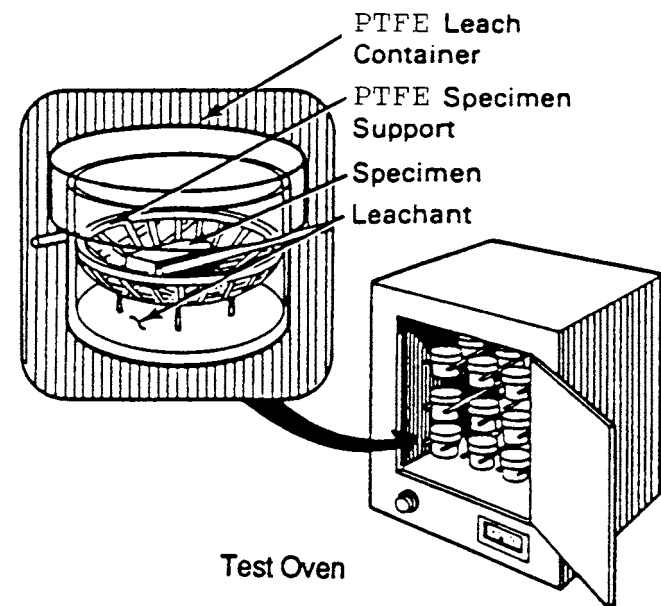


FIG. 1 Example Apparatus for Static Leach Test Method

6.2.2 Teflon vessels are considered to provide open systems because they are pervious to carbon dioxide and some water loss.

6.2.3 Stainless steel and fused silica vessels are considered to provide closed systems because they are impervious to carbon dioxide, and water loss is usually negligible.

6.3 *Test Vessel Size*—The vessels shall have a diameter-to-height ratio between 0.5 and 2.0. Leach vessel volumes will generally be between 20 mL and 1 L. The vessels shall be sufficiently impervious and have a tight-fitting lid to limit leachant loss during the test to less than 10 % of the original volume. The specimen support shall be constructed of the same material as the vessel or of equally inert material and designed to maintain the specimen near the centroid of the leach volume, but must not contact more than 5 % of the specimen surface area.

6.4 *Identification of Vessels and Cleaning History*—Vessel identification and the cleaning history of each vessel must be maintained during testing.

6.4.1 *Identification Marking*—A unique identifying number should be permanently marked on each leach vessel. The same number should be permanently marked on the companion lid.

6.4.2 *Record of Vessel Cleaning History*—Each batch of cleaned vessels shall be labeled with a unique batch number. A log book of the leach vessel number and date of cleaning shall be kept. The date can be used as the batch number identifier if only one batch has been cleaned on that date. Alternatively, a separate batch number can be assigned and recorded. In this manner, any inconsistent test responses might be traced to improper cleaning of a batch of vessels or to a problem vessel.

6.5 *Qualification of PTFE Lot for Use as Test Vessels*—Variations in manufacturing practice may cause particular lots of PTFE to have unacceptable amounts of fluoride release from PTFE vessels during leach tests. Therefore, the vessels from a particular lot must be qualified for use by performing a blank test for 28 days to ascertain and document that the fluoride release is acceptably low for 28-day tests. The suitability of a particular lot of PTFE for longer-term tests is dependent on similar checks of fluoride release in blank tests conducted for the longer test durations, which is a test requirement. That is, the fluoride level must always be checked on the blanks and leachates used during testing. It is imperative that the vessels for the blanks be from the same lot as the other vessels used for testing. Measurement of pH shall also be determined in these qualification tests, as well as in the analyses of test leachates. The test matrices in 9.5 require the use of blanks, which will further document that excessive F⁻ release from the vessel has not occurred during testing.

6.5.1 To qualify a lot of PTFE, clean three vessels as described in 6.6 and run a 28-day blank test using the three vessels at 90°C with deionized water. Measure the pH and F⁻ concentration. If the pH is in the range of 5.0 to 7.0 and the F⁻ is below 0.5 µg/ml, the lot of PTFE is acceptable for use.

