

**Procedure for determining the  
activity concentrations of lead-210 and  
polonium-210 in drinking water  
and ground water**

H-Pb-210/Po-210-TWASS-01

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# Procedure for determining the activity concentrations of lead-210 and polonium-210 in drinking water and ground water

## 1 Scope

The procedure described here serves to determine the activity concentrations of lead-210 (Pb-210) and polonium-210 (Po-210) in drinking water, mineral water and ground water. It is fit for detecting activity concentrations higher than about  $0,005 \text{ Bq}\cdot\text{l}^{-1}$ .

While simultaneously determining the two radionuclides helps to reduce the analytical effort, the applicability of the procedure is limited by the measuring uncertainty of the Po-210 activity concentration, because it will increase as the activity ratio of Pb-210 and Po-210 increases (see section 5). At activity ratios above 10, analyses separated in time have to be conducted analogous to this measuring instruction. Scenarios like this are rarely encountered in natural waters and require that the activity concentration of Po-210 be determined right after sampling (see procedure H-Po-210-TWASS-01), whereas determining the Pb-210 activity concentration can only be effected following a waiting period of 30 days.

## 2 Sampling

For the sampling of drinking water, reference is made to procedure H- $\gamma$ -SPEKT-TWASS-01 and the guidelines contained in (1).

For the sampling of ground water affected by mining activities, reference is made to procedures K- $\gamma$ -SPEKT-TWASS-01 and K-VORBEMERK-GWASS-01.

The required sample volume is determined by the requirements imposed by the analyses to be conducted, e. g., the detection limits of the activity concentration, but also by factors such as multiple analyses or the necessity of keeping samples in reserve.

