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

Part 2:
**Dissolution of MOX pellets and
powders**

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

*Partie 2: Dissolution de pastilles et poudres de MOX (ou mélanges
d'oxydes)*

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

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 samples consisting of MOX pellets or powders to provide suitable aliquots for subsequent analysis of elemental concentration and isotopic composition.

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

Part 2: Dissolution of MOX pellets and powders

1 Scope

This document specifies the dissolution of samples consisting of MOX pellets or powders to provide suitable aliquots for subsequent analysis 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, microwave denitrated oxides or sol-gel oxides);
- the degree of sintering.

Therefore, different dissolution methods are applied depending on the type of MOX sample to be dissolved.

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. A MOX mass of 0,1 g to 10 g should be sufficient for most of the analyses. Some analysis may however require more material.

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^{TM1)} 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 SiF₄. 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^{TM1)} 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 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 or uranium per gram of solution by suitable analytical methods. The solution can be used for other analyses, e.g. plutonium or uranium isotopic abundances or impurities determination.

5 Apparatus and reagents

WARNING — Because of the radiological hazard of plutonium, it shall be handled in glove boxes or hot 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 capacity up to 1 200 g and an accuracy of 0,001 g.

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 Reflux condenser.

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

5.1.6 PTFE coated tweezers.

5.2 Reagents

Use only reagents of recognized analytical grade.

1) NalgeneTM 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.

CAUTION — Prepare the reagents in accordance with the local laboratory safety instructions. Nitric acid and hydrofluoric acid are very corrosive and can cause 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, $w(\text{HNO}_3) = 65\%$, $c(\text{HNO}_3) = 14,4 \text{ mol/l}$ (density $\rho_{20\text{ °C}} \sim 1,39 \text{ g/cm}^3$).

5.2.3 Nitric acid, $c(\text{HNO}_3) = C_2 \text{ mol/l}$ prepared by dilution of concentrated nitric acid (5.2.2) with water (5.2.1).

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

5.2.5 Ammonium hydrogen bifluoride, NH_4HF_2 .

5.2.6 Mixed nitric-hydrofluoric acid solution, $c(\text{HNO}_3) = 14 \text{ mol/l}$ or 7 mol/l to 8 mol/l , $c(\text{HF}) = 0,05 \text{ mol/l}$ to $0,1 \text{ mol/l}$.

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, $c(\text{HNO}_3) = 14,4 \text{ mol/l}$, $c(\text{NH}_4\text{HF}_2) = 2 \text{ g/l}$, $c(\text{HF}) = 0,07 \text{ mol/l}$.

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) Weigh a labelled dissolution vessel with a labelled cap, m_1 .
- c) Transfer the sample into the vessel. Be very careful when transferring powder or crushed pellet 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.
- d) 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
- e) Close the vessel and weigh it again to obtain the gross mass, m_2 .

Sample mass is the difference $m_2 - m_1$.

- f) 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. about at minimum 5 ml \pm 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 solution. However, larger amounts of acid will result in an increased attack of glass dissolution vessels or may cause increased PuF₄ formation when no-glass vessels are used.

Although the solution volume decreases with heating, the heavy metal concentration for MOX product is estimated by [Formula \(1\)](#):

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

where

$(m_2 - m_1)$ 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;

0,88 is the (Pu + U)/(PuO₂ + UO₂) mass fraction.

- g) In the case of MOX powder or crushed pellet, the acid should be added slowly due to the high reaction rate between the acid and the UO₂ powder. For MOX pellet the acid can be added in one step.
- h) Swirl the vessel to bring the whole sample in contact with the acid.
- i) Place the cap on the vessel.
- j) Weigh the labelled vessel with the 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. For pellets, the temperature controller should be set in a way to bring the solution to a boil. In this case, the dissolution shall be performed under reflux conditions. For powder or crushed pellet, the temperature controller should be set at 70 °C to 110 °C.
- 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 pellets, a normal time of about 18 h or more may be necessary. Occasional gentle swirling will speed up the dissolution. For powder, a normal time less than that for pellets may be necessary.

- n) After cooling for 30 min to 2 h, weigh the labelled vessel with the original 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 MOX, the heavy metal concentration can then still be estimated by [Formula \(1\)](#).

6.2 Solution adjustment (optional)

Depending on the choice of the analytical method, the obtained dissolved MOX 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 would be 150 g Pu/l, whereas potentiometric titration or spectrophotometric assay requires far lower concentration.

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 Pu/l in an 8 mol/l matrix of nitric acid. In this instance a PuO₂ 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 .

- a) Calculate the volume V_2 of HNO₃ C_2 mol/l (5.2.3) to add to the obtained Pu solution in order to adjust the Pu concentration and acidity:

Pu concentration in g/l in the adjusted solution can be estimated by [Formula \(2\)](#):

$$[U]+[Pu] \approx \frac{(m_2 - m_1) \times 0,88}{V_1 + V_2} \times 1\,000 \quad (2)$$

To obtain element concentrations for U and Pu requires prior knowledge of the approximate U/Pu ratio of the MOX material.

Acidity in mol/l in the adjusted solution can be estimated by [Formula \(3\)](#):

$$[H^+] \approx \frac{(V_1 \times C_1) + (V_2 \times C_2)}{V_1 + V_2} \quad (3)$$

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/PuO₂ and U/UO₂ 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.

- b) After introducing V_2 of nitric acid solution (5.2.3) with a density ρ_2 , if the vessel is weighed (m_4), V_2 is given by [Formula \(4\)](#):

$$V_2 = \frac{(m_4 - m'_3)}{\rho_2} \quad (4)$$

where