6.6 *Preparation of Vessel*—New PTFE vessels and supports must be cleaned to reduce the amount of F⁻ released during testing. This cleaning is done by a special procedure using a NaOH solution, described in 6.6.1. PTFE vessels can be reused after testing provided they are cleaned before reuse. However,

reuse of PTFE test vessels and supports is not allowed in this test method when these components have been used in tests with actinide-doped specimens. This is because actinides are difficult to remove, and may not be sufficiently removed from the PTFE vessel walls by leachate acidification and the vessel/specimen support structure cleaning procedure. As these dopants may be present in very low concentrations in a leachate, contamination from the vessel walls could be potentially significant. New PTFE test vessels and supports, except fine monofilaments, shall be heated in a $200 \pm 10^\circ\text{C}$ oven for one week prior to cleaning. Both new and used PTFE vessels and PTFE specimen supports, except for fine filaments, must be cleaned according to the specified procedures. Stainless steel and fused silica vessels are cleaned according to different procedures, described in 6.6.3.

6.6.1 *New PTFE Vessels and Supports*—For new PTFE vessels and supports, clean according to 6.6.1.1-6.6.1.20. For used PTFE vessels (cleaned previously according to 6.6.1.1-6.6.1.20), skip 6.6.1.1-6.6.1.20 and clean according to 6.6.2.1-6.6.2.8.

6.6.1.1 Rinse vessels, lids, and supports with fresh high-purity water. Use at least three vessel volumes for each vessel at ambient temperature.

6.6.1.2 Fill vessels approximately 90 % full with 5 wt % NaOH solution.

6.6.1.3 Tighten lids and place vessels in an oven preheated to $110 \pm 10^\circ\text{C}$.

NOTE 2—Use this temperature when using PTFE vessels rated to 0.5 MPa or higher (see 9.4.7). For vessel designs not rated to 0.5 MPa, use an oven temperature of $95 \pm 2^\circ\text{C}$.

6.6.1.4 Retighten the vessel lids after 12 to 24 h in oven.

6.6.1.5 After 7 days in oven, remove vessels and allow to cool to room temperature.

6.6.1.6 Remove lids carefully and dispose of NaOH solution.

6.6.1.7 Rinse vessels and lids in fresh high-purity water.

6.6.1.8 Repeat 6.6.1.7.

6.6.1.9 Place vessels and lids in fresh, boiling high-purity water for a minimum of 1 h.

6.6.1.10 Repeat 6.6.1.7 and 6.6.1.9.

6.6.1.11 Allow vessels and lids to air dry for a minimum of 16 h at $90 \pm 10^\circ\text{C}$.

6.6.1.12 Fill vessels about 90 % full with fresh high-purity water at ambient temperature.

6.6.1.13 Tighten lids and place vessels in oven preheated to $90 \pm 2^\circ\text{C}$ for a minimum of 16 h.

6.6.1.14 Remove vessels and allow to cool to room temperature.

6.6.1.15 Take an aliquot of liquid from each vessel and measure pH.

6.6.1.16 If pH is below 5, repeat 6.6.1.1-6.6.1.16 until pH is above 5.

6.6.1.17 If pH is above 7, repeat 6.6.1.7-6.6.1.17.

6.6.1.18 If pH is between 5.0 and 7.0 take a second aliquot and send for ISE F⁻.

6.6.1.19 If ISE F⁻ level is $>0.5 \mu\text{g/mL}$, repeat 6.6.1.7-6.6.1.19. If ISE F⁻ is still $>0.5 \mu\text{g/mL}$ repeat 6.6.1.1-6.6.1.19.

6.6.1.20 If ISE F⁻ level is $<0.5 \mu\text{g/mL}$, a vessel is acceptable for use.

6.6.2 *Used Vessels*—Clean used PTFE vessels and supports (that is, vessels and supports that were cleaned according to 6.6.1.1-6.6.1.20 and then used for testing) according to 6.6.2.1-6.6.2.8.

6.6.2.1 Rinse vessels, lids, and supports with fresh high-purity water. Use at least three vessel volumes of water for each vessel.

6.6.2.2 Soak vessels and supports for 1 h in 0.16 M HNO₃ (1 wt % HNO₃) at $90 \pm 10^\circ\text{C}$.

6.6.2.3 Rinse again as specified in 6.6.2.1.

6.6.2.4 Soak for 1 h in high-purity water at $90 \pm 10^\circ\text{C}$.

6.6.2.5 Fill the vessels approximately 90 % full with fresh high-purity water with support in place. Close the lids and hold for at least 16 h at $90 \pm 2^\circ\text{C}$ and then measure the pH of the water from each vessel. Take an aliquot of the water from at least two vessels from each vessel batch and submit for ISE F⁻.

