

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

H- α -SPEKT-AWASS-03

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1 Scope

The procedure is suitable for the simultaneous determination of the plutonium isotopes Pu-238 and Pu-(239+240) in wastewater. It is suitable for use with wastewaters from nuclear facilities, wastewaters from users of isotopes, and raw and processed wastewaters from sewage treatment purification plants. The principles of the procedure may also be projected – if needed after enrichment by evaporation of 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

Together with uranium, plutonium is extracted by trioctylmethylammonium nitrate from a nitric acid solution, then isolated as a hexanitrate complex by anion exchange, and separated from accompanying elements (e. g., uranium, thorium, iron). Its activity is determined by measuring thin-layer counting sources that are obtained by electrochemical deposition of plutonium in hydroxide form on stainless steel discs by alpha spectrometry. Adding Pu-236 or Pu-242 with known activities as tracers serves to determine the chemical yield of plutonium. The principle of the procedure is illustrated in Figure 1.

Notes

Owing to the limited energy resolution of alpha spectrometry (half-width about 50 keV), it is impossible to analyse the lines of the plutonium isotopes Pu-239 ($E_{\alpha} = 5,157 \text{ MeV}$) and Pu-240 ($E_{\alpha} = 5,168 \text{ MeV}$) separately. It is therefore common practice to state the sum of Pu-239 and Pu-240.

If Pu-242 is available for use as a tracer, it should be given preference over Pu-236, because the Pu-242 line has a lower energy level than the alpha energies of both Pu-238 and Pu-(239 + 240) and thus excludes the possible interference of tailing effects of the Pu-236 line.

Pu-236 is often contaminated with Pu-238 of a low activity concentration whose influence on the analysis of the Pu-238 content of a sample may need to be corrected for numerically.

