

**Procedure for determining
uranium isotopes in wastewater
by alpha spectrometry**

H- α -SPEKT-AWASS-01

Authors:

Th. Bünger
H.U. Fusban[†]
H. Rühle
I. Gans

Federal coordinating office for drinking water, groundwater,
wastewater, sludge, waste and wastewater of
nuclear power plants

(Leitstelle für die Überwachung der Radioaktivität in Trinkwasser,
Grundwasser, Abwasser, Klärschlamm, Reststoffen und Abfällen)

Procedure for determining uranium isotopes in wastewater by alpha spectrometry

1 Scope

The procedure described here serves to simultaneously determine the uranium isotopes U-234, U-235 and U-238 in wastewater. It is suitable for analysing wastewaters from nuclear facilities, users of isotopes, and both processed and raw wastewater from sewage treatment plants. Salts at higher concentrations, e. g., sodium chloride, may interfere. The principles of the procedure may also be projected – if needed after enrichment by means of evaporating larger volumes – to other waters, including, e. g., ground water, drinking water and surface waters.

2 Sampling

Details on the selection of samples and sampling can be found in the procedures H- γ -SPEKT-AWASS-01 and H- γ -SPEKT-TWASS-01. A sample volume of 1 l will usually be sufficient. The water samples are stabilised with about 1 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) per litre and may then be stored in polyethylene bottles until they can be processed further.

3 Analysis

3.1 Principle of the procedure

The principle of the procedure is illustrated in Figure 1. Uranium is extracted from a nitric acid solution using trioctylmethylammonium nitrate dissolved in xylene and then separated as a hexachloron complex from associated elements (e. g., plutonium, thorium, iron) by anion exchange. Its activity is determined by alpha spectrometric measurements of thin-layer counting sources that are obtained by electrochemical deposition of the uranium in hydroxidic form on stainless steel discs. Spiking the sample with U-232 tracer of known activity is done to determine the chemical yield.

3.2 Sample preparation

The water sample is spiked with U-232 tracer (about 0,5 Bq) for determining the radiochemical yield. 5 ml of sulphuric acid ($18 \text{ mol}\cdot\text{l}^{-1}$) and 10 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) are added, too. The amount of U-232 tracer used should be such that the resulting U-232 line is of similar peak height compared to the analysed uranium isotopes. This means that higher tracer activities might be required in the case of higher activities of the analysed uranium isotopes.

The sample is fumed off (wet-ashed) to dryness. Once cooled, 2 ml of sulphuric acid ($18 \text{ mol}\cdot\text{l}^{-1}$) and 5 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) are added to the residue and fumed off to dryness once more. This step is to be repeated until the residue does no longer contain any organic constituents.

