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Nuclear fuel technology — Dissolution of plutonium dioxide-containing materials —

Part 1:
Dissolution of plutonium dioxide powders

Technologie du combustible nucléaire — Dissolution des matériaux contenant du dioxyde de plutonium —

Partie 1: Dissolution des poudres de dioxyde de plutonium

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Contents

Page

Foreword

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This document was prepared by Technical Committee ISO/TC 85, *Nuclear energy, nuclear technologies, and radiological protection*, Subcommittee SC 5, *Nuclear installations, processes and technologies*.

A list of all the parts in the ISO 18256 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document describes a method to dissolve powder samples of plutonium oxide to provide suitable aliquots for subsequent analysis of elemental concentration and isotopic composition.

Nuclear fuel technology — Dissolution of plutonium dioxide-containing materials —

Part 1:
Dissolution of plutonium dioxide powders

1 Scope

This document specifies the dissolution of powder samples of plutonium oxide for subsequent determination of elemental concentration and isotopic composition.

2 Normative references

There are no normative references in this document.

3 Terms and definitions

No terms and definitions are listed in this document.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

- ISO Online browsing platform: available at https://www.iso.org/obp
- IEC Electropedia: available at http://www.electropedia.org/

4 Summary of the method

Among the factors affecting the formation of solid solution and hence, the ease of dissolution are:

- the method of fuel fabrication (i.e. mechanically blended oxides, co-precipitated oxides, or sol-gel oxides);
- the degree of sintering.

Therefore, different dissolution methods are applied according to the type of plutonium oxide sample to be dissolved. For high-fired plutonium oxide procedure can be different.

The radiological hazard of plutonium and the need to minimize the waste shall be taken into account when choosing the mass of the sample to be dissolved. In most cases, PuO_2 masses between 0,1 g and 1 g are appropriate for the subsequent analysis.

For the highest possible assay accuracy only gravimetric dissolution methods are recommended. However for a less critical assay, volumetric dissolution may be appropriate.

For grain-size powders, the sample is transferred in a pre-weighed flask or vial made of glass, high-density polyethylene (HDPE), polytetrafluoroethylene (PTFE), Nalgene™1) or other container types, but the choice of the container has consequences.

- When using a glass dissolution vessel, the added fluoride will attack the glass (resulting in a falsification of the pre-weighed tare) but with the benefit that the fluoride is ultimately removed from the solution via release of volatile SiF_4. The resulting reduction in fluoride content of the final solution guards against the formation of insoluble plutonium fluoride (especially below 8 M), which would negatively bias the plutonium element content up to 0,1 % [or more when large quantities of hydrofluoric acid (HF) are used]. The tare mass of the etched glass vessel may be re-established by careful cleaning, drying and re-weighing of the vessel.
- HDPE, PTFE or Nalgene™1) dissolution vessels are not reactive to HF, therefore tare mass remains unaffected. However, these materials have the disadvantage that fluoride ions in the dissolution liquor promote the precipitation of insoluble plutonium fluoride when the oxidation state of plutonium is reduced from IV to III (e.g. by later volume adjustments using a low molarity acid).

An aqueous dissolving mixture comprising nitric acid (about 8 mol/l to 14 mol/l) and an effective catalytic amount of fluoride ions from either hydrofluoric acid (about 0,05 mol/l to 0,1 mol/l) or ammonium hydrogen bifluoride (about 2 g/l) is added and the pre-weighted dissolution vessel is closed with a reflux cap (or watch glass). The vessel is placed on a hotplate and heat is applied until the dissolution is completed. The solution is then ready for concentration determination of plutonium per gram of solution by suitable analytical methods. The solution can be used for other analyses, e.g. plutonium isotopic abundances or impurities determination.

Dissolution can be either performed in a closed vessel, at temperature below nitric acid boiling point, or with a reflux for higher temperature in order to accelerate the dissolution process and reduce dissolution time.

More effective dissolution of refractory (or “high fired PuO_2“) plutonium oxide (fired to T = 1 000 °C) can be carried out by forming ceric nitrate in nitric acid or by using sodium carbonate fusion.

5 Apparatus and reagents

WARNING — Because of the radiological hazard of plutonium, it shall be handled in glove boxes or hot analytical cells and extreme care shall be taken to prevent direct contact, inhalation or ingestion.