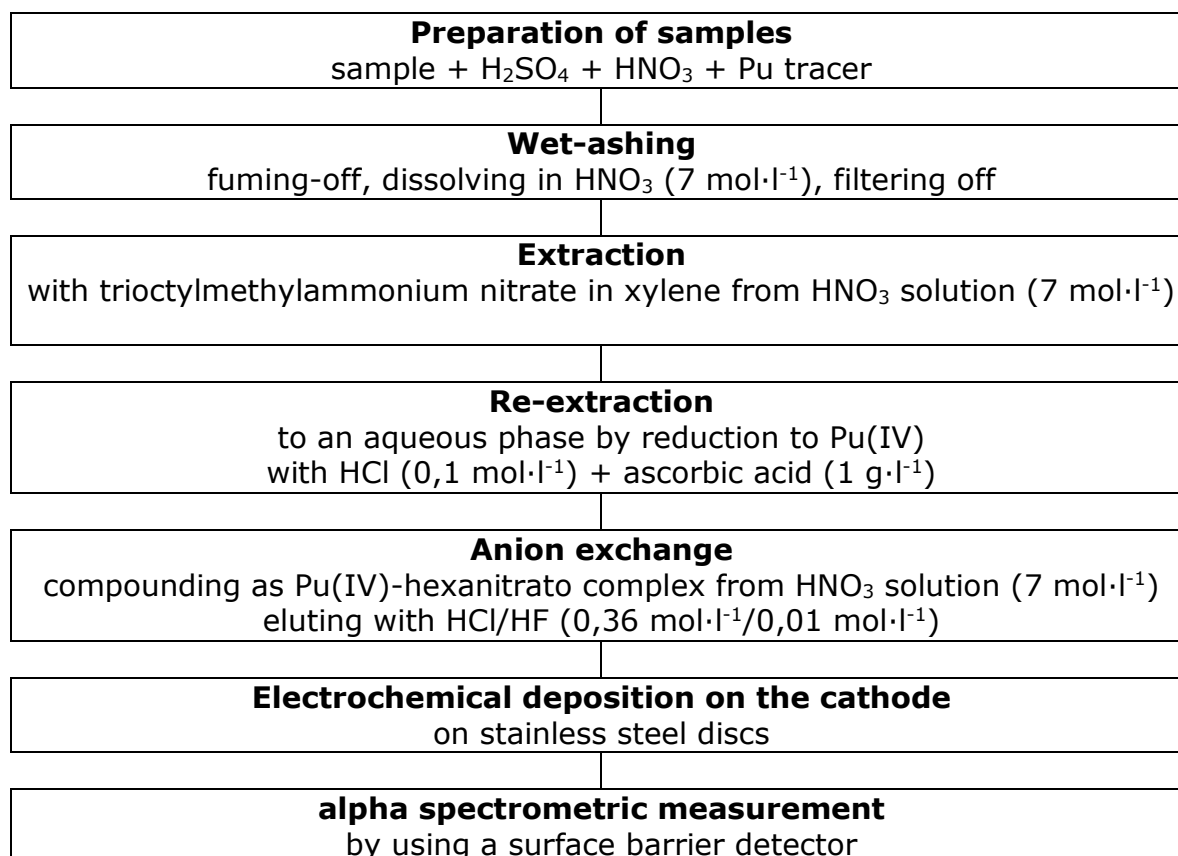


Fig. 1: Principle for determination of plutonium isotopes in wastewater

3.2 Sample preparation

An adequately large volume of the sample (normally 1 l) is spiked with Pu-236 tracer (ca. 0,5 Bq), 5 ml of sulphuric acid (18 mol·l⁻¹), and 10 ml of nitric acid (14 mol·l⁻¹) and fumed off to dryness.

Note

The activity of the Pu-236 used as a tracer should be such that the resulting Pu-236 line is of similar peak height compared to the analysed Pu-isotopes. In the case of higher activities smaller sample volumes might be used. 2 ml of sulphuric acid (18 mol·l⁻¹) and 5 ml of nitric acid (14 mol·l⁻¹) are added to the cooled residue and the dissolved residue is fumed off once more. This step needs to be repeated until the residue is free of organic constituents.

3.3 Radiochemical separation

3.3.1 100 ml of nitric acid (7 mol·l⁻¹) is added to the residue and, capped with a watch glass, dissolved by stirring at elevated temperature for about one hour; the solution is then filtered off using a frit equipped with a membrane filter (pore diameter 0,45 μ m) in order to remove traces of silicic acid. The residue 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 trioctylmethylammonium nitrate in xylene, on an automated shaker (for preparation of 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 solution may be observed. This indicates that a larger volume of nitric acid is required. The

extraction of the plutonium would then need to be done by using fresh trioctylmethylammonium nitrate solution at individual portions of about 100 ml each.

3.3.3 The plutonium is re-extracted from the washed organic phase five times, each time with 100 ml of ca. 50 °C hydrochloric acid ($0,1 \text{ mol}\cdot\text{l}^{-1}$) that contains 1 g of ascorbic acid per litre, for at least 5 minutes. The aqueous phases are combined and evaporated to dryness. The organic phase is discarded (collected in a barrel for solvent wastes).

3.3.4 The black evaporation residue is fumed off to dryness 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 residue possibly still present is light in colour.

3.3.5 50 ml of hydrochloric acid ($7 \text{ mol}\cdot\text{l}^{-1}$) is added to the residue at elevated temperature, cooled to 20 °C, and then 1 ml of sodium nitrite solution ($2,9 \text{ mol}\cdot\text{l}^{-1}$) or a spatula tip of solid sodium nitrite (foams strongly) is added in order to reduce Pu(VI) to Pu(IV). Thereafter, the solution is applied to a pre-conditioned anion exchanger (for conditioning the anion exchange, see section 7.1.1) at a through-flow speed of 1 ml to 2 ml per minute. It is then washed in succession with 120 ml of nitric acid ($7 \text{ mol}\cdot\text{l}^{-1}$) and 100 ml of hydrochloric acid ($9 \text{ mol}\cdot\text{l}^{-1}$). Throughflow and wash solutions are discarded.

