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Determination of plutonium in nitric acid solutions — Method by oxidation by cerium(IV), reduction by iron(II) ammonium sulfate and amperometric back-titration with potassium dichromate

Détermination du plutonium dans des solutions d'acide nitrique — Méthode par oxydation par le cérium(IV), réduction par le sulfate d'ammonium et de fer(II), et titrage en retour par le dichromate de potassium, suivi par ampérométrie

Reference number
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Foreword

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Determination of plutonium in nitric acid solutions — Method by oxidation by cerium(IV), reduction by iron(II) ammonium sulfate and amperometric back-titration with potassium dichromate

1 Scope and field of application

This International Standard specifies a precise and accurate analytical method for determining plutonium in nitric acid solutions. The method is almost specifically for plutonium; it is suitable for the direct determination of plutonium in materials ranging from pure product solutions, to fast reactor fuel solutions with a uranium/plutonium ratio of up to 10 : 1, either before or after irradiation.

The method recommends that the aliquot of sample be weighed and that a weight titration be used in order to obtain adequate precision. This does not preclude using any alternative technique which can be shown to give an equivalent performance.

2 Principle

2.1 Oxidation of plutonium in a 1 mol/l nitric acid solution to plutonium(VI) with cerium(IV). At this acidity, 1 mmol of cerium(IV) will oxidize more than 60 mg of plutonium(IV) in less than 5 min. Addition of sulfamic acid to prevent nitrite-induced side reactions. Reduction of excess cerium(IV) by adding, drop by drop, a sodium arsenite solution, catalysed by osmium tetroxide, a slight excess of arsenite being added. Oxidation of this excess by adding, drop by drop, a 0,2 mol/l potassium permanganate solution until an excess of permanganate is present. Reduction of the excess of permanganate by adding, drop by drop, a 0,1 mol/l oxalic acid solution, iron(III) being used to catalyse the reduction. A small excess of oxalic acid does not interfere in the subsequent plutonium determination.

2.2 These reduction and oxidation stages can be followed amperometrically and the plutonium is left in the hexavalent state. Addition of sulfuric acid followed by a measured amount of standardized iron(II) ammonium sulfate solution in excess of that required to reduce the plutonium(VI) to plutonium(IV). Amperometric back-titration of the excess iron(II) and any plutonium(III) formed to produce iron(III) and plutonium(IV) using a standard potassium dichromate solution. Regular standardization of the iron(II) ammonium sulfate by titration with a standard potassium dichromate solution.

2.3 Calculation of the plutonium content from the back-titration for the plutonium(VI) to plutonium(IV) change, by reference to the standard potassium dichromate. The latter shall be checked, either directly or indirectly, against an internationally recognized plutonium reference material, using the same titration procedure, or against NBS potassium dichromate SRM 136 C.

3 Interferences

3.1 On the basis of information currently available, the method is free from interference from up to 10 mg quantities of commonly occurring cations, including the alkali and alkaline earth metals, Al, Fe, Cr, Mn, Cu, Zn and Mo, during the titration of 30 mg of plutonium.

3.2 Vanadium interferes quantitatively as a one electron change and neptunium as a two electron change. Technetium interferes non-quantitatively and this interference is negligible. Quantities of up to 200 mg of sulfate, 1 mg of chloride or 2 mg of phosphate do not interfere. Quantities of up to 1 mg of fluoride do not interfere if 500 mg of aluminium is added to complex the fluoride.

In the specific case of irradiated fast reactor fuel solutions, quantities of up to 200 mg of uranium and fission products, equivalent to a 5 % burn-up of the fuel, do not interfere (i.e they cause less than a 0,1 % bias).

3.3 However, neptunium interferes quantitatively. For neptunium/plutonium ratios up to 10 mg/g, a correction can be applied if the neptunium content is measured independently to ± 10 %. Vanadium and technetium are normally present at levels well below 0,5 % (m/m) of the plutonium in fast reactor fuel solutions and therefore do not interfere significantly.

