INTERNATIONAL STANDARD

ISO 11597

First edition
1995-07-15

Verification of samples of uranyl or plutonium nitrate solutions by density measurements

Qualification d'échantillons de solutions de nitrate d'uranyle ou de plutonium par mesure de la masse volumique

Reference number
ISO 11597:1995(E)

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International Organization for Standardization
Case Postale 56 • CH-1211 Genève 20 • Switzerland
Printed in Switzerland

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 11597 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

Annex A forms an integral part of this International Standard. Annex B is for information only.

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Verification of samples of uranyl or plutonium nitrate solutions by density measurements

1 Scope

This International Standard establishes the use of density measurements for verifying the homogeneity of an industrial solution of uranyl or plutonium nitrate of nuclear grade, and the representativity of samples drawn from such a solution.

It is applicable to solutions of densities greater than 1,25 g/cm^3, containing 100 g/l to 400 g/l of uranium or 50 g/l to 300 g/l of plutonium, in 0,2 mol/l to 8 mol/l nitric acid. The procedure assumes that the only cause of heterogeneity of the industrial solution can be an incomplete mixing with aqueous diluents containing 0 to 7 mol/l nitric acid.

The procedure is intended to provide a quick test which can be used directly at the sampling station to accept or reject the samples taken for fissile material accountability analysis.

It requires a dip tube system for measuring the density and the volume of the solution in the tank in accordance with future International Standards.

NOTE 1 The statistical concepts used in this International Standard are described in ISO 10980.

2 Principle

2.1 The procedure is based on experimental correlations between the density, the free nitric acid concentration and the concentration of uranium (table 1) or plutonium (table 2).

2.2 The homogeneity of the solution is verified first by checking that the densities of successive samples lie within preset limits.

2.3 The representativity of the last sample is then checked by comparing its density with the average density of the bulk solution measured with a dip tube device installed in the tank.

2.4 The major steps of the procedure are as follows:

a) The relative difference in uranium or plutonium concentration D, which should not be exceeded between the concentration of the fissile element in a sample and its average concentration in the industrial solution, is selected.

b) Derive from table 1 or 2 the density difference Δ_0 which is not to be exceeded to ensure that a) is met.

c) Replicate samples are taken and the volume of solution in the tank after successive mixings of the industrial solution is measured.

d) Mixing is repeated until the densities of three successive samples agree within the selected limit Δ_0, after correction of potential evaporation losses and for given risks of non-detection, β, and false alarm, α.

e) The density of the last sample is compared with the density measured by a dip tube immersed in the industrial solution.

f) The last sample is accepted if its density agrees with the dip tube measurement within the selected limit Δ_0 and the experimental errors of measurements, for the selected risks β and α.

3 Equipment

3.1 Accountability tank, equipped with a sensor capable of measuring temperatures with an accuracy of 0,1 °C or better, with a dip tube device calibrated for measuring the density or immersing solutions with a precision and accuracy of 1 mg/cm^3 or better, and with a dip tube device suitable for measuring the level of solution in the tank with a precision and accuracy in the order of 0,1 mm.

NOTE 2 Annex A gives a method for calibrating the density dip tube.

3.2 Oscillator density meter, with a readability of 0,1 mg/cm^3, suitable for measuring the density of solutions with a precision and accuracy of 0,5 mg/cm^3 or better, and the temperature with an accuracy of 0,05 °C or better, with sample volumes of 1 ml or less.

3.3 Laboratory ultrathermostat, suitable for stabilizing and measuring the temperatures within ± 0,02 °C.

3.4 Reference thermometer, calibrated to ± 0,01 °C in the 5 °C to 35 °C temperature range.

3.5 Pycnometers, of 5 ml to 20 ml capacity, calibrated to an accuracy of 0,005 %.

3.6 Analytical balance, with a minimum capacity of 100 g and an accuracy of 0,1 mg or better.

4 Reagents

4.1 Bidistilled water.

4.2 Standard density solutions

Prepare a set of uranyl nitrate solutions. The set described in table 3 is suitable for the calibration and quality control of the oscillator density meter (3.2) over the full range of densities foreseen in this procedure. A volume of 100 ml of each solution represents an ample supply.

Measure the density of each solution with a pycnometer (3.5) at temperatures of 10 °C, 20 °C and 30 °C with an accuracy of 0,1 mg/cm^3 or better. Record the results, their repeatability and their actual accuracy.

Store the solutions in tared and sealed or tightly capped glass flasks. Measure the gross weight of the flask after closing it and just before opening it again to remove an aliquot, in order to detect any evaporation loss during storage.

Repeat the pycnometer measurement when the relative evaporation losses add up to 0,02 %.