Note

The combined throughflows may be used for the determination of the uranium content.

3.3.6 The plutonium is eluted with 100 ml of hydrochloric acid/hydrofluoric acid solution ($0,35 \text{ mol}\cdot\text{l}^{-1}$ and $0,01 \text{ mol}\cdot\text{l}^{-1}$, respectively). 1 ml of sodium hydrogen sulphate solution ($0,1 \text{ mol}\cdot\text{l}^{-1}$) is added to the eluate and evaporated to dryness on a sand bath. If it still contains significant remnants of the ion exchanger, these have to be destroyed by fuming them off repeatedly 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 picked up with 5 ml of sulphuric acid ($1,5 \text{ mol}\cdot\text{l}^{-1}$), concentrated to 2 ml, cooled and quantitatively transferred to the prepared electrolytic cell (cf. section 7.2.1 and Fig. 2). To this end, the beaker is rinsed three times with about 2 ml of sulphuric acid ($0,5 \text{ mol}\cdot\text{l}^{-1}$) each and the individual portions are added to the main solution in the electrolytic cell. 1 drop of methyl red and ammonia ($13 \text{ mol}\cdot\text{l}^{-1}$) is added to the solution 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). Electrolysis then takes ca. 4 hours at 300 mA. One minute before the electrolytic process is completed, 1 ml of ammonia solution ($13 \text{ mol}\cdot\text{l}^{-1}$) is added. After that, the content of the cell is poured off, the cell is dismantled, the steel disc is rinsed with distilled water and then dried with acetone.

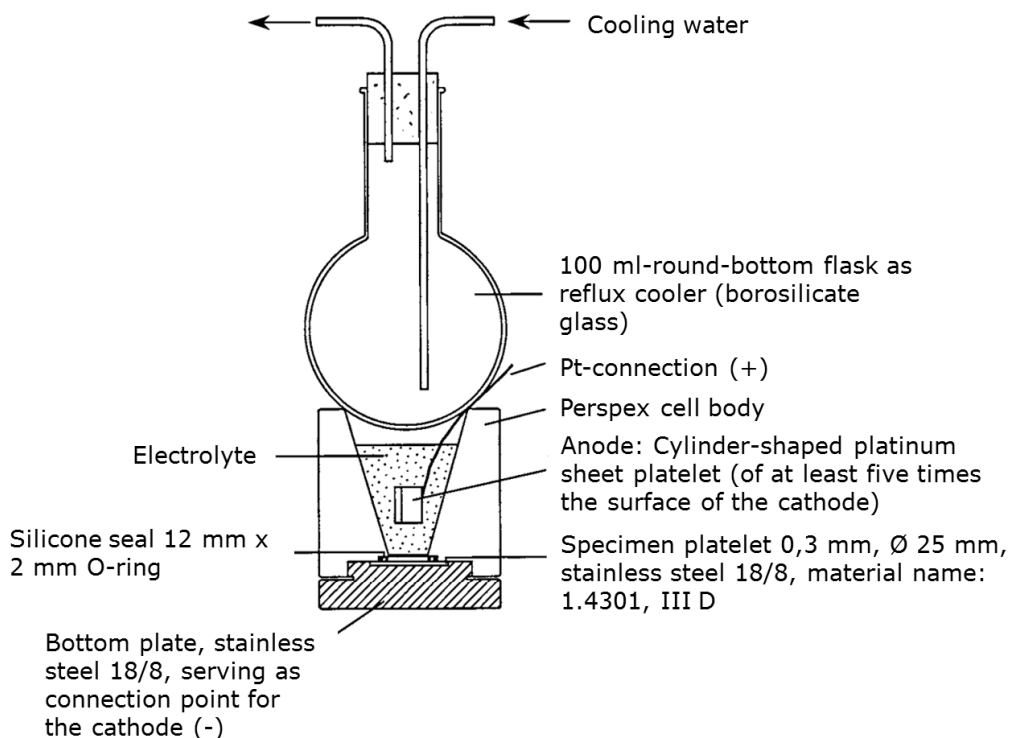


Fig. 2: Electrolytic cell

4 Measuring the activity

For basic information on alpha spectrometry, reference is made to chapter IV.2 of this procedures manual.

