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**Nuclear fuel technology — Controlled-  
potential coulometric assay of plutonium**

*Technologie du combustible nucléaire — Dosage du plutonium par  
coulométrie à potentiel imposé*

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## Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 12183 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

This second edition cancels and replaces the first edition (ISO 12183:1995), which has been technically revised.

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# Nuclear fuel technology — Controlled-potential coulometric assay of plutonium

## 1 Scope

This International Standard specifies an analytical method for the electrochemical assay of pure plutonium nitrate solutions of nuclear grade, with a total uncertainty of 0,1 % to 0,2 % at the confidence level of 0,95 for a single determination. The method is suitable for aqueous solutions containing more than 0,5 g/L plutonium and test samples containing between 4 mg and 15 mg of plutonium. Application of this technique to solutions containing less than 0,5 g/L, and test samples containing less than 4 mg of plutonium, must be demonstrated by the user as having adequate reliability for their specific application.

Preliminary purification by anion exchange is required to remove interfering substances when present in significant amounts. Purification is also appropriate in situations where the purity of the sample is unknown or when it may unpredictably fluctuate in the manufacturing process. Refer to Clause 9 for a discussion of interferences and iron corrections.

Clause 10 discusses the changes in application of the method and methodology that can be applied and important considerations when selecting measurement parameters, while still remaining within the intended scope of this International Standard.

## 2 Normative references

ISO 12183:2005

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The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 10980:1995, *Validation of the strength of reference solutions used for measuring concentrations*

## 3 Principle

The method consists of the following steps:

- test samples are prepared by weight and fumed with sulfuric acid to achieve a consistent and stable chemical form that is free from chloride, fluoride, nitrate, nitrite, hydroxylamine, and volatile organic compounds;
- when appropriate, preliminary purification by anion exchange with fuming in sulfuric acid to restore the dry plutonium sulfate chemical form in preparation for measurement;
- measuring a blank of the nitric-acid supporting electrolyte and performing an appropriate calculation to determine the background current correction applicable to the electrolysis of the test sample from charging, faradic, and residual current; [1]
- dissolution of the residue in the previously measured supporting electrolyte (the blank);

- reduction at a controlled potential that electrolyses the plutonium to greater than 99,8 % Pu<sup>3+</sup> and measurement of the equilibrium solution potential at the end of this electrolysis by control-potential adjustment; [2]
- oxidation at a controlled potential that electrolyses the plutonium to greater than 99,8 % Pu<sup>4+</sup> and measurement of the equilibrium solution potential at the end of this electrolysis by control-potential adjustment;
- periodically, the formal potential of the plutonium couple,  $E_0$ , is measured for the specific supporting electrolyte, cell components, and design;
- the result is corrected for the background current and the fraction of plutonium not electrolysed;
- coulometer calibration, traceable to electrical standards through Ohm's law and Faraday's constant, is used to convert the coulombs of integrated current from the electrolyses to equivalents of plutonium;
- quality-control plutonium standards are used to independently demonstrate measurement performance.

## 4 Reagents

Use only reagents of recognized analytical grade.

All aqueous solutions shall be prepared with double-distilled or deionized water with a resistivity greater than 10 M $\Omega$ -cm.

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4.1 **Nitric acid solution**,  $c(\text{HNO}_3) = 0,9 \text{ mol/L}$ . (standards.iteh.ai)

4.2 **Amidosulfuric acid solution**,  $c(\text{NH}_2\text{HSO}_3) = 1,5 \text{ mol/L}$ . ISO 12183:2005

4.3 **Sulfuric acid solution**,  $c(\text{H}_2\text{SO}_4) = 3 \text{ mol/L}$ . <https://standards.iteh.ai/catalog/standards/sist/975c7d44-824f-411d-a2ae-400e8d6e661/iso-12183-2005>

4.4 **Pure argon or nitrogen**, ( $\text{O}_2$  content lower than 10 parts per million).

4.5 **Pure air**, free of any organic compounds.

## 5 Apparatus

Usual laboratory equipment found in a medium-activity radiochemical laboratory suitable for work with plutonium.

