Procedure for determining thorium isotopes in wastewater by an extraction-chromatographic procedure

H-Th-AWASS-01

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Procedures manual for monitoring of radioactive substances in the environment and of external radiation
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1 Scope

The procedure described here serves to determine the thorium isotopes Th-232, Th-230 and Th-228 in wastewater samples collected from nuclear facilities, in particular from fuel assembly production plants in the context of the Guidelines for Monitoring Emissions and Immissions of Nuclear Installations (REI) Appendix B (1). The principles of the procedure may also be applied to other water samples.

2 Sampling

Details on the selection of samples and sampling techniques can be found in procedure H-γ-SPEKT-AWASS-01 of these measuring instructions. A sample volume of 0,5 l is sufficient to achieve the prescribed (1) detection limit of 0,05 $Bq \cdot l^{-1}$ and to carry out a duplicate determination according to this procedure. The water samples are stabilised by acidifying them with concentrated nitric acid (14 $mol \cdot l^{-1}$) to a pH of about 1 (about 10 ml of nitric acid per litre of wastewater).

3 Analysis

3.1 Principle of the procedure

The procedure is based on the extraction-chromatographic separation of thorium ions from uranium isotopes and other radionuclides by using specially designed columns (TEVA·Spec) for tetravalent actinides (2). The specific extraction agent that is bound to the inert carrier is a mix of tri-octyl and tri-decyl methyl ammonium chloride (Aliquat™ 336). Fig. 1 gives an overview of the analytic procedure.

For the enrichment of the actinides a phosphate precipitation is performed after which the precipitate is dissolved. This nitric sample solution is applied to a TEVA-column adsorb tetravalent thorium ions (and Pu- and Np-ions, if such are present in the sample as well) and to separate these from hexavalent U- as well as trivalent Am- and Cm-ions. The Th-isotopes retained on the column are then eluted with a hydrochloric acid, which will leave the tetravalent Pu- and Np-ions adsorbed on the column (cf. Fig. 5, Appendix).

The activity of the thorium isotopes is then measured by alpha spectrometry. The counting source is produced directly from the eluate by electrodeposition or microprecipitation with cerium fluoride (or neodymium fluoride).

For determining the yield of the radiochemical separation process, a Th-tracer is added, preferably Th-234. The described procedure will typically produce yields of about 80 %.

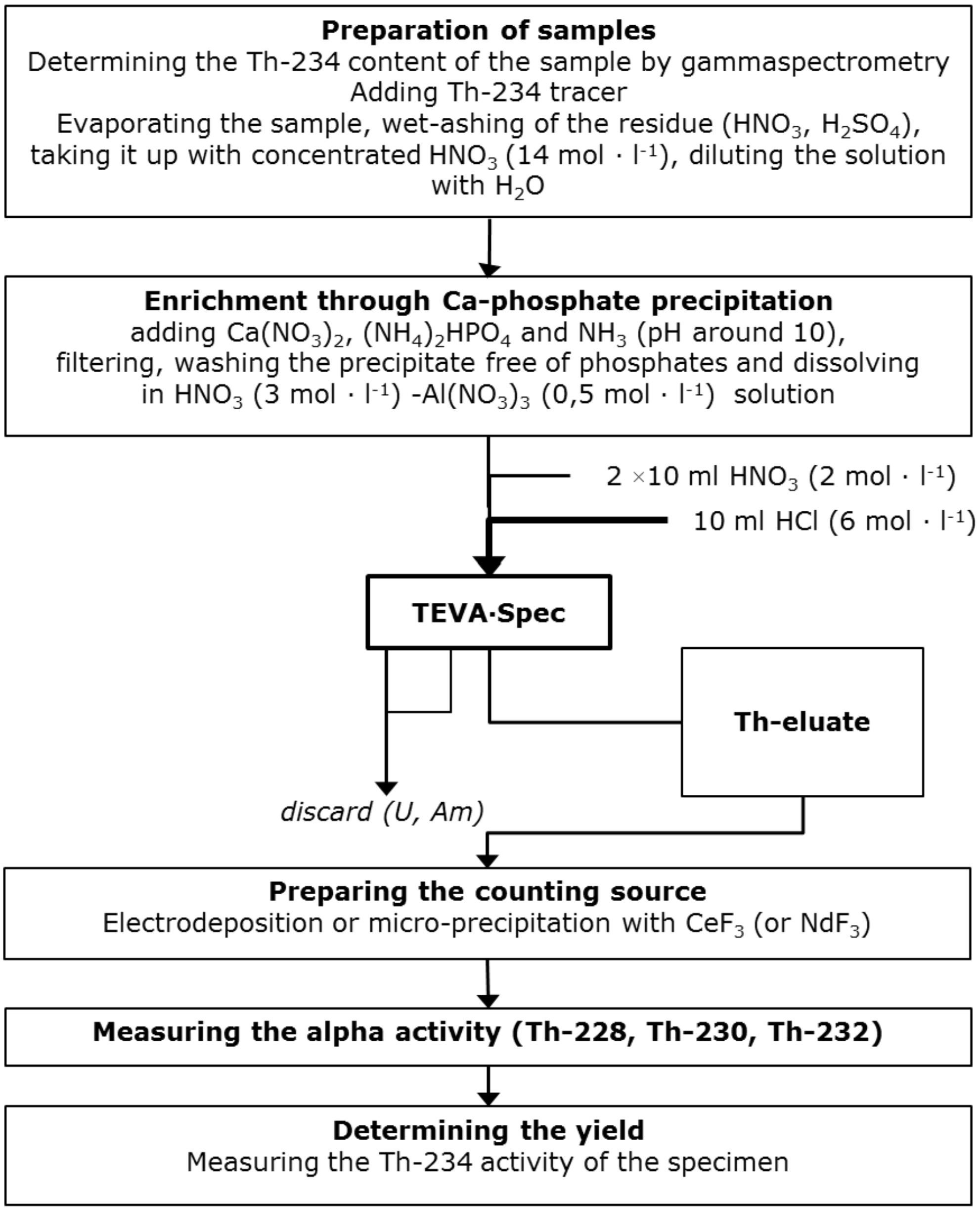

Fig. 1: Overview of the analytic procedure for determining Th-232, Th-230 and Th-228 in wastewater

3.2 Sample preparation

The sample is spiked with a defined amount of Th-234 activity, which requires that the Th-234 activity already present in the sample be known and be taken into consideration (e.g., determined by a gamma spectrometric measurement). Reliably determining the yield will be possible if the Th-234 activity ratio between tracer/sample is about 100.

