Designation: C1108 – 12

Standard Test Method for Plutonium by Controlled-Potential Coulometry[1]

This standard is issued under the fixed designation C1108; 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 describes the determination of dissolved plutonium from unirradiated nuclear-grade (that is, high-purity) materials by controlled-potential coulometry. Controlled-potential coulometry may be performed in a choice of supporting electrolytes, such as 0.9 *M* HNO_3, 1 *M* $HClO_4$, 1 *M* HCl, 5 *M* HCl, and 0.5 *M* H_2SO_4. Limitations on the use of selected supporting electrolytes are discussed in Section 5. Optimum quantities of plutonium for this procedure are 5 to 20 mg.

1.2 Plutonium-bearing materials are radioactive and toxic. Adequate laboratory facilities, such as gloved boxes, fume hoods, controlled ventilation, etc., along with safe techniques must be used in handling specimens containing these materials.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *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.*

2. Referenced Documents

2.1 *ASTM Standards:*[2]

C859 Terminology Relating to Nuclear Materials
C1009 Guide for Establishing and Maintaining a Quality Assurance Program for Analytical Laboratories Within the Nuclear Industry
C1068 Guide for Qualification of Measurement Methods by a Laboratory Within the Nuclear Industry
C1128 Guide for Preparation of Working Reference Materials for Use in Analysis of Nuclear Fuel Cycle Materials
C1156 Guide for Establishing Calibration for a Measurement Method Used to Analyze Nuclear Fuel Cycle Materials
C1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis
C1210 Guide for Establishing a Measurement System Quality Control Program for Analytical Chemistry Laboratories Within the Nuclear Industry
C1297 Guide for Qualification of Laboratory Analysts for the Analysis of Nuclear Fuel Cycle Materials
E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

3. Summary of Test Method

3.1 In a controlled-potential coulometric measurement, the substance being determined reacts at a stationary electrode, the potential of which is maintained at such a value that unwanted electrode reactions are precluded under the prevailing experimental conditions. Those substances which have reduction-oxidation (redox) potentials near that of the ion being determined constitute interferences. Electrolysis current decreases exponentially as the reaction proceeds, until constant background current is obtained. Detailed discussions of the theory and applications of this technique have been published (**1, 2, 3, 4, 5, 6**).[3] The control-potential adjustment technique (**7**) can be used to terminate the electrolysis of the specimen at constant background current without exhaustive electrolysis with considerable reduction in operating time. Use of the control-potential adjustment technique requires that the coulometer integrator be capable of operations in a bipolar mode and that the plutonium-containing solution be of high purity, that is, nuclear grade.

3.2 Plutonium(IV) is reduced to Pu(III) at a working electrode maintained at a potential more negative than the formal redox potential. Plutonium(III) is oxidized to Pu(IV) at a potential more positive than the formal redox potential. The quantity of plutonium electrolyzed is calculated from the net number of coulombs required for the electrolysis, according to Faraday's law. Corrections for incomplete reaction, derived from the Nernst equation, must be applied for electrolysis of the sample aliquot (**7, 8**).

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[1] This test method 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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[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.

[3] The boldface numbers in parentheses refer to the list of references at the end of this test method.

$$W = \frac{(Q_s - Q_b)\,M}{nFf} \tag{1}$$

where:

W = grams of plutonium,
Q_s = coulombs required by the electrolysis,
Q_b = coulombs of background current,
M = gram-atomic weight of plutonium (must be adjusted for isotopic composition),
n = number of electrons involved in the electrode reaction (for Pu(III) → Pu(IV), $n = 1$),
F = Faraday constant, coulombs/equivalent,[4] and
f = fraction of plutonium electrolyzed.

4. Significance and Use

4.1 Factors governing selection of a method for the determination of plutonium include available quantity of sample, sample purity, desired level of reliability, and equipment.

4.1.1 This test method determines 5 to 20 mg of plutonium with prior dissolution using Practice C1168.

4.1.2 This test method calculates plutonium concentration in solutions or mass fraction in solids using an electrical calibration based upon Ohm's Law and the Faraday Constant.

4.1.3 Chemical standards are used for quality control. When prior chemical separation of plutonium is necessary to remove interferences, the quality control standards should be included with each chemical separation batch (**9**).

4.2 *Committee C-26 Safeguards Statement*[5]:

4.2.1 The materials (plutonium metal, plutonium oxide or mixed oxide [(U, Pu) O_2] powders and pellets) to which this test method applies are subject to nuclear safeguards regulations governing their possession and use. Materials for use by the commercial nuclear community must also meet compositional specifications.

4.2.2 The analytical method in this test method both meets U. S. Department of Energy guidelines for acceptability of a measurement method for generation of safeguards accountability measurement data and also provides data that may be used to demonstrate specification compliance in buyer-seller interactions.

5. Interferences

5.1 Interference is caused by ions that are electrochemically active in the range of redox potentials used or by species that prevent attainment of 100 % current efficiency (for example, reductants, oxidants, and organic matter).

5.2 *Polymer*—Polymerized plutonium is not electrochemically active (**10**) and thus is neither reduced nor oxidized. The presence of polymerized plutonium will give low results. The polymer may be converted to electrochemically active species by HF treatment (**10**).

5.3 *Pu(VI)*—Plutonium(VI) is only partially reduced to Pu(III) in 1 *M* HNO_3, 1 *M* HCl, or 1 *M* $HClO_4$ supporting electrolyte solutions; therefore, the presence of Pu(VI) can lead to inaccurate results when present even as a small fraction of the total plutonium. Plutonium(VI) can be completely reduced in 0.5 *M* H_2SO_4 (**10**) or 5.5 *M* HCl (**11**) supporting electrolyte, however, quantitative reduction has not been demonstrated when the control-potential adjustment technique used in this standard test method is applied.