4 Reagents

During the analysis, use only reagents of recognized analytical grade and distilled or deionized water.

4.1 Cerium(IV) nitrate, 550 g/l solution.

Dissolve 55 g of ammonium hexanitratocerate in nitric acid solution [$c(HNO_3)$ = 1 mol/l], dilute to 100 ml using the same solution. Mix.

4.2 Iron(III) nitrate/sulfamic acid, solution.

Dilute 63 ml of concentrated nitric acid (ϱ 1,42 g/ml) to 900 ml with water. Dissolve 9,7 g of sulfamic acid and 1,95 g of iron(III) nitrate nonahydrate in this solution and dilute to 1 000 ml with water. Mix.

Prepare a fresh solution each week.

4.3 Sulfuric acid, 5,6 % (V/V) solution.

Cautiously, with stirring, add 56 ml of concentrated sulfuric acid (ϱ 1,84 g/ml) to about 900 ml of cold water; mix and dilute to 1 000 ml with water.

4.4 Osmium tetroxide, 2,5 g/l solution.

WARNING — Osmium tetroxide is volatile and the vapour attacks the eyes; it should only be handled in a fume cupboard or glove box.

Add 4 ml of concentrated sulfuric acid (ϱ 1,84 g/ml) to 36 ml of water in a glass beaker and allow to cool. Dissolve the contents of a 0,1 g ampoule of osmic acid in this solution. Store the reagent in a glass bottle with a glass stopper and do not use more than one month after preparation.

4.5 Sodium arsenite, 65 g/l solution.

WARNING — Handle with care as sodium arsenite is poisonous.

Dissolve 13 g of sodium arsenite in water and dilute to 200 ml with water. Mix.

4.6 Potassium permanganate, 6,3 g/l solution.

Dissolve 0,63 g of potassium permanganate in 100 ml water. Boil gently for 15 min, cool to room temperature and filter through a plug of glass wool.

4.7 Oxalic acid, 12,6 g/l solution.

WARNING — Handle with care as oxalic acid is poisonous.

Dissolve 1,26 g of oxalic acid dihydrate in water and dilute to 100 ml with water. Mix.

4.8 Iron(II) ammonium sulfate, 39 g/l solution.

Dissolve 3,9 g of iron(II) ammonium sulfate hexahydrate in the sulfuric acid solution (4.3) and dilute to 100 ml using the same solution. Mix. The concentration of iron(II) in this solution is standardized regularly (see clause 7).

4.9 Potassium dichromate solutions

4.9.1 Potassium dichromate, concentrated solution.

Weigh a clean, dry 1 000 ml volumetric flask to within 0,01 g (m_1). Weigh out about 2,46 g of dried potassium dichromate ($K_2Cr_2O_7$) to within 0,000 1 g (m_2) and dissolve it in water. Transfer to the tared flask, dilute to 1 000 ml with water, weigh the flask plus contents to within 0,01 g (m_3), and finally mix well. Calculate the concentration of potassium dichromate in the solution (F_1), in milliequivalents per gram of solution, correcting for purity and applying an air buoyancy correction to the mass of solid dichromate but not to the mass of solution (the apparent mass of the latter being used in 8.1) from the formula

$$F_1 = \frac{m_2}{0{,}049\ 03\ (m_3 - m_1)}$$

4.9.2 Potassium dichromate, dilute solution.

Weigh, to within 0,001 g, approximately 80 g of concentrated potassium dichromate solution (4.9.1) in a weighing bottle (m_4) and transfer the bulk of the solution to a clean 2 000 ml volumetric flask. Reweigh the weighing bottle and any remaining contents to within 0,001 g (m_5). Adjust the volume of solution in the flask to 2 000 ml with water and mix thoroughly. Calculate the dilution factor, F_2, from the formula

$$F_2 = \frac{m_4 - m_5}{2\ 000}$$

without applying any buoyancy corrections.

