ASTM INTERNATIONAL

Designation: C1108 – 23

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

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 mol/L (0.9 M) HNO_3, 1 mol/L (1 M) $HClO_4$, 1 mol/L (1 M) HCl, 5 mol/L (5 M) HCl, and 0.5 mol/L (0.5 M) H_2SO_4. Limitations on the use of selected supporting electrolytes are discussed in Section 6. Optimum quantities of plutonium for this procedure are 5 mg 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, health, and environmental practices and determine the applicability of regulatory limitations prior to use.*

1.5 *This international standard was developed in accordance with internationally recognized principles on standardization established in the Decision on Principles for the Development of International Standards, Guides and Recommendations issued by the World Trade Organization Technical Barriers to Trade (TBT) Committee.*

2. Referenced Documents

2.1 *ASTM Standards:*[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 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. Terminology

3.1 Except as otherwise defined herein, definitions of terms are as given in Terminology C859.

4. Summary of Test Method

4.1 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

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

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integrator be capable of operations in a bipolar mode and that the plutonium-containing solution be of high purity, that is, nuclear grade.

4.2 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**).

$$m_{\text{Pu}} = \frac{(Q_\text{s} - Q_\text{b})\, M}{nFf} \qquad (1)$$

where:

m_{Pu} = mass of plutonium, g,
Q_s = coulombs generated by electrolysis of sample aliquot, C,
Q_b = coulombs generated by electrolysis of supporting electrolyte (background current), C,
M = molar mass of plutonium (must be adjusted for isotopic composition), g/mol,
n = number of electrons involved in the electrode reaction (for Pu(III) → Pu(IV), $n = 1$),
F = Faraday constant, C/mol,[4] and
f = fraction electrolyzed of plutonium.

5. Significance and Use

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

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

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

5.1.3 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**).

5.2 *Fitness for Purpose of Safeguards and Nuclear Safety Application*—Methods intended for use in safeguards and nuclear safety applications shall meet the requirements specified by Guide C1068 for use in such applications.

6. Interferences

6.1 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).

6.2 *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**).

6.3 *Pu(VI)*—Plutonium(VI) is only partially reduced to Pu(III) in 1 mol/L (1 *M*) HNO$_3$, 1 mol/L (1 *M*) HCl, or 1 mol/L (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 mol/L (0.5 *M*) H$_2$SO$_4$ (**10**) or 5.5 mol/L (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.

6.4 *Iron*—In 0.5 mol/L (0.5 *M*) H$_2$SO$_4$ 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 mass fraction in the sample solution. In 1 mol/L (1 *M*) HCl, 1 mol/L (1 *M*) HNO$_3$, or 1 mol/L (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**).

6.5 *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.

6.6 *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 12.3.1.3). For aliquots of dissolved mixed oxide (MOX) fuels that have not been purified by anion exchange to remove the uranium, the sulfate ion 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 sulfate ions at >4 mmol/L in 1 mol/L (1 *M*) HClO$_4$ has been reported (**10**).

6.7 *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$_2$SO$_4$ are effective in removing fluoride.

6.8 *Oxygen*—In H$_2$SO$_4$ 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.

7. Apparatus

7.1 *Controlled-Potential Coulometer*—A coulometer with the following specifications is recommended to achieve highly precise and accurate results. (Room temperature stability of