5.4 *Iron*—In 0.5 *M* H_2SO_4 supporting electrolyte, iron is reduced and oxidized at essentially the same formal redox potentials as the Pu(III)-Pu(IV) couple and thus constitutes a direct interference. Iron must be removed by prior separation, or the effect of its presence must be corrected by a separate measurement of the iron concentration in the sample solution. In 1 *M* HCl, 1 *M* HNO_3, or 1 *M* $HClO_4$, iron interferes to a lesser extent. The effect of iron in these supporting electrolytes may be minimized by the choice of redox potentials, by a secondary titration (**10**), or by electrochemical correction (**12, 13**).

5.5 *Nitrites*—Nitrites are electrochemically active; therefore, saturated sulfamic acid solution should be added to the electrolyte in the cell to destroy any interfering nitrites when a nitric acid supporting electrolyte is used.

5.6 *Sulfate*—Because of the complexing action of sulfate on Pu(IV) and the resultant shift in the redox potential of the Pu(III)-Pu(IV) couple, that is, the formal potential, only small amounts of sulfate are tolerable in HNO_3, HCl, and $HClO_4$ electrolytes. When using these supporting electrolytes, specimens should be fumed to dryness to assure adequate removal of excess sulfate (see 11.3.1.3). For aliquots of dissolved MOX fuels that have not been purified by anion exchange to remove the uranium, the sulfate concentration after fuming will still be elevated. A formal potential should be measured for the specific U:Pu ratio and used in the calculations for these aliquots.

NOTE 1—Interference from a sulfate concentration of >0.004 *M* in 1 *M* $HClO_4$ has been reported (**10**).

5.7 *Fluoride*—Free fluoride cannot be tolerated and must be removed from the specimen. Evaporation of the specimen in HNO_3 to a low volume and fuming with H_2SO_4 are effective in removing fluoride.

5.8 *Oxygen*—In H_2SO_4 supporting electrolyte, oxygen interferes and must be removed. In HNO_3, HCl, and $HClO_4$ supporting electrolytes, oxygen may be an interference, depending upon experimental conditions. Purging the specimen with high-purity argon prior to and during the coulometric determination is recommended for all electrolytes.

6. Apparatus

6.1 *Controlled-Potential Coulometer*—A coulometer with the following specifications is recommended to achieve highly precise and accurate results. (Room temperature stability of ±1°C is recommended to ensure optimum instrument performance. Instruments with smaller output current or smaller voltage span may be satisfactory.)

Potentiostat **(6)**	
Output voltage	>25 V
Output current	>200 mA

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[4] Committee on Data for Science and Technology, CODATA, internationally recommended values for fundamental physical constants are available at URL http://physics.nist.gov/cuu/Constants/index.html.

[5] Based upon Committee C26 Safeguards Matrix (C1009, C1068, C1128, C1156, C1210, and C1297).

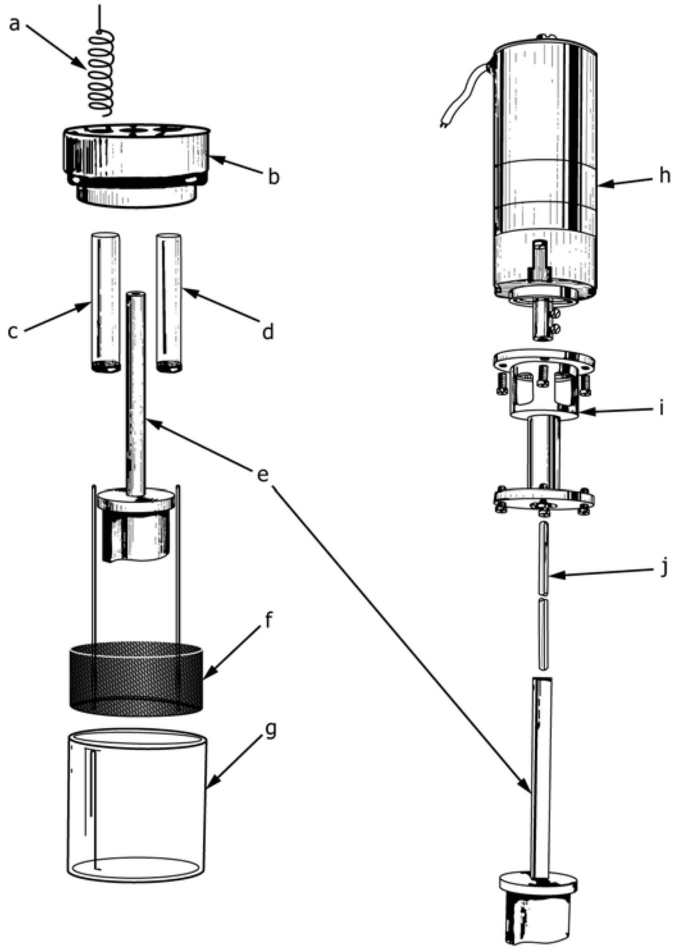

FIG. 1 Exploded View of Cell Assembly: (a) Counter Electrode, (b) Cell Head, (c) Counter Electrode Frit Tube, (d) Reference Electrode Frit Tube, (e) NBL-Designed S-Shaped Stirrer, (f) Working Electrode, (g) Sample Cell, (h) Stirrer Motor, (i) Motor Pedestal and Bearing, and (j) Stirrer Shaft