5.1 Apparatus

Normal laboratory equipment for a plutonium laboratory and, in particular, the following.

5.1.1 Analytical balance, with a 200 g capacity and an accuracy of 0,001 g or better if needed.

5.1.2 Dissolution vessels, dissolution flask or vial with a PTFE-lined screw cap.

The volume of the flask should be adapted to the volume of solution for the appropriate concentration required for subsequent analysis. PTFE-lined screw cap is recommended for the samples which will be stored for long term.

5.1.3 Glass or **PTFE reflux cap,** or **watch glass**.

5.1.4 Shielded hotplate, equipped with a temperature control unit and a fume hood.

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[1] Nalgene™ is the trademark of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of the product named. Equivalent products may be used if they can be shown to lead to the same results.

5.1.5 PTFE coated tweezers.

5.2 Reagents

Use only reagents of recognized analytical grade.

CAUTION — Prepare the reagents in accordance with the local laboratory safety instructions. Nitric acid and hydrofluoric acid are very corrosive and can caused painful burns. Hydrofluoric acid is particularly dangerous, therefore safety precautions and working instructions shall be available and understood.

5.2.1 Water, in accordance with grade 3 of ISO 3696 is recommended.

5.2.2 Concentrated nitric acid, $w(HNO_3) = 65\ \%$, $c(HNO_3) = 14{,}4$ mol/l (density $\rho_{20\,°C}$ ~1,39 g/cm^3).

5.2.3 Nitric acid, $c(HNO_3) = C_2$ mol/l prepared by dilution of concentrated nitric acid (5.2.2) with water (5.2.1). C_2 can be either 8 mol/l or 0,2 mol/l.

5.2.4 Hydrofluoric acid, $w(HF) = 40\ \%$, $c(HF) = 22$ mol/l stored in a polyethylene dropper bottle.

5.2.5 Ammonium hydrogen bifluoride, NH_4HF_2.

5.2.6 Mixed nitric-hydrofluoric acid solution, $c(HNO_3) = 14$ mol/l or 7 mol/l to 8 mol/l, $c(HF)$ approximately 0,05 mol/l to 0,1 mol/l.

The following is an example of a suitable method to prepare the solution.

In a 200 ml polyethylene flask:

— add about 1 ml of hydrofluoric acid (5.2.4);

— adjust the volume of the flask with concentrated nitric acid (5.2.2) or 7 mol/l to 8 mol/l nitric acid (5.2.3),

— homogenize.

Never add concentrated HF to a plutonium nitrate solution since this may cause precipitation of plutonium fluoride which may not be re-dissolved.

5.2.7 Mixed nitric-ammonium hydrogen bifluoride solution, $c(HNO_3) = 14$ mol/l, $c(NH_4HF_2) = 2$ g/l, $c(HF^-) = 0{,}07$ mol/l.

This reagent is prepared by dissolution of ammonium hydrogen bifluoride (5.2.5) in concentrated nitric acid (5.2.2).

6 Sample dissolution

6.1 Procedure for common plutonium containing materials

a) Calibrate the balance and check the calibration with appropriate standard weights.

b) For specific sample, weigh the sample in its original container and note the gross sampling mass, m_S.

c) Weigh a labelled dissolution vessel, including the labelled cap, m_1.

d) Transfer the sample into the vessel. The amount of powder should be between a few 100 mg and 5 g. Be very careful when transferring powder to avoid the presence of sample on the outside or in the neck of the vessel since material on the outside will induce a weighing error and powder in the neck of the vessel is difficult to recover.

e) Powders are also hygroscopic and therefore prone to moisture uptake. The weighing of powders should be carried out confidently and quickly with minimum exposure to the analytical cell atmosphere. It is preferable that such manipulations are done in a dry inert atmosphere.

f) Close the vessel and weigh it again to obtain the gross mass, m_2.

Sample mass is the difference $m_2 - m_1$.

g) Calculate the quantity of the mixed nitric-hydrofluoric acid solution (5.2.6) or mixed nitric-ammonium hydrogen bifluoride solution (5.2.7) needed, V_1, which is proportional to the sample mass and add it to the weighed sample (i.e. at minimum 5 ml ± 1 ml of solution for 1 g of solid sample are needed). It can be more according to the requirement e.g. Pu concentration and acidity of the analysis performed on the Pu solution. However, larger amounts of acid will result in an increased attack of glass dissolution vessels or may cause increased PuF_4 formation when no-glass vessels are used.

