

**Procedure for determining the
gross alpha activity concentration
in surface water**

C- α -GESAMT-OWASS-01

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Procedure for determining the gross alpha activity concentration in surface water

1 Scope

Alpha emitters found in aquatic environments are both of natural and anthropogenic origin (1 through 3). By determining the gross alpha emission, the gross concentration of alpha emitters in surface water can be determined with comparative ease. Such quantification is suitable for monitoring and recording long-term exposure as well as revealing increased releases. The procedure will not provide details on the nuclide mix present in a sample, though. If activity concentrations are found to be elevated and exceed given limits, alpha spectrometric measurements of individual nuclides need to be initiated. For conditions usually encountered in practice activity concentrations as small as $0,01 \text{ Bq}\cdot\text{l}^{-1}$ can still be detected (4 through 9).

2 Sampling

The collection of samples is described in procedure C- γ -SPEKT-OWASS-01.

3 Analysis

3.1 Principle of the method

To determine the gross alpha concentration, an aquatic sample is mixed with sulphuric acid, heated on a sand bath until fumes are emitted, and the residue is annealed at $450 \text{ }^\circ\text{C}$. The latter is then turned into a counting source of defined thickness and measured at the alpha plateau of a proportional counter.

3.2 Sample preparation

The aquatic sample is prepared as follows:

3.2.1 1 litre to 2 litres of an unfiltered aquatic sample are mixed with 5 ml to 10 ml of sulphuric acid ($1 \text{ mol}\cdot\text{kg}^{-1}$), evaporated in a ceramic dish, and heated on a sand bath until fumes are emitted under an exhaust hood. In order to obtain a sufficient amount of salt residue, water poor in salts may require that the volume of the sample to be evaporated be increased or that a defined amount of calcium chloride be added.

3.2.2 The remaining residue is annealed in a muffle furnace at $450 \text{ }^\circ\text{C}$ for 1 hour.

3.2.3 The annealed residue is weighed (m_G) and then crushed in an agate mortar.

3.3 Counting source preparation

90 mg or 1000 mg (m_u), respectively, of the finely pulverized annealed residue are turned into a paste with a little distilled water in a 60 mm or 200 mm measuring dish, respectively, distributed evenly with a pestle, and left to dry on air over night. The area fill of the sample is $3,2 \text{ mg}\cdot\text{cm}^{-2}$ in both cases. In order to improve adhesion, the surfaces of measuring dishes should have been roughed up slightly with fine sandpaper before.

4 Measuring the activity

4.1 Notes on the measurement setup

The counting source is measured with a proportional counter in a low-level measurement setup. Provision needs to be made for adequate shielding with a minimum-radiation material (5 cm to 10 cm of lead) in order to reduce the background effect to a minimum. Values of R_0 of $0,005 \text{ s}^{-1}$ to $0,02 \text{ s}^{-1}$ for 200 mm measuring dishes and R_0 of $0,0005 \text{ s}^{-1}$ to $0,004 \text{ s}^{-1}$ for 60 mm dishes are typical.

The measurements are performed with the same high-voltage setting $U_{AP,\alpha}$ (working point) at the alpha plateau of a proportional counter at which it has been calibrated (Figure 1).

As far as the model of proportional counter is concerned, one without a counter tube window is preferable over one with a counter tube window, as the former will produce significantly higher counting yields (Figure 2). Special attention needs to be paid to sufficiently pre-flushing the counter tube with counter gas prior to taking the actual measurement (typical time required for pre-flushing 30 minutes to 60 minutes, depending of the detector).

