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**Nuclear fuel technology — Determination  
of uranium in reprocessing-plant  
dissolver solution — Liquid  
chromatography method**

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



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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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

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

This second edition cancels and replaces the first edition (ISO 10981:1993), which has been technically revised.

# Nuclear fuel technology — 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 400 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 Normative references

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 8299:—<sup>1)</sup>, *Nuclear fuel technology — Determination of isotopic content and elemental uranium and plutonium concentrations of nuclear materials in nitric acid solutions — Thermal-ionization mass spectrometry*

## 3 Principle

**3.1** The sample is diluted in aqueous ascorbic acid solution until the amount of free acid of the nitric solution injected onto the reversed-phase column is lower than 0,1 mol/l in HNO<sub>3</sub> (1 < pH < 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 sufficiently by the ascorbic acid solution to keep the pH value between 1 and 3. The use of the column within this pH range gives an expected working life of the column of about one year.

NOTE 2 Pu(IV) being strongly retained on the column; its late elution may cause interference between consecutive injections. Ascorbic acid reduces Pu(IV) to Pu(III); this species is rapidly eluted and does not interfere.

Normally, a 1:50 dilution is appropriate for samples from irradiated fuel solutions from light-water reactors, and thus the mass of uranium injected onto the reversed-phase column will range between  $2 \times 10^{-3}$  µg and 10 µg.

**3.2** Ion-pair partition chromatography is performed on a grafted silica column, packed with a 5 µm granulometry stationary phase type C1 (i.e. methyl grafted).

NOTE Different types of columns can be used as long as the grafted hydrocarbon is -CH<sub>3</sub> to -C<sub>5</sub>H<sub>11</sub>. The operating conditions reported in this International Standard have been optimized for methyl (C1) or ethyl (C2) columns.

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1) To be published. (Revision of ISO 8299:1993)

3.3 The elution of uranium (chromatographic peak) is detected by UV spectrophotometry.

Fixed wavelength detectors with a band-pass filter centered around  $\lambda = 254$  nm are widely available and are easy to install in a shielded box. With a variable-wavelength detector, measurements may be performed in the range from 210 nm to 230 nm with greater sensitivity. A UV-visible diode array detector is recommended for peak conformation and to assess peak purity.

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

## 4 Reagents

Use only reagents of recognized analytical grade.

All aqueous solutions should be prepared from demineralized water with a resistivity greater than 10 M $\Omega$ -cm.

4.1 **Acetonitrile** (CH<sub>3</sub>CN), chromatography grade.

4.2 **Cetyltrimethylammonium bromide** [C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>3</sub>NBr] or **cetyltrimethylammonium hydroxide** [C<sub>16</sub>H<sub>33</sub>(CH<sub>3</sub>)<sub>3</sub>NOH].

4.3 **Sodium hydrogen sulfate** (NaHSO<sub>4</sub>).

4.4 **Ammonium sulfate** [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>].

4.5 **Ascorbic acid** solution (C<sub>6</sub>H<sub>8</sub>O<sub>6</sub>), ( $c = 5 \times 10^{-2}$  mol/l).

NOTE Ascorbic acid powder is stable. Aqueous solutions oxidize readily with air exposure. Make and use rapidly.

4.6 **Trifluoroacetic acid** solution (CF<sub>3</sub>CO<sub>2</sub>H), purity > 99 %, spectrophotometric grade.

4.7 **Mobile phase:** solution containing  $5 \times 10^{-3}$  mol/l cetyltrimethylammonium bromide (4.2) with  $2 \times 10^{-2}$  mol/l sodium hydrogen sulfate (4.3) and 0,18 mol/l ammonium sulfate (4.4) in an acetonitrile (4.1) water mixture (25 % to 75 % in volume); degassed and with 0,1 % in volume of the trifluoroacetic acid solution (4.6) added before use.

4.8 **Uranium reference solutions**, at concentrations as close as possible to the concentration of the test sample, containing typically 0,1 g/l to 400 g/l of uranium prepared from certified reference materials.

## 5 Apparatus

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

5.2 **Polytetrafluoroethylene (PTFE) filters**, with a porosity of 0,22  $\mu$ m.

5.3 **Chromatographic unit**, comprising (see Figure 1):

- a high pressure chromatographic pump;
- a four-port injection valve with an internal loop of 1  $\mu$ l;
- a chromatographic precolumn with a 3 cm length and a 4,6 mm inside diameter;
- a chromatographic column with a 10 cm length and a 4,6 mm inside diameter;

NOTE A precolumn avoids changing the whole analytical column in the case of clogging.