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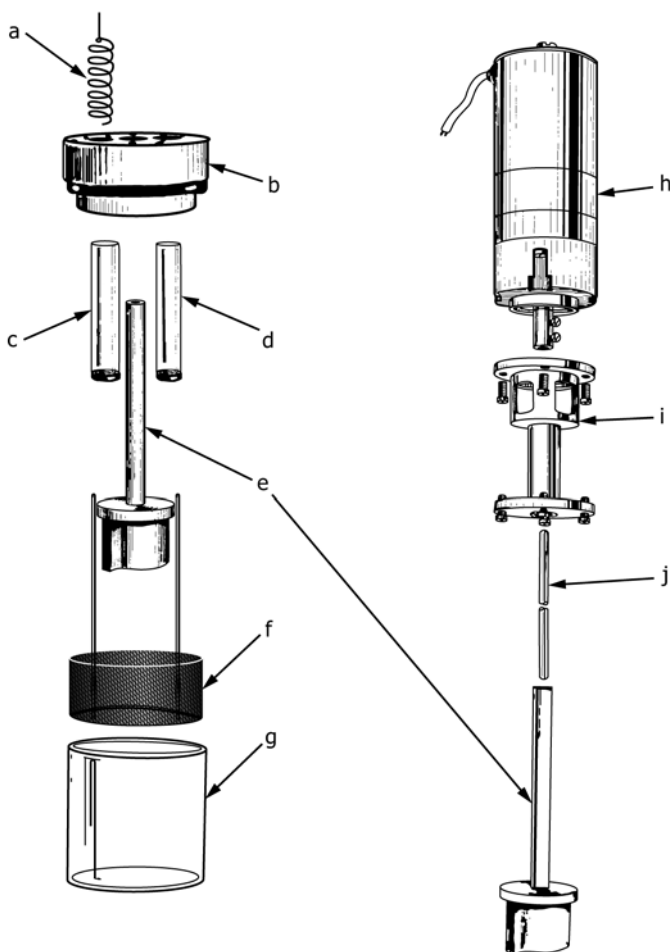
FIG. 1 Exploded View of Cell Assembly: (a) Counter Electrode,
(b) Cell Head, (c) Counter Electrode Frit Tube, (d) Reference Elec-
trode Frit Tube, (e) NBL-Designed S-Shaped Stirrer, (f) Working
Electrode, (g) Sample Cell, (h) Stirrer Motor, (i) Motor Pedestal
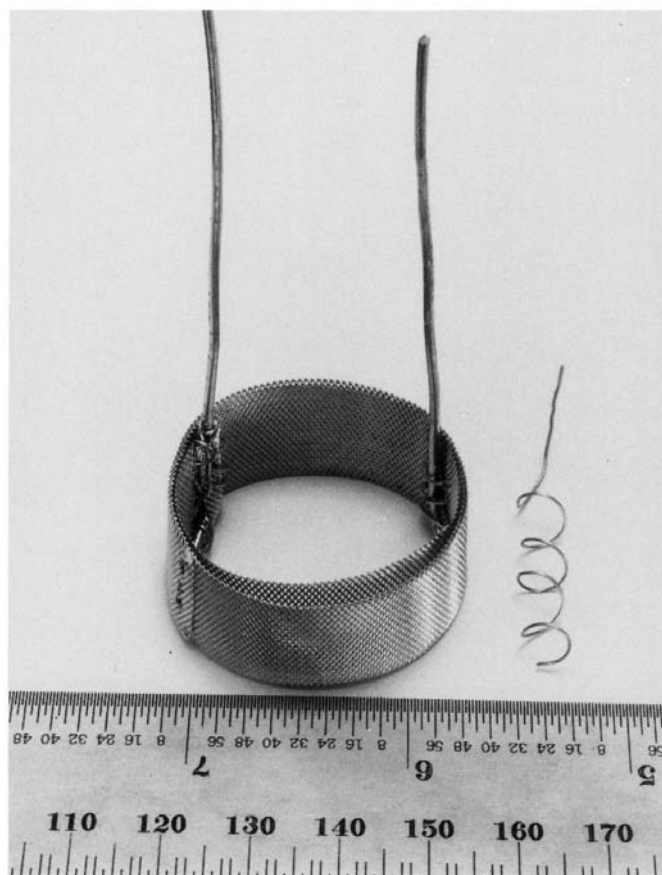and Bearing, and (j) Stirrer Shaft

FIG. 2 Working Electrode (Top View)

±1 °C is recommended to ensure optimum instrument perfor-
mance. Instruments with smaller output current or smaller
voltage span may be satisfactory.)

Potentiostat **(6)**

Output voltage	>25 V
Output current	>200 mA
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 %

7.2 *Digital Voltmeter (DVM)*—15 V range, 5½ digits accu-
rate to 0.01 % of full scale on all ranges. Input resistance
>10^{10} Ω.[5]

7.3 *Cell Assembly*—The success of controlled-potential cou-
lometric 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).

7.3.1 *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.

7.3.2 *Counter Electrode and Salt Bridge Tube*—The counter
electrode is a coiled length of 0.51 mm (0.020 in.) diameter
platinum wire (Fig. 2). Platinum with a mass fraction of
≥999.5 mg/g (that is, Pt purity of ≥99.95 %) has been used

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