## 3 Analysis

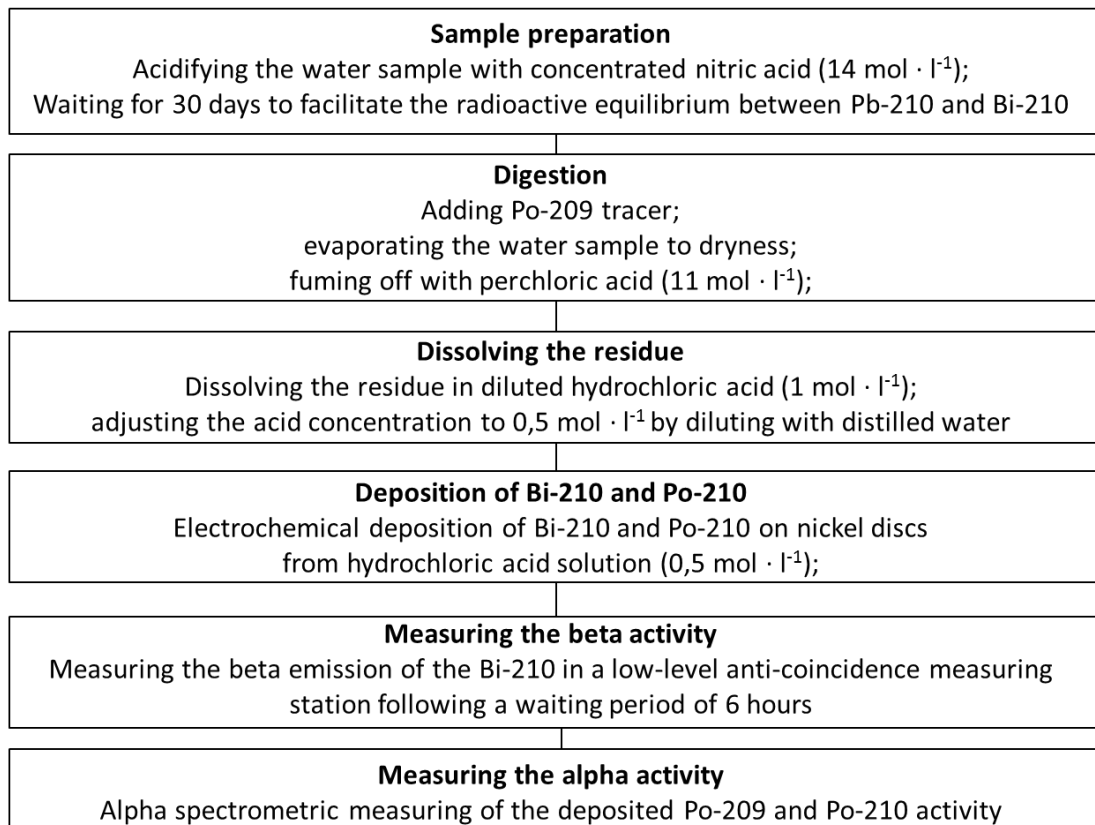
### 3.1 Principle of the procedure

The activity concentration of Pb-210 is deduced from determining the activity of its short-lived daughter nuclide bismuth-210 (Bi-210). The principles of the procedure are illustrated in Figure 1. It includes the digestion of the sample by treating it with nitric acid ( $14 \text{ mol}\cdot\text{l}^{-1}$ ) and perchloric acid ( $12 \text{ mol}\cdot\text{l}^{-1}$ ). Subsequent to a waiting period of 30 days to generate the radioactive equilibrium of Pb-210 and its decay product Bi-210 with a half-life of about 5 days, Bi-210 and Po-210 are simultaneously electrochemically deposited in elementary form on nickel from a hydrochloric acid solution. For measuring the high energy beta-radiation emitted from the decay of Bi-210 ( $E_{\beta\text{max}} = 1162 \text{ keV}$ ), the counting sources are covered with aluminium foil ( $7 \text{ mg}\cdot\text{cm}^{-2}$ ) in order to completely absorb the alpha radiation emitted by the Po-210.

### 3.2 Sample preparation

Ground water samples are typically filtered in order to separate possibly present pollutants that could potentially interfere with the analysis. This supposes that particulate radioactive substances have been dissolved when acid was added after sampling.

The sample is to be de-gassed according to procedure H-Pb-210-AWASS-01, because the radioactive decay of dissolved Rn-222 will produce Pb-210 as a decay product.



**Fig. 1:** Principle of determining the activity concentration of Pb-210 and Po-210 in water samples

### 3.3 Radiochemical separation

**3.3.1** One to four litres of the acidified water sample are spiked with Po-209 tracer in a beaker and evaporated to a volume of ca. 100 ml under continuous stirring on a hotplate with magnetic stirrer. The water is then further evaporated almost to dryness on a sand bath at a temperature of about 160 °C.

**3.3.2** 20 ml of concentrated perchloric acid (12 mol·l<sup>-1</sup>) are added to the residue from the evaporation and the solution cautiously fumed off on a sand bath to remove nitrate. This requires that the beaker holding the solution be covered with a watch glass and first stirred in the warm environment on a hotplate with magnetic stirrer for about 10 minutes in order to completely detach the residue from the bottom of the beaker. Thereafter, the solution is heated for 6 to 8 hours on a sand bath at a temperature of ca. 150 °C and swivelled occasionally. The watch glass is then removed and the solution evaporated almost to dryness.

#### Note

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

**3.3.3** After adding 100 ml of hydrochloric acid (1 mol·l<sup>-1</sup>), the residue is dissolved in a warm environment (about 50 °C) and the solution quantitatively transferred to a 250 ml-beaker, including repeated flushing with distilled water. The sample solution is then filled with distilled water to a total of 200 ml, which will produce a hydrochloric acid solution of 0,5 mol·l<sup>-1</sup>.

**3.3.4** In order to mask interfering Fe<sup>3+</sup>-ions, ascorbic acid (max. 100 mg) is stirred in at portions in a warm environment until a clear solution of light colour is obtained.