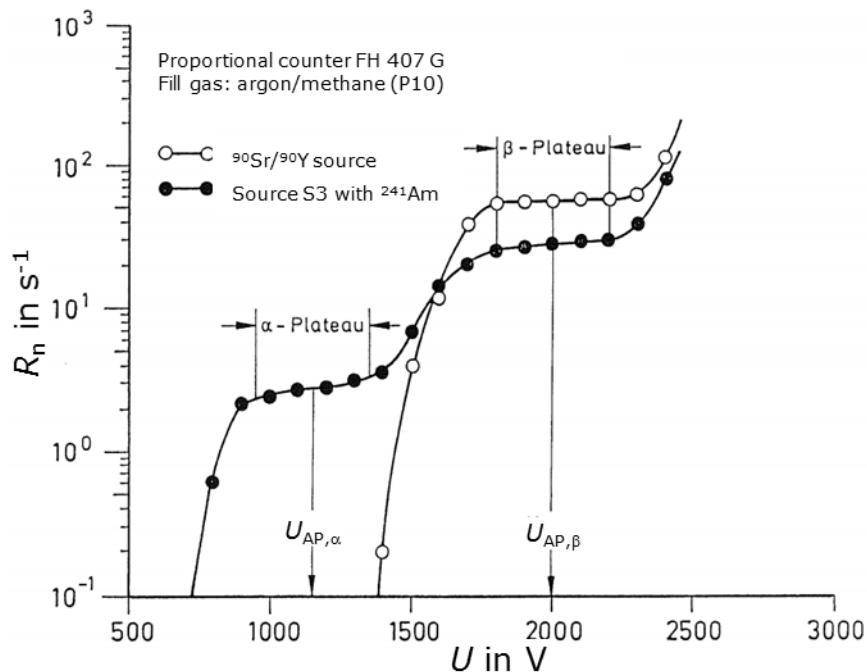


Fig. 1: Counter tube characteristics of a proportional counter with alpha and beta plateaus and the corresponding working voltages, $U_{AP,\alpha}$ and $U_{AP,\beta}$, recorded with a standard source Am-241 and Sr-90/Y-90, respectively.

Measurement periods, t_m , are typically set to 6000 s. The background count rate, R_0 , is to be monitored continuously in order to detect any contamination or other disturbances. Also, the efficiency, ε , needs to be checked regularly against sources of known activity.

For the purpose of comparability, the sensitivity of a measurement setup can be characterized with a so-called figure of merit (FOM). With the measuring conditions fixed (efficiency, ε ; mass of the prepared counting source, m_u ; mass of the annealed residue m_G ; background effect count rate, R_0), the FOM of a counting configuration can be stated as follows:

$$\text{FOM} = \frac{\varepsilon^2 \cdot \left(\frac{m_u}{m_G} \cdot V \right)^2}{R_0} \quad (1)$$

This indicates that the quality of a measurement can be improved in efficiency by increasing the efficiency, ε , or the sample volume, V , rather than by reducing the background effect, R_0 . The FOM values of carefully shielded and adjusted low-level measuring station range from 5 l² to 20 l²·s when 200 mm-measuring dishes are employed.

4.2 Calibration of the measurement setup

If samples of unknown origin are to be examined, the measurement setup must always be calibrated using Am-241. The energy of the alpha radiation of this nuclide ($E_\alpha = 5,486$ MeV and $5,443$ MeV) lies in the central energy range of commonly found alpha emitters. This tends to prevent under- and over-estimations when it comes to measuring alpha emitters that are lower or higher in energy, respectively. Calibration using U_{nat} can only be justified if the activity concentration, $C_{G\alpha}$, is based for the greater part on uranium. The lower energy of the alpha radiation of natural uranium isotopes (U-234: $4,775$ MeV and $4,722$ MeV; U-238: $4,198$ MeV and $4,151$ MeV; U-235: $4,398$ MeV, $4,366$ MeV and others) results in a much-reduced efficiencies, ε , so that the concentration of alpha emitters with moderate to elevated energies is easily over-estimated (see procedure C- α -GESAMT-SEDIM-01). In addition, uranium available from commercial sources sometimes originates from uranium enrichment installations and contains a largely unknown composition of isotopes.

In order to minimize matrix effects, the calibration must be performed using (nearly) the same material that will also be encountered in the samples to be analysed. The influence of the energy-dependence of the alpha efficiency needs to be minimized by choosing counting sources that are as thin as possible ($3,2$ mg·cm⁻²) (4, 5, 8).

The calibration is to be performed as follows:

4.2.1 Depending on the salt content, 10 litres to 20 litres of an unfiltered sample of river water are mixed with 50 ml to 100 ml of sulphuric acid (1 mol·kg⁻¹), evaporated successively in a ceramic dish, and finally left to give off all fumes on a sand bath under an exhaust hood. Be aware of sulphur trioxide vapours.

4.2.2 The residue is annealed in a muffle furnace at 450 °C for 1 hour.

4.2.3 After it has cooled down, the annealed residue is finely pulverized in an agate mortar or ball mill.

4.2.4 Calibration sources are produced by exactly weighing a sufficiently large amount of the finely pulverized annealed residue in a ceramic dish and turning it into paste with a small amount of distilled water.

4.2.5 A precisely dosed volume of an Am-241 solution with a known activity concentration, $C_{\text{Am-241}}$, is added to this paste and homogenized thoroughly. The specific activity, $a_{\text{Am-241}}$, of the calibration sources should be ca. 60 Bq·g⁻¹.

4.2.6 The source marked thus is then dried in a drying oven at 105 °C for 2 hours and thereafter annealed at 450 °C for 1 hour.

4.2.7 The annealed residue marked with Am-241 is now finely pulverized in a mortar or ball mill. Possible contaminations are recorded by means of suitable checks of mass and activity during the preparation process as well as by wipe tests in the actual work areas.