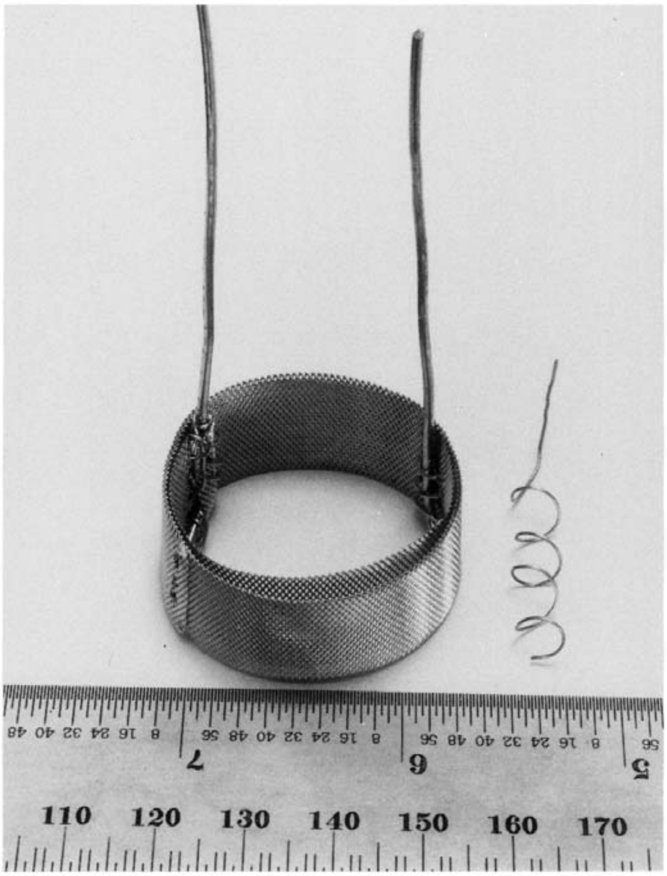

FIG. 2 Working Electrode (Top View)

Open-loop response d-c gain	$>10^5$
Unity-gain bandwidth	>300 kHz
Full-power response	>10 kHz (slewing rate 0.5 V/μs)
Voltage zero offset stability	>1-mV long term
Input d-c resistance	>50 MΩ
Input d-c current	<50 nA
d-c control voltage span	±4 V
Resolution, hum, and drift	<1 mV
Stability through extreme of line and load variation	±5 mV
Digital Integrator (**14**)	
Nonlinearity of V/F converter	<0.01 % full scale
Full scale set-point	adjustable to ±0.01 % of full scale
Input offset voltage set-point	adjustable to ±0.01 % of full scale
Output readability	<1 μg Pu
Integrating capacity	>10 C
Bias	<0.01 %

6.2 *Digital Voltmeter,* 15-V range, 5½ digits accurate to 0.01 % of full scale on all ranges. Input resistance $>10^{10}$ Ω.[6]

6.3 *Cell Assembly*—The success of controlled-potential coulometric methods is strongly dependent on the design of the cell. The cell dimensions, electrode area, spacing, and stirring rate are important parameters in a design that will minimize the time required for titration. The following components are required for the recommended cell assembly (Fig. 1).

6.3.1 *Cell*—The coulometry cell is fabricated from a cut-off 50-mL borosilicate glass beaker with an inside diameter of 38 mm and a height of 42 mm; the cut edges are rounded and polished smooth. Other cells conforming to these dimensions are satisfactory.

6.3.2 *Counter Electrode and Salt Bridge Tube*—The counter electrode is a coiled length of 0.51-mm (0.020-in.) diameter platinum wire. The salt bridge tube is unfired high-silica glass[7] filled with the supporting electrolyte solution.

6.3.3 *Reference Electrode and Salt Bridge Tube*—The reference electrode is a miniature saturated-calomel electrode (SCE).[8] The salt bridge is identical to the salt bridge described in 6.3.2 and is also filled with supporting electrolyte solution.

6.3.4 *Working Electrode,* fabricated from either 8Au8-5/0 expanded annealed-gold metal or from 45-mesh platinum gauze (Fig. 2).

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[6] A Hewlett-Packard 3455A DVM has been found to exceed these specifications.

[7] Either a test tube with unfired Vycor bottoms of Type 7930 glass obtained from Corning Glass Works, or a 0.5 cm long, 0.5-cm diameter rod of unfired Vycor Type 7930 sealed into one end of a glass tube with heat-shrinkable TFE-fluorocarbon tubing, has been found satisfactory for this application.

[8] A Fisher Calomel Reference Electrode Catalog No. 13-639-79 has been found satisfactory.

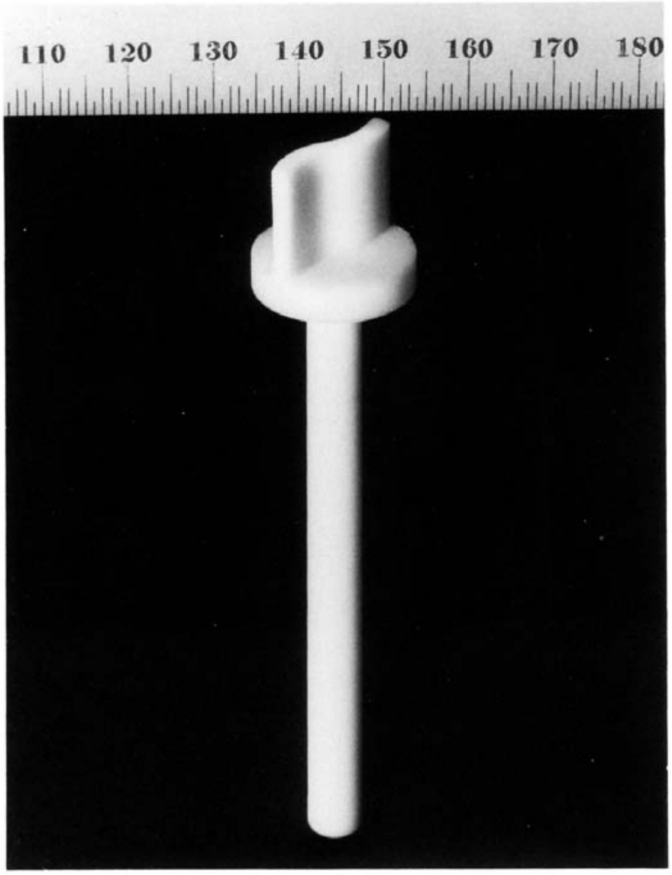

FIG. 3 S-Shaped Stirrer

6.3.4.1 Store and condition the working electrode in accordance with instruction in Section 10.

6.3.5 *Stirrer*—Several types of stirrers have performed satisfactorily. A paddle-type stirrer capable of being driven at 1800 r/min by a synchronous motor, or a magnetically driven stirring bar, is adequate. Magnetic stirring slightly simplifies the arrangement of the cell cap. For optimum stirring efficiency with freedom from losses due to splashing, an S-shaped polytetrafluoroethylene stirrer (Fig. 3) **(15)** driven by synchronous motor is recommended.

