

Procedure for determining airborne particulate uranium and plutonium in air near the ground by alpha spectrometry

A- α -SPEKT-AEROS-01

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1 Scope

The procedure described here is suitable for determining airborne particulate uranium and plutonium in air near the ground in accordance with the General Administrative Regulation on the Integrated Measuring and Information System imposed by the Precautionary Radiation Protection Act (AVV-IMIS) of 27 September 1995 (1).

2 Sampling

Samples are collected as described in the procedure A- γ -SPEKT-AEROS-01 of this procedures manual.

3 Analysis

3.1 Principle of the method

The principle of this method is illustrated in the schematic diagram of Figure 1.

Following the processing of the Luwa-Gelb filter medium (see A- γ -SPEKT-AEROS-01), uranium and plutonium are extracted from the hydrochloric acid solution by means of tris-(2-ethyhexyl)-amine. Re-extraction with ammonium iodide in a hydrochloric acid solution then separates the plutonium fraction from the uranium fraction. The plutonium fraction is then purified with an ion exchanger. The uranium is extracted from the uranium fraction and is purified through extraction with tri-n-octylphosphine oxide. To prepare a counting source with a uranium- or plutonium thickness small enough to be suitable for analysis by alpha spectrometry, both the uranium and plutonium are precipitated through electrolysis.

To determine the chemical yield of uranium and plutonium respectively, the radionuclides U-232 and Pu-236, with their known activities, are added as tracers.

3.2 Sample preparation

The charged filters are pressed and reduced to ash in a ceramic crucible at temperatures that are gradually increased to ca. 450 °C in a 5-hour process.