**3.3.5** This solution is then used to electrochemically deposit Bi-210, Po-209 and Po-210 on a nickel disc at 90 °C over a period of 20 hours. The disc is placed in a special bracket made of polytetrafluoroethylene (PTFE) in such a manner that the deposition is limited to one side. The bracket is positioned in the beaker as to ensure an even stirring of the solution. Covering the beaker takes care of minimising the loss of water through evaporation.

#### Note

Before its use, the nickel disc is purified by briefly dipping it in hot, concentrated nitric acid and rinsing it immediately thereafter with distilled water. The background count rate of the purified and dried disc is then determined by measuring its beta- and alpha-activities. Previously used nickel discs can be used again after purification if the count rates measured as background effect lie below predetermined values.

**3.3.6** Following the deposition, the bracket with the nickel disc is removed from the solution and the point of time,  $t_2$ , recorded. The nickel disc is unclipped from its bracket, flushed with distilled water, and dried in air.

## 4 Measuring the activity

### 4.1 General

The spontaneous deposition of Bi-210 and Po-210 on nickel is based upon the electromotive series of the elements involved. As a matter of principle, all those elements and their isotopes that are nobler than bismuth will be deposited.

Po-210 as well as other deposited radionuclides and their daughter nuclides will interfere with the measuring of the beta-activity of the Bi-210.

Interfering radionuclides in natural water samples are Bi-214, Bi-212 and their daughter nuclides Po-212, Po-214 and Tl-208 of the Th-232 decay chain. They are so short-lived that it will take only a few hours for them to have decayed to such an extent that they will no longer interfere with the measuring process.

### 4.2 Measurement

After the deposition process has been completed and a waiting period of at least 5 hours observed, the beta activity of the aluminium foil-covered nickel disc is measured in a low-level anti-coincidence measuring station. The measuring period is about 60000 s. The reference point of time for the activity of the counting source,  $t_{3, \text{Bi-210}}$ , is reached after half the measuring period has elapsed.

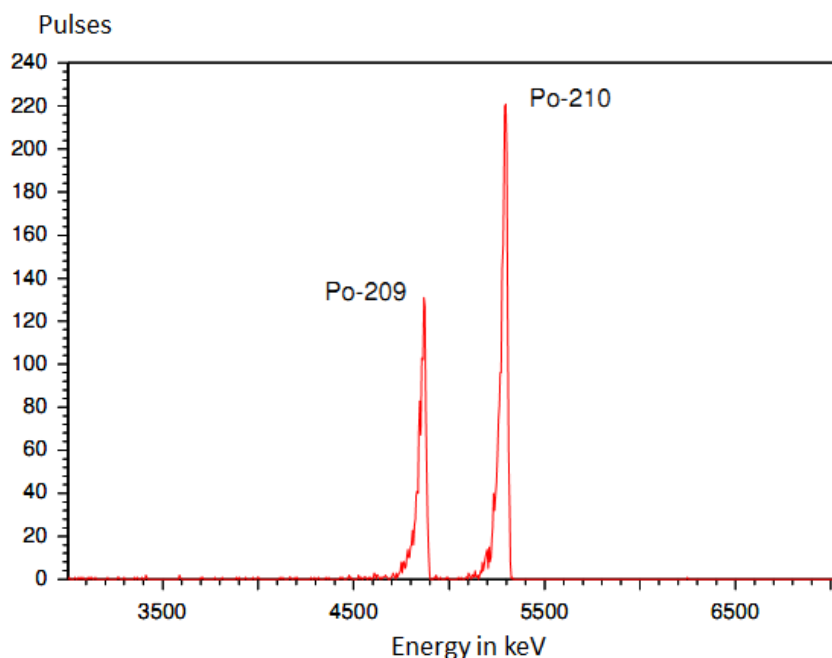
The alpha radiation of the Po-210 is suppressed by keeping the nickel discs covered with aluminium foil. The mass per unit area of the aluminium foil of  $7 \text{ mg} \cdot \text{cm}^{-2}$  is selected thus as to have it absorb low-energy beta radiation as well as alpha radiation to a threshold of about 5,5 MeV while weakening the beta radiation of the Bi-210 merely by 9 %.