6.3.6 *Inert Gas Inlet Tube*—A polyvinyl chloride tube, approximately 3 mm in outside diameter (1 mm in inside diameter), is inserted so that its tip is about 10 mm above the surface of the electrolyte solution. The gas flow is adjusted so that the surface of the solution is depressed almost 3 mm. The gas is high-purity argon. While inert gas is not required for all electrolytes, it is recommended for this procedure.

6.4 *Quartz Heating Lamps*—Optimum heating or evaporating efficiency without bumping of solutions, or both, is obtained using overhead heating with quartz heat lamps[9] controlled by a variable power supply. However, with proper care, other conventional means of heating may be used.

6.5 *Hot Plate*—Recommended for heating during the plutonium oxidation state adjustment with hydrogen peroxide.

6.6 *Quartz Clock Timer,* accurate to 0.001 s.

6.7 *100-Ω Precision Resistor,* accurate to better than 0.01 %.[10]

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.[11] 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.[12]

7.2 *Argon,* greater than 99.99 % purity.

7.3 *Hydrochloric Acid,* concentrated hydrochloric acid (HCl, specific gravity 1.19).

7.4 *Hydrochloric Acid* (1 *M*), prepare by diluting 85 mL of hydrochloric acid to 1 L with water.

7.5 *Hydrochloric Acid-Nitric Acid-Hydrofluoric Acid Mixture* (5.4 *M* HCl-1.6 *M* HNO_3-0.014 *M* HF)—Prepare by slowly adding 450 mL hydrochloric acid, 100 mL nitric acid, and 10 drops hydrofluoric acid to 450 mL water in a polytetrafluoroethylene beaker. Cool and store in a tetrafluoroethylene (TFE) fluorocarbon bottle.

7.6 *Hydrofluoric Acid,* concentrated hydrofluoric acid (HF, 48 %).

7.7 *Hydrogen Peroxide,* 30 % solution of hydrogen peroxide (H_2O_2).

7.8 *Nitric Acid,* concentrated nitric acid (HNO_3, specific gravity 1.42).

7.9 *Nitric Acid* (8 *M*)—Prepare by diluting 500 mL nitric acid to 1 L with water.

7.10 *Nitric Acid* (0.9 *M*)—Prepare by diluting 57 mL of nitric acid to 1 L with water.[13]

7.11 *Perchloric Acid* (1 *M*)—Prepare by diluting 85 mL of perchloric acid ($HClO_4$, specific gravity 1.76) to 1 L with water.

7.12 *Plutonium Standard Solution*—Dissolve plutonium metal (NBL CRM 126, current issue) in an Erlenmeyer flask by slow addition of approximately 30 mL of hydrochloric acid-nitric acid-hydrofluoric acid mixture. Add 30 mL of 8 *M*

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[9] Quartz heating lamps and Quartz epiradiator lamps, Model 534 RCL, 500 watts, 120 V (Atlas Electric Supplies, P.O. Box 1300, Hialeah, Florida, 33011) have been found to be satisfactory.

[10] A Julie 100-Ω precision resistor number NB102A, accurate to 0.0015 %, has been found satisfactory.

[11] *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.

[12] All reagents should be prepared with 18-MΩ-cm deionized (demineralized) water.

[13] 0.9 *M* HNO_3 is used because the range from 0.8 to 1.0 *M* HNO_3 provides a stable formal potential for the Pu^{3+}/Pu^{4+} couple.

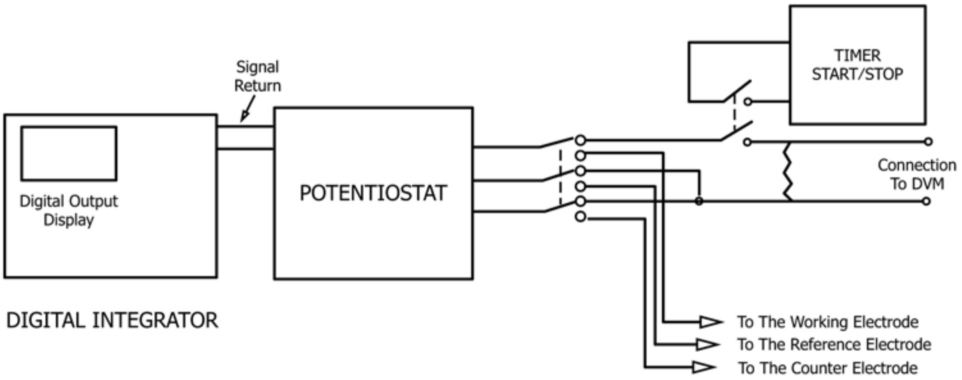

FIG. 4 Coulometer with Digital Integrator

HNO_3; evaporate to less than 15 mL. Transfer to a tared container with the 8 *M* HNO_3 and dilute to about 100 mL with 8 *M* HNO_3 prior to aliquotting. Proceed to 11.3.1.3.

7.13 *Sulfamic Acid* (NH_2SO_3H), saturated solution.

7.14 *Sulfuric Acid* (0.5 *M*)—Prepare by adding 28 mL of sulfuric acid (H_2SO_4, specific gravity 1.84) to water with constant stirring and dilute to 1 L.

7.15 *Sulfuric Acid* (3 *M*)—Prepare by adding 167 mL of sulfuric acid (H_2SO_4, specific gravity 1.84) to water with constant stirring and dilute to 1 L.

