

Rapid procedure for determining the gross alpha activity concentration in drinking water

H- α -GESAMT-TWASS-02

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1 Scope

This procedure serves to determine the gross alpha activity concentration of natural radionuclides in drinking water as well as in spring and mineral waters with low iron and salt contents (iron concentrations $< 1 \text{ mg}\cdot\text{l}^{-1}$, sum of calcium and magnesium concentrations $< 500 \text{ mg}\cdot\text{l}^{-1}$). It is suitable for monitoring radioactive parameters in accordance with Art. 7 of the Ordinance for Drinking Water (Trinkwasser-Verordnung TrinkwV 2001) (1).

The radionuclides contributing to the considered sum parameter, i. e. gross alpha activity, are in particular the uranium isotopes U-238, U-235 and U-234 as well as Ra-226 and Po-210. The noble gas Rn-222 is ignored in this procedure, as it will be removed in the course of preparing the sample. The short-lived isotope Ra-224 (half-life 3,63 days) of the thorium decay chain can only be detected if the analysis is conducted immediately after sampling. Also to be taken into consideration is that the activity ratio between Pb-210 and Po-210 in the water sample will change if they are not in radioactive equilibrium at the time of sampling. It is therefore generally advisable to avoid extended storage periods for samples taken. For calculating the gross alpha activity concentration, only the time of measuring can be given as the reference point of time.

The procedure is simple to execute, but requires that a liquid scintillation counter (LSC) with alpha/beta discrimination be available. Measuring periods of between 100 minutes and 200 minutes and sample volumes of 0,3 l to 0,5 l will produce detection limits of $15 \text{ mBq}\cdot\text{l}^{-1}$ to $30 \text{ mBq}\cdot\text{l}^{-1}$. A second measuring process 3 days to 6 days later will furthermore provide information on the extent of the contribution by Ra-226 to the gross alpha activity concentration.

2 Sampling

The general requirements for representative sampling and sampling techniques according to DIN Standard 38402 Parts 13 and 14 (2, 3) have to be complied with. In this conjunction, reference is also made to H-VORBEMERK-TWASS-01 and procedure H- γ -SPEKT-TWASS-01.

Sampling for screening purposes with the aim of checking drinking waters (or supply networks) for an exceeded gross standard dose of 0,1 mSv (according to TrinkwV 2001) may be collected from water supply plants or even end users.

A sample volume of 1 litre will normally suffice. Suitable for storage and transport are sample bottles made of polyethylene or glass of the type commonly employed in water analyses. The samples are preserved by acidifying them with nitric acid ($14 \text{ mol}\cdot\text{l}^{-1}$) to a $\text{pH} < 2$.