- 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.

## 6 Procedure

### 6.1 Calibration

**6.1.1** Use at least two uranium reference solutions (4.8) at concentrations bracketing those of the samples to be analysed.

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

NOTE 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).

**6.1.3** Dilute to 100 ml with ascorbic acid solution (4.5) and homogenize.

**6.1.4** Inject 1  $\mu$ l of the diluted reference solution into the sampling loop.

**6.1.5** Elute with the mobile phase reagent (4.7) at a 1 ml/min flow rate. The retention time of uranium is approximately 5 min. It is completely eluted after about 8 min.

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

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

**6.1.8** Repeat operations 6.1.2 to 6.1.7 with the other reference solution(s).

### 6.2 Analysis of the sample

#### 6.2.1 Treatment of the sample

Filter the test sample by means of a PTFE filter (5.2); then aliquot 2 ml of this solution into a 100 ml calibrated flask. Dilute to 100 ml with the ascorbic acid solution (4.5) and homogenize.

#### 6.2.2 Chromatographic measurement

Inject 1  $\mu$ l of the diluted sample into the sampling loop and then proceed with steps 6.1.5 to 6.1.7.

## 7 Expression of results

Calculate the uranium concentration from the measured peak area using a linear interpolation. The low concentration standard should be not less than 95 % of the high concentration standard.

## 8 Precision and accuracy

### 8.1 General

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 to 35 000 MWd/t and 45 batches of dissolver solutions of gas-cooled reactor fuel irradiated at 5 500 MWd/t.

### 8.2 Repeatability

The coefficient of variation (including all steps of Clause 6) is of the order of 0,4 % to 0,6 % at concentrations of 200 g/l of uranium and using the appropriate integration range. The use of an automatic diluter improves this coefficient of variation to 0,2 %.

### 8.3 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 in accordance with ISO 8299.

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

It is recommended that evaluation of errors has to be done by users for each specific situation.

## 9 Interferences

### 9.1 Plutonium

Plutonium (III) does not interfere. Plutonium (IV) and (VI) may adversely affect the uranium peak when the U/Pu ratio is less than 100. However, the ascorbic acid solution (4.5) used for the dilution steps 6.1.3 and 6.2.1, reduces plutonium to its trivalent state at room temperature. This species does not interfere. This procedure is suitable for use on one-month-aged PUREX solutions. On longer aged solutions, the amount of ascorbic acid added should be increased.