4.1 Calibration

The electrochemically deposited plutonium 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-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 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 counting yield (e. g., by a factor of 5 to 10). If the sample throughput is low, this may be compensated by increasing the measurement period. Observing a wider distance between counting source and detector is particularly recommendable when inexperienced laboratory staff is trained in alpha spectrometric measurement procedures.

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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 efficiency on the measuring geometry need to be applied (e. g., according to (7)). Further annotations on this subject can be found in chapter IV.2 of this procedures manual.

4.2 Measurement

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

Note

As a result of an impure, i. e., amorphous or coarsely crystalline, electrochemical deposition of the plutonium on the steel disc or contamination of the counting source, a significant broadening of the energy lines may be noted during the alpha spectrometric measurement (in particular towards the lower energy range). In such a case, purifying the counting source will improve the quality of the analysis. To this end, the plutonium 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 distilled water. The solution is then evaporated to dryness and treated further as from step 3.3.4.

A typical alpha spectrum of a wastewater sample from a nuclear fuel processing facility is illustrated in Figure 3.

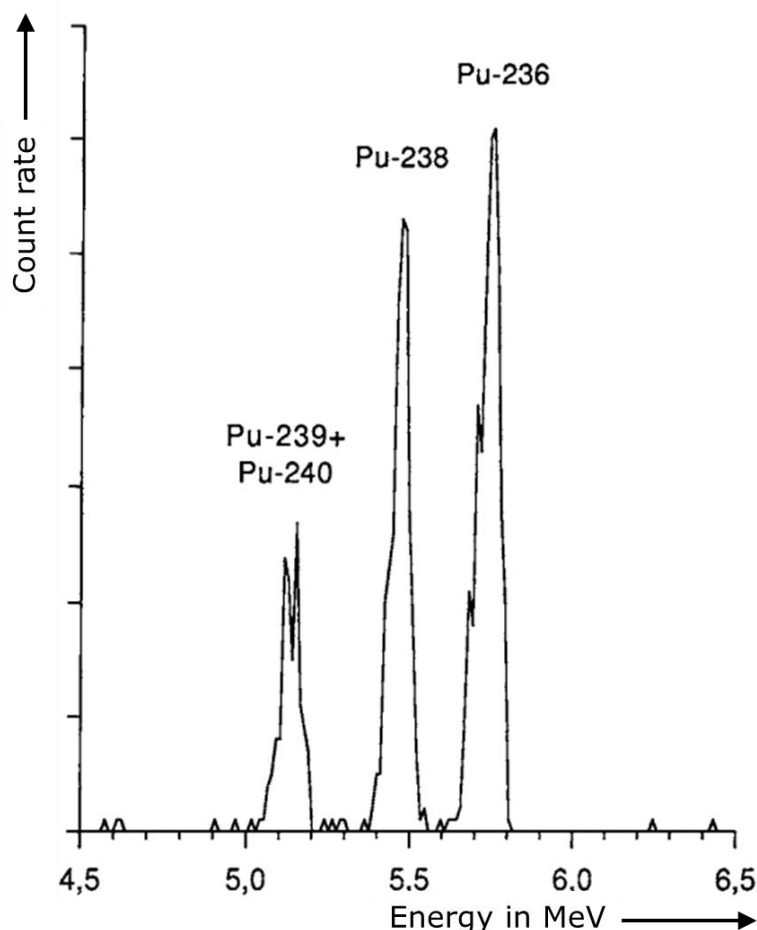


Fig. 3: Alpha spectrum of a plutonium sample

5 Calculation of the results

The activity concentrations, c_r , of the individual plutonium isotopes is calculated according to equation (1)

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

where

- φ_A calibration factor, in Bq·s;
- η chemical yield; < 1;
- $\rho_{\alpha,r}$ 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.

