INTERNATIONAL STANDARD

ISO 12803

First edition
1997-09-15

Representative sampling of plutonium nitrate solutions for determination of plutonium concentration

Échantillonnage représentatif de solutions de nitrate de plutonium en vue de déterminer la concentration du plutonium

Reference number
ISO 12803:1997(E)

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.

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.

International Standard ISO 12803 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, subcommittee SC 5, *Nuclear fuel technology*.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central
Printed in Switzerland

Representative sampling of plutonium nitrate solutions for determination of plutonium concentration

1 Scope

This International Standard describes the basic precautions necessary to ensure that installed tank mixing and sampling systems achieve representative samples from a batch of pure final-product plutonium nitrate solution free from organic compounds and suspended solids, and that the samples remain representative until used.

NOTE — When this International Standard is applied, it can be shown that the difference between the plutonium concentration of the samples, taken from the batch, and the average concentration of plutonium in the solution is less than 0,2 %.

2 Rationale

Plutonium processing plants vary in design, process and installation. Therefore standard procedures for sampling of plutonium nitrate storage tanks cannot be established. However, the necessity for representative samples of the tank contents is absolutely fundamental for accurate plutonium measurement.

The chemical and physical properties of plutonium nitrate solutions introduce many factors which can hinder representative sampling. These include:

a) storage in shielded tanks for radiation protection, with consequently long sample lines;

b) storage in tanks of very complex geometry for criticality control purposes, with a consequent need for prolonged mixing to avoid stagnant zones;

c) high density and viscosity, particularly at the highest plutonium concentrations, leading to prolonged mixing to avoid significant density differences within a single tank;

d) the possible presence of a second phase, either precipitated plutonium species or organic liquids, which would make totally representative sampling essentially impossible;

e) the tendency for plutonium(IV) nitrate to undergo hydrolysis and polymerization at low acidity, high concentration and high temperature;

f) high yields of radiolytic off-gases, particularly at high plutonium-238 or high plutonium(VI) content, leading to the build-up of gas mixtures under pressure, and the possibility of incorrect volume measurements;

g) high evaporation rates, due to both self-heating and self-radiolysis, especially if mixing is by gas sparging;

h) temperatures above ambient, leading to thermal expansion of solution and the tank and the possibility of incorrect volume measurements.

Many of the problems mentioned can be avoided or controlled by appropriate engineering at the design stage. However, it is essential that for each storage tank installation a mixing and sampling procedure is drawn up and is experimentally verified as yielding truly representative samples. After any plant modification, the mixing and sampling procedures shall be revalidated. Finally, the tank shall be equipped with a means of accurately measuring the total quantity of solution present or transferred at the time of sampling.

Equally, the samples taken shall be handled and stored in such a manner that the subsequent analytical measurements can be reliably related to the tank contents and the time of sampling. Plutonium nitrate solutions undergo concentration changes during storage, due to both unusually high evaporation rates and high yields of radiolytic off-gases. The recommended handling and storage techniques are designed to reduce to acceptable low levels any changes arising between sampling and analysis, or at least to allow adequate correction for unavoidable changes during storage.

However, even with these procedures it should be remembered that sample stability is very dependent upon the container material. If impermeable materials are used for the container, it shall be capable of containing the radiolytic gas pressure. More permeable materials allow radiolytic gases to diffuse away, but also allow water vapour to diffuse out. The container material shall resist corrosion by the acidic plutonium solution. The seal shall prevent physical loss of plutonium during storage and when a container is being opened.

3 Tank mixing and sampling

The following recommendations are given to reduce systematic and random sampling errors to a tolerably low level.

3.1 The plutonium nitrate solution should be thoroughly homogenized to ensure that the solution is uniform in isotopic, chemical and physical charateristics.

To achieve this, a verified mixing procedure should be drawn up for each installation. The mixing time and conditions will need to consider effects due to:

a) tank geometry, including the possibility that some parts of the tank may not be effectively circulated under some conditions;

b) differences in temperature and/or density between different parts of the tank;

c) the mechanics of the homogenization procedure used (i.e. stirring, sparging or recirculation).

3.2 The tank contents should be free from any organic phase and undissolved or precipitated solids. If any organic phase is visible, or suspended solids are present at a concentration greater than 0,01 $g \cdot l^{-1}$, the tank contents should be filtered or centrifuged before sampling.

3.3 The plutonium concentration should be such that it remains well within the solubility limit for both the free nitric acid concentration and likely temperature range experienced by the tank. Typically, for a free nitric acid concentration of 2 $mol \cdot l^{-1}$ and a temperature of 20 °C, plutonium concentrations of the order of 300 $g \cdot l^{-1}$ are acceptable.

3.4 As far as possible, use short direct sampling lines with small cross-section. The sampling system used should be shown to have negligible effect on solution concentrations (e.g. due to evaporation or cross-contamination during sampling).