4.9.3 Verification of the concentration

The concentration of the potassium dichromate solutions should be verified by comparison with an appropriate internationally recognized plutonium reference material : either pure plutonium metal (for example, NBS SRM 949e or EC NRM 10) or pure PuO_2 (EC NRM 122) may be used. The comparison should be made by taking at least three separate solutions of the selected reference material through the standard procedure.

Compare the mean result with the certified plutonium content; the potassium dichromate concentration (F_1) is acceptable if the agreement is better than 0,1 %.

Alternatively, the potassium dichromate solution may be verified by direct comparison with NBS potassium dichromate SRM 136 C, by analysing a pure plutonium solution using the method specified in this International Standard.

5 Apparatus

Normal laboratory equipment for a plutonium laboratory, and

5.1 Microammeter, capable of measuring up to 50 µA with a sensitivity of 0,01 µA.

5.2 Current source (constant potential), capable of supplying up to 50 µA at a constant potential, variable up to 500 mV.

5.3 Electrodes (pair), identical gold spade electrodes, having a surface area of about 0,5 cm^2 per side.

5.4 Magnetic stirrer, capable of controlled, low speed operation, without splashing.

5.5 Weighing burettes, soft-walled, polythene bottles, of 20 to 100 ml capacity, with a fine jet, suitable for adding the iron(II) ammonium sulfate (4.8) and potassium dichromate (4.9.1) solutions.

5.6 Dropping bottles, giving a drop size of about 0,01 ml, used for adding the arsenite, permanganate and oxalate solutions; the small drop size is of paramount importance in controlling the reactions described in 6.3 to 6.5.

5.7 Delivery pipette, capable of delivering 0,1 ml increments, to within ± 1 %, of the dilute potassium dichromate solution (4.9.2).

6 Procedure

6.1 Fill a clean, dry sample weighing bottle with sample solution and weigh to within 0,000 1 g (m_6). Transfer a portion of the sample, containing between 10 and 60 mg of plutonium and not more than 10 milliequivalents of free acid, to a 100 ml beaker and reweigh the sample weighing bottle to within 0,000 1 g (m_7).

NOTE — Any alternative method of measuring the sample aliquot shall be shown to be accurate to better than 0,05 %. An air buoyancy correction may be required if the corresponding plant measurement is on an absolute weight basis.

6.2 Add 1 ml of the cerium(IV) nitrate solution (4.1), wash down the walls of the beaker with 30 ml of the iron(III) nitrate/sulfamic acid solution (4.2) and insert the gold electrodes (5.3). Stir gently for 5 min and apply a potential (usually 200 to 300 mV) to the electrodes to give a current of 15 to 20 µA.

NOTE — The electrodes are inserted at this stage as the redox cycling process appears to prevent passivation of the electrodes. The successive redox stages are followed amperometrically.

6.3 Add 0,1 ml of the osmium tetroxide solution (4.4). Add the sodium arsenite solution (4.5), drop by drop, until the observed current falls to a steady reading of about 10 µA.

Continue to add single drops of the sodium arsenite solution, waiting 10 s between each addition, until one single drop results in a momentarily negative current reading. At this stage, wash down the walls of the beaker with 10 ml of the iron(III) nitrate/sulfamic acid solution.

NOTE — A typical amperometric curve for the cerium(IV)/arsenic(III) reaction is shown in figure 1. As each drop of arsenite solution is added, the observed current may decrease during mixing and then return to a steady reading. This current falls as more arsenite is added and the reaction proceeds, falling more rapidly as complete reduction of the cerium(IV) is approached. A few seconds after the addition of the final drop of the arsenite solution, the current decreases rapidly to a negative reading (− 3 to − 4 µA) before drifting up again to about + 6 µA [see figure 1a)].