5.1 Worked example

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

- φ_A = 5,46 Bq·s;
- η = 0,472 (47,2 %);
- $\rho_{\alpha,r}$ = 1,0;
- t_m = 158230 s (44 h);
- R_0 = $5,7 \cdot 10^{-5}$ s⁻¹ in the region of the Pu-238 line;
- R_0 = $3,2 \cdot 10^{-5}$ s⁻¹ in the region of the Pu-(239+240) line;
- R_g = $3,86 \cdot 10^{-4}$ s⁻¹ in the region of the Pu-238 line;
- R_g = $5,06 \cdot 10^{-4}$ s⁻¹ in the region of the Pu-(239+240) line;
- R_n = $3,29 \cdot 10^{-4}$ s⁻¹ in the region of the Pu-238 line;
- R_n = $4,74 \cdot 10^{-4}$ s⁻¹ in the region of the Pu-(239+240) line;
- V = 1 l.

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

$$c_{\text{Pu-238}} = 3,81 \cdot 10^{-3} \text{ Bq} \cdot \text{l}^{-1}$$

$$c_{\text{Pu-(239+240)}} = 5,48 \cdot 10^{-3} \text{ Bq} \cdot \text{l}^{-1}$$

5.2 Consideration of uncertainties

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

When assessing the total uncertainty of the calculated activity concentration, c_r , the uncertainty incurred from determining the efficiency (calibration error) and the uncertainty associated with determining the chemical yield need to be taken into account beside the statistical counting uncertainty, s , while the uncertainty incurred from determining the sample volume used can be neglected. The relative uncertainty in the efficiency ranges around ± 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 long measurement times, the following mean background count rates were determined in the regions of the lines of Pu-238 as well as Pu-239 + Pu-240 with the measuring configuration used:

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
Pu-238	5,49	20	$5,7\cdot 10^{-5}$	$2,9\cdot 10^{-6}$
Pu-(239+240)	5,15	20	$3,2\cdot 10^{-5}$	$1,6\cdot 10^{-6}$

Applying equation (2.4) of section 2.1.2 of chapter IV.5 and measurement periods of t_m (sample) and t_0 (background effect) of 84600 s , a calibration factor of $\varphi_A = 5,46 \text{ Bq}\cdot\text{s}$ and a value of $k_{1-\alpha} + k_{1-\beta} = 4,65$, the detection limit for the activity of, e. g., Pu-(239+240), will produce a value of about $1,4 \text{ mBq}$.

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 $V = 1 \text{ l}$ and achieving a radiochemical yield of $\eta = 0,472$ ($47,2\%$) will produce a detection limit of about $3 \text{ mBq}\cdot\text{l}^{-1}$ for the activity concentration of Pu-(239+240).

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 mol·l⁻¹;
- Anion exchanger: DOWEX[™] 1 × 2, 100 mesh to 200 mesh, Cl⁻-form;
- Ascorbic acid, $\text{C}_6\text{H}_8\text{O}_6$;
- Eluent HCl/HF: 0,36 mol·l⁻¹ and 0,01 mol·l⁻¹, respectively;
- Hydrofluoric acid, HF: 23 mol·l⁻¹;
- Methyl red: 0,01 mol·l⁻¹ in ethanol;
- Sodium hydrogen sulphate, NaHSO_4 : 0,1 mol·l⁻¹;
- Sodium nitrite, NaNO_2 : 2,9 mol·l⁻¹;
- Pu-242- or Pu-236 tracer solution, ca. 300 Bq·l⁻¹ (e.g., from. Amer-sham/Buchler);
- Purifier, e.g., RBS-50 or Mucasol concentrates: 10 % solution;
- Hydrochloric acid, HCl: 0,1 mol·l⁻¹; 8 mol·l⁻¹ and 9 mol·l⁻¹;
- Nitric acid, HNO_3 : 7 mol·l⁻¹ and 14 mol·l⁻¹;
- Sulphuric acid, H_2SO_4 : 0,5 mol·l⁻¹; 1,5 mol·l⁻¹ and 18 mol·l⁻¹;
- Sea sand, washed with acid and annealed;
- Trioctylmethylammonium chloride [$(\text{C}_8\text{H}_{18})_3 \cdot \text{CNH}_3$]Cl: 10 % solution in xylene;
- 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 24 h, the anion exchanger is elutriated without air bubbles in the column and conditioned with 100 ml of nitric acid (7 mol·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 mol·l⁻¹) each immediately before the extraction. This will produce the required trioctylmethylammonium nitrate. The aqueous phases are discarded. The organic phase is used for the extraction process.

