

INTERNATIONAL  
STANDARD

**ISO**  
**10981**

First edition  
1993-06-15

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**Determination of uranium in reprocessing  
plant dissolver solution — Liquid  
chromatography method**

**iTeh STANDARD PREVIEW**

*Dosage de l'uranium dans les solutions de dissolution des usines de  
retraitement — Méthode par chromatographie en phase liquide*

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INTERNATIONAL

**ISO**



Reference number  
ISO 10981:1993(E)

## Foreword

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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 10981 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Sub-Committee SC 5, *Nuclear fuel technology*.

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

Printed in Switzerland

# Determination of uranium in reprocessing plant dissolver solution — Liquid chromatography method

## 1 Scope

This International Standard specifies an analytical method for determining the uranium concentration between 0,1 g/l and 500 g/l in nitric acid solutions of irradiated fuel from light water reactors, gas cooled reactors and fast breeder reactors. It specifies how interference by nitrite and plutonium ions is prevented. The other constituents of fuel solutions do not interfere.

This method is suitable for process control but not for accountancy purposes.

## 2 Principle

**2.1** The sample is diluted in aqueous ascorbic acid solution until the amount of free acid of the nitric solution injected into the chromatograph is lower than 0,1 mol/l in  $\text{HNO}_3$ .

NOTE 1 The column is destroyed when the pH of the solution in contact with the stationary phase is either lower than 1 or higher than 9. To avoid any plutonium hydrolysis the pH of the solution has to be lower than 3. With the procedure described in this International Standard, the sample is diluted enough into the mobile phase to keep the pH value between 1 and 3.

Normally a 1:50 dilution is appropriate for samples from light water reactor irradiated fuel solutions and thus the mass of uranium injected into the chromatographic column is between  $2 \times 10^{-3} \mu\text{g}$  and  $10 \mu\text{g}$ .

**2.2** Ion-pair partition chromatography is performed on a grafted silica column, packed with a 5 mm granulometry stationary phase type C1.

NOTE 2 Different types of columns may be used as long as the grafted hydrocarbon is  $-\text{CH}_3$  to  $-\text{C}_5\text{H}_{11}$ . The operating conditions reported in this International Standard have been optimized for C1 or C2 columns.

**2.3** The elution of uranium is detected by UV spectrophotometry at a wavelength,  $\lambda$ , of 254 nm.

**2.4** The peak area is measured by integration and the result is obtained by comparison with the measurements of standards performed under the same conditions.

## 3 Reagents

Use only reagents of recognized analytical grade.

All aqueous solutions shall be prepared from demineralized water with a resistivity greater than 10  $\text{M}\Omega\cdot\text{cm}$ .

**3.1 Acetonitrile** ( $\text{CH}_3\text{CN}$ ), chromatography grade.

**3.2 Cetyltrimethylammonium bromide** [ $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{NBr}$ ].

**3.3 Sodium hydrogen sulfate** ( $\text{NaHSO}_4$ ).

**3.4 Ammonium sulfate** [ $(\text{NH}_4)_2\text{SO}_4$ ].

**3.5 Ascorbic acid** solution, ( $\text{C}_6\text{H}_8\text{O}_6$ )  
 $c = 5 \times 10^{-2} \text{ mol/l}$ .

**3.6 Mobile phase**, solution containing  $5 \times 10^{-3} \text{ mol/l}$  of cetyltrimethylammonium bromide (3.2) and  $2 \times 10^{-2} \text{ mol/l}$  of sodium hydrogen sulfate (3.3) and 0,18 mol/l ammonium sulfate (3.4) in an acetonitrile (3.1) water mixture [25% (V/V)/75% (V/V)]; degas before use.

**3.7 Uranium reference solutions**, at concentrations as close as possible to the concentration of the test sample, containing typically 50 g/l to 450 g/l of uranium prepared from certified reference materials.

## 4 Apparatus

Usual laboratory equipment found in a high-activity laboratory analysing solutions containing uranium, plutonium and fission products and

**4.1 Polytetrafluoroethylene (PTFE) filters**, with a porosity of 0,22  $\mu\text{m}$ .

**4.2 Chromatographic unit**, comprising (see figure 1)

- a high pressure chromatographic pump;
- a four-port injection valve with an internal loop of 1  $\mu\text{l}$ ;
- a chromatographic column with a 13 cm length and a 4,6 mm inside diameter;
- a spectrophotometric detector, capable of operation at a wavelength,  $\lambda$ , of 254 nm;
- an automatic calculator/integrator;
- a system for transferring the prepared sample to the chromatographic valve.