Once measuring the beta activity has been completed, the aluminium foil is removed and the activities of the Po-210 and Po-209 tracer are determined alpha spectrometrically. Ion-implanted semiconductor detectors are employed for measuring the alpha activity. The measuring process is conducted in the same geometric arrangement as the one previously used for calibrating. A typical measuring period would be 60000 s. The reference point of time for the activity of the counting source,  $t_{3, \text{Po-210}}$ , is reached after half the measuring period has elapsed. Figure 2 illustrates as an example the alpha spectrum of the polonium isotopes deposited on a nickel disc.

Basic information on alpha spectrometry is contained in chapter IV of this procedures manual.

#### Note

An alternative to alpha spectrometrically determining the activity is employing procedures for determining the total alpha activity by way of, e. g., scintillation probes and ZnS(Ag)-scintillators. Determining the chemical yield by using Po-209 as a tracer will not be possible in these cases, though.



**Fig. 2:** Alpha spectrum of Po-210 deposited from a water sample and the added tracer, Po-209

### 4.3 Calibration

The detection efficiency of the measuring configuration for the beta radiation of Bi-210 and the alpha radiation of Po-210, respectively, are determined on the basis of calibration sources manufactured from certified activity standards. The geometry of the calibration sources has to correspond to that used for analysing the sample. When calibrating with Bi-210, paying attention to covering the nickel disc with aluminium foil is of major importance. The detection efficiency is then calculated according to equation (1):

$$\varepsilon_r = \frac{(R_{gK,r} - R_{0,r})}{A_{K,r}} \quad (1)$$

#### Note

The absorption of the beta radiation to be measured by aluminium foil with an area-related mass of  $7 \text{ mg}\cdot\text{cm}^{-2}$  amounts to 9 %. This absorption does not need to be taken into consideration for calculating the activity concentration of the Pb-210 if the same aluminium foil is used for measuring both the counting source and the calibration source.

Equation (2) is applied to calculate the relative standard measurement uncertainty of the detection efficiency:

$$\frac{s(\varepsilon_r)}{\varepsilon_r} = \sqrt{\frac{\frac{R_{gK,r}}{t_{mK}} + \frac{R_{0,r}}{t_0}}{(R_{gK,r} - R_{0,r})^2} + \left(\frac{s(A_{K,r})}{A}\right)^2} \quad (2)$$

The symbols in equations (1) and (2) have the following meaning:

- $\varepsilon_r$  detection efficiency for the radionuclide  $r$ , in  $\text{Bq}^{-1}\cdot\text{s}^{-1}$ ;
- $R_{gK,r}$  gross count rate of the calibration source used, in  $\text{s}^{-1}$ ;
- $R_{0,r}$  background count rate within the corresponding measuring range, in  $\text{s}^{-1}$ ;
- $A_{K,r}$  activity of the calibration source used, in Bq;

- $t_{mk}$  duration of the calibration source measurement, in s;  
 $t_0$  duration of the background measurement, in s;  
 $s(A_{K,r})$  standard measurement uncertainty of the activity of the particular calibration source, in Bq.

The measuring period for determining the detection efficiency depends on the activity of the calibration source used. It needs to be selected as to not exceed a value of 5 % for the statistical counting uncertainty.

## 5 Calculation of the results

### 5.1 Equations

The activity concentration,  $c_{r,t_1}$ , of the radionuclide  $r$  that needs to be determined at the point of time of sampling,  $t_1$ , is calculated with the aid of the activity measured at the point of time of deposition on nickel and by taking into account the period of time between sampling and deposition.