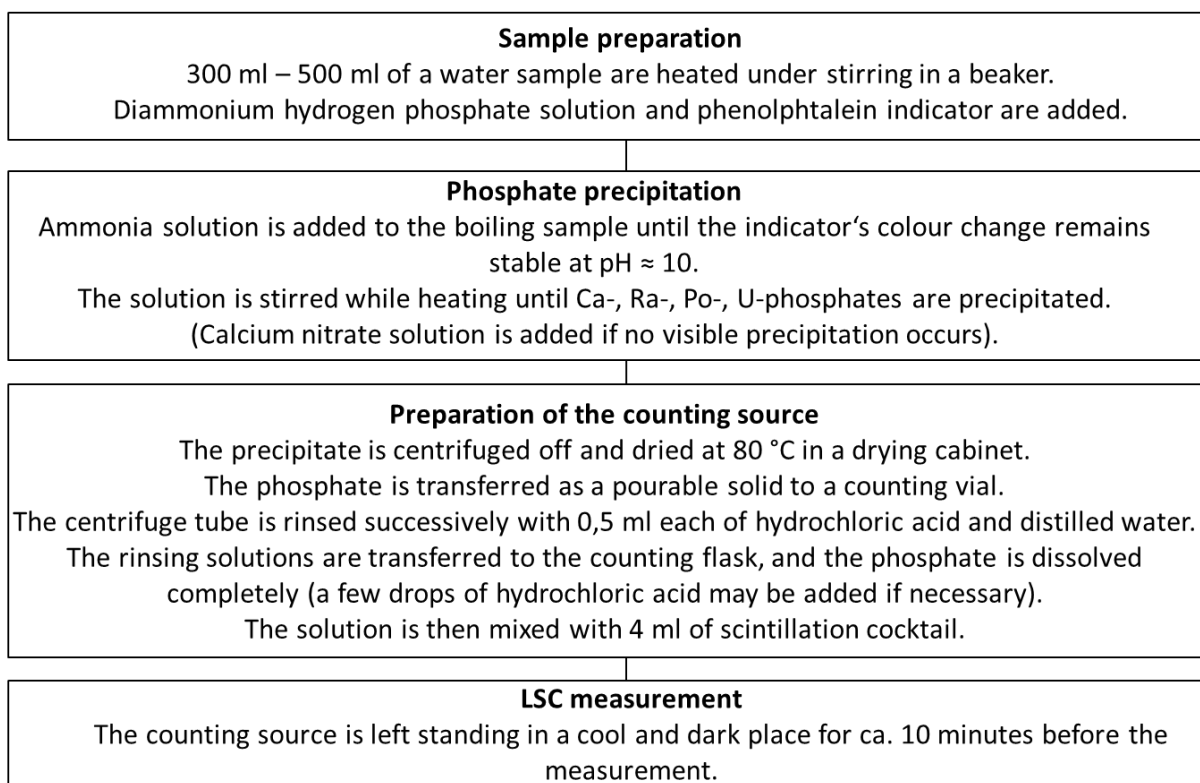


Fig. 1: Overview of the procedure for determining the gross alpha activity concentration in drinking water

3 Analysis

3.1 Principle of the procedure

The procedure is based upon co-precipitating uranium, radium and polonium with calcium phosphate, dissolving the phosphates in hydrochloric acid, and then measuring the solution in a liquid scintillation counter. The individual steps of the procedure are illustrated in Figure 1.

In the case of a low number of samples, conducting dual analyses is recommended, but substantially increasing measuring periods should be avoided because of the possible ingrowth of Rn-222 and its short-lived decay nuclides.

Note

Owing to its short half-life of 3,82 days, Rn-222 grows in rapidly from the Ra-226 present. It will only take 12 hours from the separation for the Rn-222 activity to account for about 10 % of the Ra-226 activity. With the decay nuclides of Rn-222 having half-lives in the range of minutes and even seconds and comparable activities that will contribute to the count rate, the gross alpha activity concentration may be overestimated relative to its Ra-226 content.

3.2 Radiochemical separation

3.2.1 300 ml to 500 ml of the water sample are heated to boiling under stirring in a beaker. After adding 2 drops of phenolphthalein indicator solution and 2 ml of diammonium hydrogen phosphate solution ($3,2 \text{ mol}\cdot\text{l}^{-1}$), ammonia solution ($13,5 \text{ mol}\cdot\text{l}^{-1}$) is used to adjust the pH to about 10 (indicator colour change towards red). Stirring the solution while heating is continued for a few more minutes, then the beaker is taken from the hotplate, and the stirring magnet removed.

Note

Drinking water typically contains enough calcium and magnesium to immediately cause clearly visible precipitates. If this should not be the case, however, 1 ml of calcium nitrate solution ($1,25 \text{ mol}\cdot\text{l}^{-1}$) is added drop by drop to the boiling solution.

3.2.2 Following a period allowing the phosphate precipitates to cool and sediment, the supernatant clear solution is decanted off and the precipitate is quantitatively transferred to a centrifuge tube. The precipitate is centrifuged off, the supernatant solution discarded, and the precipitate is dried at $80 \text{ }^\circ\text{C}$ in a drying cabinet for ca. 30 minutes.

3.2.3 The dry phosphate precipitate is pulverized with a glass rod and transferred via a small glass funnel to a counting vial with a nominal volume of 7 ml. The centrifuge tube is then successively flushed with 0,5 ml of hydrochloric acid ($4 \text{ mol}\cdot\text{l}^{-1}$) and 0,5 ml of distilled water, and these solutions are likewise added via the glass funnel to the measuring vial. Following the short yet vigorous shaking of the capped flask, the precipitate should have dissolved completely. If the precipitate does not dissolve completely, more drops of hydrochloric acid ($4 \text{ mol}\cdot\text{l}^{-1}$) need to be added until a clear solution free of residue is obtained.