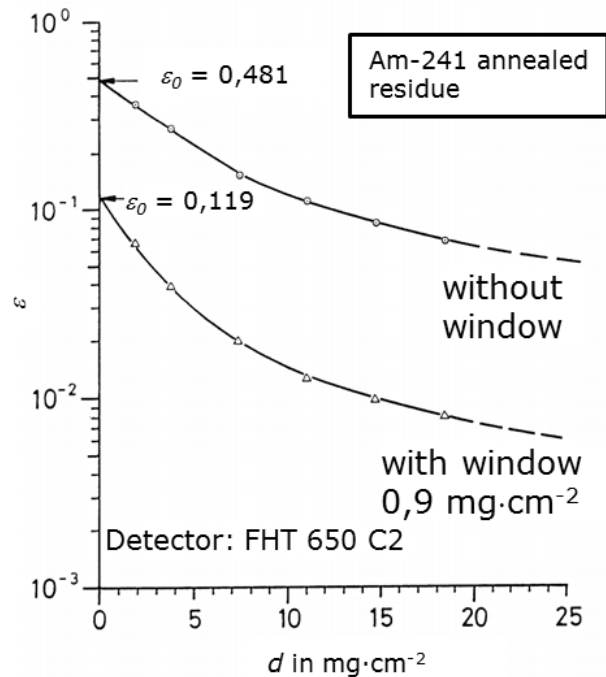


Fig. 2: Efficiencies, $\varepsilon_{\text{Am-241}}$, for annealed residues from river water samples marked with Am-241, measured with and without counter windows, as a function of the area fill, d

4.2.8 To verify the influence of the area fill, d , on the efficiency, $\varepsilon_{\text{Am-241}}$, precisely measured amounts of the marked annealed residue, m_u , are turned into a paste with a small amount of distilled water in 60 mm- or 200 mm-measuring dishes and homogeneously distributed with a pestle. The calibration sources are left to dry on air over night. If necessary, the surfaces of the measuring dish should have been roughed up slightly with fine sandpaper before to improve adhesion.

The calibration curve should be measured in the range from $1 \text{ mg}\cdot\text{cm}^{-2}$ to $25 \text{ mg}\cdot\text{cm}^{-2}$, depending on the area fill (Fig. 2). This will ensure that the gross alpha activity concentration can also be determined in water samples that require deviating from the recommended area fill of $3,2 \text{ mg}\cdot\text{cm}^{-2}$.

4.2.9 From the weighed portion, m_u (g), and the known specific activity of the marked annealed residue, $a_{\text{Am-241}}$ ($\text{Bq}\cdot\text{g}^{-1}$), the required efficiency, $\varepsilon_{\text{Am-241}}$, per area fill, d ($\text{mg}\cdot\text{cm}^{-2}$), can be derived from the following equation:

$$\varepsilon_{\text{Am-241}} = \frac{R_g - R_0}{m_u \cdot a_{\text{Am-241}}} = \frac{R_n}{m_u \cdot a_{\text{Am-241}}} \quad (2)$$

The dependency of the efficiency, $\varepsilon_{\text{Am-241}}$, of a typical counting configuration with and without a counting tube window, on the area fill, d , is shown as an example in Figure 2. Here, the samples are annealed residues of water samples doped with Am-241. From Figure 2, the efficiency $\varepsilon_{\text{Am-241}}$ can be extracted for any given sample thickness. A dedicated estimation of the self-absorption is not necessary under these conditions.

4.3 Interferences

Interferences of the gross alpha activity concentration in water samples during the measurement process must be expected if the voltage point, $U_{AP, \alpha}$, has been selected too high on the alpha plateau of the proportional counter so that a more substantial amount of the beta emitters, which are potentially contained in the sample, is metered as well (Figure 1).

5 Calculation of the results

The activity concentration, $c_{G\alpha}$, of a water sample is calculated as follows:

$$c_{G\alpha} = \frac{R_g - R_0}{\varepsilon_{Am-241} \cdot \frac{m_u}{m_G} \cdot V} = \frac{R_n}{\varepsilon_{Am-241} \cdot q_u \cdot V} \quad (3)$$

with

$$\frac{m_u}{m_G} = q_u$$

It is not normally required to take into account the radioactive decay between collecting the sample and its measurement, considering the long half-lives of the alpha emitters of interest.

The statistical uncertainty, s_n , of the net count rate, R_n , of gross alpha measurement can be calculated from the following relationship:

$$s_n = \sqrt{\frac{R_0}{t_0} + \frac{R_g}{t_m}} \quad (4)$$

This produces the statistical uncertainty of the gross alpha measurement $s(c_{G\alpha})$:

$$s(c_{G\alpha}) = \frac{s_n}{\varepsilon_{Am-241} \cdot q_u \cdot V} \quad (5)$$

or the relative standard deviation, $s(c_{G\alpha})/c_{G\alpha}$ (variation coefficient):

$$\frac{s(c_{G\alpha})}{c_{G\alpha}} = \frac{s_n}{\varepsilon_{Am-241} \cdot q_u \cdot V \cdot c_{G\alpha}} \quad (6)$$

Errors in weighing and calibration, respectively, can usually be neglected vis-à-vis the statistical uncertainty of the gross alpha measurement.