3.5 Before starting sampling, sampling lines should be rinsed with the solution to be sampled. To prevent cross-contamination, the first sample collected should be rejected.

3.6 Samples should be taken either during recirculation of the solution or during its transfer to another tank.

3.7 Sample containers should be completely dry. Sample volume should exceed half of the bottle volume. Several samples should be taken, if possible from different parts of the tank, and with the shortest practicable time intervals between samples. It is recommended that individual samples are analysed for plutonium content. It is recommended to record the date of sampling for each sample.

3.8 For routine use with a verified mixing and sampling procedure, density measurements can be used to test homogeneity. The density of the plutonium nitrate solution should be sufficiently different from the density of any likely diluent (see ISO 11597[1)]).

1) ISO 11597:1995, *Verification of samples of uranyl or plutonium nitrate solutions by density measurement.*

The density of each sample should be measured, preferably within 30 min of sampling, and the density differences compared using the homogeneity test. Provided the homogeneity requirements are met, a bulk of the individual samples may be analysed for plutonium content.

3.9 The total liquor content of the tank should be measured at the time of sampling, with an accuracy comparable to that achieved on subsequent plutonium measurements on the samples.

4 Sample storage

The following procedures are given to ensure that the sample concentration at the time of analysis can be related to the sample concentration at the time of sampling.

4.1 Clearly mark samples to ensure unequivocal identification.

4.2 Fill the samples of plutonium nitrate solution into suitable clean and dry stoppered leakproof bottles. A volume of 5 ml to 10 ml of plutonium nitrate solution in a 15 ml bottle (or *pro rata* for larger bottle sizes) is recommended as the best compromise between evaporation effects and container pressurization by radiolytic gases.

4.3 Whenever possible, handle and store the bottle at ambient temperature in an upright position without wetting the neck of the bottle, to avoid both sample concentration and liquor condensation effects around the bottle stopper.

4.4 Close immediately after filling or removal of an aliquot. Beware of radiolytic gas pressure when removing the bottle stopper.

4.5 Complete the analysis of the sample within 48 h, or alternatively apply one of the techniques described in 4.6, 4.7 or 4.8 from the time of sampling.

4.6 Weight correction techniques:

a) Use sample bottles that are proven to have a tare weight stable to better than 0,001 g under long-term glovebox storage conditions.

b) Weigh the empty sample bottle plus stopper after application of all identification marks, which shall be permanent and stable. Record the mass as w_1.

c) Weigh the sample bottle plus stopper after filling with sample. Record the mass as w_2.

d) Store and handle the sample bottle in order to keep it clean, dry and dust-free; ensure that the solution does not wet the neck of the bottle. Regularly check that the bottle stopper is in place.

e) Just before use, remove and replace the stopper to release any gas pressure and reweigh the sample bottle plus stopper and sample. Record the mass as w_3.

f) Use a portion of the stored sample for analysis within 48 h of reweighing (for mass w_3). Calculate the true concentration of analyte y from the measured concentration x using the expression:

$$y = \frac{w_3 - w_1}{w_2 - w_1} x$$

g) Analysis based on this storage technique becomes less reliable if storage time and conditions do not satisfy the following criterion: the mass change during storage should be less than 1 % of the sample mass, i.e.

$$(w_2 - w_3) < 0{,}01\ (w_2 - w_1)$$

4.7 Pre-weighed aliquot technique:

a) Within 48 h of taking the samples, weigh the required number of appropriately sized aliquots into separate, sealable containers. Record the mass of each aliquot. Ensure that each container is uniquely identified.

b) Seal the containers and store them in an upright position, under conditions that keep the container clean, dry and free from dust.

c) For analysis, open the container and quantitatively transfer the contents to the analysis equipment. Wash out the storage container and its seal with dilute acid and add the washing to the sample in the analysis equipment. The volume, strength and type of acid used should be compatible with the chosen analytical technique.

d) There is no time limit for the application of this storage technique. However, storage containers and conditions shall be chosen such that radiolysis gas pressure does not rupture the container, that the aliquot remains in solution and that the whole aliquot can be recovered for analysis without risk of contamination from the container exterior during washout.

4.8 Sample dilution technique:

The stability of concentrated samples can be improved by diluting the sample to ~ 20 $g \cdot l^{-1}$ plutonium before storage, using mass/mass dilution techniques.

4.9 For samples stored longer than four months, a plutonium-241 decay correction should be applied.

5 Verification

Because plant installations differ in detail, the mixing and sampling procedures shall be verified before use. Any subsequent changes in plant or operation shall be considered for possible sources of error.

Similarly, laboratory storage conditions vary from laboratory to laboratory. The suitability of proposed storage conditions shall be verified before use. Subsequent changes in laboratory techniques, container materials, plutonium concentration or isotopic composition shall be considered for possible sources of error.