Note

Since a homogeneous mixture of sample solution and scintillation cocktail needs to be prepared for the LSC measurement, the solvent volume will typically be limited. Manufacturers' data on the sample uptake capacities of their scintillation cocktails may prove useful here. Ultima Gold AB™, for example, is a scintillation cocktail that has been developed specifically for alpha/beta discrimination processes and can take up a maximum of 2,25 ml of hydrochloric acid ($2 \text{ mol}\cdot\text{l}^{-1}$) per 10 ml of scintillation cocktail (4).

3.2.4 The sample solution is mixed with 4 ml of a suitable scintillation cocktail and stored in a cool and dark place for ca. 10 minutes prior to measuring.

4 Measuring the activity

4.1 General

The relevant alpha emitters, U-238, U-234, Ra-226 and Po-210, with their energies between 4100 keV and 5300 keV may be present at most varying activity ratios in drinking water. They are accompanied by energy-rich beta emitters such as Pa-234m (Th-234) with $E_{\beta\text{max}} = 2280 \text{ keV}$ or Bi-210 with $E_{\beta\text{max}} = 1162 \text{ keV}$. Ac-228 with $E_{\beta\text{max}} = 2100 \text{ keV}$, a short-lived decay product of Ra-228, may in some instances be present in a water sample at an activity concentration that exceeds that of the mentioned alpha emitters.

The presence of high-energy beta emitters and the variability in the composition of the counting sources, which cannot be avoided in routine analyses and result in a varying quench, impact on the quantitative discrimination of alpha and beta emissions. Determining a suitable discrimination threshold is therefore of particular importance.

Note

The separate recording of alpha and beta emissions is based upon the analysis of pulse-shapes in modern liquid scintillation counters, i. e., the pulses are distinguished according to their decay characteristics. Making this distinction becomes increasingly difficult as the quench increases. If the selection of the discriminator threshold is too low, beta radiation will be recorded for a large part within the alpha measuring range, while, on the other hand, alpha emissions will be recorded in the beta range if the discriminator threshold is too high.

In contrast to nuclide-specific LSC measuring, the detection efficiency of alpha radiation as a function of the quench parameter of the sample cannot reasonably be corrected by calculation. Firstly, the dependency of the detection efficiency from the quench value is low, and secondly, the impact of the beta radiation on the count rate within the alpha range changes with the quench parameter as well. In routine operations, it is not even expedient to repeat the measuring process of individual counting sources with a discriminator threshold that is modified according to the quench value.

4.2 Calibration

The calibration process comprises determining a discriminator threshold for optimally separating the alpha and beta emissions and at the same time determining the detection efficiency for alpha radiation at quench values of real counting sources.

Note

In contrast to commercially available unquenched alpha and beta calibration sources, a lower discriminator threshold and an increased rate of misclassifications (fraction of alpha radiation recorded within the beta measuring range and vice versa) must be expected when measuring real samples, because the sample will provide a less ideal composition for the energy transfer, which in turn causes a significantly higher quench.

For calibration purposes, an Am-241 solution with known activity and, e. g., a (Sr-90 + Y-90)-solution is used. Also Th-234, which is relatively easy to produce from natural uranium (see procedure H-Th-AWASS-01), is a beta emitter suitable for this purpose. The deciding factor here is that a radionuclide with a high maximum beta radiation energy is employed.

Two counting sources are prepared whose chemical composition should largely correspond to the real counting sources, but of which one will contain exclusively radionuclides that emit beta radiation and the other those that emit alpha radiation. To this end, ca. 20 mg of calcium phosphate are dissolved in 1 ml of hydrochloric acid ($2 \text{ mol} \cdot \text{l}^{-1}$) each in two counting vials and spiked with the smallest volume possible (in the μl -range) of the radionuclide solution. The activity added amounts to at least a few Becquerels in order to produce sufficiently high count rates during short measuring periods. After mixing in 4 ml of scintillator cocktail each and waiting for a short while, the two counting sources are measured successively at various discriminator threshold settings while ensuring that the two measuring ranges for alpha and beta radiation will cover the entire available energy range. The quench can be increased for the next measuring series by adding 5 μl to 10 μl of carbon tetrachloride to the counting sources.