6.4 Stir gently for at least 1 min, but not more than 2 min, after adding the final drop of the arsenite solution. Then immediately add the potassium permanganate solution (4.6), drop by drop, until the current falls to about 2 µA [see figure 1b)].

Add one further drop, which will result in a sharp increase in current to about 10 µA and a stable pink colour. Wash down the beaker walls with 10 ml of the iron(III) nitrate/sulfamic acid solution and stir for 3 min.

During this period, weigh the weighing burettes (5.5), filled with the iron(II) ammonium sulfate solution (4.8) (m_8) and the concentrated potassium dichromate solution (4.9.1) (m_9), to within 0,000 1 g in each case.

NOTE — Between 0,12 and 0,17 ml of the permanganate solution should be required, if the optimum excess of arsenite has been added at the appropriate stage in the procedure outlined in 6.3.

6.5 Add the oxalic acid solution (4.7), drop by drop, until the addition of one further drop causes no further reduction in current [see figure 1c)]. The pink permanganate colour should disappear. Add five drops (about 0,05 ml) in excess. Wash down the walls of the beaker with 10 ml of sulfuric acid solution (4.3).

6.6 Add sufficient iron(II) ammonium sulfate solution from a weighing burette to reduce the plutonium(VI) and leave a suitable excess for the titration. Wash down the beaker walls with 5 to 10 ml of sulfuric acid solution.

NOTE — 1 g of iron(II) ammonium sulfate solution will reduce approximately 10 mg of plutonium(VI); 0,5 to 1 g of the iron(II) ammonium sulfate solution is a suitable excess for titration. A pale blue colour, due to plutonium(III), is visible when a suitable excess of iron(II) has been added, provided that other coloured ions are absent.

6.7 Stir gently for 3 to 5 min. Ensure that the microammeter (5.1) is showing a steady current of 10 to 20 µA.

NOTE — A rapidly falling current indicates that insufficient iron(II) has been added.

6.8 Add the concentrated potassium dichromate solution from the weighing burette until just before the end point, i.e. until the current reading is about 5 µA. Wash down the walls of the beaker with sulfuric acid solution.

NOTE — Figure 2 shows a typical titration curve. Initially, the decrease in current per drop of titrant is very small, but approach to the end point is indicated by progressively larger decreases in current.

6.9 Continue the titration by adding 100 µl increments of the dilute potassium dichromate solution (4.9.2) from a delivery pipette. After each addition, record the current reading; continue the titration until at least two current readings after the end point (indicated by a steady, low current) have been recorded.

NOTES

1 Sufficient concentrated potassium dichromate solution should be added in the first part of the titration so that between two and ten 100 µl increments of the dilute potassium dichromate solution are needed to reach the end point.

2 If the titration end point is accidentally overshot, a few more drops of the 0,1 mol/l iron(II) ammonium sulfate solution can be added, allowing the end point to be approached a second time.

6.10 Locate the exact end point from a graph of current versus number of 100 µl increments of the dilute potassium dichromate solution. The end point is the number of increments (n_1) at the point of intersection shown in figure 2.

6.11 Reweigh the weighing burettes containing the iron(II) ammonium sulfate solution (m_{10}) and the potassium dichromate solution (m_{11}), to within 0,000 1 g in each case.

7 Standardization of the iron(II) ammonium sulfate solution

NOTE — The iron(II) ammonium sulfate solution should be standardized at least once a day and the factor recorded on a control chart.

7.1 Add 0,5 ml of the cerium(IV) nitrate solution to a 100 ml beaker and wash down the beaker walls with 30 ml of the iron(III) nitrate/sulfamic acid solution. Insert the electrodes, stir gently for 5 min and apply a potential to the electrodes to give a current of 15 to 20 µA.

7.2 Follow the basic procedure as outlined in 6.3 to 6.5, recording the masses of the burettes containing the iron(II) ammonium sulfate solution (m_{12}) and the concentrated potassium dichromate solution (m_{13}).