If samples are not stored for longer than three months, determining the activity concentration of the long-lived Pb-210 (half-life 22,3 a) does not require a correction to be applied for the decay during the period of time between sampling,  $t_1$ , and deposition,  $t_2$ . Amounting only to some 0,8 %, the decrease in activity over three months is negligible ( $C_{Pb-210,t_2} = C_{Pb-210,t_1}$ ).

Relating the activity concentration of the Po-210 (half-life 138,4 d) to the point of time of collecting the sample ( $t_1$ ) requires that the Pb-210 activity concentration of the sample be known. If Pb-210 and Po-210 are in radioactive equilibrium, which cannot be supposed to be the case in naturally occurring waters, no correction is applied. At higher (or lower) Pb-210 activity concentrations in the water, the Po-210 activity ingrowing (respectively diminishing) during the waiting period is to be corrected mathematically.

#### 5.1.1 Equations for calculating the activities of Bi-210 and Po-210 in the counting source

The activity  $A_{r,t_2}$ , of the radionuclide to be determined,  $r$ , at the point of time of its deposition,  $t_2$ , is calculated according to equation (3):

$$A_{r,t_2} = \frac{(R_{g,r} - R_{0,r})}{\varepsilon_r \cdot \eta_r} \cdot f_{3,r} \quad (3)$$

The calculation of the correction factor,  $f_{3,r}$  for the decay of Bi-210 or Po-210, respectively, during the period from the end of the deposition process and the half-way point of time of the measuring process is conducted according to equation (4):

$$f_{3,r} = e^{-\frac{\ln 2 \cdot t_{A,r}}{t_r}} \quad (4)$$

The symbols in equations (3) and (4) have the following meaning:

- $A_{r,t_2}$  activity of the Bi-210 or Po-210 at the point of time of deposition, in Bq;  
 $R_{g,r}$  gross count rate of the counting source, in  $s^{-1}$ ;  
 $R_{0,r}$  background count rate, in  $s^{-1}$ ;  
 $\varepsilon_r$  detection efficiency of the measuring process, in  $Bq^{-1} \cdot s^{-1}$ ;

- $\eta_r$  chemical yield of determining the radionuclide;  
 $f_{3,r}$  correction factor;  
 $t_r$  half-life of Bi-210 or Po-210, respectively, in s;  
 $t_{A,r}$  period of time between the end of the deposition process ( $t_2$ ) of Bi-210 or Po-210, respectively, and the halfway point of time of the measuring process ( $t_{3,r}$ ) of the beta- and alpha-activity, respectively, of Bi-210 or Po-210, respectively, in s ( $t_{A,r} = t_{3,r} - t_2$ ).

The chemical yield of the Po-210 analysis is calculated according to (5):

$$\eta_{\text{Po-210}} = \frac{(R_{g,\text{Tr}} - R_{0,\text{Tr}})}{A_{\text{Tr}} \cdot \varepsilon_{\text{Po-210}}} \quad (5)$$

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

- $R_{g,\text{Tr}}$  gross count rate of the tracer, in  $\text{s}^{-1}$ ;  
 $R_{0,\text{Tr}}$  background count rate within the energy range of the tracer peak, in  $\text{s}^{-1}$ ;  
 $A_{\text{Tr}}$  Po-209 tracer activity added, in Bq.

Because the chemical yield cannot be determined while the Pb-210 activity concentration is measured with the tracer added, it needs to be determined separately on the basis of repeated measuring of Pb-210 in samples with a comparative matrix structure. Own investigations to determine yields showed a mean chemical yield of  $(90 \pm 5) \%$  for this procedure under the described conditions for deposition from samples of drinking and mineral water.

#### Note

Larger amounts of bismuth (several tens of milligrams) and the elements that are co-deposited with bismuth will interfere with the electrochemical deposition and produce lower yields. This becomes particularly important when the yield is to be determined with the aid of Pb-210/Bi-210 solutions with known activities, because some of the commercially available activity standards will contain substantial amounts of the relevant elements as carriers.