4.3 Dip tube calibration solutions

Prepare two aqueous solutions of sodium nitrate or uranyl nitrate with densities bracketing the range of densities expected in the industrial solutions. Prepare a volume of solution sufficient for a careful rinsing of the empty tank and for filling it enough to immerse fully the density dip tube.

Measure the density of the dip tube calibration solutions with an accuracy of 0,1 mg/cm^3 or better, at the temperatures of 10 °C, 20 °C and 30 °C with a pycnometer (3.5). Record the measurements, their repeatability and their actual accuracy.

5 Calibration of the oscillator density meter

5.1 Select two standard solutions of uranyl nitrate (4.2) with densities bracketing the expected densities of the industrial solution.

5.2 Bring the two standard solutions and the density meter to a temperature as close as possible to the temperature of the industrial solution.

5.3 Calibrate the oscillator density meter (3.2) with the two standard solutions (4.2).

6 Evaporation losses

This clause describes the principle of a procedure for determining the change in the density of the solution due to evaporation losses between two consecutive mixing operations.

6.1 The volume V_k and the density ρ_k of the solution in the tank with the relevant dip tubes are measured after the k^{th} mixing operation and before taking the k^{th} test sample.

6.2 V'_k is the total volume of the test sample taken after the same mixing operation, and ρ'_k its density measured with the density meter (3.2).

6.3 e_k is the relative increase (in %) of the uranium or plutonium concentration due to evaporation of the solution during the k^{th} mixing operation. According to the balance of the masses of solution between the $(k-1)^{\text{th}}$ and the k^{th} mixing:

$$e_k = \left[\frac{(V_{k-1}\rho_{k-1} + V'_{k-1}\rho'_{k-1})}{V'_k\rho_k} - 1 \right] \times 100 \qquad \ldots (1)$$

6.4 An estimate, δ_k, of the corresponding change in the average density of the solution in the tank is derived from table 1 or 2.

7 Procedure for testing the homogeneity of the solution

7.1 Select the acceptable limit D for relative differences in uranium or plutonium concentrations.

7.2 Derive from table 1 or 2, as appropriate, the acceptable limit Δ_0 for density differences at the expected concentrations in heavy metal ions and free nitric acid.

7.3 Select the risk of non-detection β and the risk of false alarm α.

7.4 Read in table 4 the corresponding values of the parameters L_α and L_β.

7.5 Verify that Δ_0 is sufficiently larger than the standard deviation of the readibility r of the density meter (3.2), and satisfies the following inequation:

$$\Delta_0 \geqslant \sqrt{2}\,(L_\alpha + L_\beta)r \qquad \ldots (2)$$

7.6 If this is not the case, select either larger values for D and Δ_0 or greater risks α or β in order to satisfy inequation (2).

7.7 Mix the solution in the tank for a time T, sufficient to obtain a homogeneous solution.

7.8 Draw a sample out of the tank and measure the temperature in the tank, t, to a tenth of a degree, the differential pressure at the density dip tube, p, the level of the solution in the tank and its volume, V, at that time.

7.9 Adjust the density meter (3.2) and the sample to a temperature t' as close as possible to the temperature in the tank, and maintain t' constant to ± 0,02 °C.

7.10 With the oscillator density meter (3.2), measure the density of 10 or more aliquots of the sample at temperature t', if the repeatability of these measurements is not already known.

7.11 Call s the measured or known value of the standard deviation of the density meter measurements.

7.12 Use the following equation to calculate the number n of replicate density measurements necessary to detect a change of density Δ_0 between two successive samples, with the selected risks α and β:

$$n = \frac{2(L_\alpha + L_\beta)^2 s^2}{\Delta_0^2} \qquad \ldots (3)$$

7.13 Resume mixing of the industrial solution for a time $T/2$.

7.14 Draw another sample i and measure again the temperature in the tank, t_i, the differential pressure at the density dip tube, p_i, the level of the solution in the tank and its volume, V_i, at that time.

7.15 Verify that the volume of solution in the tank has remained constant within experimental errors, or estimate the change δ_i in the average density of the solution in the tank due to evaporation losses in accordance with clause 6.