7.3 Add about 5 g of the iron(II) ammonium sulfate solution from a weighing burette. Wash down the beaker walls with 5 to 10 ml of the sulfuric acid solution.

7.4 Follow the basic procedure as outlined in 6.7 to 6.11, recording the final masses of the burettes containing the iron(II) ammonium sulfate solution (m_{14}) and the potassium dichromate solution (m_{15}), and the number of increments at the end point (n_2).

8 Expression of results

8.1 Method of calculation

8.1.1 Calculate the standardization factor for the iron(II) ammonium sulfate solution, F_3, from the formula

$$F_3 = \frac{0{,}1\, n_2 F_2 + (m_{13} - m_{15})}{m_{12} - m_{14}}$$

where

F_2 is the potassium dichromate dilution factor (see 4.9.2);

n_2 is the number of increments at the end point (see 7.4);

$m_{13} - m_{15}$ and $m_{12} - m_{14}$ are, respectively, the masses of the potassium dichromate solution and the iron(II) ammonium sulfate solution, determined in the standardization titration of the iron(II) ammonium sulfate solution (see 7.2 and 7.4).

8.1.2 Calculate the plutonium content, P_1, of the sample solution expressed in milligrams of plutonium per gram of sample solution, from the formula

$$P_1 = \frac{F_1 A_r \{F_3 (m_8 - m_{10}) - [0{,}1\, n_1 F_2 + (m_9 - m_{11})]\}}{2\,(m_6 - m_7)}$$

where

F_1 is the potassium dichromate concentration (see 4.9.1);

A_r is the relative atomic mass of the plutonium (see 8.1.3);

F_3 is the standardization factor for the iron(II) ammonium sulfate solution (see 8.1.1);

$m_8 - m_{10}$ and $m_9 - m_{11}$ are, respectively, the masses of the iron(II) ammonium sulfate solution and the potassium dichromate solution, determined in the sample titration (see 6.4 and 6.11);

n_1 is the number of increments at the sample end point (see 6.10);

F_2 is the potassium dichromate dilution factor (see 4.9.2);

$m_6 - m_7$ is the mass of the sample, expressed in grams (see 6.1).

8.1.3 Calculate the relative atomic mass of the plutonium, A_r, in the sample material from the formula

$$A_r = \left(\frac{m_{238}}{238{,}050} + \frac{m_{239}}{239{,}052} + \frac{m_{240}}{240{,}054} + \frac{m_{241}}{241{,}057} + \frac{m_{242}}{242{,}059} + \frac{m_{244}}{244{,}064} \right)^{-1}$$

where m_{238}, m_{239}, etc. are the mass fractions of the plutonium isotopes ^{238}Pu, ^{239}Pu, etc., determined by mass spectrometry in the plutonium sample.

8.2 Correction for neptunium

Calculate the corrected plutonium concentration, Pu, from the formula

$$Pu = P_1 \left(1 - N \frac{237}{239}\right)$$

where

P_1 is calculated in accordance with 8.1.2;

N is the molar ratio of neptunium to plutonium in the sample which shall be measured or calculated with an accuracy of ± 10 %.

8.3 Repeatability

The coefficient of variation for a single determination is better than 0,1 % when the method is applied to a pure plutonium solution. A slight deterioration in performance shall be expected when the method is used in a remote-handling facility with highly radioactive solutions.

8.4 Bias

The bias of the method is less than 0,1 % when applied to pure plutonium solutions and less than 0,3 % when applied to irradiated fuel solutions.

9 Test report

The test report shall include the following information :

a) identification of the sample;

b) the reference of the method used;

c) the results and method of expression used;

d) any unusual features noted during the test;

e) any operations not included in this International Standard or regarded as optional.