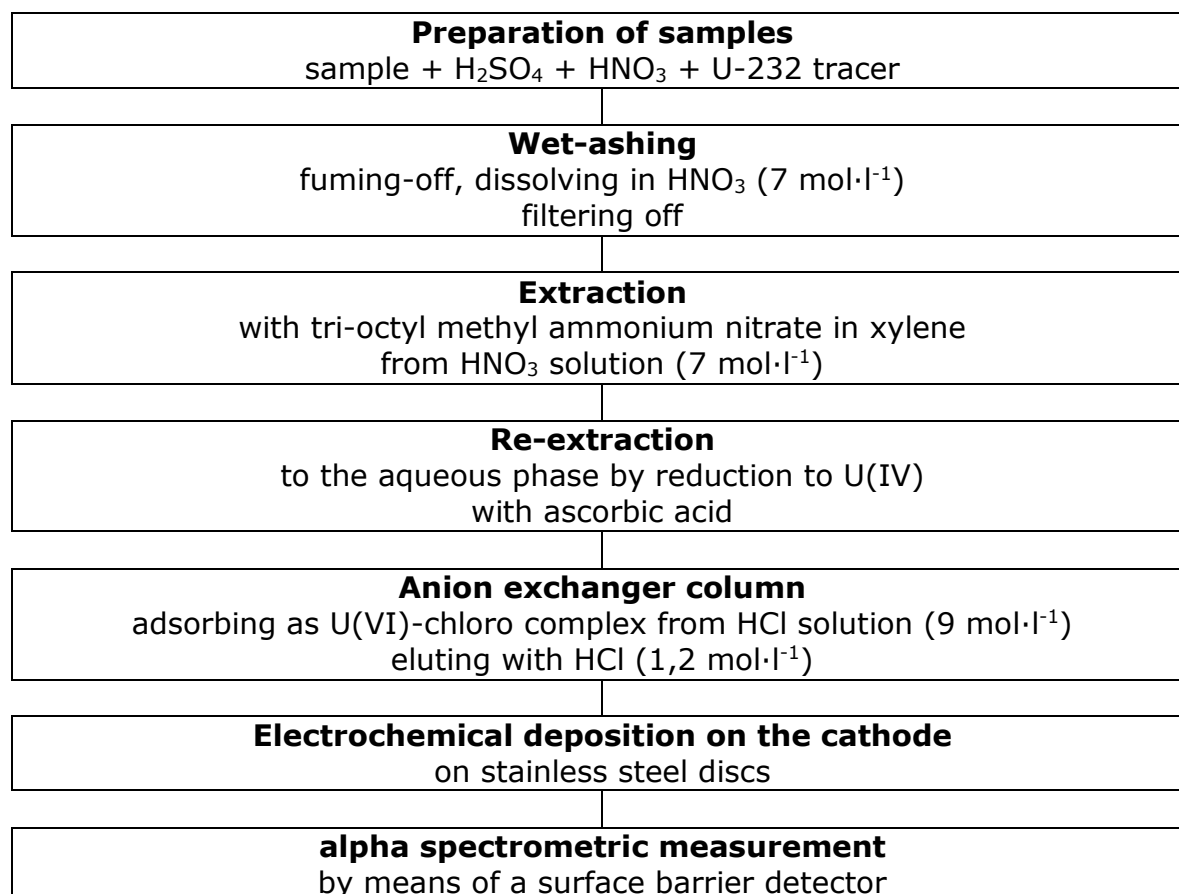


Fig. 1: Principle of determining uranium isotopes in wastewater

3.3 Radiochemical separation

3.3.1 100 ml of nitric acid (7 mol·l⁻¹) are added to the residue in order to dissolve it by stirring at elevated temperature for about one hour after capping with a watch glass. The solution is then filtered off via a frit equipped with a membrane filter (pore diameter 0,45 μ m) in order to remove insoluble substances (e. g., silicic acid). The filter cake is discarded.

3.3.2 The filtrate is left to cool to about 20 °C. Liquid-liquid extraction is performed twice for a minimum of 5 minutes each, using 50 ml of tri-octyl methyl ammonium nitrate in xylol, e. g., on an automated shaker (for conditioning the solvent, see section 7.1.2). The two organic phases (top) are combined and washed once with 50 ml of nitric acid (7 mol·l⁻¹).

Note

When processing large volumes of wastewater (> 1 l), precipitates of salts in the cooled filtrate may be observed. This indicates that a larger volume of nitric acid is required for dissolving. The extraction of uranium is then carried out using a correspondingly large volume of trioctylmethylammonium nitrate solution.

3.3.3 The uranium is then re-extracted from the washed organic phase five times, each time with 100 ml of ca. 50 °C hydrochloric acid (0,1 mol·l⁻¹) that contains 1 g of ascorbic acid per litre (shaking time 5 minutes each). The aqueous phases are combined and evaporated to dryness. The organic phase is discarded (collected in a bin for solvent wastes).

3.3.4 The black evaporation residue is wet-ashed with 5 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) and 2 ml of sulphuric acid ($18 \text{ mol}\cdot\text{l}^{-1}$). This process is to be repeated until the possibly still present residue is light in colour.