7.2 Equipment

- Stainless steel discs (V2A steel, austenitic, $\varnothing = 25$ mm, thickness 0,3 mm);
- Electrolytic cell: see Fig. 2;
- Direct-current generator, if possible with current stabiliser;
- Ion exchanger columns: length 20 cm, $\varnothing = 1,5$ cm, frit G0;
- Membrane filter, pore diameter 0,45 μm ;
- Measuring station for alpha spectrometry, consisting of:
surface barrier detector (e.g., with 400 mm² active surface, 100 μm 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;

- U-233 and Am-241 standard sources (e. g., from Commissariat à l'Énergie Atomique, Laboratoire de Metrologie des Rayonnements Ionisants);
- Basic equipment of a radiochemical laboratory.

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 ($0,5 \text{ mol}\cdot\text{l}^{-1}$) and thereafter with distilled water.

References

- (1) Anderson, R. F., Fleer, A. P.: Determination of Natural Activities and plutonium in Marine Particulate Material, *Analytical Chemistry* 54 (1982), pp. 1142 ff.
- (2) Delle Site, A., Santori, G., Bazzarri, S.: Determination of plutonium-239 in Animal Tissues and Excreta. The Application of Liquid Scintillation Counting and Extraction Chromatography. RT/PROT (74) 23, Comitato Nazionale Energia Nucleare, Roma, Sept. 1973
- (3) Frindik, O.: α -spectrometrische Methoden zur Bestimmung von Plutonium und Uran in Lebensmitteln, biologischem Material and Böden. BFE-Bericht 1980/6, Bundesforschungsanstalt für Ernährung, Karlsruhe, Juli 1980
- (4) Godoy, J. M., Schüttelkopf, H., Pimpl, M.: Die Bestimmung von Pu-241 durch Flüssigszintillationsspektrometrie in der Umgebung des Kernforschungszentrums Karlsruhe. Kfk 3531, Kernforschungszentrum Karlsruhe GmbH, Hauptabteilung Sicherheit, April 1983
- (5) Harley, J. H.: EML Procedures Manual HASL 300, Environmental Measurements Laboratory of U. S. Department of Energy, E-Pu-01 bis E-Pu-09
- (6) Pimpl, M., Schüttelkopf, H., Afsar, M.: Die Plutonium-Kontamination des Rheins: Die Kontamination der Sedimente. Kfk 2892, Kernforschungszentrum Karlsruhe GmbH, Hauptabteilung Sicherheit, Dez. 1979
- (7) Schüttelkopf, H.: Entwicklung einer Analysenmethode für Plutonium im Femtogramm/gramm-Bereich und ihre Anwendung auf Umweltproben. Kfk 3035, Kernforschungszentrum Karlsruhe GmbH, Hauptabteilung Sicherheit, Sept. 1981
- (8) Schwochau, K., Astheimen, L., Schenk, H. J., Witte, E. G.: On the Extraction of uranium from Sea Water by a Complexing Resin, *Zeitschrift für Naturforschung* 37b (1982), pp. 214 ff.