The relative standard measurement uncertainty of the activity of the radionuclide  $r$  is calculated according to equation (6):

$$\frac{s(A_{r,t_2})}{A_{r,t_2}} = \sqrt{\frac{\frac{R_{0,r}}{t_0} + \frac{R_{g,r}}{t_m}}{(R_{g,r} - R_{0,r})^2} + \left(\frac{s(\varepsilon_r)}{\varepsilon_r}\right)^2 + \left(\frac{s(\eta_r)}{\eta_r}\right)^2} \quad (6)$$

### 5.1.2 Equations for calculating the activity concentrations of Pb-210 and Po-210

#### 5.1.2.1 Equation for calculating the activity concentration of Pb-210

The activity concentration of Pb-210 in a water sample at the point of time of sampling is calculated by using equation (3) according to equation (7):

$$C_{\text{Pb-210}, t_1} = \frac{A_{\text{Bi-210}, t_2}}{V} \quad (7)$$



wherein:

$C_{\text{Pb-210}, t_1}$  the activity concentration of Pb-210 at the point of time of sampling, in  $\text{Bq}\cdot\text{s}^{-1}$ ;

$V$  the volume of the sample used, in l.

The relative standard measurement uncertainty of the activity concentration of Pb-210 determined at the point of time of sampling,  $t_1$ , is calculated according to chapter IV.5 of this procedures manual after equation (8):

$$\frac{s(C_{\text{Pb-210}, t_1})}{C_{\text{Pb-210}, t_1}} = \frac{s(A_{\text{Pb-210}, t_2})}{A_{\text{Pb-210}, t_2}} \quad (8)$$

The relative standard measurement uncertainty of the chemical yield,  $s_{\text{Bi-210}}(\eta) \cdot \eta^{-1}$ , of the spontaneous deposition of Bi-210 has been experimentally determined by means of repeat analyses of known Pb-activity concentrations. When analysing salt-deficient waters of drinking water quality, it will typically range around 5 %. The relative standard measuring uncertainty of the volume is negligibly small compared to the other contributions.

### 5.1.2.2 Equation for calculating the activity concentration of Po-210

The exact calculation of the activity concentration of Po-210 at the point of time of sampling,  $t_1$ , is conducted according to the equations described in the literature (Bateman equations) (3). Applying these complex differential equations will not necessarily be required if combined standard measurement uncertainties of 20 % to 30 % can be tolerated. If this is the case, calculating the activity concentration of Po-210 may be based upon an empirically deduced approximation in the form of the simplified equation (12) by incorporating the equations (3) through (5) and (9) through (11):

$$C_{\text{Po-210}, t_1} = \frac{(A_{\text{Po-210}, t_2} - A_{\text{Pb-210}, t_1} \cdot f_5) \cdot f_4}{V} \quad (9)$$

with:

$$f_4 = e^{\frac{\ln 2 \cdot t_B}{t_{\text{Po-210}}}} \quad (10)$$

$$\begin{aligned} f_5 = & \frac{t_{\text{Pb-210}}}{t_{\text{Pb-210}} - t_{\text{Bi-210}}} \cdot \frac{t_{\text{Pb-210}}}{t_{\text{Pb-210}} - t_{\text{Po-210}}} \cdot e^{\frac{-\ln 2 \cdot t_B}{t_{\text{Pb-210}}}} + \\ & + \frac{t_{\text{Pb-210}}}{t_{\text{Bi-210}} - t_{\text{Pb-210}}} \cdot \frac{t_{\text{Bi-210}}}{t_{\text{Bi-210}} - t_{\text{Po-210}}} \cdot e^{\frac{-\ln 2 \cdot t_B}{t_{\text{Bi-210}}}} + \\ & + \frac{t_{\text{Po-210}}}{t_{\text{Po-210}} - t_{\text{Bi-210}}} \cdot \frac{t_{\text{Pb-210}}}{t_{\text{Po-210}} - t_{\text{Pb-210}}} \cdot e^{\frac{-\ln 2 \cdot t_B}{t_{\text{Po-210}}}} + \\ & + \frac{A_{\text{Bi-210}, t_1}}{A_{\text{Pb-210}, t_1}} \cdot \left[ \frac{t_{\text{Bi-210}}}{t_{\text{Bi-210}} - t_{\text{Po-210}}} \cdot \left( e^{\frac{-\ln 2 \cdot t_B}{t_{\text{Bi-210}}}} - e^{\frac{-\ln 2 \cdot t_B}{t_{\text{Po-210}}}} \right) \right] \end{aligned} \quad (11)$$