### 9.2 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.

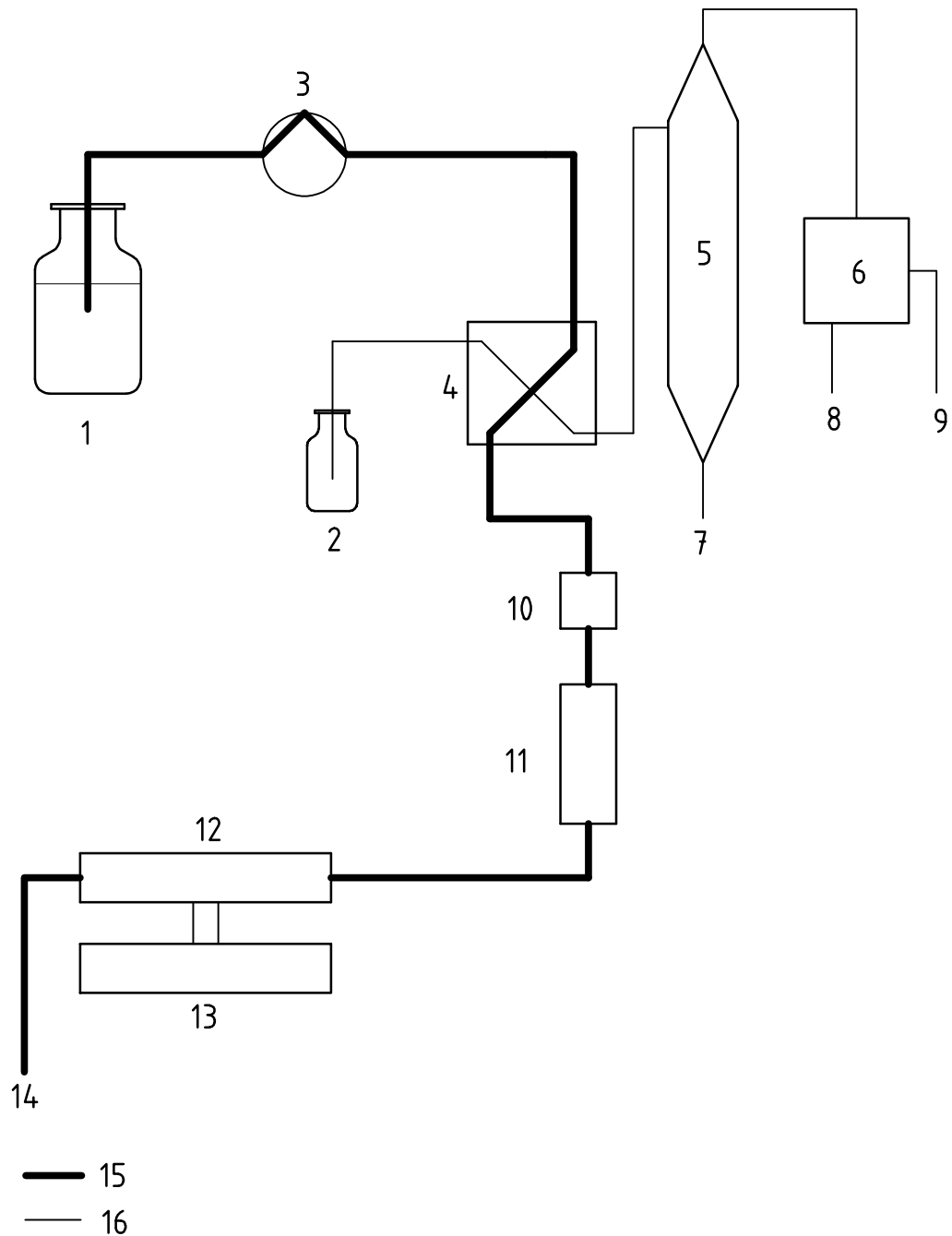
### 9.3 Nitrite anions

Nitrite anions interfere if they are present. However, the ascorbic acid solution (4.5) used for the dilution in steps 6.1.3 and 6.2.1 reduces the nitrite ions and prevents any interferences.



Table 1

| Elements | Concentration<br>g/l | Elements | Concentration<br>g/l |
|----------|----------------------|----------|----------------------|
| B        | 0,1                  | Ba       | 0,7                  |
| P        | 0,1                  | Mo       | 1,9                  |
| Na       | 22,0                 | Ce       | 0,2                  |
| Mg       | 5,0                  | Rh       | 0,3                  |
| Ca       | 0,1                  | Zr       | 4,0                  |
| Fe       | 10,2                 | La       | 1,0                  |
| 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       | 40,0                 | Gd       | 0,1                  |



**Key**

- |   |                       |
|---|-----------------------|
| 1 mobile phase                            | 9 pressurized water   |
| 2 sample                                  | 10 3 cm precolumn     |
| 3 chromatographic pump                    | 11 10 cm long column  |
| 4 injection valve with 1 µl sampling loop | 12 UV detector        |
| 5 separator                               | 13 integrator         |
| 6 venturi                                 | 14 waste              |
| 7 waste                                   | 15 mobile phase pipes |
| 8 waste                                   | 16 sample pipes       |

**Figure 1 — Chromatographic unit flow-sheet**

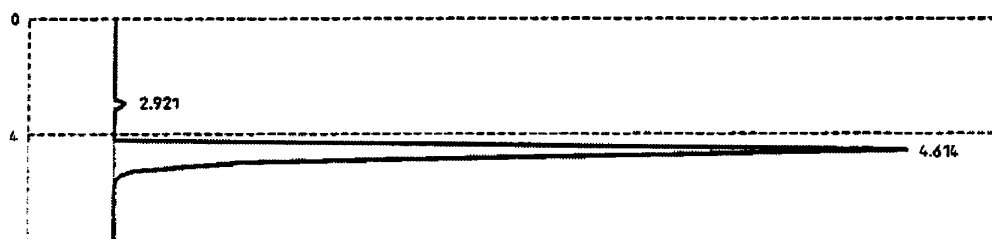
## Annex A (informative)

### Example of computer output from chromatography package

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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



**\*\* 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:0FILEC**

**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 — Example of a uranium concentration determination using a computer-based chromatography package

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