The results of calibrating a TRICARB 3170 TR/SL with the calibration sources of Am-241 and (Sr-90 + Y-90) described above are illustrated as an example in Figure 2. The quench is specified as a device-specific parameter (here: a transformed spectral index = tSIE), with a low value corresponding to a strong quench. The quench of real counting sources with compositions matching the description provided here would typically range between tSIE-values of 450 and 350, less than that in exceptional cases.

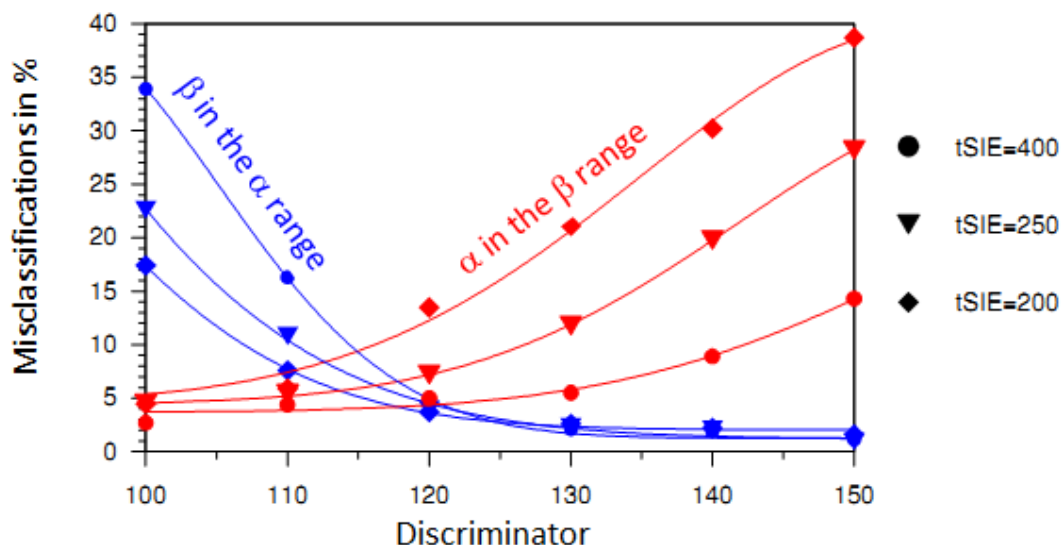


Fig. 2: Misclassification of alpha and beta radiation at varying quench relative to the discrimination threshold

The proportions of misclassification, q_α and q_β , respectively, (5) characterise the contribution of the count rate during the measurement of the alpha emitting counting source, e. g., Am-241, within the beta measuring range (q_α) respectively the contribution of the count rate during the measurement of the beta emitting counting source, e. g., (Sr-90 + Y-90), within the alpha measuring range (q_β). They are calculated according to equation (1):

$$q_\alpha = \frac{R_{\alpha,K}}{R_{\alpha,K} + R_{\beta,K}}, \quad q_\beta = \frac{R_{\alpha,K}}{R_{\alpha,K} + R_{\beta,K}} \quad (1)$$

where

q_α misclassification of alpha radiation within the beta measuring range;

q_β misclassification of beta radiation within the alpha measuring range;

$R_{\alpha,K}$ net count rates within the beta measuring range when measuring an alpha calibration source, in min^{-1} ;

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Figure 2 demonstrates that the optimal discriminator threshold is found at the point of intersection of two curves with an identical quench value and that the particular quench determines the position of the point of intersection. At tSIE-values between 200 and 400, the discriminator threshold has been selected at a value of 115, which will keep the degree of misclassifications within an acceptable range of 5 % to 10 %. While the degree of misclassified alpha radiation will be low at the commonly observed tSIE-values around 400 and the detection efficiency lies at 95 %, the alpha activity must be expected to be slightly overestimated if beta radiation is present within a comparable activity range. The alpha radiation would only be underestimated by more than 10 % if the sample quench was strong (tSIE-values < 200). It is for this reason that measurements at tSIE-values below 200 are not analysed further; in these cases the analysis is repeated (see section 5.2).