After the tracer has been added, the water sample is evaporated to dryness and the residue is (if need be several times) fumed off with 10 ml of concentrated nitric acid (14 mol·l^{-1}) and 5 ml of concentrated sulphuric acid (18 mol·l^{-1}) in order to completely remove any organic constituents. The sample is then taken up with ca. 5 ml of concentrated nitric acid and dissolved in about 50 ml of distilled water under stirring in a warm environment.

Note
In the appendix of this instruction, two procedures for preparing Th-234 tracers and the required determination of their activities are outlined. In principle it would also be possible to use other thorium isotopes as tracers. However, neither the tracer nuclide itself or its decay products may interfere with the alpha spectrometric measurements of the Th-232, Th-230 and Th-228 activities. Similarly, the yield can only then reliably be determined if the thorium isotopes that are to be determined or their short-lived decay products do not interfere with the measurement of the tracer activity. Being a beta emitter, Th-234 will conform to these requirements. The alpha energies and emission probabilities of other relevant thorium isotopes are listed in chapter IV.6 of this procedures manual.

3.3 Radiochemical separation

3.3.1 A few drops of phenolphthalein solution, 0,5 ml of calcium nitrate solution (1,25 $mol \cdot l^{-1}$), and 2 ml of diammonium hydrogen phosphate solution (3,2 $mol \cdot l^{-1}$) are added to the sample.

3.3.2 Keeping the sample warm, concentrated ammonia (13,5 $mol \cdot l^{-1}$) is added drop by drop while stirring until a colour change of the indicator towards red is observed (pH 9 to 10), which will cause a phosphate precipitation. Following another 5 minutes of stirring, the beaker is covered with a watch glass and left to stand at room temperature for ca. 2 hours to allow the voluminous precipitate to settle.

3.3.3 The precipitate is filtered off via a white-ribbon filter and washed twice with about 10 ml of distilled water. Using a clean new beaker, the precipitate is dissolved in 15 ml to 20 ml of a nitric acid (3 $mol \cdot l^{-1}$) – aluminium nitrate (1 $mol \cdot l^{-1}$) solution (the filter needs to be rinsed thoroughly).

3.3.4 A TEVA-column (2 ml in column bed volume, 0,7 g resin) is conditioned with 5 ml of a nitric acid (3 $mol \cdot l^{-1}$) – aluminium nitrate (0,5 $mol \cdot l^{-1}$) solution.

3.3.5 The sample solution obtained in step 3.3.3 is applied to the conditioned column, which will extract the tetravalent Th-, Pu- and Np-ions from the sample solution and retain them on the carrier. The beaker is rinsed with 10 ml of nitric acid (2 $mol \cdot l^{-1}$) and this solution is applied to the column after the sample solution has run through. In order to completely remove the uranium isotopes adsorbed on the column, it is washed once more with 10 ml of nitric acid (2 $mol \cdot l^{-1}$). The run-off of the sample and the wash solutions are discarded.

3.3.6 The thorium ions bound to the carrier are eluted with 10 ml of hydrochloric acid (6 $mol \cdot l^{-1}$), using a clean beaker or a LSC-vial to collect the eluate. The eluate is processed further for measuring the alpha-activity.

Note
In order to obtain an estimate of the chemical yield directly after the separation, the eluate is measured with a liquid-scintillation counter. Within minutes, radioactive equilibrium between Th-234 and its short-lived daughter nuclide Pa-234m (half-life 1,17 minutes) is established. The high-energy beta-emitter Pa-234m with its maximum beta-energy of 2,28 MeV creates Cerenkov-radiation in a light-permeable medium that can be measured without the need of adding a scintillation cocktail. A typical Cerenkov-spectrum is illustrated in Figure 4 (Appendix).

3.3.7 The column is washed for storage with 5 ml of nitric acid (0,1 $mol \cdot l^{-1}$) and left to stand closed with a little supernatant.

Note
The TEVA-column may be reused several times. If bound Pu- and Np-ions need to be removed, the resin is washed with 20 ml of hydrochloric acid (1 $mol \cdot l^{-1}$) before storage.

3.3.8 The counting source may be prepared by either of two procedures. Either, the eluate is processed further with the aim to deposit the thorium as a hydroxide on a stainless steel disc by electrochemical means, or thorium fluoride is precipitated with cerium fluoride (or neodymium fluoride) directly from the eluate.

3.3.9 The steel disc with its layer of precipitated $Th(OH)_4$ or ThF_4 on the filter is measured by alpha spectrometry. The yield is then verified by measuring the activity of the Th-234. This may be achieved by either measuring the steel disc by gamma spectrometry, or by an LSC-measurement of the Cerenkov-radiation of the Pa-234m after the separated $Th(OH)_4$-layer has been removed from the steel disc completely with a few drops of concentrated nitric acid. The chemical yield is calculated as the quotient of the measured and the added Th-234 activities while taking into account the decay time.