6.6.2.6 Repeat 6.6.2.4 and 6.6.2.5 until the pH is in the range of 5.0 to 7.0 and the F⁻ is $<0.5 \mu\text{g/mL}$.

6.6.2.7 If the pH and fluoride requirements cannot be achieved by three repetitions of 6.6.2.4 and 6.6.2.5, then repeat the cleaning procedure starting at 6.6.2.1.

6.6.2.8 Dry vessels and lids at $90 \pm 10^\circ\text{C}$ for a minimum of 16 h and store inside a clean environment until used.

6.6.3 *Stainless Steel and Fused Silica Vessels*—The procedures in 6.6.1 and 6.6.2 are specifically for PTFE vessels. When using other inert vessels, such as fused silica or 304L stainless steel, variations of these procedures are appropriate.

6.6.3.1 Clean fused silica vessels using 6.6.2.1-6.6.2.8 except delete the check for F⁻, which is specific to PTFE containers.

6.6.3.2 Degrease new 304L stainless steel vessels and lids without gaskets and ultrasonically clean in 95 % ethanol for approximately 5 min (in order to remove any residual grease or oil left from machining operations) and then clean using the following procedure:

6.6.3.3 Rinse three times in high-purity water.

6.6.3.4 Submerge in 0.16 M HNO₃ (1 wt % HNO₃) for 1 h at $90 \pm 10^\circ\text{C}$.

6.6.3.5 Rinse three times with high-purity water at ambient temperature.

6.6.3.6 Submerge the vessels and lids in fresh high-purity water for 1 h at $90 \pm 10^\circ\text{C}$.

6.6.3.7 Rinse with fresh high-purity water at ambient temperature.

6.6.3.8 Fill the vessel 80 to 90 % full with high-purity water. Close the lid and leave in a $90 \pm 2^\circ\text{C}$ oven for a minimum of 16 h.

6.6.3.9 Remove the vessels from the oven and cool to room temperature, then take a cooled aliquot of the water and measure the pH.

6.6.3.10 If the pH is not in the range of 5.0 to 7.0, repeat 6.6.3.6-6.6.3.9.

6.6.3.11 If the pH is not in the range of 5.0 to 7.0 after 3 repetitions of 6.6.3.6-6.6.3.9, repeat the cleaning steps starting at 6.6.2.2.

6.6.3.12 Dry the vessels in a $90 \pm 10^\circ\text{C}$ oven for a minimum of 16 h and then cool to room temperature. If the vessels are not used immediately, close the vessels and store in a clean environment until needed.

6.6.4 *Cleaning of Used Stainless Steel and Fused Silica Vessels*—When stainless steel or fused silica vessels are reused subsequent to their use with radioactive specimens, residual contamination may be present. The vessels shall be cleaned before reuse using 0.16 M HNO_3 (1 wt % HNO_3) and high-purity water until the level of the radioactive element of interest is below the detectable level using the analytical method employed for concentration measurement of the leachate. Stainless steel vessels are also checked for Si contamination before reuse.

6.6.4.1 Rinse the vessel and lid with high-purity water. Fill the vessel 80 to 90 % full with 0.16 M HNO_3 (1 wt % HNO_3). Reseal the vessel and place in an oven at $90 \pm 2^\circ\text{C}$ for a minimum of 16 h to acid strip any radionuclides adhering to the interior of the vessel.

6.6.4.2 Check the acid stripped solution for radioactivity. Repeat 6.6.4.1 until the radioactivity of the acid strip solution is reduced below the background.

6.6.4.3 Remove the gasket and discard. Rinse vessels and lids thoroughly with high-purity water at ambient temperature. Take precautions to prevent contamination of the vessel interior with any radionuclides present on the exterior of the vessel or in the work environment.

6.6.4.4 Fill the vessel 80 to 90 % full with fresh high-purity water. Close the lid using a new, cleaned gasket (see 6.6.5) and place in oven at $90 \pm 2^\circ\text{C}$ for at least 24 h.