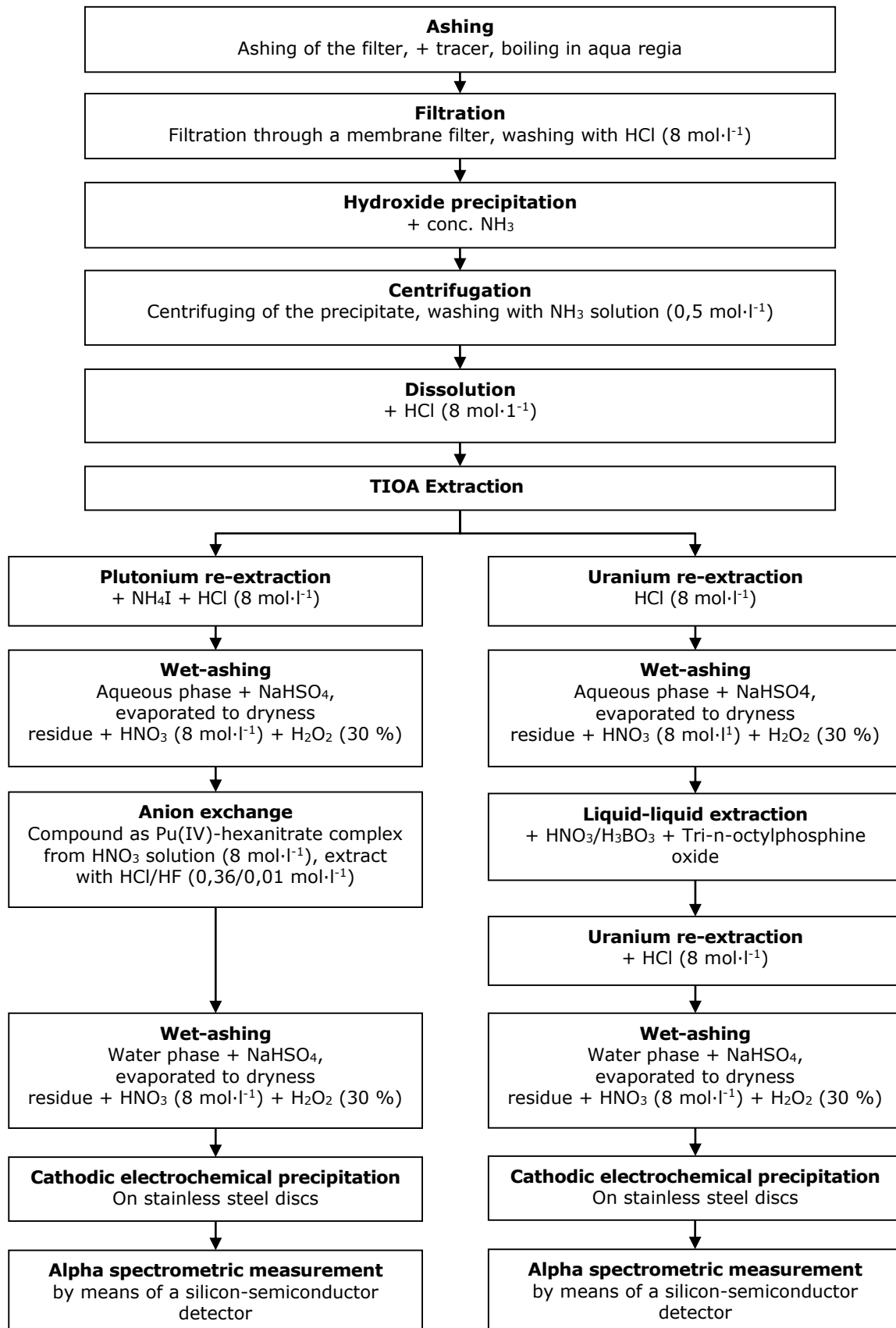


Fig. 1: Schematic diagram of uranium/plutonium separation

3.3 Radiochemical separation

3.3.1 Chemical extraction of ash

3.3.1.1 Using a beaker (covered), the ashed filters are mixed with the tracer solution and freshly prepared aqua regia and stirred at a weak boil for one hour.

3.3.1.2 The solution is filtered off via a membrane filter (No. 11301), and the filter washed with hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) to completely eliminate the aqua regia.

3.3.1.3 The filtrate is mixed with 3 ml hydrogen peroxide 30 %, followed by boiling down the hydrogen peroxide on a sand bath.

3.3.1.4 The solution is transferred to a beaker and diluted with distilled water to ca. 300 ml. While stirring and heating it, concentrated ammoniac solution is added drop by drop to adjust the pH to between 7 and 8. Then, an additional 30 ml of ammoniac solution is added.

3.3.1.5 The precipitated hydroxides are left to mature over night (ca. 12 hours).

3.3.1.6 The hydroxides are centrifuged off and washed with ammoniac solution ($0,5 \text{ mol}\cdot\text{l}^{-1}$). The supernatant solution is discarded.

3.3.2 Plutonium and uranium extraction with tris-(2-ethylhexyl)-amine

Tris-(2-ethylhexyl)-amine is commonly known as triisooctylamine and therefore referred to in the following by its abbreviation, TIOA.

3.3.2.1 The hydroxide residue is dissolved in hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) during heating and mixed with 3 ml of hydrogen peroxide solution (30 %) after having cooled. Excess hydrogen peroxide is eliminated by heating the solution on a sand bath (covered). The solution is then cooled in a water bath and stored.

3.3.2.2 Pre-treatment of the TIOA solution (2,6 g \pm 3,2 ml TIOA in 23,4 g \pm 27 ml xylene):

- a) The TIOA solution is mixed with 30 ml of distilled water and shaken for 5 minutes, and
- b) then mixed with 30 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) and shaken for 5 minutes.
- c) Procedures a) and b) are repeated.

3.3.2.3 The HCl solution from 3.3.2.1 is transferred to a separating funnel, mixed with 30 ml of the prepared TIOA solution and shaken for 1 minute. The aqueous phase is discarded.

3.3.3 Plutonium re-extraction

3.3.3.1 The TIOA phase is mixed twice with 30 ml freshly prepared, hot ammonium iodide solution (0,42 g of NH_4I in 60 ml of HCl $8 \text{ mol}\cdot\text{l}^{-1}$) and shaken for 2 minutes each. Each of the organic phases is retained.