3.4 Counting source preparation

3.4.1 Electrodeposition

1 ml of sodium hydrogen sulphate solution (0,1 $mol \cdot l^{-1}$) is added to the eluate, then evaporated to dryness on a sand bath, and the residue fumed off with 2 ml of concentrated nitric acid (14 $mol \cdot l^{-1}$) and 1 ml of concentrated sulphuric acid (18 $mol \cdot l^{-1}$). This will destroy organic substances that have been washed off the column. The residue is then heated and dissolved with 10 ml of sulphuric acid (1,5 $mol \cdot l^{-1}$), cooled to room temperature, and the solution then transferred to the electrolytic cell. The sample vessel is rinsed twice with 2 ml of sulphuric acid (0,5 $mol \cdot l^{-1}$) each, and the rinsing water is added to the cell as well. Following the addition of 1 ml of ammonium oxalate solution (0,16 $mol \cdot l^{-1}$) and one drop of methyl-red solution, concentrated ammonia (13,5 $mol \cdot l^{-1}$) is added slowly until the solution turns yellow. Thereafter, sulphuric acid (1,5 $mol \cdot l^{-1}$) is added dropwise until the solution turns red, and the pH is subsequently adjusted to 2,4 to 2,5 by adding another three drops of sulphuric acid (1,5 $mol \cdot l^{-1}$) (the pH needs to be checked with acilite paper). The thorium isotopes are then electrochemically deposited on the steel disc at a current of 0,75 A to 1 A for 1,5 hours. In order to prevent the solution from evaporating, the electrolytic cell is covered with a round-bottomed flask that is continuously flushed with cold water. One minute before the electrolytic process is completed, 1 ml of ammonia is added. The cell is dismounted, the steel discs rinsed with distilled water and then dried with acetone. The counting source is labelled and its alpha activity measured.

3.4.2 Micro-precipitation

0,2 ml of the cerium or neodymium carrier solution and 1 ml of hydrofluoric acid 40 % is added to the eluate under stirring with a glass rod. Approx. 30 minutes later, it is filtered through an acid-resistant membrane filter with a pore size of 0,1 µm by vacuum suction. The sample vessel is flushed with 5 ml of distilled water and the fluoride precipitate washed with this flush water. It is then washed further with 3 ml of ethanol. The membrane filter is dried on air and glued to a labelled steel disc (e .g., with double-sided sticky tape).

4 Measuring the activity

Si-semiconductor detectors are employed for measuring alpha activity. Basic information on alpha spectrometry is contained in chapter IV.2 of this procedures manual.

4.1 Calibration

The measuring configuration is calibrated by means of calibration sources (e. g., U-233 and Am-241) with known activities in negligibly thin layers. It is important, though, that the diameters of the active layers of the calibration and the counting sources be identical. Being the quotient of activity (at an emission probability of 100 %) and the net count rate, the calibration factor, φ_A, is constant throughout the relevant energy spectrum from 4 MeV to 7 MeV.

The energy calibration needs to be monitored at regular intervals, for example with standard sources that contain several alpha emitters.

4.2 Measurement

The measurement of the counting sources is based on the same geometric configuration as that which was used for calibrating. Measuring periods will typically be at least 10 hours. The measuring chamber and the detector should be checked for possible contaminations at regular intervals, e. g., by measuring the background effect with blank sources.

The alpha spectra of an electrochemically deposited counting source and a micro precipitated counting source on a membrane filter from the analysis of a water sample (duplicate determination) are illustrated in Figure 2. The measuring periods amounted to 70000 seconds here.

5 Calculation of the results

The activity concentrations of the thorium isotopes, c_r, contained in the wastewater sample at the date of sampling are calculated according to equation (1):

$$c_r = \frac{\varphi_A \cdot \left(R_{g,r} - R_{0,r}\right)}{V \cdot \eta \cdot p_\alpha} \cdot e^{\lambda_r \cdot t_A} \tag{1}$$

where

c_r	activity concentration of the radionuclide r, in $Bq \cdot l^{-1}$;
φ_A	calibration factor for a certain geometry, in Bq·s;
p_α	emission probability of alpha radiation of the analysed energy of the respective isotope;
$R_{g,r}$	gross count rate of the main energy of the alpha radiation of the radionuclide r, in s^{-1};
$R_{0,r}$	background count rate within the range of channels at E_α, in s^{-1};
V	sample volume used, in l;
η	chemical yield (see equation 2);
λ_r	decay constant of the Th-isotope, in s^{-1};
t_A	the time between the measurement and the reference date of collecting the sample, in s.

Note

A decay correction in calculating the activity concentration of the wastewater sample to the date of sampling is only required for Th-228 (half-life 1,913 years, $\lambda_{Th\text{-}228}$ = $1{,}15 \cdot 10^{-8}$ s^{-1}).

The difference in the emission probabilities p_α is only of importance for the thorium isotopes Th-227 and Th-229.