4.3 Measurement

Limiting the alpha measuring range by determining a range of channels within which pulses are counted depends on the pulse-height spectra at low and higher quench values (see Figure 3).

Using a real sample of drinking water containing elevated U-238 and U-234 activity concentrations, Figure 3 illustrates the impact of the quench on the pulse-height spectra during the measuring process. The increased quench in the repeat measuring of the counting source was created by adding 10 μl of carbon tetrachloride. It caused a shift of the spectrums towards the lower energy range and a much poorer energy resolution. The count rate and as a consequence, the detection efficiency remained almost constant, though.

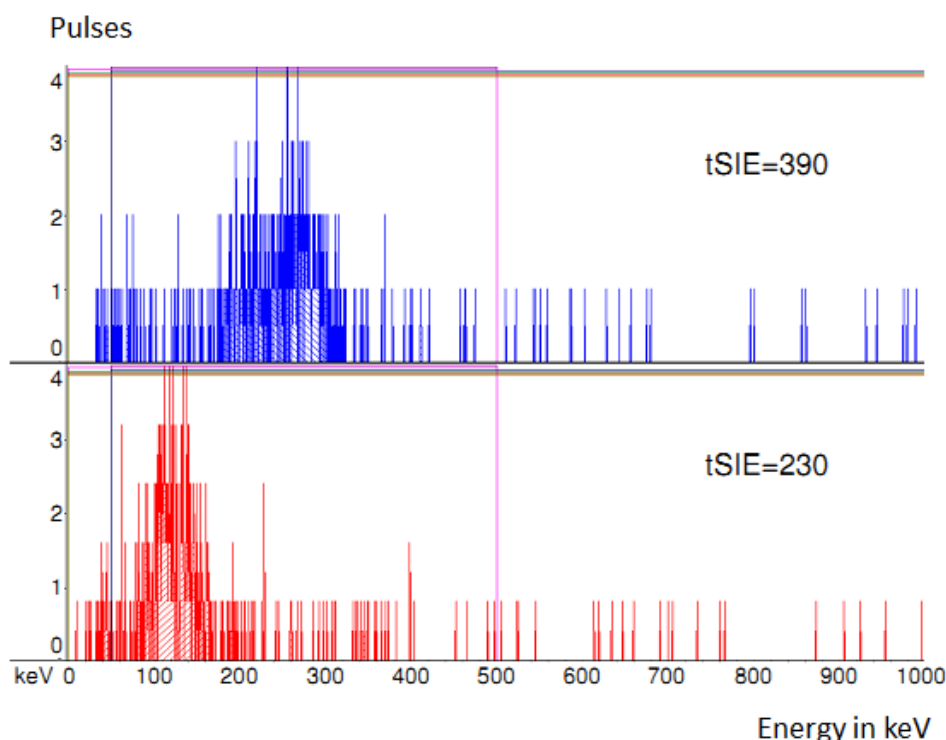


Fig. 3: Counts per channel within the alpha measuring range from measuring a counting source containing uranium with various quench values (tSIE)

An alpha measuring range from 50 keV through 500 keV has been determined to be suitable for routine measuring; this facilitates reaching a background count rate of $0,01 \text{ s}^{-1}$.

The common measuring period is 100 minutes; if four or more counting sources need to be processed successively, the possible ingrowth of Rn-222 needs to be taken into consideration, while a shorter measuring period will be of advantage if Ra-226 is the major contributor to the gross alpha activity concentration.

Repeating the measuring process after 3 to 5 days can provide indications whether Ra-226 is the dominant alpha emitter. Compared to the original measuring result, it will cause the count rate to be approximately twice as high at this point of time.