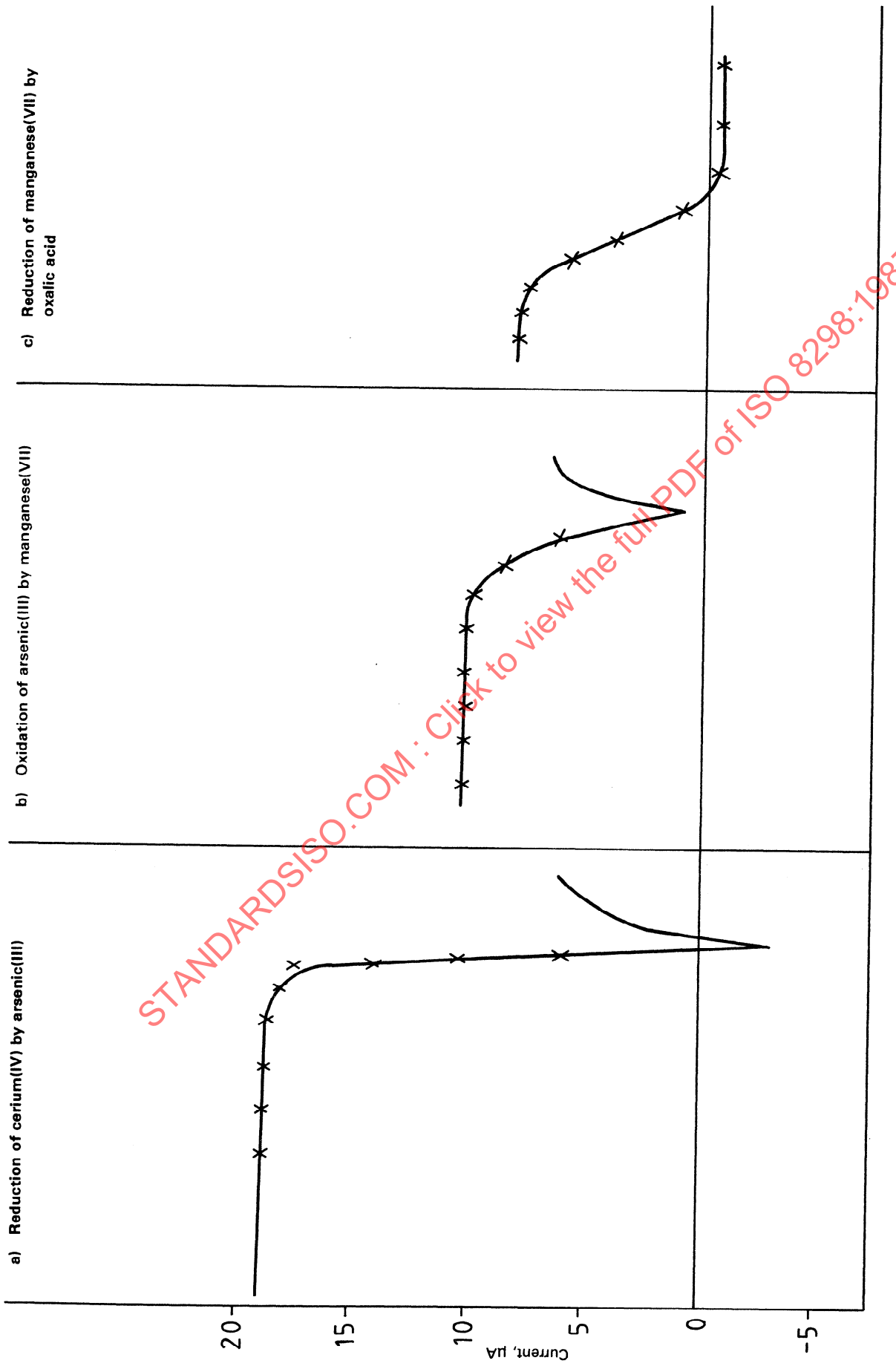

Figure 1 — Amperometric detection of intermediate reactions