3.3.3.2 The aqueous phases are collected in an evaporation pan, mixed with 1 ml of sodium hydrogen sulphate solution ($1 \text{ mol}\cdot\text{l}^{-1}$), and evaporated to dryness.

3.3.3.3 The residue is moistened with concentrated nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) and wet-ashed by adding 5 to 10 drops of hydrogen peroxide (30 %). This procedure is repeated until the residue is clear of all organic residues (TIOA) and iodine (yellowish white colouration of the residue).

3.3.4 Uranium re-extraction

3.3.4.1 The retained TIOA phase is purified by shaking it in 30 ml of hydrochloric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) for 5 minutes. The aqueous phase is discarded.

3.3.4.2 The TIOA phase is then mixed twice with 30 ml of hydrochloric acid ($0,1 \text{ mol}\cdot\text{l}^{-1}$) each and shaken for 5 minutes each. The TIOA phase is then discarded.

3.3.4.3 The aqueous phases are collected in an evaporation pan, mixed with 1 ml of sodium hydrogen sulphate ($1 \text{ mol}\cdot\text{l}^{-1}$) and evaporated to dryness.

3.3.4.4 The residue is moistened with concentrated nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) and wet-ashed by adding 5 to 10 drops of hydrogen peroxide (30 %). The procedure is repeated until the residue has been liberated of all organic residues (see 3.3.3.3).

3.3.5 Cleansing of the plutonium fraction

3.3.5.1 An ion exchange column (see Fig. 2) is fitted with a glass wool plug, ca. 5 ml of exchange resin (Dowex 1 x 4, 50 mesh – 100 mesh, suspended in distilled water), and another glass wool plug. The column is conditioned with 30 ml of nitric acid ($8 \text{ mol}\cdot\text{l}^{-1}$).

3.3.5.2 The plutonium residue is dissolved by warming it in 10 ml of nitric acid ($8 \text{ mol}\cdot\text{l}^{-1}$), mixed with 0,1 ml of a freshly prepared sodium nitrite solution (1 g of sodium nitrite in 5 ml of water), and left standing in a warm environment for 20 minutes.

3.3.5.3 The dissolved plutonium fraction is added to the column. Its flow-rate should be ca. 1 ml per minute.

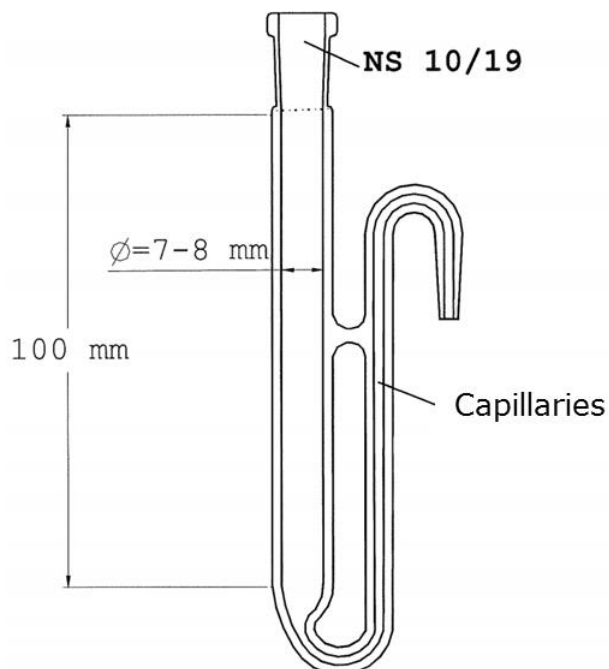


Fig. 2: Ion exchange column

3.3.5.4 The column is rinsed with 30 ml of nitric acid ($8 \text{ mol}\cdot\text{l}^{-1}$) and 50 ml of hydrochloric acid ($10 \text{ mol}\cdot\text{l}^{-1}$).

3.3.5.5 Extraction is effected with a solution made from hydrochloric acid ($0,36 \text{ mol}\cdot\text{l}^{-1}$) and hydrofluoric acid ($0,01 \text{ mol}\cdot\text{l}^{-1}$), corresponding to 35 ml of HCl (32 %) and 0,5 ml of HF (40 %) per 1 litre of water.