Although the solution volume decreases with heating, the plutonium concentration in g/l for fairly pure PuO_2 is estimated by the following formula:

$$[\mathrm{Pu}]=\frac{(m_2-m_1)\times 0{,}88}{V_1}\times 1\,000 \quad (1)$$

$$[\mathrm{Pu}]=\frac{m_S\times 0{,}88}{V_1}\times 1\,000 \quad (2)$$

where

$(m_2 - m_1)$ or m_S	is the sample mass, in g;
V_1	is the volume of the mixed nitric-hydrofluoric acid solution or mixed nitric-ammonium hydrogen bifluoride solution, in ml, with a density ρ_1;
0,88	is the $Pu/Pu0_2$ mass fraction.

i) Place the cap on the flask.

h) Swirl the vessel to bring the whole sample in contact with the acid and to avoid that powder becomes airborne.

j) Weigh the labelled vessel with the original cap, m_3.

k) Replace the cap with a reflux cap (or watch glass) and store the original cap in a safe place.

l) Put the vessel on the hotplate. The temperature controller should be set at 90 °C ± 5 °C to avoid boiling. Another way to proceed is to use a reflux system to increase heating temperature in order to accelerate the dissolution process and reduce dissolution time.

m) Make a visual assessment of whether dissolution is complete (a green, brown or green/brown coloured solution, no more reaction, no undissolved residues). Otherwise, continue the heating procedure.

For µ-size powder particles:

- a normal dissolution time of about 7 h to 8 h may be necessary for temperature set at 90 °C;
- at higher temperature, using a reflux heating device the dissolution time could be reduced to 1 h or 2 h.

High fired PuO_2 powder can take much longer to dissolve.

Occasional gentle swirling will speed up the dissolution.

n) After cooling for 30 min to 2 h, weigh the labelled flask with the cap, m'_3, and check that mass lost during dissolution $\frac{m_3 - m'_3}{m_3}$ is less than that defined in accordance with the intended accuracy of the analysis performed later.

NOTE This is important when a volumetric analytical method is used. For gravimetric methods this requirement is less important.

For instance, criteria can be $\frac{m_3 - m'_3}{m_3} < 1\ \%$.

In the solution of dissolved Pu, the Pu concentration, [Pu], can then still be estimated by Formula (1).

6.2 Solution adjustment (optional)

Depending on the choice of the analytical method, the dissolved plutonium solution may need further dilution with pure nitric acid solution to reach an appropriate concentration. For example, the target value for assay by K-edge densitometry is 150 g of Pu/l, whereas potentiometric titration or spectrometric assay requires far lower concentrations.

Never add pure water to a plutonium nitrate solution as this results in the formation of Pu colloids which may remain invisible to some analytical techniques. When volume adjustments are needed, diluted nitric acid solution rather than water should be used.

Some techniques may also have specific requirement regarding the molarity of the final solution matrix. Using spectrophotometry as a specific example, optimum assay conditions may stipulate 20 g of Pu/l in an 8 mol/l matrix of nitric acid. In this instance, a PuO_2 mass of 0,5 g and a volume, V_1, of 10 ml of fluorated nitric acid is appropriate and may be adjusted with 6 ml of a 0,2 mol/l nitric acid solution, V_2.

Calculate the volume V_2 of HNO_3 C_2 mol/l (5.2.3) to add to the obtained Pu solution in order to adjust Pu concentration and acidity.

Pu concentration in g/l in the adjusted solution can be estimated by Formula (3):

$$[\mathrm{Pu}] \approx \frac{(m_2 - m_1) \times 0{,}88}{V_1 + V_2} \times 1\,000 \tag{3}$$

Acidity in mol/l in the adjusted solution can be estimated by Formula (4):

$$[\mathrm{H}^+] = \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2} \tag{4}$$

where

$(m_2 - m_1)$	is the sample mass, in g;
V_1	is the volume of nitric-hydrofluoric acid solution or mixed nitric-ammonium hydrogen bifluoride solution, in ml;
V_2	is the volume of nitric acid solution for adjustment, in ml;
0,88	is the conversion Pu/$Pu0_2$ coefficient;
C_1	is the acidity of the concentrated nitric acid (about 14 mol/l);
C_2	is the acidity of the nitric acid used for adjustment.