3.3.5 The residue is wet-ashed with 5 ml of hydrochloric acid ($9 \text{ mol}\cdot\text{l}^{-1}$), and dissolved in 100 ml of hydrochloric acid ($9 \text{ mol}\cdot\text{l}^{-1}$). It is then briefly heated to boiling point before the solution is left to cool to room temperature once more. Thereafter, the solution is applied to a pre-treated anion exchanger (for conditioning the exchanger, see section 7.1.1) at a rate of 1 ml to 2 ml per minute.

3.3.6 The anion exchanger is washed first with 120 ml of hydrochloric acid solution of ammonium iodide and then with 80 ml of hydrochloric acid ($9 \text{ mol}\cdot\text{l}^{-1}$). The wash solutions are discarded. For elution of uranium 100 ml of hydrochloric acid ($1,2 \text{ mol}\cdot\text{l}^{-1}$) are applied to the exchanger column. The eluate is evaporated to a dryness. If it still contains significant remnants of the ion exchanger, these have to be destroyed by fuming them off with 2 ml of sulphuric acid ($18 \text{ mol}\cdot\text{l}^{-1}$) and 5 ml of nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$).

3.3.7 The dry residue is dissolved at elevated temperatures with 1 ml of sodium hydrogen sulphate solution ($0,1 \text{ mol}\cdot\text{l}^{-1}$) and 4 ml of sulphuric acid ($1,5 \text{ mol}\cdot\text{l}^{-1}$), cooled to room temperature, and transferred to the prepared electrolytic cell (see section 7.2.1 and Fig. 2). The beaker is rinsed three times with ca. 2 ml sulphuric acid ($0,5 \text{ mol}\cdot\text{l}^{-1}$) each; the wash solutions are transferred to the cell and one drop of methyl red is added to the combined solution. Thereafter, ammonia solution ($13 \text{ mol}\cdot\text{l}^{-1}$) is added to the point of colour change. By adding a few drops of sulphuric acid ($1,5 \text{ mol}\cdot\text{l}^{-1}$), the pH is adjusted to a value of 2,4 to 2,5 (verified with Acilit[®] paper).

3.3.8 The uranium is then electrochemically deposited on the cathode at 300 mA for four hours. One minute before the electrolytic process is completed, 1 ml of ammonia solution ($13 \text{ mol}\cdot\text{l}^{-1}$) is added. The cell is dismantled. The steel disc is rinsed with distilled water and then dried with acetone. The cell, seal and bottom plate are rinsed with distilled water, and the upper part of the cell and a fresh steel disc (for the next analysis) are stored in RBS solution.

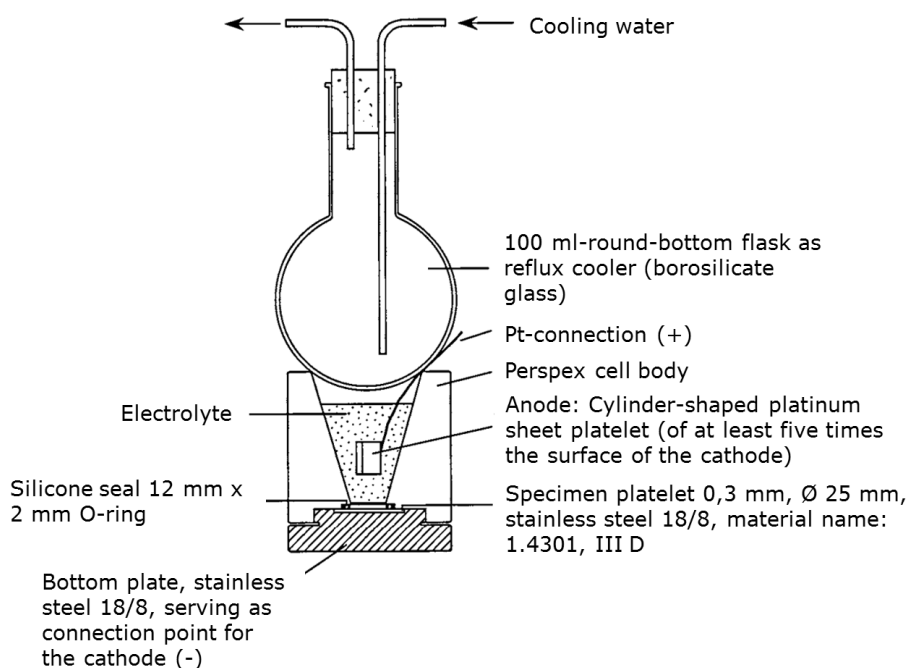


Fig. 2: Electrolytic cell

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4 Measuring the activity

For basic information on alpha spectrometry, please refer to chapter IV.2 of this procedures manual.