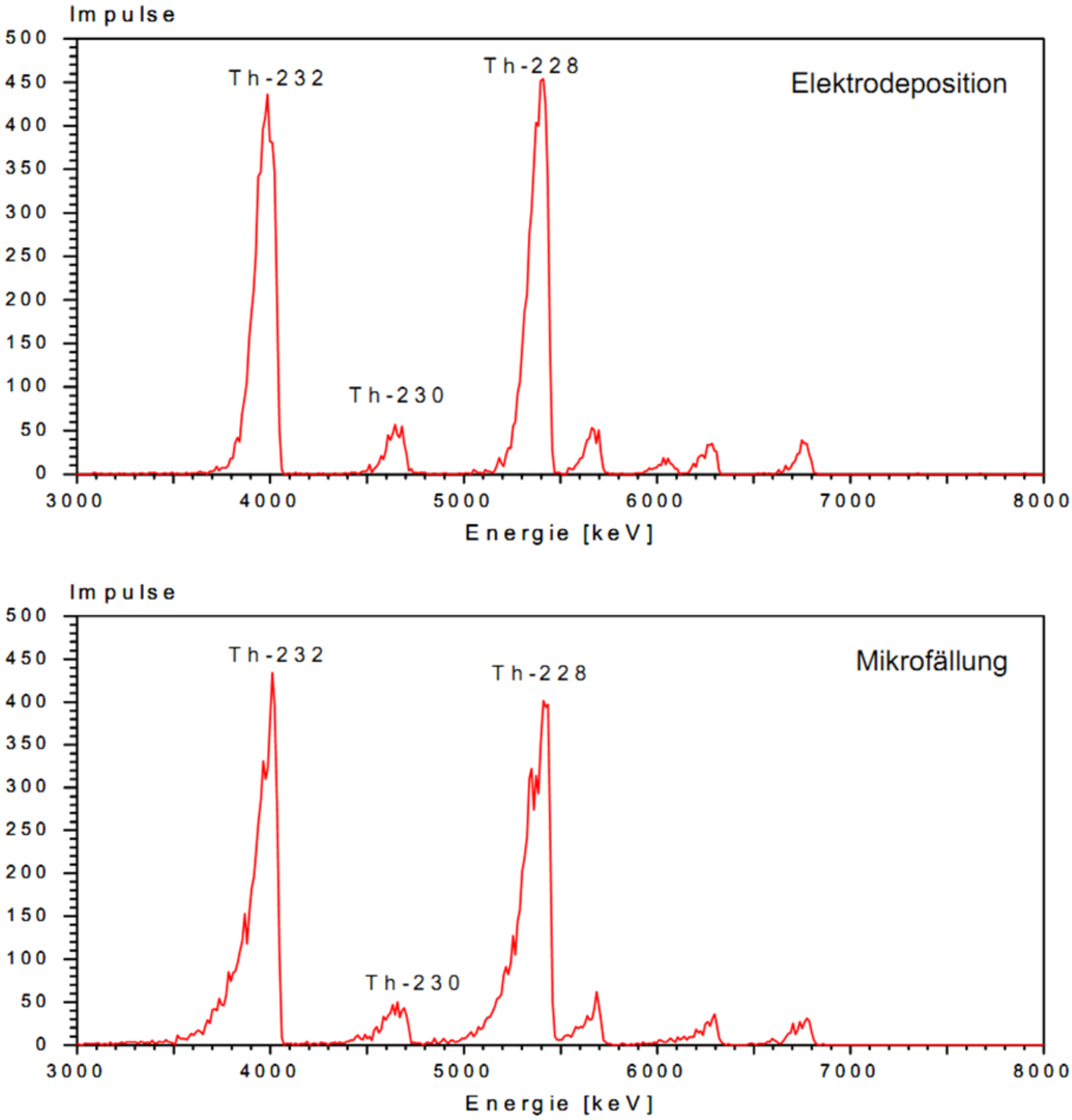

Fig. 2: Alpha spectra of different counting sources of a water sample

The chemical yield of the thorium is calculated as the ratio of the Th-234 activity after the measurement of the alpha activity to the Th-234 activity added as tracer, taking into account the decay correction, according to equation (2):

$$\eta = \frac{\varphi \cdot \left(R_g - R_0\right)}{A_{Tr} \cdot e^{-\lambda_{Th\text{-}234} \cdot t_B}} \tag{2}$$

Here, following symbols are used for the measurement by gamma spectrometry or LSC-measurement of Th-234 activity (cf. sections 3 and 4 in the Appendix):

φ	calibration factor, in Bq·s;
R_g	gross count rate of the counting source, in s^{-1};
R_0	background count rate, in s^{-1};
A_{Tr}	activity of the Th-234 tracer used, in Bq;
$\lambda_{Th\text{-}234}$	decay constant of Th-234, in s^{-1} ($3{,}33 \cdot 10^{-7}\ s^{-1}$);
t_B	time between the measurement and the reference time at which the tracer was added, in s.

The relative standard deviations of the activity concentrations of the thorium isotopes that are to be determined are calculated according to equation (3):

$$\frac{s\left(c_r\right)}{c_r} = \sqrt{\left(\frac{s\left(R_{n,r}\right)}{R_{n,r}}\right)^2 + \left(\frac{s\left(\varphi_A\right)}{\varphi_A}\right)^2 + \left(\frac{s\left(\eta\right)}{\eta}\right)^2} \tag{3}$$

where

$\frac{s(c_r)}{c_r}$	relative standard deviation of the activity concentration of the Th-isotope r;
$\frac{s(R_{n,r})}{R_{n,r}}$	relative standard deviation of the net count rate, $R_{n,r}$;
$\frac{s(\varphi_A)}{\varphi_A}$	relative standard deviation of the calibration factor, φ_A;
$\frac{s(\eta)}{\eta}$	relative standard deviation of the chemical yield, η.

The relative standard deviation of the net count rate is calculated according to equation (4):

$$\frac{s\left(R_{n,r}\right)}{R_{n,r}} = \frac{1}{R_{n,r}} \cdot \sqrt{\frac{R_{g,r}}{t_m} + \frac{R_{0,r}}{t_0}} \tag{4}$$

in which the following factors are introduced in addition to the symbols already defined:

$R_{n,r}$	net count rate of the thorium isotope, in s^{-1};
t_m	duration of counting source measurement, in s;
t_0	duration of background measurement, in s;

Experience indicates that the relative standard deviation of the calibration factor ranges around 5 % to 10 %, while that of the chemical yield is about 10 %.

5.1 Worked example

The following values from the analysis of a wastewater sample are used to calculate the activity concentrations of Th-232, Th-230 and Th-228 and the corresponding standard deviations of these activity concentrations. The Th-234 content of the sample determined by gamma spectrometry was below the detection limit of 1,5 $\mathrm{Bq \cdot l^{-1}}$.

$V = 0{,}20$ l;
$A_{\mathrm{Tr}} = 52$ Bq of Th-234;
$t_{\mathrm{A}} = 7{,}776 \cdot 10^{6}$ s (90 d).

Determining the yield by measuring the Cerenkov-radiation of Pa-234m:

$\varphi = 1{,}53\ \mathrm{Bq \cdot s}$;
$R_0 = 2{,}8 \cdot 10^{-1}\ \mathrm{s^{-1}}$;
$R_{\mathrm{g}} = 24{,}17\ \mathrm{s^{-1}}$;
$t_{\mathrm{B}} = 2{,}59 \cdot 10^{5}$ s (3 d).