6.6.4.5 Remove vessels from oven, then take an aliquot of the water and measure the pH. Take another aliquot and measure the radioactivity. For stainless steel vessels, also measure the Si content of the solution.

6.6.4.6 If the pH is not in the range of 5.0 to 7.0 or the measured radioactivity is not at the background level, or Si is detected for stainless steel vessels, repeat 6.6.4.3-6.6.4.5.

6.6.4.7 If three repetitions of 6.6.4.3-6.6.4.5 do not result in a pH of 5.0 to 7.0, low radioactivity, and Si <1 ppm for stainless steel vessels, then repeat the cleaning starting at 6.6.4.1.

6.6.4.8 Dry vessels, lids, and gaskets at $90 \pm 2^\circ\text{C}$ for a minimum of 16 h and store in a clean environment until needed.

6.6.5 *Cleaning of New PTFE Gaskets for Stainless Steel Vessels*—Clean new PTFE gaskets for stainless steel vessels using the following method:

6.6.5.1 Handle the gaskets only with clean tongs.

6.6.5.2 Clean each gasket ultrasonically in 95 % ethanol for approximately 10 min.

6.6.5.3 Clean each gasket under flowing high-purity water at ambient temperature for approximately 3 min.

6.6.5.4 Bake each gasket in an oven at $200 \pm 10^\circ\text{C}$ for a minimum of 4 h.

6.6.5.5 Immerse each cooled gasket in fresh high-purity water in a boiling water bath for a minimum of 2 h.

6.6.5.6 Dry gaskets at $90 \pm 10^\circ\text{C}$ for a minimum of 16 h and store in a clean environment until needed.

6.7 *Oven*—The test oven must be capable of controlling the temperature of the test vessels to within 1°C over the range of 40° to 100°C . Determine the zone within the loaded chamber that is constant within 1°C of the target temperature using at least ten points of temperature measurement. A temperature recorder or other monitoring device must be provided to ensure that the desired temperature has been maintained for the duration of the test. When radioactive specimens are used, ensure that self-heating does not prevent the maintenance of the desired leaching temperature (see Note 1). Brief fluctuations from the desired temperature are allowable when specimens are placed in or removed from the test oven, but the cumulative time of these fluctuations outside 1°C of the target temperature must not exceed 5 % of the test period and no fluctuation may be more than 5°C above the target temperature.

6.8 *Balances*—Balances shall provide the following accuracies, depending on the materials being weighed:

Leachant + vessels	within 0.25 % of the leachant mass
Chemical reagents	within 1 % of the reagent mass
Specimens	within 0.5 mg

6.9 *Volume Measurement*—Measure leachant volumes gravimetrically or with pipettes, burettes, or flasks calibrated as described in Table 1 (see also 6.10) and accurate to within 1 % or better.

6.10 *Solution Analysis*—Measure solute concentrations using equipment standardized with standards traceable to NIST, preferably, or other recognized organizations, such as EPA or USGS. Determine and report precision and bias. Although analytical results should normally be accurate within 10 % of the reference solution when checked by individual measurements on reference solutions, this may not be possible when concentrations in the solution approach detection limits. The detection limits for each analysis must accompany the reported result. Various analytical techniques can be used to determine the solute concentrations in leachates, including inductively coupled plasma spectroscopy (see Test Methods C1109 or EPA SW846a, or both), direct current plasma spectroscopy, atomic absorption emission spectroscopy, and neutron activation. Selection of a specific technique depends on specific test objectives and the particular solutes of interest. For radioactive elements such as actinides and fission products, where low amounts may be of interest, radiochemistry/radiation counting may be needed or desirable. Use of blanks and simulated leachates, as discussed in Section 10, help ensure that high-quality data are obtained.

6.11 *pH Measurement*—Measure the pH to an accuracy of 0.1 unit using a calibrated meter. Use Test Methods D1293, Method A and commercial buffers to make this measurement. When measuring the pH of deaerated solutions, make the measurement under an argon atmosphere.

6.12 *pH Measurement in Brines:*

6.12.1 Determination of pH, defined as the negative logarithm of hydrogen ion activity, in concentrated brines using standard glass electrodes is complicated by two principal factors: (1) a significant liquid junction potential and (2) significant differences between hydrogen ion concentrations and activities. The result is usually a measured pH value that is significantly smaller than the actual value.