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3.3.5.6 The extract is collected in an evaporation pan, mixed with 1 ml of sodium hydrogen sulphite solution ($0,1 \text{ mol}\cdot\text{l}^{-1}$), and evaporated to dryness.

3.3.5.7 The residue is wet-ashed with concentrated nitric acid and hydrogen peroxide (see 3.3.3.3).

3.3.6 Purification of the uranium fraction

3.3.6.1 A tri-n-octylphosphine oxide (TOPO) solution is prepared as follows (always freshly prepared):

- a) 2,3 g of TOPO are dissolved in 20 ml of n-heptane ($0,3 \text{ mol}\cdot\text{l}^{-1}$), then
- b) mixed with 20 ml of ammonium carbamate solution ($1 \text{ mol}\cdot\text{l}^{-1}$) 10 % and shaken for 5 minutes,
- c) mixed twice with 20 ml of nitric acid ($2 \text{ mol}\cdot\text{l}^{-1}$) and shaken for 5 minutes each, and
- d) mixed with 20 ml of the nitric/boric acid mixture ($2 \text{ mol}\cdot\text{l}^{-1} \text{ HNO}_3$ with 25 g H_3BO_3 per litre) and shaken for 5 minutes.

3.3.6.2 The uranium residue from 3.3.4.4 is dissolved in 20 ml of the warm nitric/boric acid solution (see 3.3.6.1 d) and added to the prepared TOPO solution. This solution is shaken for 10 minutes after which the aqueous phase is discarded.

3.3.6.3 The organic phase is mixed three times with 20 ml of the nitric/boric acid solution (see 3.3.6.1 d) each and shaken for 5 minutes each time, and then again mixed with 20 ml of nitric acid ($2 \text{ mol}\cdot\text{l}^{-1}$) and shaken for another 5 minutes.

3.3.6.4 The organic phase is left standing over night (ca. 12 hours) in a closed vessel.

3.3.6.5 In order to re-extract the uranium from the TOPO solution, the solution is mixed four times with 5 ml of ammonium carbamate solution 10 % each and shaken for 5 minutes each.

3.3.6.6 The aqueous solutions are collected in a new separation funnel and shaken in 20 ml of n-heptane for 5 minutes for purification.

3.3.6.7 The aqueous phase is collected in an evaporation pan, mixed with 1 ml of sodium hydrogen sulphate solution ($0,1 \text{ mol}\cdot\text{l}^{-1}$) and evaporated to dryness. The organic phase is discarded.

3.3.6.8 The residue is wet-ashed with nitric acid/hydrogen peroxide (see 3.3.3.3).

3.3.7 Preparation of the electrolysis

3.3.7.1 The Teflon cellular body is cleansed in a 10 % Extran solution.

3.3.7.2 The silicone seals are boiled in a 10 % Extran solution, and briefly dipped into sulphuric acid 1 %, rinsed with distilled water, and dried. Seals prepared thus can be stored dry.

3.3.7.3 The stainless steel disc are cleansed in Labosol solution 5 % in an ultrasonic cleaning tank, and then rinsed with distilled water. The stainless steel disc prepared thus are stored in ethanol (p. a.) and rinsed with distilled water prior to use.

3.3.8 Electrolysis for uranium and plutonium

3.3.8.1 The cellular body is mounted (see Fig. 3) and tested for leakage with distilled water.

3.3.8.2 The dry residue of plutonium or uranium is mixed with 2 ml of concentrated nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) and 0,5 ml of concentrated sulphuric acid ($18 \text{ mol}\cdot\text{l}^{-1}$), and are heated on a sand bath until SO_3 vapour is emitted.