Alpha spectrometry:

$\frac{s(\varphi_{\mathrm{A}})}{\varphi_{\mathrm{A}}} = 0{,}1$;
$\frac{s(\eta)}{\eta} = 0{,}1$;
$\varphi_{\mathrm{A}} = 3{,}67\ \mathrm{Bq \cdot s}$;
$t_0 = 300000$ s;
$t_{\mathrm{m}} = 70000$ s;
$R_{0,\mathrm{Th\text{-}232}} = 3{,}3 \cdot 10^{-5}\ \mathrm{s^{-1}}$;
$R_{0,\mathrm{Th\text{-}230}} = 2{,}7 \cdot 10^{-5}\ \mathrm{s^{-1}}$;
$R_{0,\mathrm{Th\text{-}228}} = 1{,}1 \cdot 10^{-4}\ \mathrm{s^{-1}}$;
$R_{\mathrm{g,Th\text{-}232}} = 2{,}36 \cdot 10^{-2}\ \mathrm{s^{-1}}$;
$R_{\mathrm{g,Th\text{-}230}} = 5{,}91 \cdot 10^{-3}\ \mathrm{s^{-1}}$;
$R_{\mathrm{g,Th\text{-}228}} = 2{,}57 \cdot 10^{-2}\ \mathrm{s^{-1}}$.

The following results are obtained according to equations (1), (2), (3) and (4):

$$\eta = \frac{1{,}53 \cdot (24{,}17 - 0{,}28)}{52 \cdot e^{-3{,}33 \cdot 10^{-7} \cdot 2{,}59 \cdot 10^{5}}} = 0{,}766$$

$$c_{\mathrm{Th\text{-}232}} = \frac{3{,}67 \cdot \left(2{,}36 \cdot 10^{-2} - 3{,}3 \cdot 10^{-5}\right)}{0{,}2 \cdot 0{,}766}\ \mathrm{Bq \cdot l^{-1}} = 0{,}565\ \mathrm{Bq \cdot l^{-1}}$$

$$\frac{s\left(R_{\mathrm{n,\,Th\text{-}232}}\right)}{R_{\mathrm{n,\,Th\text{-}232}}} = \frac{1}{2{,}3567 \cdot 10^{-2}} \cdot \sqrt{\frac{2{,}36 \cdot 10^{-2}}{7 \cdot 10^{4}} + \frac{3{,}3 \cdot 10^{-5}}{3 \cdot 10^{5}}} = 0{,}023$$

$$\frac{s\left(c_{\mathrm{Th\text{-}232}}\right)}{c_{\mathrm{Th\text{-}232}}} = \sqrt{0{,}023^{2} + 0{,}1^{2} + 0{,}1^{2}} = 0{,}143$$

$$c_{\mathrm{Th\text{-}232}} = (0{,}565 \pm 0{,}081)\ \mathrm{Bq} \cdot \mathrm{l}^{-1}$$

$$c_{\mathrm{Th\text{-}230}} = (0{,}141 \pm 0{,}021)\ \mathrm{Bq} \cdot \mathrm{l}^{-1}$$

$$c_{\mathrm{Th\text{-}228}} = (0{,}670 \pm 0{,}096)\ \mathrm{Bq} \cdot \mathrm{l}^{-1}$$

5.2 Consideration of uncertainties

General information on assessing uncertainties and analysing spectra are contained in chapter IV of this procedures manual.

As in the example given above, the standard deviations of the results of the analysis lie in a range of 15 % to 20 %, and around 40 % in the case of low activity concentrations near the detection limit. The main factors influencing the standard deviation are the measurement uncertainties, uncertainties incurred from the calibration factor, and the uncertainty of the chemical yield. An additional contribution must be included in calculating the standard deviation of the Th-230 activity concentration if the Th-234 tracer used is contaminated with Th-230 (see the procedure in the Appendix for preparing a Th-234 tracer). The uncertainty incurred from adding Th-230 activity is included as an additional term in the Gaussian error propagation. In this case, the Th-230 activity concentration of the sample is calculated according to equation (5) (analogously to equation (1)); the activity added via the tracer needs to be subtracted from the total activity of Th-230 determined via its alpha spectrum.

$$c_{\mathrm{Th\text{-}230}} = \frac{\varphi_{\mathrm{A}} \cdot \left(R_{\mathrm{g,\,Th\text{-}230}} - R_{\mathrm{n,\,Tr}} - R_0\right)}{V \cdot \eta} \tag{5}$$

with

$$R_{\mathrm{n,\,Tr}} = \frac{A_{\mathrm{Th\text{-}230,\,Tr}} \cdot \eta}{\varphi_{\mathrm{A}}} \tag{5a}$$

where

$R_{\mathrm{g,Th\text{-}230}}$	gross count rate of the alpha energy of the Th-230, in s^{-1};
$R_{\mathrm{n,Tr}}$	net count rate of the separated Th-230 activity that does not originate from the sample, in s^{-1};
$A_{\mathrm{Th\text{-}230,Tr}}$	activity added via the tracer, in Bq.

If Th-229 is used as a tracer, Th-230 present in the sample may cause lines to overlap and so disturb the determination of the yield or even render it impossible. Determining the activity of Th-230 will then be equally unreliable or impossible. In this case it is advisable to repeat the analysis with Th-234 tracer.

Incompletely separated constituents of the matrix of the sample or the presence of other radionuclides, such as plutonium or neptunium from columns that have been reused, may create additional sources of uncertainty for measuring activities. Quantifying such uncertainties is usually impossible in practice, and the analysis may need to be repeated with a smaller sample volume and a new column.

6 Characteristic limits of the procedure

Calculating the detection limits of the thorium isotope activities is based on time preselection, small number of background counts, and different measuring periods for the counting sources prepared from the samples and for the background effects according to equation (6):

$$G_{\mathrm{r}} = \frac{\varphi_{\mathrm{A}}}{p_{\alpha}} \cdot \left[\left(k_{1-\alpha} + k_{1-\beta} \right) \cdot \sqrt{R_{0,\mathrm{r}} \cdot \left(\frac{1}{t_{\mathrm{m}}} + \frac{1}{t_0} \right)} + \frac{1}{4} \cdot \left(k_{1-\alpha} + k_{1-\beta} \right)^2 \cdot \left(\frac{1}{t_{\mathrm{m}}} + \frac{1}{t_0} \right) \right] \tag{6}$$

with

$p_\alpha = 1$ for Th-232, Th-230 and Th-228.

In addition to the symbols already used:

G_r	detection limit of the activity of the individual isotope, in Bq;
$k_{1-\alpha}$, $k_{1-\beta}$	quantile of the normal distribution.