5.1 **Analytical balance**, capable of weighing after installation in radiological containment with an accuracy of 0,1 mg, or less. (The test sample size must be correspondingly greater than the minimum 1 g size, if the accuracy, as installed, does not meet this 0,1 mg criteria.)

5.2 **Weighing burette**, glass or plastic; the material selection is not critical provided it maintains a stable tare weight and is not susceptible to static charge.

5.3 **Equipment for sample evaporation in the coulometric cell**, comprising the following:

- an overhead radiant heater or hotplate with a means of temperature adjustment;
- for optimum evaporation rate and to minimize the concentration of acid fumes, an air supply with the delivery tube directed towards the surface of the liquid may be used;

- additional design feature to control acid fumes, including vapour capture and local neutralization may be appropriate depending upon facility design and requirements.

The evaporation/fuming apparatus shall be adjusted to provide both rapid and well-controlled evaporation, followed by fuming to dryness of the plutonium sulfate test sample. The apparatus shall prevent mechanical loss of the test-sample solution from boiling and spattering during the process and from contamination by chemicals, which may be used to neutralize acid vapours.

The equipment in Figure 1 is suitable.

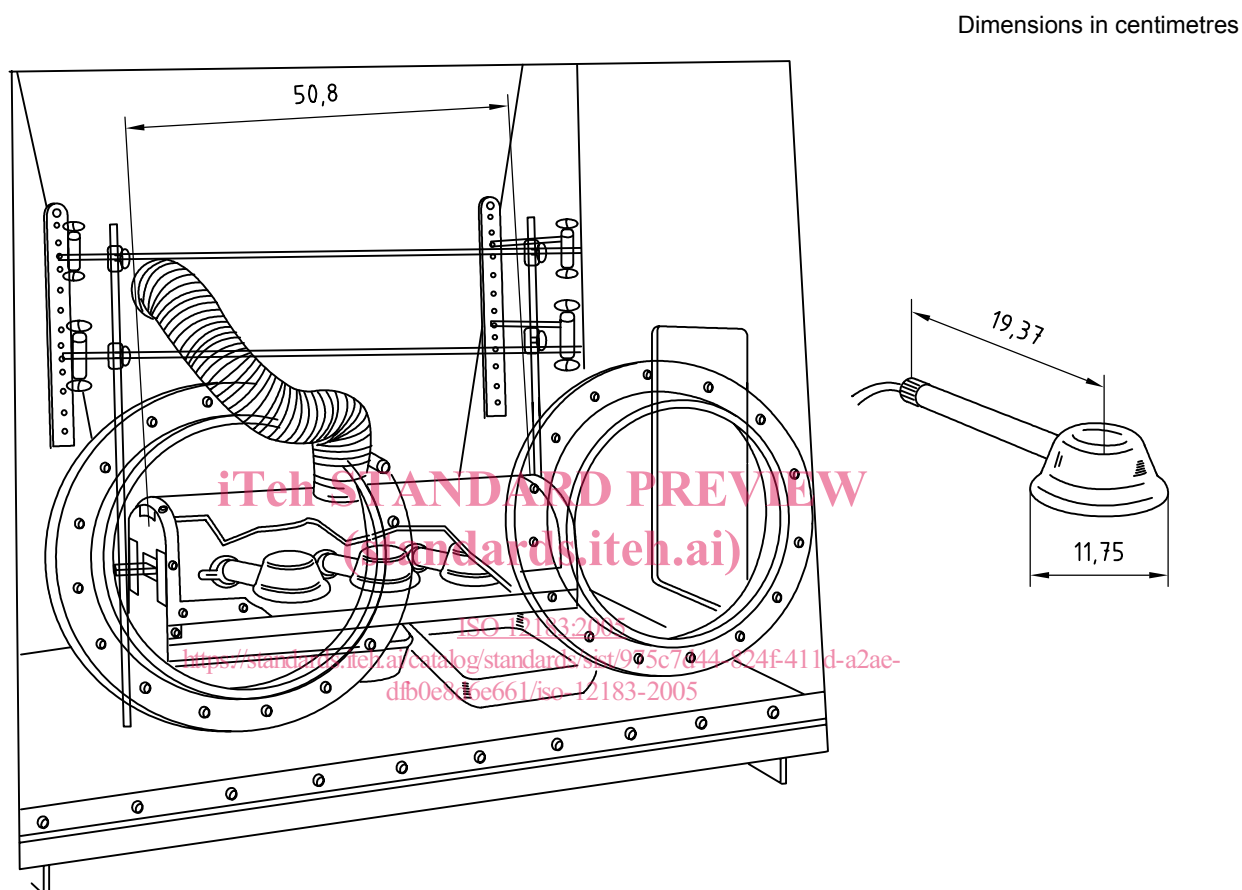


Figure 1 — Sample evaporation system

#### 5.4 Controlled-potential coulometer.

The following equipment is suitable (see Figure 2).

##### 5.4.1 Coulometer-cell assembly, comprising the following:

- a stirrer motor with a rotation frequency of at least  $1\ 000\ \text{min}^{-1}$ ;

NOTE Adjustable-speed motors allow optimizing for individual cell designs. Stirring motors powered by isolated direct-current supplies have the advantage of reducing electrical noise that is superimposed on the blank and test-sample electrolysis current signal sent to the integrator.

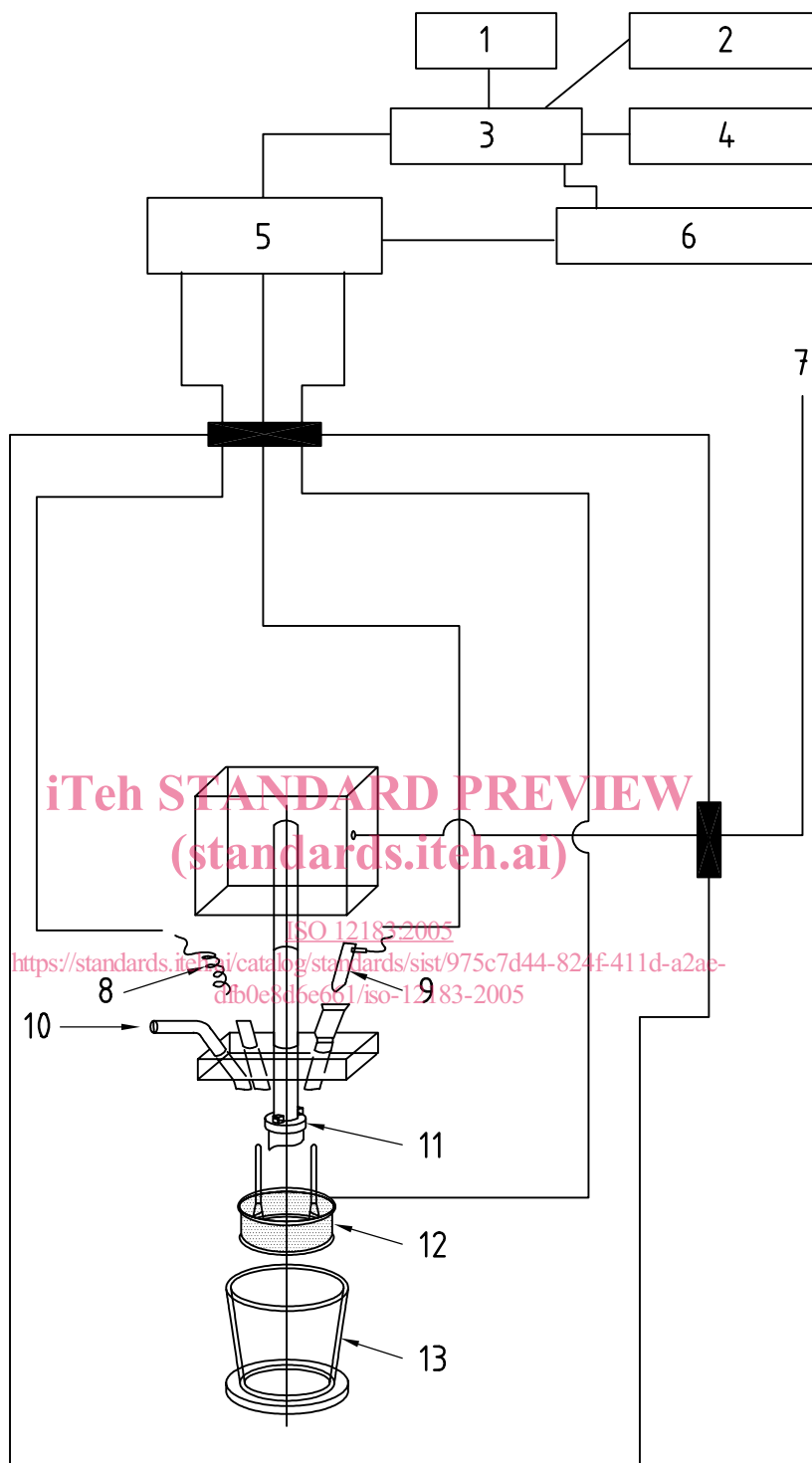
- a cylindrical or tapered glass coulometric cell of capacity 50 mL, or less, with an O-ring seal and a lid suitable for the following internal equipment:
  - an inlet tube for inert gas, to exclude atmospheric oxygen;