4.1 Calibration

The electrochemically deposited uranium isotopes are measured by means of a measuring station for alpha spectrometry. This may be, for example, a surface barrier detector that is run in a vacuum (ca. 10^3 Pa residual pressure) at ca. 100 V and connected to a multi-channel analyser with a data-output unit.

The detection efficiency of the measuring configuration is calibrated with solid U-233 and Am-241 calibration sources with known activities and negligibly thin layers (see section 7.2). The calibration factor is nearly constant within a range from ca. 3 MeV through 7 MeV.

For its part, the energy calibration is verified with the aid of solid (commercially available) calibration sources that contain several alpha emitters (e. g., U-233, Pu-239, Am-241, Cm-244, Cf-250 and Cf-252).

Notes

The detection efficiency depends to a large extent on the active surface area of the detector and the distance between counting source and detector. In case of a small distance (< 5 mm) there may be a risk, in particular if the electrolytic deposition has been poor and in the case of samples with higher activity, that the detector might be contaminated by the recoil effect of the alpha decay. While this can be prevented by choosing a larger distance (e. g., 30 mm), it will also substantially reduce the detection efficiency (e. g., by a factor of 5 to 10). If the sample throughput is low, this may be compensated by increasing the measurement period. Measuring at a larger distance between counting source and detector is particularly recommendable when inexperienced laboratory staff is trained in alpha spectrometric measurement procedures.

When calibrating a measuring station, it needs to be ensured that the calibration sources used have the same diameters as the counting sources. If this is not the case, numerical corrections for the dependency of the detection efficiency on the measuring geometry need to be applied (e. g., according to equation (7)). For further notes on this subject, please refer to chapter IV.2 of this procedures manual.

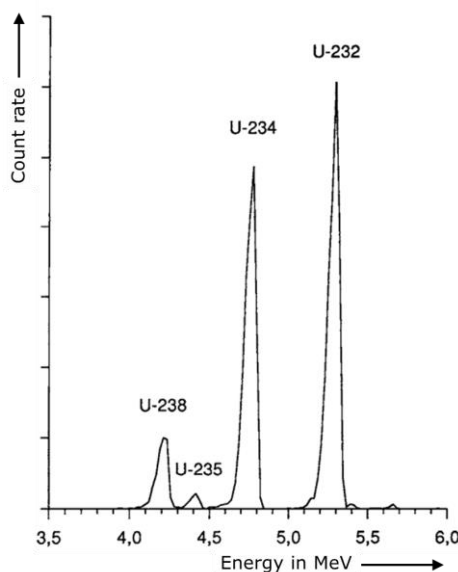


Fig. 3: Alpha spectrum of a uranium sample containing enriched uranium

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4.2 Measurement

The sample is measured in the same geometric configuration as the one used for calibration. Typical measurement periods are 10 hours and more.

Note

As a result of a bad, i. e., amorphous or coarsely crystalline, electrochemical deposition of the uranium on the steel disc or contamination of the counting source, a significant broadening of the energy lines may be observed during the alpha spectrometric measurement (in particular towards the lower energy range). In such a scenario, purifying the counting source will improve the quality of the analysis. To this end, the uranium is detached from the steel disc with a little hydrochloric acid ($8 \text{ mol} \cdot \text{l}^{-1}$) for about one second and rinsed off with water. The solution is then evaporated to a dry extract and treated further as from step 3.3.5.

A typical alpha spectrum of a wastewater sample from a plant processing nuclear fuels is illustrated in Figure 3. It refers to enriched uranium. For comparative purposes, Figure 4 illustrates the spectrum of a uranium sample with a natural isotopic composition.