3.3.8.3 The residue is cooled and then mixed with 3 ml of distilled water and 2 drops of thymol-blue indicator 0,02 %.

3.3.8.4 The solution is transferred to the electrolytic cell together with 6 ml of sulphuric acid 1 %.

3.3.8.5 The pH is adjusted to 2,5 with ammoniac gas (indicator will assume salmon colouring).

3.3.8.6 The electrolytic cell is connected to a constant current generator.

3.3.8.7 The cellular body is covered with an ice-cooled round-bottomed flask and placed on a deep-cooled metal block.

3.3.8.8 The cell is electrified with a current of 1,5 A for a period of 1,5 hours. Deviations of up to 10 % are permissible with regard to both duration and current.

3.3.8.9 Upon completion of the electrodepositing process, 10 ml of ammoniac solution 2,5 % are filled into the cellular body and left to mix for 1 minute.

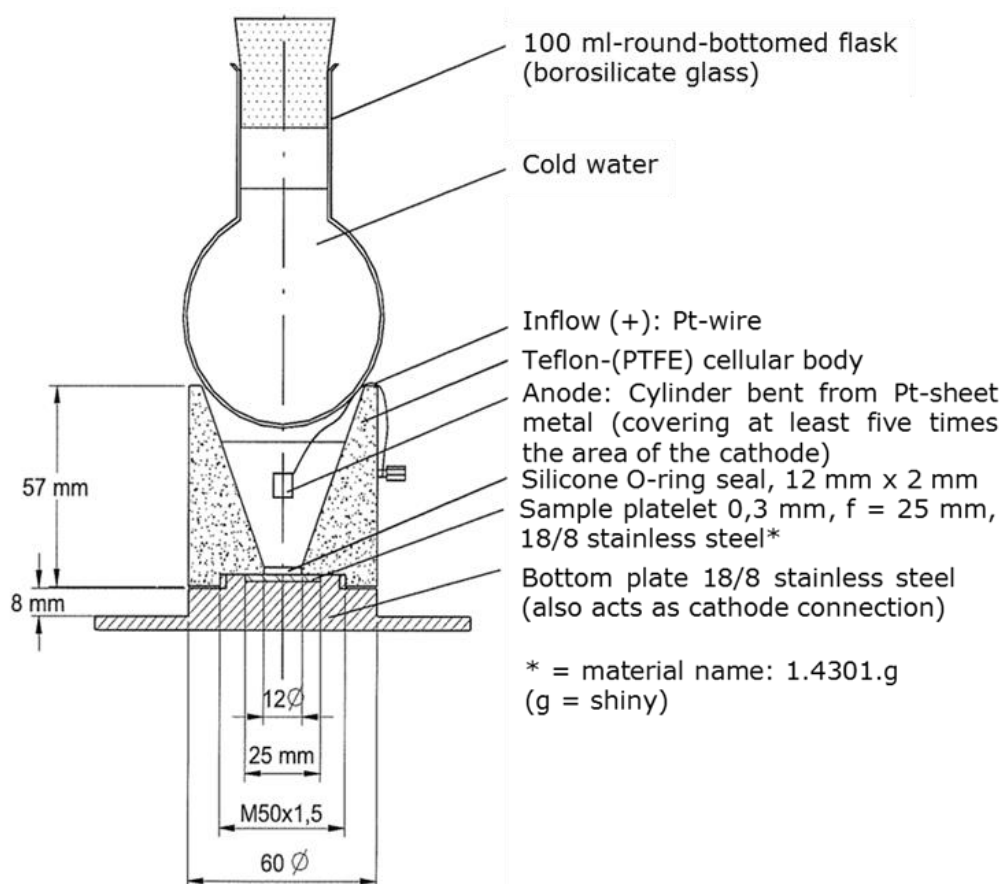


Fig. 3: Electrolytic cell

3.3.8.10 The contents of the cell are poured out, and the cathode is disconnected from the circuit.

3.3.8.11 The cell is rinsed with a solution of ammonium nitrate 1 % in an ammoniac solution 1 %. The anode can then be detached and power switched off.

3.3.8.12 The stainless steel disc is removed from the cell, rinsed with ammoniacal ethanol (pH 8), and dried by briefly, yet strongly, heating it on a hotplate.