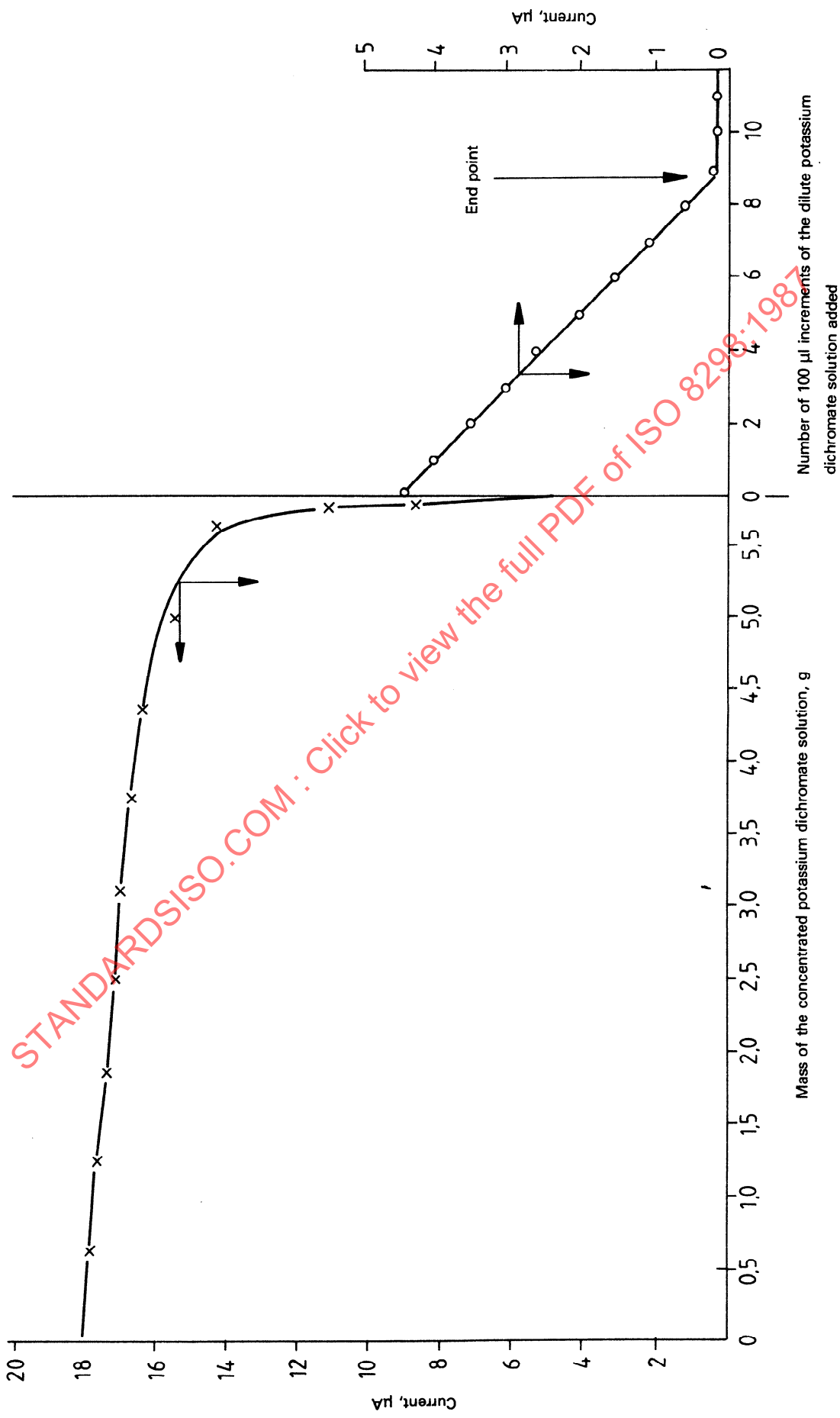

Figure 2 — Typical amperometric titration curve