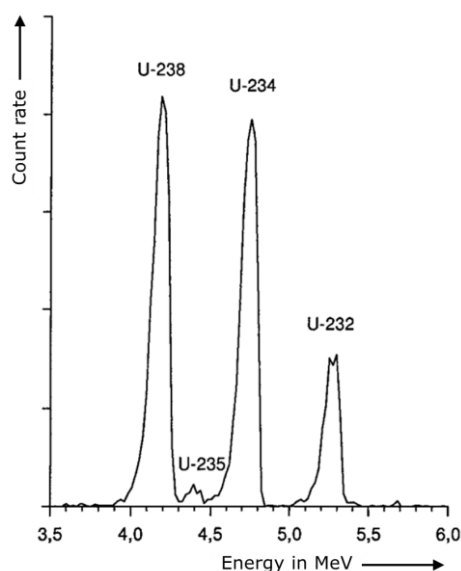


Fig. 4: Alpha spectrum of a uranium sample with a natural isotopic composition

5 Calculation of the results

The activity concentration, c_r , of an individual uranium isotope, r , is calculated according to equation (1)

$$c_r = \frac{\varphi_A}{V \cdot \eta \cdot p_{\alpha,r}} \cdot (R_g - R_0) \quad (1)$$

where

φ_A calibration factor, in Bq·s;

η chemical yield; < 1 ;

$p_{\alpha,r}$ emission probability of alpha radiation of the nuclide r ;

R_g gross count rate in the region of the line at $E_{\alpha,r}$ in s^{-1} ;

R_0 mean background count rate in the range of channels at $E_{\alpha,r}$ in s^{-1} ;

V volume of the sample used, in l.

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5.1 Worked example

The following data have been obtained from analysing the uranium content of a wastewater sample:

φ_A	= 5,46 Bq·s;
η	= 0,636 (63,6 %);
$\rho_{\alpha r}$	= 0,74 for U-235;
t_m	= 60000 s;
R_0	= $6,3 \cdot 10^{-5} \text{ s}^{-1}$ in the region of the U-234 line;
R_0	= $6,3 \cdot 10^{-5} \text{ s}^{-1}$ in the region of the U-235 line;
R_0	= $8,8 \cdot 10^{-5} \text{ s}^{-1}$ in the region of the U-238 line;
R_g	= $9,77 \cdot 10^{-3} \text{ s}^{-1}$ in the region of the U-234 line;
R_g	= $3,33 \cdot 10^{-4} \text{ s}^{-1}$ in the region of the U-235 line;
R_g	= $7,50 \cdot 10^{-3} \text{ s}^{-1}$ in the region of the U-238 line;
R_n	= $9,70 \cdot 10^{-3} \text{ s}^{-1}$ in the region of the U-234 line;
R_n	= $2,70 \cdot 10^{-4} \text{ s}^{-1}$ in the region of the U-235 line;
R_n	= $7,41 \cdot 10^{-3} \text{ s}^{-1}$ in the region of the U-238 line;
V	= 0,25 l.

Applying equation (1), the activity concentrations of the U-isotopes yield the following values:

$$c_{\text{U-234}} = 0,33 \text{ Bq} \cdot \text{l}^{-1}$$

$$c_{\text{U-235}} < 0,003 \text{ Bq} \cdot \text{l}^{-1} \text{ (see section 6)}$$

$$c_{\text{U-238}} = 0,25 \text{ Bq} \cdot \text{l}^{-1}$$

5.2 Consideration of uncertainties

For calculating the standard deviation of the statistical counting uncertainty, reference is made to chapter IV.5 of this procedures manual.

When assessing the total uncertainty of the calculated activity concentration, c_i , the uncertainty incurred from determining the detection efficiency (calibration uncertainty) and the uncertainty incurred from determining the chemical yield need to be taken into account next to the statistical counting uncertainty, s , while the uncertainty associated with determining the sample volume used can be neglected. The relative uncertainty in the detection efficiency ranges around $\pm 5 \%$, while the relative uncertainty in the chemical yield fluctuates, depending on the achieved chemical yield, around a mean value of between $\pm 5 \%$ and 10% .