7.16 *Sulfuric Acid-Hydrofluoric Acid Mixture* (8.1 *M* H_2SO_4-2.9 *M* HF)—Prepare by adding 45 mL of sulfuric acid (H_2SO_4, specific gravity 1.84) to 45 mL of water with constant stirring. Add 10 mL of hydrofluoric acid, cool, and store in a TFE-fluorocarbon polymer bottle.

8. Hazards

8.1 Review the material safety data sheets and safety procedures in the laboratory's safety manual before performing this procedure.

8.2 Hydrofluoric acid and acid mixtures containing HF are highly corrosive and can severely burn skin, eyes, and mucous membranes. Hydrofluoric acid is similar to other acids in that the initial extent of a burn depends on the concentration, the temperature, and the duration of contact with the acid. Hydrofluoric acid differs from other acids because the fluoride ion readily penetrates the skin, causing destruction of deep tissue layers. Unlike other acids that are rapidly neutralized, hydrofluoric acid reactions with tissue may continue for days if left unattended. Due to the serious consequences of hydrofluoric acid burns, prevention of exposure or injury of personnel is the primary goal. Utilization of appropriate laboratory controls (hoods) and wearing adequate personal protective equipment to protect from skin and eye contact is essential. Acute exposure to HF can cause painful and severe burns upon skin contact that require special medical attention. Chronic or prolonged exposure to low levels on the skin may cause fluorosis.

8.3 Elemental plutonium is reactive and evolves hydrogen and other gases during dissolution; assure that the dissolution reactions are complete before sealing closed vessels.

8.4 Pressure protection and pressure relief is required when supplying compressed gas services to a glovebox or other types of radiological containment units.

8.5 Handling of hot acids during electrode conditions and aliquot fuming requires appropriate ventilation of fumes and safe handling practices for hot, corrosive materials.

9. Calibration of Instrument

9.1 The type of instrumentation recommended herein **(16, 17)** includes an electronic integrator circuit. The digital (voltage-to-frequency) integrator develops a series of pulses, the sum of which is proportional to the integrated current generated during electrolysis. Establish the relationship between coulombs of electricity and integrator output by calibration. (See 9.2 and 9.3.)

9.2 *Adjustment of the Digital Integrator:*

9.2.1 Adjust the full-scale and input offset voltage trim pots on the voltage-to-frequency converter (V/F) using the digital voltmeter and a frequency counter[14] in accordance with the manufacturer's procedure and recommended frequency for this adjustment.

9.3 *Electrical Calibration:*

9.3.1 Connect the circuit as shown in Fig. 4, with the potentiostat leads connected to the calibration precision resistor rather than the cell. Place the timer in the STOP (open circuit) position. Connect the digital voltmeter to the integrator output.

9.3.2 Place the potentiostat and the integrator in the operating mode.

9.3.3 Place the timer in the START (circuit closed) position.

9.3.4 After 150 s, use the DVM to record the potential drop, P,[15] across the resistor, R.

9.3.5 After 300 s, place the timer in the STOP (circuit open) position.

9.3.6 After stopping the timer, record the final integrator output, pulses.

9.3.7 Record the time required for calibration, s.

9.3.8 Repeat calibrations as required.

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[14] A Hewlett Packard 3458 digital multimeter has been found satisfactory.

[15] A time-averaged voltage measured during the duration of the calibration may be substituted for the voltage measured at the midpoint of the calibration.

9.3.9 Calculate the electrical calibration factor, C_e, in equivalents Pu/pulse, as follows:

$$C_e = \frac{Pt}{RVF} \qquad (2)$$

where:

P = potential drop across the precision resistor, V,
R = value of the precision resistor, Ω,
V = integrator output signal (from 9.3.6), pulses,
t = time of calibration, s, and
F = the Faraday constant, C/equivalent.

10. Conditioning

10.1 Achieving a consistent response from the gold or platinum working electrode requires proper storage and conditioning.

10.1.1 Storing gold and platinum working electrodes in 8 *M* HNO_3 when not in use is normally adequate to maintain satisfactory electrode response.

10.1.2 Rinsing with 8 *M* HNO_3 between specimens may be applied, as needed, to maintain satisfactory electrode response. (Satisfactory response may be defined as the ability of the electrode to oxidize and reduce the supporting electrolyte to 1 to 2 µA constant background current in about 3 min with the current following an exponential curve.)

10.1.3 If such electrode response is not obtained, the following electrode reconditioning treatments, in increasing order of severity, have been found to be successful in restoring response. The gold electrode may be: (*1*) briefly dipped in ambient temperature concentrated HCl and thoroughly rinsed with 8 *M* HNO_3; (*2*) briefly dipped in warm or hot[16] concentrated HCl and thoroughly rinsed with 8 *M* HNO_3; (*3*) briefly dipped in aqua regia and thoroughly rinsed with HNO_3; or (*4*) soaked 10 min in the sulfuric acid-hydrofluoric acid mixture (8.16), the residual acid removed by fuming and the hot electrode quenched in 8 *M* HNO_3. After each treatment, the electrode is stored in 8 *M* HNO_3 overnight. Following overnight storage, conditioning, that is, alternating reduction and oxidation of the supporting electrolyte with and without plutonium, may be required to achieve desired electrode performance.

10.1.3.1 The platinum electrode may be subjected to any of the above treatments, or it may be: (*1*) heated to red heat in a gas flame and quenched in 8 *M* HNO_3 or (*2*) heated in a furnace to 900°C and quenched in 8 *M* HNO_3. Do not use these latter treatments on gold electrodes as melting may occur.

10.2 The electrode storage and conditions steps above should also be applied to the platinum counter electrode when cell performance problems are observed.

11. Procedure

11.1 *Specimen Preparation:*

11.1.1 Weigh a sample, approximately 1 g, so that the overall weighing uncertainty is ≤0.01 %. If homogeneity of material or representativeness of samples cannot be assured, take multiple subsamples according to a statistically designed plan.