5 Calculation of the results

5.1 Equations

The gross alpha activity concentration, c , at the time of measurement is calculated according to equation (2):

$$c = \frac{\varphi_A \cdot [(R_{g,\alpha} - R_{0,\alpha}) \cdot (1 - q_\beta) - (R_{g,\beta} - R_{0,\beta}) \cdot q_\beta]}{(1 - q_\alpha - q_\beta) \cdot V \cdot \eta} \quad (2)$$

For measuring processes in which a relative standard uncertainty of ca. 20 % is acceptable, the activity concentration, c , can be calculated according to the simplified equation (3):

$$c = \frac{\varphi_A \cdot (R_{g,\alpha} - R_{0,\alpha})}{V \cdot \eta} \quad (3)$$

The following quantities are introduced for equations (2) and (3) in addition to the symbols already defined:

- c gross alpha activity concentration, in Bq·l⁻¹;
- φ_A calibration factor, in Bq·s;
- V volume of the sample, in l;
- η chemical yield (typically between 0,95 and 1);
- $R_{g,\alpha}$ gross count rate within the alpha measuring range, in s⁻¹;
- $R_{0,\alpha}$ background count rate within the alpha measuring range, in s⁻¹;
- $R_{g,\beta}$ gross count rate within the beta measuring range, in s⁻¹;
- $R_{0,\beta}$ background count rate within the beta measuring range, in s⁻¹.

The relative standard measuring uncertainty of the alpha activity concentration is derived according to the Gaussian law of error propagation by applying equation (4):

$$\frac{s(c)}{c} = \sqrt{\left(\frac{s(R_{n,\alpha})}{R_{n,\alpha}}\right)^2 + \left(\frac{s(\varphi_A)}{\varphi_A}\right)^2 + \left(\frac{s(\eta)}{\eta}\right)^2} \quad (4)$$

with

- $\frac{s(c)}{c}$ relative standard measuring uncertainty of the gross alpha activity concentration;
- $\frac{s(R_{n,\alpha})}{R_{n,\alpha}}$ relative standard measuring uncertainty of the net count rate, $R_{n,\alpha}$;
- $\frac{s(\varphi_A)}{\varphi_A}$ relative standard measuring uncertainty of the calibration factor;
- $\frac{s(\eta)}{\eta}$ relative standard measuring uncertainty of the chemical yield.

The relative standard measuring uncertainty of the net count rate is calculated according to equation (5):

$$\frac{s(R_{n,\alpha})}{R_{n,\alpha}} = \frac{1}{R_{n,\alpha}} \sqrt{\frac{R_{g,\alpha}}{t_m} + \frac{R_{0,\alpha}}{t_0}} \quad (5)$$

in which the following quantities are introduced in addition to those already defined:

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

5.2 Worked example

Aside from a discriminator threshold set at 115 and a tSIE-value of 410, the following analytic data are available for determining the gross alpha activity concentration in a sample of drinking water:

- $V = 0,3$ l; $t_m = t_0 = 6000$ s;
 $\varphi_A = 1,0$ Bq·s; $R_{0,\alpha} = 0,01$ s^{-1} ;
 $\eta = 1,0$; $R_{g,\alpha} = 0,085$ s^{-1} .

which will produce a result for the analysis of:

$$c = \frac{0,085 - 0,01}{0,3} \text{ Bq} \cdot \text{l}^{-1} = 0,25 \text{ Bq} \cdot \text{l}^{-1}$$

$$\frac{s(R_{n,\alpha})}{R_{n,\alpha}} = \frac{1}{0,075} \cdot \sqrt{\frac{0,085 + 0,01}{6000}} = 5,3 \cdot 10^{-2}$$

$$\frac{s(c)}{c} = \sqrt{(0,053)^2 + (0,2)^2 + (0,1)^2} = 0,23$$

The value of the gross alpha activity concentration in the sample of drinking water at the point of time of measuring amounts to:

$$c = (0,25 \pm 0,06) \text{ Bq} \cdot \text{l}^{-1}$$

5.3 Consideration of uncertainties

Problems may arise during LSC measuring according to this procedure, e. g., in a case where groundwater is treated for the production of drinking water. Here, matrix components may intensify the colouration during the precipitation of phosphates in hydrochloric acid and create a strong quench of the counting source. The yellow-coloured chlorido complex that has been formed with iron ions is typically destroyed by adding 20 μl of 40 % hydrofluoric acid ($23 \text{ mol} \cdot \text{l}^{-1}$), colouration induced by other impurities, however, cannot normally be removed at this stage. In such a scenario, it may be necessary to carefully evaporate a smaller volume of the water sample to dryness and wet-ash it with nitric acid and hydrogen peroxide. The analysis must then be repeated.