In the case of activity concentrations that range in the region of the example given above (ca. $2 \text{ Bq} \cdot \text{l}^{-1}$), a total relative uncertainty of about $\pm 10 \%$ must be expected, whereas significantly lower activity concentrations will come with $\pm 20 \%$ and more.

6 Characteristic limits of the procedure

For calculating the characteristic limits, reference is made to chapter IV.5, sections 2.1, 2.3 and 4.8 of this procedures manual. The approach for determining the detection limit is based on interpreting the full peak width b (in channels) of an alpha line as an integral measurement that is taken with a single-channel analyser.

In practice, the background count rate, R_0 , of blind samples needs to be determined that are produced under the exact same conditions as the samples to be analysed. The background count rates recorded as a result may be higher than those of a blank sample such as an untreated steel disc.

The magnitude of achievable detection limits is estimated in the following example:

For measurement with long measurement periods, the following mean background effect count rates were determined at the line energies of U-234, U-235 and U-238:

Isotope	Mean α -energy (MeV)	Base width of line, b (channels)	R_0 in s^{-1} within range b	R_0 in s^{-1} per channel
U-234	4,75	18	$6,3 \cdot 10^{-5}$	$3,5 \cdot 10^{-6}$
U-235	4,39	9	$6,3 \cdot 10^{-5}$	$7,0 \cdot 10^{-6}$
U-238	4,19	16	$8,8 \cdot 10^{-5}$	$5,5 \cdot 10^{-6}$

According to equation (2.4) of section 2.1.2 of chapter IV.5 and measurement periods, t_m (sample) and t_0 (background effect) of 84600 s, a calibration factor of $\varphi_A = 5,46$ Bq·s and a value of $k_{1-\alpha} + k_{1-\beta} = 4,65$ will produce the following values as the detection limit G :

U-234: 1,7 mBq

U-235: 2,3 mBq

U-238: 1,8 mBq

The detection limits, g_r , for the activity concentrations are obtained according to equation (2):

$$g = \frac{G}{V \cdot \eta \cdot p_{\alpha,r}} \quad (2)$$

Using a wastewater sample volume of $V = 0,25$ l and achieving a radiochemical yield of $\eta = 0,64$ (64 %) will produce a detection limit for U-234 of about $11 \text{ mBq} \cdot \text{l}^{-1}$, for U-235 of about $14 \text{ mBq} \cdot \text{l}^{-1}$, and for U-238 of about $12 \text{ mBq} \cdot \text{l}^{-1}$.

7 Catalogue of chemicals and equipment

7.1 Chemicals

All chemicals used should be of the purity grade "pro analysi":

- Acetone, $\text{CH}_3\cdot\text{CO}\cdot\text{CH}_3$;
- Acilit® paper, pH 0,5 to 5,0;
- Ammonia NH_3 : 13 $\text{mol}\cdot\text{l}^{-1}$;
- Ammonium iodide solution: 8,7 g NH_4I in 240 ml of hydrochloric acid (9 $\text{mol}\cdot\text{l}^{-1}$); **this solution needs to be prepared freshly prior to use!**
- Anion exchanger: DOWEX 1 \times 2, 100 mesh to 200 mesh, Cl^- -form;
- Ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$;
- Methyl red: 0,01 $\text{mol}\cdot\text{l}^{-1}$ in ethanol;
- Sodium hydrogen sulphate, NaHSO_4 : 0,1 $\text{mol}\cdot\text{l}^{-1}$;
- Purifier, e. g., RBS-50 or Mucosal concentrates: 10 % solution;
- Hydrochloric acid, HCl : 0,1 $\text{mol}\cdot\text{l}^{-1}$, 1,2 $\text{mol}\cdot\text{l}^{-1}$, 8 $\text{mol}\cdot\text{l}^{-1}$ and 9 $\text{mol}\cdot\text{l}^{-1}$;
- Nitric acid, HNO_3 : 7 $\text{mol}\cdot\text{l}^{-1}$ and 14 $\text{mol}\cdot\text{l}^{-1}$;
- Sulphuric acid, H_2SO_4 : 0,5 $\text{mol}\cdot\text{l}^{-1}$, 1,5 $\text{mol}\cdot\text{l}^{-1}$ and 18 $\text{mol}\cdot\text{l}^{-1}$;
- Sea sand, washed with acid and annealed;
- Trioctylmethylammonium chloride $[(\text{C}_8\text{H}_{18})_3\cdot\text{CNH}_3]\text{Cl}$: 10 % solution in xylene;
- U-232 tracer solution, ca. 300 $\text{Bq}\cdot\text{l}^{-1}$ (e. g., from Amersham-Buchler, Brunswick);
- Xylene, isomer mix, $\text{C}_6\text{H}_4\cdot(\text{CH}_3)_2$.