TABLE 1 Formal Redox Potentials of Pu(III)-Pu(IV) Couples in Various Supporting Electrolytes (10, 11)

Electrolyte	Concentration, M	$E^{o\prime}$, Volt Versus Saturated Calomel Electrode
$HClO_4$	1.0	0.71
	2.5	0.72
HCl	0.1	0.76
	0.25	0.75
	1.0	0.72
	3.0	0.68
	5.0	0.67
HNO_3	0.5	0.69
	1.0	0.69
	1.5	0.65
H_2SO_4	0.25	0.50
	0.5	0.49
	1.0	0.48

11.1.2 Dissolve the sample using an appropriate acid or acidic salt. After dissolution, volatilize the HF, if used, by evaporating to a low volume of nitric acid. Transfer to a tared container with 8 *M* HNO_3 and determine mass of solution (the weighing uncertainty should be ≤0.01 %).

11.1.3 Aliquot, by weight, a quantity of solution sufficient to contain 5 to 20 mg Pu, directly into a coulometry cell.[17] Add 1 mL 3 *M* H_2SO_4 (or 6 mL 0.5 *M* H_2SO_4) to the cell. Heat gently to dense fumes of SO_3, then fume the $Pu(SO_4)_2$ to dryness. The heating volatilizes HCl, HF, HNO_3, and excess H_2SO_4.

11.1.4 If Pu(VI) is known or suspected to be present, perform the treatment described in 11.1.5, otherwise proceed directly to 11.1.6.

11.1.5 Add 10 mL 8 *M* HNO_3, one drop 3 *M* H_2SO_4 (or 6 drops of 0.5 *M* H_2SO_4), and two drops 30 % H_2O_2 to the cell. Cover with a watchglass to prevent solution losses due to effervescing from oxygen evolution.[18] Allow the sample to stand at least two hours, during which time the solution turns blue (indicating Pu^{3+}). Heat gently to oxidize the Pu^{3+} to Pu^{4+} and to destroy excess H_2O_2(solution will turn green).[19] Remove watchglass and rinse with 6 *N* H_2SO_4 into the cell. Fume the sample to dryness as in 11.1.3.

11.1.6 Repeat the fuming step.[20] Proceed to 11.2.

NOTE 2—As an alternative to peroxide oxidation state adjustment or for samples with lower purity or high iron content not covered by this procedure, use the ferrous ion oxidation state adjustment technique followed by anion-exchange purification **(18)**.

11.2 *Coulometric Measurement:* [21]

NOTE 3—Measurements described in 11.2.3 are made during the

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[16] The higher the temperature, the more aggressive the treatment. Temperatures in the range from 50 to 70°C are typically effective. Ensure that hazards with handling acids at elevated temperatures are addressed in the work area where the electrode treatment is performed.

[17] Adjust the solution weight so that the combined uncertainty for the overall weighing process of each 5 to 20-mg aliquot of plutonium is 0.01 % with a coverage factor of 2.

[18] Sulfuric acid is critical to the oxidation state adjustment step as it prevents formation of insoluble plutonium dioxide on the cell walls and coverglass.

[19] A hot plate set at 120°C is recommended for this heating step.

[20] After cooling the solution, the coulometry cell may be covered with a 2 by 2-in. (50 by 50-cm) piece of parafilm to prevent sample loss or contamination prior to measurement.

[21] The procedure is based on a modification of a method described in *Analytical Chemistry*, Vol 50, 1978, p. 216.

electrolysis of the supporting electrolyte (11.2.1) and the sample (11.2.2).

11.2.1 *Electrolyte Blank:*

11.2.1.1 Add 18 to 20 mL of supporting electrolyte to a clean cell. If nitric acid supporting electrolyte is used, add three drops of saturated sulfamic acid to the supporting electrolyte.

11.2.1.2 Attach the cell to the cell head and stir the solution at 1200 to 1400 r/min.

11.2.1.3 Purge with an argon gas at flow rate sufficient to cause a 3-mm dimple to form in the solution surface.

11.2.1.4 Reduce the electrolyte at 0.28 V more negative than the formal potential (see Section 11.3 and Table 1) until the current decreases to 30 µA, at which time adjust the control potential to 0.18 V more negative than the formal potential.

11.2.1.5 Allow the solution to equilibrate for about 1 min. Record the potential difference between the working electrode and reference electrode, B_{red}, at their respective connections to the coulometer.

11.2.1.6 Adjust the potentiostat controls for oxidation of the supporting electrolyte.

11.2.1.7 Oxidize the electrolyte at 0.23 V more positive than the formal potential. After a time equivalent to five cell constants (see 11.2.3), adjust the control potential to 0.18 V more positive than the formal potential.

11.2.1.8 After 300 s total elapsed time, record the integrator output, E_B, and the amperes of constant background current, A_B.[22]

11.2.1.9 Record the working electrode versus reference electrode potential difference as before, (B_{ox}).

11.2.2 *Sample:*

11.2.2.1 Transfer the electrolyte (from 11.2.1) using a transfer pipet to a cell containing the dried plutonium sample.

11.2.2.2 Attach the cell to the cell head.

11.2.2.3 Stir at 1200 r/min, or higher,[23] and purge with argon gas.

11.2.2.4 Reduce the sample at 0.28 V more negative than the formal potential until the current decreases to <200 µA. Adjust the control potential until the current is approximately zero (±2 µA).

11.2.2.5 Record the potential between the working and reference electrodes, S_{red}. Turn the integrator to the operating position.

11.2.2.6 Adjust the potentiostat controls for oxidation of the sample.

11.2.2.7 Oxidize the sample at 0.23 V more positive than the formal potential until the current decreases to about 100 µA. Adjust the control potential until the current is approximately zero (±2 µA).

11.2.2.8 Record the integrator output, E_s, at 300 s.[24] Record the amperes of constant background current, A_s.[22] [$A_s \approx A_B$].