## 5 Procedure

### 5.1 Calibration

**5.1.1** Use at least two uranium reference solutions (3.7) at concentrations bracketing those of the samples to be analysed.

**5.1.2** Aliquot 2 ml of the uranium reference solution into a 100 ml calibrated flask.

NOTE 3 With an automatic diluter, the volume of the sample and thus the volume of the wastes can be reduced (for example, 0,5 ml in 25 ml).

**5.1.3** Dilute to 100 ml with ascorbic acid solution (3.5) and homogenize.

**5.1.4** Inject 1  $\mu\text{l}$  of the diluted reference solution into the sampling loop.

**5.1.5** Elute with the mobile phase reagent (3.6) at a 1 ml/min flow rate. The retention time of uranium is roughly 5 min. It is completely eluted after about 8 min.

**5.1.6** Measure the peak areas by means of the integrator.

**5.1.7** After each analysis, rinse the sampling line with a nitric acid solution (0,1 mol/l for example) to avoid cross-contamination or crystallisation by evaporation of the remaining sample.

**5.1.8** Repeat 5.1.2 to 5.1.7 with the other reference solution(s).

## 5.2 Analysis of the sample

### 5.2.1 Treatment of the sample

Filter the test sample by means of a PTFE filter (4.1); then aliquot 2 ml of this solution into a 100 ml calibrated flask. Dilute to 100 ml with the ascorbic acid solution (3.5) or demineralized water and homogenize.

### 5.2.2 Chromatographic measurement

Inject 1  $\mu\text{l}$  of the diluted sample into the sampling loop and then proceed with steps 5.1.5 to 5.1.7.

## 6 Expression of results

Calculate the uranium concentration from the measured peak area using the linear interpolation. The concentration range which encompasses the reference solutions and the unknown samples shall be less than 5 % of the reference solution concentration.

## 7 Precision and accuracy

The following estimates of the performance of the procedure are based on the statistical evaluation of duplicate analyses performed on about 200 batches of dissolver solutions from light water reactor fuel irradiated from 20 000 MWd/t to 35 000 MWd/t and 45 batches of dissolver solutions of gas cooled reactor fuel irradiated at 5 500 MWd/t.

### 7.1 Repeatability

The coefficient of variation is of the order of 0,4 % to 0,6 % at concentrations of 200 g/l of uranium if the proper integration range is selected. The use of an automatic diluter improves this coefficient to 0,2 %.

### 7.2 Systematic errors

The mean of duplicate results obtained by this method differed by  $-0,1\%$  to  $+0,4\%$  from the mean of duplicate results obtained by isotopic dilution mass spectrometry (see ISO 8299).

The coefficient of variation of the systematic error is of the order of 0,4 % or less.

## 8 Interferences

### 8.1 Plutonium

Plutonium (III) does not interfere. Plutonium (IV) and (VI) can adversely affect the uranium peak when the U/Pu ratio is less than 100. In that case, the ascorbic

acid solution (3.5) used for the dilution steps 5.1.3 and 5.2.1, reduces plutonium to its trivalent state.

## 8.2 Fission products (FP) and other elements

The elements given in table 1 which are present in an actual FP concentrate solution do not affect the base line in the region of interest of the spectrum when present in concentrations less than those specified.

## 8.3 Nitrite anions

Nitrite anions interfere if they are present. In that case, the ascorbic acid solution (3.5) used for the dilution in steps 5.1.3 and 5.2.1 reduces the nitrite ions.