7.16 With the density meter (3.2) measure the density, ρ'_i, of n aliquots of the sample i at temperature t'.

7.17 Calculate the means $\overline{\rho'}_i$ and $\overline{\rho'}_{i-1}$ of n density measurements of samples i and $i-1$, all densities being measured at the same temperature t'. Calculate their difference Δ_i, corrected if appropriate for the change δ_i due to evaporation losses:

$$\Delta_i = \overline{\rho'}_i - \overline{\rho'}_{i-1} - \delta_i \qquad \ldots (4)$$

7.18 Repeat steps 7.13 to 7.17 as long as

$$\Delta_i \geqslant L_\alpha \sqrt{\frac{2}{n}}\, s \qquad \ldots (5)$$

7.19 Whenever the difference Δ_j for sample j becomes smaller than the limit value:

$$\Delta_j < L_\alpha \sqrt{\frac{2}{n}}\, s \qquad \ldots (6)$$

repeat steps 7.13 to 7.17 once more and verify that Δ_{j+1} is also smaller than the limit value:

$$\Delta_{j+1} < L_\alpha \sqrt{\frac{2}{n}}\, s \qquad \ldots (7)$$

8 Procedure for testing the representativity of the sample

8.1 Proceed with steps 7.1 to 7.19.

8.2 Use the dip tube pressure measurement p_{j+1} to calculate the density ρ_{j+1} of the solution in the tank when sample $j+1$ was taken.

8.3 Accept sample $j+1$ for accountability analysis if

$$|\bar{\rho}'_{j+1} - \bar{\rho}_{j+1}| \leqslant L_\alpha \sqrt{s'^2 + s'^2_0 + \frac{s^2}{n} + s_0^2} \qquad \ldots (8)$$

where

s'_0 and s_0 are the standard deviations of the systematic errors of the dip tube and density meter measurements, respectively;

s' is the standard deviation of the repeatability of the dip tube measurements.

9 Example

9.1 Apply the procedure to a solution of plutonium nitrate containing 100 g/l of plutonium and 8 mol/l free nitric acid, the potential diluent being 3 mol/l nitric acid.

9.2 Take $D = 0{,}31$ % as the acceptable limit for differences in plutonium concentrations.

9.3 According to table 2 b):

$$\Delta_0 = 1{,}0 \text{ mg/cm}^3$$

9.4 Let

$r = 0{,}1$ mg/cm^3

$s = 0{,}3$ mg/cm^3

$s_0 = 0{,}2$ mg/cm^3

$s' = 0{,}5$ mg/cm^3

$s'_0 = 0{,}5$ mg/cm^3

and select $\beta = \alpha = 10$ %

9.5 According to table 4:

$L_\alpha = 1{,}65$

$L_\beta = 1{,}28$

9.6 Verify inequation (2):

$$\sqrt{2}\,(L_\alpha + L_\beta)r =$$

$$\sqrt{2}\,(1{,}65 + 1{,}28) \times 0{,}1 = 0{,}41 \text{ mg/cm}^3$$

$$\Delta_0 = 1{,}0 \text{ mg/cm}^3$$

Thus

$$\Delta_0 > \sqrt{2}\,(L_\alpha + L_\beta)r$$

9.7 Use equation (3) to calculate the number n of replicate density measurements required:

$$n = \frac{2(1{,}65 + 1{,}28)^2 \times 0{,}3^2}{1{,}0^2} = 1{,}54$$

Take $n = 2$.

9.8 Accept sample $j+1$ if

$$\Delta_{j+1} < \sqrt{2} \times 1{,}65 \times \frac{0{,}3}{\sqrt{2}}$$

$$< 0{,}49 \text{ mg/cm}^3$$

9.9 Use sample $j+1$ for accountability analyses if

$$|\bar{\rho}'_{j+1} - \bar{\rho}_{j+1}| \leqslant 1{,}65\sqrt{0{,}5^2 + 0{,}5^2 + 0{,}2^2 + \frac{0{,}3^2}{2}}$$

$$\leqslant 1{,}26 \text{ mg/cm}^3$$

9.10 In such a case, there is a 10 % risk that the density of the sample $j+1$ actually differs from the density of the industrial solution by a value:

$$\Delta_1 = (L_\alpha + L_\beta)\sqrt{s'^2_0 + s'^2 + s_0^2 + \frac{s^2}{n}}$$

$$= (1{,}65 + 1{,}28)\sqrt{0{,}5^2 + 0{,}5^2 + 0{,}2^2 + \frac{0{,}3^2}{2}}$$

$$= 1{,}7 \text{ mg/cm}^3$$

This would correspond to a relative difference D_1 in the plutonium concentration:

$$D_1 = 0{,}31 \times \frac{1{,}7}{1{,}0}$$

$$= 0{,}53 \text{ \%}$$

Table 1 — Correlation between the concentration and density changes in uranyl nitrate solutions