The detection limits of the activity concentrations, g_{r} ($\mathrm{Bq \cdot l^{-1}}$), are calculated according to equation (7) taking into account the sample volume used, the chemical yield, and the decay time between collecting the sample and the measurement, with a correction for the decay time being once more of importance only for Th-228:

$$g_{\mathrm{r}} = \frac{G_{\mathrm{r}}}{V \cdot \eta} \cdot \mathrm{e}^{\lambda_{\mathrm{r}} \cdot t_{\mathrm{A}}} \tag{7}$$

Inserting the values given in section 5.1 and $k_{1-\alpha} + k_{1-\beta} = 4{,}645$, the following detection limits are obtained:

$$G_{\mathrm{Th\text{-}232}} = 3{,}67 \cdot \left[4{,}645 \cdot \sqrt{\frac{3{,}3 \cdot 10^{-5}}{7 \cdot 10^{4}} + \frac{3{,}3 \cdot 10^{-5}}{3 \cdot 10^{5}}} + \frac{1}{4} \cdot 4{,}645^{2} \cdot \left(\frac{1}{7 \cdot 10^{4}} + \frac{1}{3 \cdot 10^{5}} \right) \right] \mathrm{Bq \cdot l^{-1}} =$$

$$= 0{,}76 \cdot 10^{-3}\ \mathrm{Bq \cdot l^{-1}}$$

$$g_{\mathrm{Th\text{-}232}} = \frac{0{,}76 \cdot 10^{-3}}{0{,}2 \cdot 0{,}77}\ \mathrm{Bq \cdot l^{-1}} = 4{,}9 \cdot 10^{-3}\ \mathrm{Bq \cdot l^{-1}}$$

$G_{\mathrm{Th\text{-}232}} = 0{,}76$ mBq $\qquad g_{\mathrm{Th\text{-}232}} = 4{,}9\ \mathrm{mBq \cdot l^{-1}}$

$G_{\mathrm{Th\text{-}230}} = 0{,}81$ mBq $\qquad g_{\mathrm{Th\text{-}230}} = 5{,}3\ \mathrm{mBq \cdot l^{-1}}$

$G_{\mathrm{Th\text{-}228}} = 0{,}85$ mBq $\qquad g_{\mathrm{Th\text{-}228}} = 6{,}0\ \mathrm{mBq \cdot l^{-1}}$

7 Catalogue of chemicals and equipment

7.1 Chemicals

The extraction-chromatographic separation requires ready-to-use columns or loose resin, respectively, that are available under the trade name TEVA Resin (by Eichrom Industries Inc.).

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

- Concentrated nitric acid, HNO_3 ($14\ mol \cdot l^{-1}$),
  furthermore, HNO_3 solutions with the following concentrations:
  6 mol·l^{-1} (420 ml of concentrated HNO_3 per litre),
  3 mol·l^{-1} (210 ml of concentrated HNO_3 per litre),
  2 mol·l^{-1} (140 ml of concentrated HNO_3 per litre),
  1 mol·l^{-1} (70 ml of concentrated HNO_3 per litre),
  0,1 mol·l^{-1} (7 ml of concentrated HNO_3 per litre);
- Concentrated hydrochloric acid, HCl ($14\ mol \cdot l^{-1}$),
  and diluted HCl solutions with the following concentrations:
  6 mol·l^{-1} (590 ml of concentrated HCl per litre),
  1 mol·l^{-1} (96 ml of concentrated HCl per litre);
- Concentrated sulphuric acid, H_2SO_4 ($18\ mol \cdot l^{-1}$),
  and H_2SO_4 solutions with the following concentrations:
  1,5 mol·l^{-1} (83 ml of concentrated H_2SO_4 per litre),
  0,5 mol·l^{-1} (28 ml of concentrated H_2SO_4 per litre);
- Hydrofluoric acid ($23\ mol \cdot l^{-1}$) 40 %;
- Ammonia solution ($13,5\ mol \cdot l^{-1}$) 25 %;
- Sodium hydrogen sulphate solution ($0,1\ mol \cdot l^{-1}$): 12 g of $NaHSO_4$ dissolved in 1 l of H_2O;
- Methyl-red solution (0,5 %, in ethanol);
- Phenolphthalein solution (1 %, in ethanol);
- Calcium nitrate solution ($1,2\ mol \cdot l^{-1}$): 14 g of $Ca(NO_3)_2 \cdot 4H_2O$ in 50 ml of H_2O;
- Diammonium hydrogen phosphate solution ($3,2\ mol \cdot l^{-1}$): 42,2 g $(NH_4)_2HPO_4$ dissolved in 100 ml of H_2O;
- HNO_3 ($3\ mol \cdot l^{-1}$)–$Al(NO_3)_3$ ($1\ mol \cdot l^{-1}$) solution: 75,0 g of $Al(NO_3)_3 \cdot 9H_2O$ dissolved in 200 ml of HNO_3 ($3\ mol \cdot l^{-1}$);
- Ammonium oxalate solution ($0,16\ mol \cdot l^{-1}$): 5 g of ammonium oxalate monohydrate [$(NH_4)_2C_2O_4 \cdot H_2O$] dissolved in 250 ml of H_2O;
- Carrier solution for micro-precipitation with CeF_3 or NdF_3;
- Cerium carrier: 155 mg of $Ce(NO_3)_3 \cdot 6H_2O$ dissolved in 100 ml of 1 M HCl:
- Neodymium carrier: 11,7 mg of Nd_2O_3 dissolved in 100 ml of 1 M HNO_3.

7.2 Equipment

- Measuring station for alpha spectrometry;
- Electrolytic cell and stainless steel discs (V2A steel, Ø 25 mm, thickness 0,3 mm);
- Vacuum-suction apparatus and acid-resistant membrane filters (pore size: 0,1 µm);
- Basic equipment of a radiochemical laboratory.