4 Measuring the activity

The measurement by alpha spectrometry is performed by using silicon semiconductor detectors. Further details on alpha spectrometry can be found in chapter IV.2 of this procedures manual.

5 Calculation of the results

The calculation of the activity concentration, c_r , of the radionuclide, r , to be identified in the air is derived from the equation (4.51b) given in chapter IV.5 of this procedures manual, using the following equation (1):

$$c_r = \frac{A_{Tr} \cdot (N_p - q \cdot N_{p,0})}{V \cdot (N_{Tr} - q \cdot N_{Tr,0})} \quad (1)$$

where:

- A_{Tr} activity of the tracers added, in Bq;
- V air volume throughput of the sample, in m^3 ;
- t_m duration of counting source measurement, in s;
- t_0 duration of background measurement, in s;
- q ratio t_m/t_0 ;
- N_p number of gross counts in the region of the line of the radionuclide, r ;
- $N_{p,0}$ number of background counts in the region of the radionuclide r ;
- N_{Tr} number of gross counts in the region of the line of the trace;
- $N_{Tr,0}$ Number of background counts in the region of the line of the trace;

It is assumed that the region of interest for the evaluation of the radionuclides has been chosen in such a manner that all lines of a radionuclide are included and the sum of the emission probabilities of the respective lines equals 1.

The standard deviation, $s(c_r)$, of the activity concentration is derived from equation (4.51b) given in chapter IV.5 of this procedures manual, using the following equation (2):

$$s(c_r) = c_r \cdot \sqrt{\frac{N_p + q^2 \cdot N_{p,0}}{(N_p - q \cdot N_{p,0})^2} + \frac{N_{Tr} + q^2 \cdot N_{Tr,0}}{(N_{Tr} - q \cdot N_{Tr,0})^2} + \frac{s^2(A_{Tr})}{A_{Tr}^2}} \quad (2)$$

where:

- $s(A_{Tr})$ standard deviation of the activity of the tracer, in Bq.

5.1 Worked example

The following is an example of data obtained from an analysis of uranium content:

Air volume throughput	50042,0 m ³
Measurement period of the counting source	150000 s
Measurement period of the background effect	150000 s
Activity of the U-232 tracer added	(2,44 · 10 ⁻² ± 0,077 · 10 ⁻²) Bq
Gross count number in the range of the U-238 line	3365
Background count number in the range of the U-238 line	2
Gross count number in the range of the U-232 line	5838
Background count number in the range of the U-232 line	7

This results in an activity concentration of U-238 and its standard deviation of:

$$c_r = \frac{2,44 \cdot 10^{-2} \cdot (3365 - 1 \cdot 2)}{50042 \cdot (5838 - 1 \cdot 7)} \text{ Bq} \cdot \text{m}^{-3} = 2,81 \cdot 10^{-7} \text{ Bq} \cdot \text{m}^{-3}$$

$$s(c_r) = 2,81 \cdot 10^{-7} \cdot \sqrt{\frac{3365 + 1^2 \cdot 2}{(3365 - 1 \cdot 2)^2} + \frac{5838 + 1^2 \cdot 7}{(5838 - 1 \cdot 7)^2} + \frac{0,077 \cdot 10^{-2}}{2,44 \cdot 10^{-2}}} \text{ Bq} \cdot \text{m}^{-3} =$$

$$= 1,08 \cdot 10^{-8} \text{ Bq} \cdot \text{m}^{-3}$$

and thus produces a result of:

$$c_r = (2,8 \pm 0,1) \cdot 10^{-7} \text{ Bq} \cdot \text{m}^{-3}$$

5.2 Consideration of uncertainties

The main contributor to the uncertainty of the activity concentration is the statistical uncertainty in the number of background counts. To a lesser extent, the uncertainty of the tracer activity (3 %) and the uncertainty of the air volume throughput (ca. 2 %) contribute. In comparison, the uncertainty of the decay time can be neglected.

6 Characteristic limits of the procedure

Identification of the detection limit of the procedure requires the preparation and analysis of a dummy sample under the same conditions as those applied to the counting source. Note that the count rate of the dummy sample may actually be higher than that of an empty sample, e. g., an untreated steel disc.