Note

Owing to its relatively low boiling and melting points, the element polonium is volatile at high temperatures. Polonium in the form of a chloride sublimates at about 200 $^{\circ}\text{C}$, and at about 500 $^{\circ}\text{C}$ as an oxide; organically bonded polonium must be expected to experience losses through sublimation already at temperatures above 100 $^{\circ}\text{C}$.

The combined standard measuring uncertainty of the gross alpha activity concentration is determined by counting statistical errors as well as uncertainties stem-

ming from the alpha/beta discrimination and, as a consequence, the uncertainty of the calibration factor. Staff should have some experience with performing and analysing LSC measurements in order to avoid the two major sources of errors:

- setting an unsuitable discriminator threshold, and
- neglecting sample-specific quench values as a result of different compositions of the counting sources.

The contribution of the relative standard measuring uncertainty of $s(R_{n,\alpha}) \cdot R_{n,\alpha}^{-1}$ to the gross uncertainty of the measurand plays a more significant role only in cases of low pulse rates or short measuring periods. The relative standard measuring uncertainty of the calibration factor depends on the variation limit of the composition of the counting sources. In order to not constrict the range of admissible tSIE-values too much, an uncertainty of the calibration factor of about 20 % must be expected ($s(\varphi_A) \cdot \varphi_A^{-1} = 0,2$). Experience from exemplarily determining the yield of individual nuclides indicates that the systematic contribution arising from the indeterminable chemical yield ranges around 10 %. Determining the chemical yield of this procedure is effected with specifically manufactured counting sources that only contain radionuclides that do not emit beta radiation (e. g., Am-241 or Po-208) and come as certified activity standards. Determining the yield routinely for each and every counting source is not possible.

Samples should not be stored for extended periods of several months in order to avoid misinterpretations on the basis of altered activity ratios in the water sample (e. g., through the ingrowth of Po-210 from excess Pb-210).

6 Characteristic limits of the procedure

6.1 Equations

The detection limit of the gross alpha activity concentration is calculated according to chapter IV.5 of this procedures manual for adequately large background count number according to equation (6):

$$g = \frac{k_{1-\alpha} + k_{1-\beta}}{V \cdot \eta} \cdot \varphi_A \cdot \sqrt{R_{0,\alpha} \cdot \left(\frac{1}{t_0} + \frac{1}{t_m} \right)} \quad (6)$$

in which the following quantities are introduced in addition to those already defined:

- g detection limit of the gross alpha activity concentration, in $\text{Bq} \cdot \text{l}^{-1}$;
 $k_{1-\alpha}, k_{1-\beta}$ quantiles of the normal distribution (type I and type II errors).

6.2 Worked example

Using a sample volume of 0,3 l, a duration of background and counting source measurement of 100 minutes each, a background count rate of $0,60 \text{ min}^{-1}$ (see section 5.2), and applying quantile values of $k_{1-\alpha} = 3$ and $k_{1-\beta} = 1,645$ will produce a result of:

$$g = 0,028 \text{ Bq} \cdot \text{l}^{-1}$$

A detection limit of the gross alpha activity concentration of $0,012 \text{ Bq} \cdot \text{l}^{-1}$ can be achieved by applying a measuring period of 200 minutes and using a sample volume of 0,5 l.

7 Catalogue of chemicals and equipment

7.1 Chemicals

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

- Ammonia solution, NH_3 13,5 mol·l⁻¹ (25 %);
- Diammonium hydrogen phosphate solution, $(\text{NH}_4)_2\text{HPO}_4$ 3,2 mol·l⁻¹,
42,2 g dissolved in 100 ml of water;
- Calcium nitrate solution, $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ 1,2 mol·l⁻¹,
14 g dissolved in 50 ml of water;
- Hydrofluoric acid, HF 23 mol·l⁻¹ (40 %);
- Phenolphthalein solution 1 % in ethanol;
- Nitric acid, HNO_3 14 mol·l⁻¹;
- Hydrochloric acid, HCl 4 mol·l⁻¹;
- Scintillation cocktail e. g., Ultima Gold AB™.

7.2 Equipment

- Basic equipment of a radiochemical laboratory for determining low activity concentrations in environmental media, in particular hotplates with magnet stirrers, sand baths, a drying cabinet, and a centrifuge;
- Liquid scintillation counter with alpha/beta discrimination.

References

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