TABLE 1 Required Calibration Schedule

Measurement	Device	Frequency Check and Methods
Temperature	thermocouple or thermometer	6 months NIST standard or ice/boiling water
	electronics or temperature probe (without sensor)	6 months against a calibrated millivolt source
Length	micrometer	6 months standard foils, gage blocks
Mass	balance	3 months NIST standard masses
Chemical concentration	analytical method	3 months NIST standards, where possible, 2 times daily (routine), secondary standards
pH	pH meter	each day of use with commercial buffer solutions, and at intervals of 30 to 60 min during measurements. See Test Methods D1293 and 6.11 for pH measurement guidance
Volume	volumetric flasks	use certified flasks 3 months by measuring the mass of pure water contained
	pipettes	3 months by measuring the mass of pure water contained
Activity	counting techniques	twice a day, before and after counting NIST or NIST-traceable standard isotope source of interest

6.12.2 A potential at the junction between the reference electrode filling solution and the sample solution (“liquid junction potential”) is present any time these two solutions are different. The potential arises from the interdiffusion of ions in the two solutions. Since these ions diffuse at different rates, the electrical charge will be carried unequally across the junction. This results in a potential whose magnitude and stability depends on the composition of the solutions as well as the type of junction. Glass pH electrodes are usually standardized against buffers to establish the pH scale. These buffer solutions, however, are of much lower ionic strength than concentrated brines, so that significantly different liquid junction potentials are present in the two cases. The usual result in a saturated brine is a measured pH value that is one or more pH units smaller than the actual value.

6.12.3 In addition, changes in ion activity coefficients as a function of ionic strength can be important in pH measurements. (Activity is equal to the product of concentration and the activity coefficient.) Activity coefficients are usually unity in dilute solutions. However, in solutions of high ionic strength, average cation-anion activity coefficients can be much larger than unity (for example, greater than 10 for HCl in saturated magnesium chloride solutions). Because glass electrodes respond to ion activities, not to concentration, there can be a large effect on the measured pH value. The situation is complicated by a lack of activity coefficient data in concentrated brines and a similar lack of theoretical models applicable to such solutions.

6.12.4 Considerable caution must be exercised, therefore, when attempting to interpret brine pH measurements. Liquid junction and ion activity coefficient effects will result in measured pH values being shifted significantly from the true pH (based on H⁺ ion activities). However, for a given brine system, these contributions should be constant for a large portion of the pH scale, such that trends in the pH will be unaffected. If major changes in brine composition occur during a given experiment, even trends in measured pH may be suspect. In this test method, the reference brine is a diluted brine derived from analysis of Brine A for the Salado Region

in New Mexico.⁵ Other simulated, site-specific reference brines may be used depending on the particular application of the test. The bulk composition of the brine solution is not likely to change significantly in leach tests, and the measurement of pH to indicate trends of the actual pH during testing is expected to be valid. For distilled water and the silicate water, the measurement of pH is relatively straightforward.

6.13 *Calibration and Standards*—Calibrate all instruments used in these tests initially, and periodically, to minimize possible errors due to drift. [Table 1](#) shows the methods and the minimum frequency of calibration for the various devices used. Use standardization procedures that are published by recognized authorities such as NIST or ASTM.

7. Leachant Preparation and Storage

7.1 *General Chemicals and Procedures*—Use chemicals of reagent grade or better that conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.⁶

7.1.1 It is recommended that each chemical be analyzed to determine if impurities, once the leachant is prepared, will exceed detection limits of the leachate analysis system to be used. If impurities will cause detection limits to be exceeded, obtain a different batch of the chemical or use an ultrapure chemical. Good laboratory practice should be used at all times to minimize contamination of the leachant.

7.2 *Water*—The water referred to in this procedure is air-saturated (except when deaerated solutions are required), reagent water Type I or II conforming to Specification [D1193](#), which has a total impurity level, including organics, of less than 0.1 mg/L.

⁵ Molecke, M. A., “A Comparison of Brines Relevant to Nuclear Waste Experimentation,” *Sandia Report SAND83-0516*, Sandia National Laboratories, 1983.

⁶ *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.