(Relative change in uranium concentration, D (in %), for a density change Δ_0 of 0,001 0 g/cm^3)

a) Uranium in 0,2 mol/l nitric acid		
Concentration, g/l **(Density,** g/cm^3**)**	**Diluent**	D %
400 (1,54)	Water	0,19
	3 mol/l HNO_3	0,23
	8 mol/l HNO_3	0,34
300 (1,40)	Water	0,25
	3 mol/l HNO_3	0,32
	8 mol/l HNO_3	0,62
200 (1,27)	Water	0,37
	3 mol/l HNO_3	0,57
	8 mol/l HNO_3	3,70
100 (1,14)	Water	0,72
	3 mol/l HNO_3	2,39
	8 mol/l HNO_3	0,92
b) Uranium in 3 mol/l nitric acid		
Concentration, g/l (**Density**, g/cm^3)	**Diluent**	D %
300 (1,49)	Water	0,20
	3 mol/l HNO_3	0,25
	8 mol/l HNO_3	0,40
200 (1,36)	Water	0,28
	3 mol/l HNO_3	0,38
	8 mol/l HNO_3	0,87
100 (1,23)	Water	0,43
	3 mol/l HNO_3	0,77
	8 mol/l HNO_3	5,43
NOTE — D is practically proportional to Δ_0 when $\Delta_0 \leqslant 0,002$ g/cm^3.		

Table 2 — Correlation between the concentration and density changes in plutonium nitrate solutions

(Relative change in plutonium concentration, D (in %), for a density change Δ_0 of 0,001 0 g/cm^3)

a) Plutonium in 3 mol/l nitric acid		
Concentration, g/l **(Density,** g/cm^3**)**	**Diluent**	D %
300 (1,54)	Water	0,18
	3 mol/l HNO_3	0,24
	8 mol/l HNO_3	0,34
200 (1,40)	Water	0,25
	3 mol/l HNO_3	0,36
	8 mol/l HNO_3	0,64
100 (1,26)	Water	0,38
	3 mol/l HNO_3	0,72
	8 mol/l HNO_3	6,49
50 (1,19)	Water	0,52
	3 mol/l HNO_3	1,36
	8 mol/l HNO_3	1,84
b) Plutonium in 8 mol/l nitric acid		
Concentration, g/l **(Density,** g/cm^3)	**Diluent**	D %
300 (1,70)	Water	0,14
	3 mol/l HNO_3	0,17
	8 mol/l HNO_3	0,22
200 (1,56)	Water	0,18
	3 mol/l HNO_3	0,22
	8 mol/l HNO_3	0,32
100 (1,42)	Water	0,24
	3 mol/l HNO_3	0,31
	8 mol/l HNO_3	0,58
50 (1,35)	Water	0,29
	3 mol/l HNO_3	0,40
	8 mol/l HNO_3	0,98

NOTE — D is practically proportional to Δ_0 when $\Delta_0 \leqslant 0,002$ g/cm^3.

Table 3 — Composition of reference solutions recommended for the calibration of the oscillator density meter

Reference solutions	Concentrations		Approximate density
	Uranium g/l	Free nitric acid mol/l	g/cm^3
1	100	0	1,23
2		3,0	
3		8,0	
4	200	0	1,36
5		3,0	
6		8,0	
7	300	0	1,49
8		3,0	
9		8,0	
10	400	0	1,63
11		3,0	
12		8,0	

Table 4 — L_α and L_β

Risk α or β	L_β	L_α
0,000 03	4,00	3,90
0,000 5	3,30	3,44
0,001	3,09	3,30
0,01	2,33	2,58
0,05	1,65	1,96
0,10	1,28	1,65
0,25	0,67	1,15
0,50	0,00	0,67

Annex A
(normative)

Calibration of the density dip tube

NOTE 3 The calibration of the density dip tube will be covered in a future International Standard.

Use solutions (4.3) to calibrate the density dip tube. This is best done at the time of the tank volume calibrations.

A.1 Empty and dry the tank.

A.2 Start with the dip tube calibration solution (4.3) of lowest density.

A.3 Rinse the tank, if possible, with the minimum amount of standard solution (4.3) and empty the tank again as completely as possible.

A.4 Fill the tank with the standard solution (4.3) so that the density dip tubes are completely immersed.

A.5 Let the solution, the tank and its ancillary equipment reach thermal equilibrium.

A.6 Start a slow bubbling in the dip tubes of about 3 bubbles per minute.

A.7 When the readings become stable, measure the temperature of the solution, t, to a tenth of a degree and the differential pressure p at the density dip tube with a precision of 1 Pa.

A.8 Correct all experimental data and calculate the calibration factor F_0.

A.9 Repeat steps A.3 to A.8 with the dip tube calibration solution (4.3) of highest density.

A.10 Verify, after temperature corrections, that the calibration factors $F_{0,1}$ and $F_{0,2}$ obtained with the two solutions (4.3) respectively agree within experimental errors.

A.11 If this is the case, adopt the arithmetic mean of the calibration factors as calibration constant:

$$F_0 = \frac{F_{0,1} + F_{0,2}}{2} \qquad \text{... (A.1)}$$

A.12 If this is not the case, check for a potential source of systematic error and eliminate it.