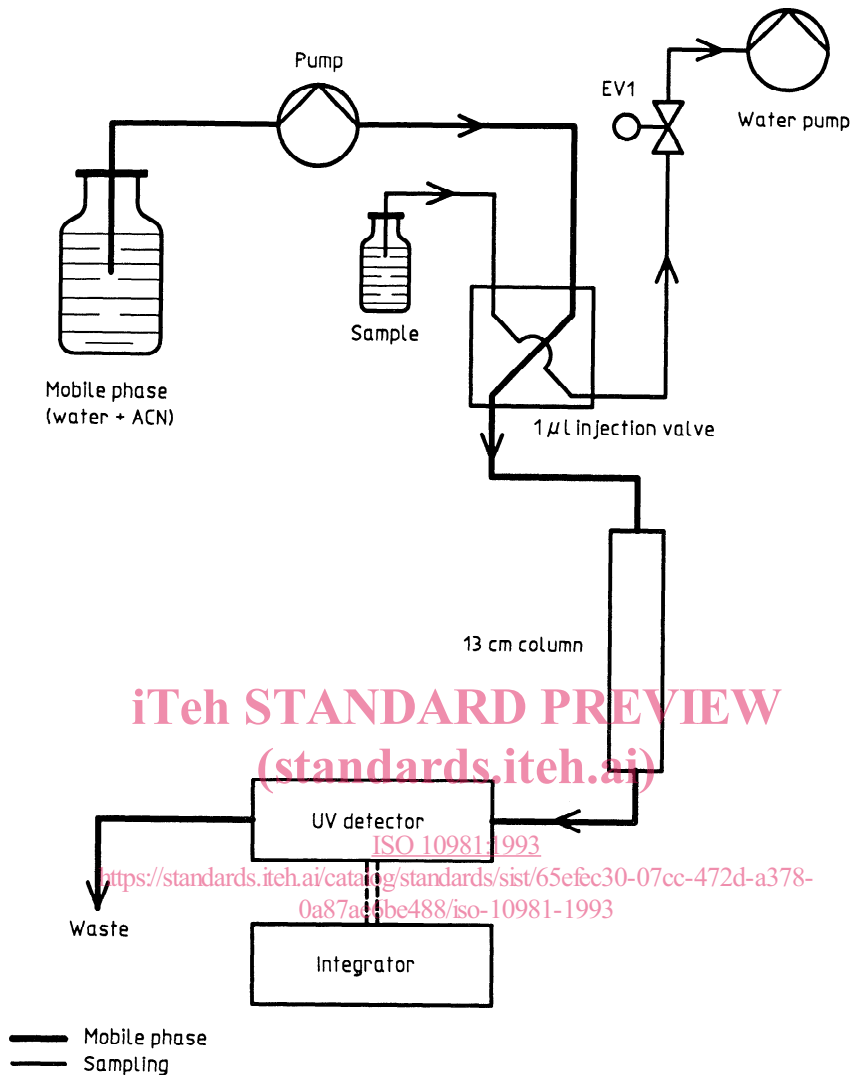
Table 1

Element	Concentration g/l	Element	Concentration g/l
B	0,1	Ba	0,7
P	0,1	Mo	1,9
Na	22	Ce	0,2
Mg	5	Rh	0,3
Ca	0,1	Zr	4
Fe	10,2	La	1
Cr	0,1	Sr	0,1
Ni	2,2	Pr	1,1
Mn	10,5	Nd	1,7
Cu	0,2	Ru	0,3
Al	40	Gd	0,1

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Figure 1 — Chromatographic unit flow sheet

## Annex A (informative)

### Example of computer output from chromatography package

Figure A.1 shows an example of a uranium concentration determination using a computer-based chromatography package.

```
OPERATEUR           =5
CONCENTRATION       =251.7 G/L
DILUTION            =50
SENSIBILITE DETECTEUR =0.1
```

C-R4A CHROMATOPAC CH=1 REPORT No.=121 CHROMATOGRAM=P:E98012.C03 92/04/12 14:52:



\*\* CALCULATION REPORT \*\*

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	2.921	1599	98				
	2	4.614	193039	7093		1	133.6107	U
TOTAL			194639	7192			133.6107	

\*\* ANALYSIS FILE \*\* N:@FILEC

PROCESSING PARAMETERS

WIDTH (sec)	20	SLOPE (uV/min)	44.75
DRIFT (uV/min)	100	MIN.AREA (Count)	500
T.DBL (min)	0	STOP.TM (min)	8
ATTEN (2^X mV)	3	SPEED (mm/min)	5
METHOD (0~8)	4	W/B (0:WINDOW 1:BAND)	0
WINDOW (%)	20	SPL.WT	100
IS.WT	1	CALIB POINTS (1~8)	1

IDENTIFICATION TABLE

IDNO	Name	Time	Band	Conc	Factor(1)	Factor
1	U	4.57		251.7	0.000692143	

Figure A.1

**Annex B**  
(informative)

**Bibliography**

- [1] ISO 8299:1993, *Determination of isotopic content and concentration of uranium and plutonium in nitric acid solution — Mass spectrometric method.*
- [2] MULLER, J.P., COJEAN, J. and DELOGE, A. Uranium determination in nuclear fuel reprocessing solutions by liquid chromatography. *Analysis*, 1987, Vol. 15(5), pp. 209-216.

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