- a chemically inert stirrer, designed to prevent splashing, centrally located, and connected to a stirrer motor;
- a working electrode made of gold (99,99 %) and consisting of a gold wire welded or machined to a cylindrical gold wire frame, nominally 15 mm high and 20 mm in diameter, around which is welded or machined a very fine gold mesh. The gold mesh may be of several layers (e.g. four layers);
- a glass tube plugged at the bottom end with a 2,5 mm thick sintered-glass disc (pore size < 0,01 µm), filled with nitric acid (4.1) and the tip positioned within the ring of the working electrode;
- a reference electrode, saturated calomel electrode (SCE), or other reference electrodes as described in 10.3, housed in the glass tube;
- another glass tube, similar to the first one, also filled with nitric acid (4.1), and mounted within the ring of the working electrode;
- an auxiliary electrode consisting of a platinum wire, 0,5 mm to 3,0 mm in diameter, housed in the glass tube;

The diameter of the glass tube and sintered-glass disc used to house the auxiliary electrode may be larger than the glass tube used for the reference electrode. The flow rate of the solution through both glass discs shall be less than 0,05 mL/h.

- a) A thermocouple for measuring the temperature of the test-sample solution is an optional feature. If it is not possible to measure the solution temperature either during or immediately following the analysis, then a thermometer inside the containment unit may be used to estimate the solution temperature from the ambient air temperature. An accuracy of  $\pm 0,1$  °C is recommended.
- b) For optimum potential control, design the cell assembly to position the sintered-glass discs of the glass tubes to meet the following requirements: [ISO 12183:2005](https://standards.iteh.ai/catalog/standards/sist/975c7d44-824f-411d-a2ae-11b111111111)
- the reference electrode connection is 1 mm to 2 mm from the working electrode;
  - the distance between auxiliary and reference electrode discs is less than or equal to the distance between the auxiliary electrode disc and the nearest point on the working electrode.
- c) The hole for the stirrer shaft provides a gas vent. Except for the stirrer passage, all openings in the lid shall be relatively gastight such that the inert-gas flow rate selected is sufficient to quickly degas oxygen from the supporting electrolyte and the test-sample solution and to prevent in-leakage of atmospheric oxygen. For ease of operation and consistent performance, the gas-flow inlet tube may be designed to direct all or part of the inert gas toward the test-sample solution, such that a 2 mm to 4 mm dimple is produced on the sample solution without causing the solution to splash. For cell assemblies with an optimized design and fit, degassing is accomplished in 5 min or less.