5.1 Worked example

Measuring the activity concentration, $c_{G\alpha}$, in a sample of surface water

Duration of background measurement	t_0	60 000 s
Duration of counting source measurement	t_m	6 000 s
Efficiency of the measurement configuration	ε_{Am-241}	0,29
Background count rate	R_0	0,0167 s ⁻¹
Gross count rate	R_g	0,0333 s ⁻¹
Mass of the annealed residue	m_G	1,5 g
Mass of the counting source	m_u	1,0 g
Volume of the evaporated sample	V	2 l

Following equation (3), this produces an activity concentration, $c_{G\alpha}$, of:

$$c_{G\alpha} = \frac{0,033 - 0,0167}{0,29 \cdot 0,67 \cdot 2} \text{ Bq} \cdot \text{l}^{-1} = 0,043 \text{ Bq} \cdot \text{l}^{-1}$$

The associated statistical counting uncertainty, $s(c_{G\alpha})$ is calculated according to equations (4) and (5):

$$\sqrt{\frac{\frac{0,0167}{60000} + \frac{0,033}{6000}}{0,29 \cdot 0,67 \cdot 2}} \text{ Bq} \cdot \text{l}^{-1} = 0,0062 \text{ Bq} \cdot \text{l}^{-1}$$

The result of the gross alpha measurement with the associated uncertainty therefore reads:

$$c_{G\alpha} = (43 \pm 6) \text{ mBq} \cdot \text{l}^{-1}$$

or

$$c_{G\alpha} = 43 \text{ mBq} \cdot \text{l}^{-1} \pm 14 \%$$

6 Characteristic limits of the procedure

6.1 Decision threshold

The decision threshold, $g_{G\alpha}^*$, that can be attained determining the gross alpha activity concentration of water samples can be calculated as a good approximation according to the following relationship:

$$g_{G\alpha}^* = \frac{k_{1-\alpha}}{\varepsilon_{Am-241} \cdot q_u \cdot V} \cdot \sqrt{\frac{R_0}{t_m} \cdot \left(1 + \frac{t_m}{t_0}\right)} \quad (7)$$

A measurement configuration using a 200-mm measuring dish, a background count rate of $R_0 = 0,017 \text{ s}^{-1}$, a measurement period of the sample of $t_m = 6000 \text{ s}$ and that of the background effect of $t_0 = 60\,000 \text{ s}$, a water volume of $V = 2 \text{ litres}$, a total amount of annealed residue of $m_G = 1,5 \text{ g}$, a mass of the counting source of $m_u = 1,0 \text{ g}$, and an efficiency of $\varepsilon_{Am-241} = 0,29$, the detection limit is $g_{G\alpha}^* = 0,014 \text{ Bq} \cdot \text{l}^{-1}$ for a confidence coefficient of $k_{1-\alpha} = 3$.

6.2 Detection limit

The detection limit can be calculated from the confidence coefficient, $k_{1-\beta}$, for type II errors and based on the decision threshold, $g_{G\alpha}^*$, as follows (see chapter IV.5 of this procedures manual):

$$g_{G\alpha} = \frac{k_{1-\alpha} + k_{1-\beta}}{k_{1-\alpha}} \cdot g_{G\alpha}^*$$

For $k_{1-\beta} = 1,645$, the detection limit of the procedure can thus be given as $g_{G\alpha} = 0,022 \text{ Bq}\cdot\text{l}^{-1}$. Attention is explicitly drawn to particulars in measurement conditions that limit the probability of the error β occurring (type II error) and so ensure a power of $1-\beta$.

7 Catalogue of chemicals and equipment

7.1 Chemicals

- Am-241 solution with known activity concentration (activity standard) e. g. from the Phys.-Tech. Bundesanstalt, 38116 Brunswick;
- Natural uranium oxide, certified;
- Sulphuric acid, H_2SO_4 , $1 \text{ mol}\cdot\text{kg}^{-1}$;
- Fill gas: argon/methane (P10 gas);
- Calcium chloride solution, $219 \text{ g}\cdot\text{kg}^{-1} \text{ CaCl}_2\cdot 6 \text{ H}_2\text{O}$, in distilled water.

7.2 Equipment

- Low-level measurement station with proportional counter and computer-supported analysis unit;
- Surface heater;
- Drying oven;
- Muffle furnace;
- Ceramic dishes;
- Agate mortar or ball mill (e. g., Pulverisette manufactured by A. Fritsch, 55743 Idar-Oberstein);
- Basic equipment of a laboratory.

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