The fundamentals for calculating detection limits are described in chapter IV.5 section 4.8 of this procedures manual. The evaluation of an alpha line with a defined base width is regarded as an integral measurement taken with a mono-channel analyser.

In the case of tracer nuclides, the activity-related calibration factor, φ_A , is not explicitly known. By formally introducing the (fictitious) chemical yield, η , to the equation (3):

$$\eta = \frac{N_{\text{Tr}} + q \cdot N_{\text{Tr},0}}{\varepsilon \cdot t_m \cdot A_{\text{Tr}}} \quad (3)$$

where:

ε detection efficiency of the measuring system, in $\text{Bq}^{-1} \cdot \text{s}^{-1}$.

The representation of the activity-related calibration factor, φ_A , required for the calculation of the detection limit according to chapter IV.5 section 2.1 is obtained from the following equation (4):

$$\varphi_A = \frac{t_m \cdot A_{\text{Tr}}}{N_{\text{Tr}} - q \cdot N_{\text{Tr},0}} \quad (4)$$

Using the numerical values from the sample calculation in chapter 5.1 and $k_{1-\alpha} + k_{1-\beta} = 4,645$, the detection limit, G , is obtained for the activity of U-238:

$$G_{\text{U-238}} = 8,41 \cdot 10^{-5} \text{ Bq}$$

Given an air volume throughput of 50042 m^3 , the detection limit, g , of the activity concentration of U-238 is:

$$g_{\text{U238}} = 1,68 \cdot 10^{-9} \text{ Bq} \cdot \text{m}^{-3}$$

7 Catalogue of chemicals and equipment

7.1 Chemicals

All chemicals should, as far as possible, be utilized at the purity grade '*pro analysi*'.

- Ammoniac gas (99,8 %);
- Ammoniac solution (13 mol·l⁻¹);
- Ammoniac solution (0,5 mol·l⁻¹);
- Ammonium carbamate;
- Ammonium nitrate;
- Ammonium iodide;
- Boric acid;
- Ethanol (96 %);
- Cleaning solution (e.g., Extran MA 01, alkaline, by Merck);
- Hydrofluoric acid (20 mol·l⁻¹);
- Glass wool;
- Ion exchanger resin (Dowex 1 x 4, 50 mesh – 100 mesh);
- Cleaning solution for ultrasonic cleaning tank (e.g., Labosol S by neoLab);
- Membrane filter (Sartorius No. 11301);
- n-heptane;
- Sodium hydrogen sulphate;
- Sodium nitrite;
- Nitric acid, concentrated (14 mol·l⁻¹);
- Nitric acid (8 mol·l⁻¹);
- Hydrochloric acid (8 mol·l⁻¹);
- Hydrochloric acid (10 mol·l⁻¹);
- Sulphuric acid, concentrated (18 mol·l⁻¹);
- Thymol-blue indicator;
- Tris-(2-ethylhexyl)-amine (triisooctylamine, abbreviated to TIOA);
- Tri-n-octylphosphine oxide (TOPO);
- Hydrogen peroxide (30 %);
- Xylene (isomer mix).

7.2 Equipment

Alpha spectrometry:

- Alpha spectrometry workstation with surface barrier layer counter or ion-implanted detector and multi-channel analyser.

Electrolysis:

- Stainless steel disc: V2A steel, austenitic, Ø 25 mm, thickness 0,5 mm, polished;
- Direct-current generator with constant-value current regulator for up to 3 A;
- Silicone seal washers.

Miscellaneous:

- Evaporation pan;
- Muffle furnace;
- Ceramic crucible;
- Sand bath;
- Separation funnel;
- Ultrasonic cleaning tank;
- usual equipment of a radiochemical laboratory.

References

- (1) The Ministry of the Environment, Nature Conservation and Reactor Safety (ed.): Common Administrative Regulations on the Integrated Measuring and Information System according to the Precautionary Radiation Protection Act, Bundesanzeiger 47, Number 200a dated 24. October 1995