11.2.2.9 Record the working electrode versus reference electrode potential, S_{ox}.

TABLE 2 Correction Factors for Fraction Plutonium Electrolyzed at 25°C ($f = f\,' - f\,''$)

Oxidation		Reduction	
$S_{ox} - E^{\circ\prime}$	$f\,'$	$S_{red} - E^{\circ\prime}$	$f\,''$
0.05	0.875012	−0.05	0.124988
0.10	0.980004	− 0.10	0.019996
0.15	0.997094	− 0.15	0.002906
0.18	0.999094	− 0.18	0.000906
0.20	0.999584	− 0.20	0.000416
0.22	0.999809	−0.22	0.000191
0.25	0.999941	− 0.25	0.000059

11.2.2.10 Measure the solution temperature, T, using a thermometer with an uncertainty of ≤0.5°C.[25]

11.2.3 *Time Constants:*

11.2.3.1 Time constants of the cell (τ_1, τ_2) are determined from measurements taken during the electrolysis of the supporting electrolyte and of the sample, respectively. Determination of the time constants during each electrolysis is not required as long as parameters such as cell geometry, electrode condition, and stirring rate remain reproducible. Fluctuations in the cell constants of less than 20 % can be tolerated. As an alternative, plots of current versus time or log current versus time may be taken during each electrolysis to provide visual evidence that reproducible cell conditions are being attained.

11.2.3.2 During both the elctrolyte blank and sample measurements, record the electrolysis currents at two times, t_1 and t_2, when the electrolysis current is following an exponentially curve, such as 100 ± 1 s and at 200 ± 1 s after the start of the electrolysis.[26]

11.2.3.3 Calculate each time constant as follows:

$$\tau = \frac{t_2 - t_1}{\ln i_2/i_1} \tag{3}$$

where:

τ = time constant, s,
t_1 = time of first current reading, s,
t_2 = time of second current reading, s,
i_1 = current at t_1, A, and
i_2 = current at t_2, A.

11.2.3.4 If gross variations in τ are observed, electrode condition or matrix differences between electrolyte and sample should be investigated before proceeding with sample analysis.

11.3 *Determination of the Formal Potential, E°′:*

11.3.1 A determination of the formal potential is required for the calculation of the fraction of plutonium electrolyzed (13.1), and should be performed periodically.[27]. A satisfactory determination of the formal potential is described.

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[22] The sign of A_B has been arbitrarily designated (+), oxidation current; and (−), reduction current.

[23] Select stirring rate based on cell design and stirrer configuration. Avoid splashing of the specimen and electrolysis current interruptions from the vortex.

[24] If blank and sample oxidation are not done for the same length of time, a constant background current correction is required. See Section 12.

[25] Depending on the flow rate of the argon gas in the measurement cell assembly, the solution is typically 1 to 3°C cooler than the ambient temperature because of the cooling effect from gas expansion above the solution. The solution temperature should be measured during the plutonium oxidation step or promptly after completing the oxidation.

[26] For the blank, the current reading at time t_2 should be taken when it is at least 10 µA above the constant background current, so that the assumption of an exponential curve is valid.

[27] The formal potential should be measured whenever the reference electrode is replaced or when the measurement system has not been used for an extended period of time. The frequency selected for periodic formal potential measurements should be chosen by the user based upon measurement data quality objective and consequence of failure.

11.3.1.1 After completion of the coulometric measurements on a standard or sample (9.2), repeat the reduction (11.2.2.3 through 11.2.2.5).

11.3.1.2 Oxidize the sample at 0.23 V more positive than the formal potential until the integrator output approaches $E_s/2$. Adjust the control potential such that the current becomes approximately zero (±50 μA)[28] when the integrator output equals $E_s/2$. At this time the Pu(IV)/Pu(III) ratio will be sufficiently close to unity such that the control potential will equal the formal potential within the required accuracy.

11.3.1.3 Record the working electrode versus reference electrode potential, $E°'$. (Literature values for $E°'$ for different electrolytes are given in Table 1.)

11.3.2 The formal potential determination for sample and standard should agree within 0.005 V. The source of differences greater than 0.005 V must be resolved to ensure achieving the stated precision and accuracy of the test method. Differences in the formal potentials measured for samples and standards do not necessarily indicate a shift in the formal potential of the plutonium system. Electroactive impurities can cause a bias in the measurement of the formal potential while complexing impurities can shift the formal potential of the plutonium system. These differences can be eliminated by purification of the sample or standard using an anion-exchange (11.1.5) or other suitable separation method.

12. Calculation

12.1 Calculate the fraction of the plutonium electrolyzed, f **(1, 7)** (see Table 2).

$$f = \frac{\exp\left|\frac{S_{ox} - E°'}{N}\right|}{1 + \exp\left|\frac{S_{ox} - E°'}{N}\right|} - \frac{\exp\left|\frac{S_{red} - E°'}{N}\right|}{1 + \exp\left|\frac{S_{red} - E°'}{N}\right|} \quad (4)$$

where:

E°' = formal potential of Pu(III)/Pu(IV) couple, and

N = $R(T + 273.16)/nF$. Where R is the molar gas constant.[29] T is the sample solution Celsius temperature; $n = 1$ for Pu(III)/Pu(IV) couple, and F is the Faraday constant.

12.2 Constant background current correction, V_c:

$$V_c = \frac{(t_s - t_B)\, A_B}{C_e F} \quad (5)$$

where:

t_s *and* t_B = time for sample and blank oxidation, respectively, s,

A_B = constant background current during the blank determination, A,

C_e = integrator electrical calibration factor, equivalents Pu/pulse, and

F = Faraday constant, coulombs/equivalent.

12.3 Plutonium Content:

$$\% \text{ Pu} = \frac{V_s - \frac{V_B\,(S_{ox} - S_{red})}{(B_{ox} - B_{red})} - V_c}{Sf} MC_e \times 100 \quad (6)$$

where:

V_B and V_s = integrator output for the blank and the sample, respectively,

C_e = calibration factor (8.3.9), equivalents Pu/count,

f = fraction electrolyzed, from Table 2,

S = sample in aliquot, g,

B_{ox}, B_{red}, S_{ox}, and S_{red} = potential difference between working electrode and reference electrode for the blank oxidation/reduction and the sample oxidation/reduction, respective, V, and

M = gram atomic ($n = 1$) weight of plutonium (adjusted for isotopic composition).