- |   |                                   |    |  |
|---|-----------------------------------|----|--|
| 1 | video                             | 8  | auxiliary (or counter) electrode in bridge tube filled with supporting electrolyte |
| 2 | printer                           | 9  | reference electrode in bridge tube filled with supporting electrolyte              |
| 3 | control computer                  | 10 | inert gas  |
| 4 | keyboard                          | 11 | stirrer  |
| 5 | potentiostat and integrator       | 12 | working electrode  |
| 6 | voltmeter digital                 | 13 | cell   |
| 7 | AC or DC power for stirring motor |    |  |

Figure 2 — Coulometric-cell assembly connections

**5.4.2 Measuring unit**, comprising the following [3,4].

- a) **A potentiostat** with the desired range of electrolysis potentials for plutonium measurement and the following capabilities:
- a high power, minimum current output capability of 250 mA;
  - a quick-response control-potential circuit, maximum rise-time from zero volts to the desired control potential of 1 ms, with maximum voltage overshoot of 1 mV;
  - a control amplifier with a common-mode rejection of 90 dB or greater;
  - automatic control-potential adjustment, with an output stepping capability resolution of 0,001 V, or less;
  - a voltage-follower amplifier used to isolate the reference electrode (electrometer), with a minimum input impedance of  $10^{11} \Omega$ ;
  - detection capability for monitoring the full range of the electrolysis currents, including a sensitivity of 0,5  $\mu\text{A}$  at zero current.

NOTE This procedure assumes that the coulometer has two accurate potentiometers for selecting the oxidation and reduction potentials, although this is not a system requirement.

- b) **A coulometric integrator** capable of being read to  $\pm 10 \mu\text{C}$  and able to integrate currents varying from 1  $\mu\text{A}$  to 150 mA. (Refer to 6.1.4 for integrator capabilities and calibration requirements.)
- The control-potential system should not drift more than  $\pm 1 \text{ mV}$  and the integration system should not drift more than 0,005 % during routine measurements (between electrical calibrations), over the range of temperatures to which the control-potential circuitry will be exposed. The system should be located in a cabinet having adequate temperature control to limit electronic drift within the specified accuracy, if the room temperature varies excessively.
  - An electronic clock, accurate within the selected range to better than 0,002 %.
  - A system for generating a known constant current, stable to 0,002 % over the range of temperatures to which the constant-current circuitry will be exposed. This system will be used for electrical calibration of the integration circuit of the coulometer, as described in 6.1.4.
  - The cable connecting the potentiostat to the cell should be a three-wire conductor, twisted-shielded cable, preferably with the shield grounded at the potentiostat. Gold connectors at the cell are recommended to avoid contact problems from corrosion.

**5.5 Digital voltmeter (DVM)**, having an accuracy of  $\pm 0,001 \%$  of the voltage reading in the range 0,5 V to 10 V, and 0,01 % of the voltage reading in the range 100 mV to 500 mV, with an input impedance of  $10^{10} \Omega$  or greater. This accuracy is required for electrical calibration, as described in 6.1.4.

**5.6 Regulated power:** equipment should be protected with an uninterruptable power supply that provides a regulated voltage of  $\pm 1 \%$  of the national standard, and provides appropriate surge-protection features.

## 6 Procedure

### 6.1 Plutonium determination

#### 6.1.1 Weighing the test sample, with an accuracy of 0,01 %.

The test sample may be weighed after delivery into a tared coulometer cell and the apparent mass corrected for the air buoyancy effect using Equation (1).

Alternatively, the test sample may be delivered by weighing into the coulometer cell, as follows:

NOTE Care is needed to avoid any loss of microdrops. During weighing of the polyethylene weighing burette, the problem of static electricity is eliminated by contact between the dropping tube and a copper plate connected to the ground or a similar arrangement.

For test samples with concentrations greater than 15 g/L of plutonium, the solution should be diluted by weight so that all weights are greater than 1 g and the overall weighing uncertainty remains acceptably small.

- a) Fill a polyethylene weighing burette with the solution to be analysed.
- b) Weigh the burette to 0,1 mg.
- c) Deliver a test sample of at least 1 mL, drop by drop, into a coulometric cell.
- d) Weigh the burette again to 0,1 mg.
- e) The mass difference gives the apparent mass,  $m_a$ , of the test sample in the cell.
- f) Correct the apparent mass of the test sample for the air buoyancy affect using Equation (1):

$$m_{\text{Real}} = m_a \times \frac{1 - (D_a/D_b)}{1 - (D_a/D_s)} \quad (1)$$

where

$D_a$  is the density of air, which is a function of temperature, pressure, and humidity, but typically is 0,001 16 g/cm<sup>3</sup> to 0,001 2 g/cm<sup>3</sup>;

$D_b$  is the density of the stainless steel weights used in modern analytical balances, 8,0 g/cm<sup>3</sup>;

$D_s$  is the density of the test sample.