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Appendix

Procedure for the preparation of a Th-234 tracer and determining its activity

1 Ion exchange (Th-234 activities from ca. 10^4 Bq through $5 \cdot 10^4$ Bq)

10 g of uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ (58000 Bq of U-238) are dissolved in ca. 20 ml of concentrated nitric acid (14 $mol \cdot l^{-1}$). After cautiously adding 10 ml of concentrated sulphuric acid (18 $mol \cdot l^{-1}$) (the violent reaction requires that this be done under a fume hood and wearing protective goggles!), the solution is fumed off on a sand bath at a medium heating level. The residue is dissolved in 100 ml of hydrochloric acid (9 $mol \cdot l^{-1}$) and this solution applied to a conditioned anion exchanger column [150 g strongly alkaline anion exchanger resin, Cl^--form, pre-treated with about 200 ml of hydrochloric acid (9 $mol \cdot l^{-1}$)]. While the uranyl ions are retained on the column, the thorium ions will run through with the mobile phase. The run-off is collected in a 1 l-beaker and the time of completion is recorded as the reference time for the separation of the Th-234. The anion exchanger is washed twice with ca. 200 ml of hydrochloric acid (9 $mol \cdot l^{-1}$) each and the wash solutions are combined with the run-off.

Note

After the Th-234 has been separated, the uranyl ions retained on the column are eluted with about 200 ml of diluted hydrochloric acid (1,2 $mol \cdot l^{-1}$). The eluate is evaporated; the residue may be used again for preparing tracers after a sufficient waiting period has permitted the regeneration of Th-234 (cf. Table 1).

The solution containing the thorium is evaporated to dryness on a sand bath and the residue once more wet-ashed with 10 ml of concentrated nitric acid (14 $mol \cdot l^{-1}$) and 5 ml of concentrated sulphuric acid (18 $mol \cdot l^{-1}$). This residue is now dissolved in 20 ml of hydrochloric acid (9 $mol \cdot l^{-1}$) and purified once more by way of anion exchange. This makes use of a smaller column with about 50 g of resin [strongly alkaline anion exchanger resin, Cl^--form, conditioned with about 50 ml of hydrochloric acid (9 $mol \cdot l^{-1}$)]. After the Th-solution has been applied and has run through, the exchanger is washed with 100 ml of hydrochloric acid (9 $mol \cdot l^{-1}$). The wash solution and the run-off are combined, evaporated, and the residue is fumed off once with 10 ml of concentrated nitric acid and 5 ml of concentrated sulphuric acid. The remaining residue is then heated and dissolved in ca. 50 ml of diluted nitric acid (0,1 $mol \cdot l^{-1}$) under stirring and the solution transferred to a 250 ml-volumetric flask. The beaker is rinsed twice with ca. 20 ml of diluted nitric acid (0,1 $mol \cdot l^{-1}$) and the rinsing solutions are added to the volumetric flask. Thereafter, the solution is filled to the calibration mark with nitric acid (0,1 $mol \cdot l^{-1}$).

The Th-234 solution produced thus may be contaminated with Th-230. The Th-230 content therefore has to be determined by alpha spectrometry prior to use. This measurement should consist of three independent runs with 10 ml of tracer solution each. The Th-230 activity that is added to the samples together with the Th-234 tracer needs to be taken into account for calculating the Th-230 activity concentration of the sample and the corresponding standard deviation (cf. section 5.2) as well as for calculating the detection limit.

Depending on the waiting period for the Th-234, tracers with activity concentrations of up to 200 Bq·ml^{-1} may be prepared thus.

The Th-234 activity concentration of the tracer solution is determined either by gamma spectrometry or by measuring the Cerenkov-radiation.

Note
Repeated reuse of the uranium salt for separating Th-234 will decrease the simultaneously washed-out Th-230 activity and thus the degree of impurity of the tracer solution.

2 Extraction-chromatography (Th-234 activities from ca. 50 Bq through 250 Bq)

The preparation process of the tracer is illustrated in Figure 3. A solution containing 5 mg to 20 mg of uranium is evaporated to dryness and the residue dissolved in 10 ml of hydrochloric acid (8 mol·l^{-1}). This solution is applied to a TEVA-column that has been conditioned with 5 ml of hydrochloric acid (8 mol·l^{-1}), which will cause the uranium to be retained in the form of a chlorido complex on the column and the thorium ions contained in the solution to be washed out with hydrochloric acid. Thereafter, the column is washed with 10 ml of hydrochloric acid (6 mol·l^{-1}). Once the wash solution has run through (the column must not run dry), the column is closed and left standing to allow for the regeneration of Th-234 (the column must be labelled and the date recorded). The combined hydrochloric acid solutions are discarded; aside from Th-234, they will also contain Th-230 and other radionuclides of the U-238 decay chain.

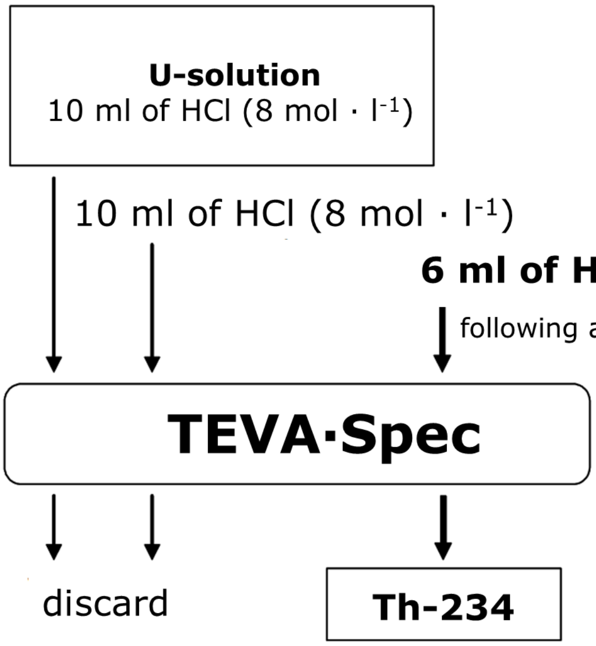

Fig. 1: Principle of preparing Th-234 via a TEVA·Spec column

Th-234 may be eluted at least ten times from the uranium-charged column, provided that the required waiting periods have been observed to facilitate the regeneration. This requires that 6 ml to 8 ml of hydrochloric acid (6 $mol \cdot l^{-1}$) be applied to the column, the date recorded, and the column left resting. These Th-234 solutions will not normally be contaminated with Th-230, but checking the first eluate accordingly is nevertheless recommended. A contamination of the Th-234 elutes with U-238 and U-234 (at activities in the mBq range) is possible, however. This will not affect the described Th-determination process, though, as the U-isotopes are extracted from the sample during analysis as well.