13. Use of Standards

13.1 Chemical standards should be used for quality control to verify proper and consistent performance of this test method.

14. Precision and Bias[30]

14.1 An interlaboratory comparison was performed (see Practice E691) in which six laboratories each measured two subsamples from each of two samples of plutonium dioxide (PuO_2). Each subsample was dissolved and coulometric measurements, using the laboratory's choice of electrolyte and working electrode material, were performed on two separate days. Thus, each laboratory performed four measurements on each sample. The unweighted mean of all 48 observations was 87.732 wt % Pu (0.065 % relative difference from the assigned value). Statistical analysis of the 48 data points revealed that the data from one laboratory, less experienced with the test method, were statistical outliers and were excluded from the subsequent analysis. The unweighted mean of the 40 remaining observations was 87.672 wt % Pu (–0.004 % relative difference from the assigned value). Based on an analysis of variance, the within-laboratory standard deviation (sometimes called "repeatability," see Practice E691) was ±0.100 wt % Pu (0.115 % relative to an assigned value of 86.676 wt % Pu); the between-laboratory standard deviation (sometimes called "reproducibility," see Practice E691) was ±0.439 wt % Pu (0.506 % relative to the assigned value).

14.2 A recovery of 99.99 %, RSD 0.05 % ($n = 40$), on NBS SRM 949e was obtained over a six-month period by three experienced analysts using anion-exchange separation. This fact, coupled with the agreement (within 0.004 %) between the interlaboratory mean and the assigned value, indicates that the test method exhibits no statistically significant bias.

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[28] In the region near the formal potential, it will be difficult to adjust the current exactly to zero as small changes in the control potential cause large shifts in the equilibrium Pu(IV)/Pu(III) ratio.

[29] Committee on Data for Science and Technology, CODATA, internationally recommended values for fundamental physical constants are available at URL http://physics.nist.gov/cuu/Constants/index.html.

[30] Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:C26-1005.

15. Keywords

15.1 controlled-potential coulometry; coulometry; electroanalytical method for plutonium; plutonium analysis; plutonium assay using electrolysis; plutonium concentration

REFERENCES

(1) Delahay, P., *New Instrumental Methods in Electrochemistry*, Instrumental Publishers, Inc., New York, NY, Chapters 11–13, 1954 .

(2) Lingane, J. J., *Electroanalytical Chemistry*, 2nd ed., Interscience Publishers, Inc., New York, NY, Chapter XIX, 1958.

(3) DeFord, D. D., and Miller, J. W., "Coulometric Analysis," *Treatise on Analytical Chemistry*, I. M. Kolthoff and P. L. Elving, eds., Interscience Publishers, Inc., New York, NY, Part I, Vol 4, 1963.

(4) Abresch, K., and Classen, I., *Coulometric Analysis*, translated by L. L. Levenson, Chapman, and Hall, Ltd., London, 1965.

(5) Shults, W. D., " Coulometric Methods," *Standard Methods of Chemical Analysis*, 6th ed., F. J. Welcher, ed., D. Van Nostrand Co., Inc., Princeton, NJ, Vol III, Chapter 23, 1966.

(6) Harrar, J. E., " Techniques, Apparatus, and Analytical Applications of Controlled-Potential Coulometry," *Electroanalytical Chemistry*, J. A. Bard, ed., Vol 8, 1975, pp. 1–167.

(7) Holland, M. K., Weiss, J. R., and Pietri, C. E., *Analytical Chemistry*, Vol 50, 1978, p. 236.

(8) Bingham, C. D., " Application of a Correction Factor for Unelectrolyzed Species in Controlled-Potential Coulometry," *NBL-289*, January 1979, p. 59.

(9) Mitchell, W. G., Spaletto, M. I., Lewis, K., Soriano, M. D., and Smith, M. M., " The Effect of Ion-Exchange Purification on the Determination of Plutonium at the New Brunswick Laboratory," NBL-323, July 1990.

(10) Shults, W. D., *Talanta*, Vol 10, 1963, pp. 833–849.

(11) Jackson, D. D., Hollen, R. M., Roensch, F. R., and Rein, J. E., "Controlled-Potential Coulometric Determination of Plutonium with a Hydrochloric Acid-Sulfamic Acid Electrolyte and Phosphate Complexing," *Analytica Chimica Acta*, Vol 117, 1980, p. 205.

(12) Holland, M. K., and Weiss, J. R., "Application of an Electrochemical Correction for Iron Impurity in the Controlled-Potential Coulometric Determination of Plutonium," *NBL-292* , October 1979, p. 28.

(13) Holland, M. K., and Lewis, K., "Controlled-Potential Determination of Plutonium with Concurrent Correction for a Second Reversible Couple," *Analytica Chimica Acta*, Vol 149, 1983, p. 167.

(14) Frazzini, T. L., Holland, M. K., Weiss, J. R., and Pietri, C. E., "A Digital Integrator for Controlled-Potential Coulometry," *Analytica Chimica Acta*, Vol 129, 1981, p. 125.

(15) Holland, M. K., Weiss, J. R., and Pietri, C. E., "The New Brunswick Laboratory Controlled-Potential Coulometric Method for the Determination of Plutonium," *NBL-299*, June 1981.

(16) Holland, M. K., and Cordaro, J. V., "An Automated Instrument for Controlled-Potential Coulometry: System Documentation," SRS, DP–1751, June 1988.

(17) Mitchell, W. G., Troutman, D., and Lewis, K., "Automation of the New Brunswick Laboratory Controlled-Potential Coulometric Method for Plutonium," NBL-320, November 1988 .

(18) Freeman, B. P., Pietri, C. E., and Weiss, J. R., "Separation of Plutonium from Impurities by Anion Exchange Methods," *NBL-292*, October 1979, p. 32.