In addition to applying an air buoyancy correction to the mass of the test sample, air buoyancy corrections should be applied to all mass measurements (including any bulk-material mass measurements). This correction is required to eliminate systematic errors that can exceed 0,1 % for solutions. The correction is less for solids, but can still be significant.

#### 6.1.2 Preparation of the test sample

- a) Add 1 mL of sulfuric acid solution (4.3) to the coulometric cell containing the test sample.
- b) Place the cell containing the test sample into the sample evaporation system and evaporate the liquid in the test sample.
- c) Evaporate at a temperature sufficient to evolve SO<sub>3</sub> fumes, and continue until SO<sub>3</sub> fumes are no longer observed and a residue of plutonium sulfate (orange-coloured precipitate) is formed. Do not allow the solution to boil or splash as this will cause mechanical loss.

The colour of the plutonium sulfate is dependent on the type of lighting used in the laboratory. Under fluorescent lighting, the dried sulfate is coral pink. Degradation of plutonium sulfate to plutonium oxide should not be expected, even after baking the residue, unless extreme temperatures are employed. Failure to use high-purity reagents, anion-exchange resins washed free of resin fines, and heating equipment that is not well maintained and clean can produce visible black residue in combination with the dried sulfate powder. These residues could be mistaken for plutonium oxide, and, depending on their composition, might interfere in subsequent measurements.

- d) Allow the test sample to cool to room temperature.
- e) If the presence of significant amounts of impurities is suspected, purify the plutonium in the test sample by a suitable purification process, then repeating the sulfuric acid fuming step as detailed in 6.1.2. Anion-exchange separation as outlined in Annex A is an effective purification process.

**6.1.3 Electrode pretreatment**

Electrode conditioning is critical and shall be repeated periodically. The laboratory shall therefore have the capability to perform aggressive electrode treatments. The following techniques may be used individually, or in combination with each other, to treat the working and auxiliary electrodes:

- storing in 8 mol/L nitric acid (recommended as the general overnight practice);
- soaking in concentrated sulfuric acid containing 10 % hydrofluoric acid, followed by 8 mol/L nitric acid;
- boiling in nitric acid;
- soaking in aqua regia (limited to several minutes to prevent damage to the working electrode);
- flaming the platinum auxiliary electrode to white or red heat.

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Electrode treatment may be performed on a preventative basis, at the beginning and/or the end of the day that the electrode is used. Alternatively, treatment may be on an "as needed" basis, particularly in the case of failure to obtain optimum electrode performance when measuring either the blank or the test sample. The typical background current levels should be relatively constant for a given installation and are normally used as indicators of the desired performance.

Each day, or more often as desired, before performing the actual blank determination, further conditioning of the electrodes is achieved by performing the following sequence of electrolyses.

- a) Assemble the cell lid complete with the electrodes and other internal equipment (see 5.4.1).
- b) Take a clean dry coulometric cell and add sufficient nitric acid solution (4.1) to immerse the working electrode, and the sintered-glass tips of the reference and auxiliary electrode tubes.
- c) Add one drop of amidosulfuric acid solution (4.2).
- d) Firmly fit the cell under the lid.
- e) Start the stirrer at the desired speed. (Using the maximum speed, while avoiding splashing or forming any excessive vortex that would interrupt electrical connections, is recommended.)
- f) Open the gas inlet and maintain a sufficient flow of inert gas throughout the electrolysis period. (Inadequate purging to remove oxygen can be mistaken for an electrode-conditioning problem.)
- g) Preselect the oxidation potential at  $E_0 + 0,32$  V and the reduction potential at  $E_0 - 0,36$  V.
- h) After degassing for 5 min, start the oxidation and oxidize at  $E_0 + 0,32$  V until a residual current of 10  $\mu$ A is obtained.