The Th-234 activity of the eluate is determined either by gamma spectrometry or by measuring its Cerenkov-radiation. Depending on the waiting period for regeneration (s. Table 1), tracers with activities of up to 250 Bq of Th-234 may be prepared.

Tab. 1: Selected values of the relative Th-234 activity as a function of waiting periods observed after the last Th-separation, calculated according to $A_{\mathrm{Th-234}} = \left(1 - e^{\lambda_{\mathrm{Th-234}} \cdot \Delta t}\right) \cdot A_{\mathrm{U-238}}$

Waiting period in days	Relative Th-234 activity
10	0,2499
20	0,4374
30	0,5780
40	0,6835
50	0,7626
60	0,8219
70	0,8664
80	0,8998
90	0,9249
100	0,9436

3 Determining the activity by gamma spectrometry

For measuring the Th-234 activity, an n-type germanium detector (detection efficiency > 30 %) is suitable. The line is analysed at 63 keV, as it is unperturbed by other radionuclides with the exception of Th-232. Disturbances by Th-232 will not be relevant owing to the activity ratios (Th-234/Th-232 ≥ 1000).

The calibration process makes use of a uranium solution with a known activity concentration of U-238 in radioactive equilibrium with Th-234 for two different measuring geometries. A small vial (e. g., of 20 ml in volume) is suitable for determining the activity concentration of the Th-234 tracer solution, whereas determining the chemical yields requires a certain "filter geometry". For the latter, a filter is charged with a known U-238 activity (at radioactive equilibrium with Th-234) while ensuring that the dimensions of the active area correspond to those of the counting sources that are to be used later. The filter is glued to a steel disc and the steel disc centred and affixed at a defined distance above the detector. A plastic ring may be used to hold it, for example. Further guidelines for calibration and the analysis of spectra are included in chapter IV.I of this procedures manual.

4 Determining the activity by measuring the Cerenkov-radiation

The Cerenkov-radiation that is emitted in a light-permeable medium at high beta energies is measured in a liquid scintillation counter without the need of a scintillation cocktail. When using 20 ml-PE-vials, a solution volume of 10 ml to 15 ml, and a measuring range from 0 keV to max. 50 keV, the detection efficiency of Pa-234m with its maximum beta-energy of 2,28 MeV will be about 65 %. The beta radiation of the Th-234 with its maximum energy of 193 keV does not contribute to the Cerenkov-radiation. For measuring activities of ca. 10 Bq of Pa-234m, measuring periods of 30 minutes are sufficient (twice the relative standard deviation of the net count rate < 5 %). Quench and luminescence effects will not be observed in this case.

Calibration is carried out with a Th-234 solution whose activity concentration has been determined in advance by gamma spectrometry. Uranium solutions with known U-238 activities are not suitable for determining the calibration factor, as radionuclides of the U-238 decay chain apart from Pa-234m (Bi-214, Bi-210) will create Cerenkov-radiation.

The background effect is determined by using 10 ml of hydrochloric acid (6 mol·l^{-1}) [eluent for Th-234] in 20 ml-PE-vials.

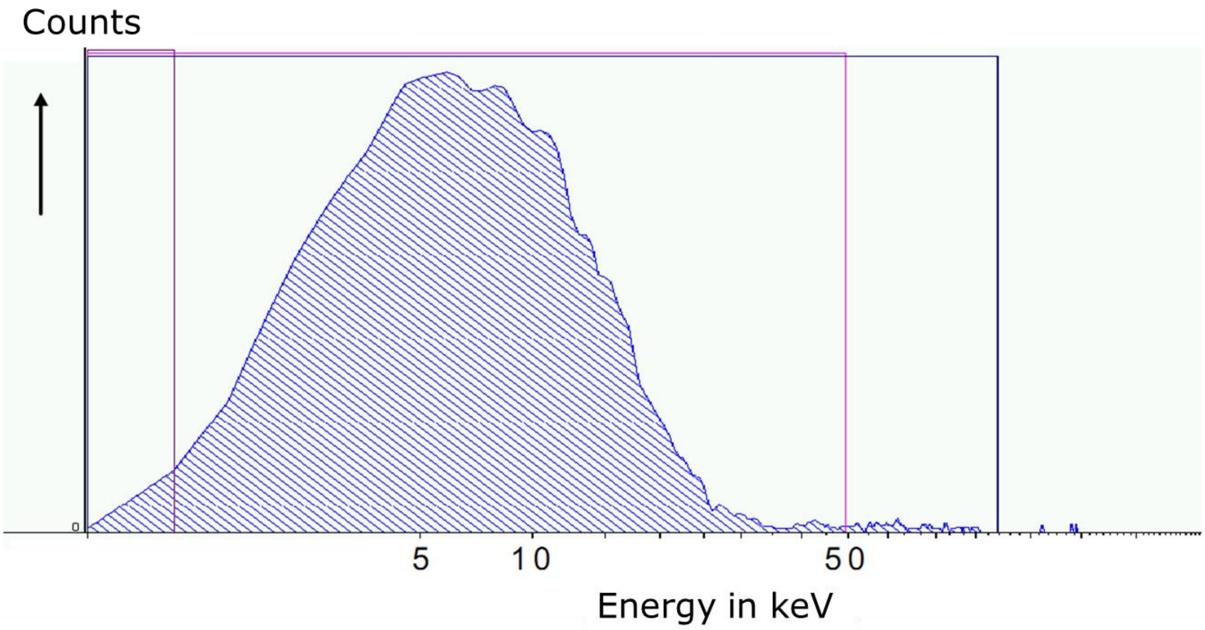

Fig. 2: Cerenkov-spectrum of Th-234/Pa-234m in 10 ml of HCl solution (6 mol·l^{-1})