7.1.1 Pretreatment of the anion exchanger

After having been soaked in distilled water for about 1 hour, the anion exchanger is elutriated without air bubbles in the column for about 2/3 of the column volume and conditioned with 100 ml of hydrochloric acid (9 $\text{mol}\cdot\text{l}^{-1}$) immediately before the prepared sample solution is applied.

7.1.2 Pretreatment of the extraction agent

100 ml of trioctylmethylammonium chloride (10 % solution in xylene) are washed twice with 50 ml of nitric acid (7 $\text{mol}\cdot\text{l}^{-1}$) each immediately before the extraction. This will produce the required tri-octyl methyl ammonium nitrate. The aqueous phases are discarded. The organic phase is used for the extraction process.

7.1.3 Purifying the U-232 tracer solution and determining the activity concentration

U-232 produces Th-228 as a daughter nuclide with a half-life of 1,8 years. The latter decays into short-lived alpha emitters that may interfere with the measuring process. It is for this reason that the tracer solution needs to be purified at intervals of about 6 months. This is done by evaporating a volume of tracer solution from a U-232 mother solution that will cover the needs for an extended period of time, dissolving it in hydrochloric acid (9 $\text{mol}\cdot\text{l}^{-1}$), and purifying it by anion exchange according to steps 3.3.5 and 3.3.6. The purification step with ammonium iodide/hydrochloric acid may be omitted here. The evaporated eluate is then dissolved in a warm environment with a little nitric acid (1 $\text{mol}\cdot\text{l}^{-1}$) and thereafter diluted with distilled water to a concentration of about 150 $\text{Bq}\cdot\text{l}^{-1}$. Its activity is measured fol-

lowing the electrochemical deposition of 1 ml to 2 ml of the solution according to steps 3.3.7 and 3.3.8. A 100 % deposition may be supposed.

7.2 Equipment

- Stainless steel discs (V2A steel, austenitic, $\varnothing = 25$ mm, thickness 0,3 mm);
- Electrolytic cell: see Fig. 2;
- Ion exchanger columns: length 20 cm, $\varnothing = 1,5$ cm, frit G0;
- Measuring station for alpha spectrometry, consisting of: surface barrier counter (e. g., with 400 mm² active surface, 100 μ m depth of the depletion zone, 25 keV resolution), vacuum measuring chamber, vacuum pump, power supply, amplifier, analogue-digital converter (ADC), multi-channel pulse peak analyser, data recording device;
- Automated shaker;
- Basic equipment of a radiochemical laboratory;
- U-233 and Am-241 standard sources (e. g., from Commissariat à l'Énergie Atomique, Laboratoire de Metrologie des Rayonnements Ionisants).

7.2.1 Preparing the electrolytic cell

The electrolytic cell and the stainless steel disc are stored in RBS-50 solution (ca. 10 %). Prior to electrolysis, the cell needs to be warmed for about 10 minutes in the RBS-50 solution and then needs to be thoroughly rinsed with distilled water. After having been treated with RBS-50, the stainless steel disc is to be rinsed thoroughly with sulphuric acid (0,5 mol·l⁻¹) and thereafter with distilled water.

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Further references, in particular those relating to measuring techniques, are provided in chapter IV.2 of this procedures manual.