Supposing and approximating the following:

$$A_{\text{Pb-210},t_1} = A_{\text{Pb-210},t_2} \quad \text{and} \quad \frac{A_{\text{Bi-210},t_1}}{A_{\text{Pb-210},t_1}} = 1$$

as well as:

$$\frac{t_{\text{Pb-210}}}{t_{\text{Pb-210}} - t_{\text{Po-210}}} = 1,017 \approx 1 \quad \text{and} \quad e^{\frac{-\ln 2 \cdot t_B}{t_{\text{Pb-210}}}} \approx 1$$

ultimately the simplified equation (12) is derived:

$$C_{\text{Po-210},t_1} = \frac{A_{\text{Pb-210},t_2} \cdot (1 - f_4) + A_{\text{Po-210},t_2} \cdot f_4}{V} \quad (12)$$

wherein (equations (9) through (12)):

$C_{\text{Po-210},t_1}$  activity concentration of the Po-210 at the point of time of sampling, in  $\text{Bq} \cdot \text{s}^{-1}$ ;

$t_B$  period of time between sampling and the end of the deposition process, in s;

$t_{\text{Po-210}}$  half-life of Po-210, in s;

$t_{\text{Bi-210}}$  half-life of Bi-210, in s;

$t_{\text{Pb-210}}$  half-life of Pb-210, in s;

$A_{\text{Bi-210},t_1}$  supposed Bi-210 activity at the point of time of sampling, in Bq;

$A_{\text{Pb-210},t_1}$  determined Pb-210 activity at the point of time of sampling, in Bq.

The relative standard measurement uncertainty of the activity concentration of Po-210 at the point of time of sampling,  $t_1$ , is calculated according to equations (6) and (13). This will take into account both the standard measurement uncertainties of the activities of Pb-210 and Po-210 at the point of time of their deposition,  $t_2$ , and the ratio  $C_{\text{Pb-210},t_1} \cdot C_{\text{Po-210},t_1}^{-1}$  at the point of time  $t_1$ . It will furthermore make provision for decay and ingrowth corrections for the period of time  $t_B$  between sampling and deposition in the factor  $f_4$  and a 5 % standard uncertainty arising from the unknown activity ratio between Pb-210 and Bi-210 at the point of time  $t_1$ .

$$\frac{s(C_{\text{Po-210},t_1})}{C_{\text{Po-210},t_1}} = \sqrt{(1 - f_4)^2 \cdot \left(\frac{A_{\text{Pb-210}}}{A_{\text{Po-210},t_1}}\right)^2 \cdot \left(\frac{s(A_{\text{Pb-210}})}{A_{\text{Pb-210}}}\right)^2 + 0,05^2 + f_4^2 \cdot \left(\frac{A_{\text{Po-210},t_2}}{A_{\text{Po-210},t_1}}\right)^2 \cdot \left(\frac{s(A_{\text{Po-210},t_2})}{A_{\text{Po-210},t_2}}\right)^2} \quad (13)$$

The relative standard measurement uncertainty of the calculated Po-210 activity concentration at the point of time of sampling,  $t_1$ , increases as the ratio  $C_{\text{Pb-210},t_1} \cdot C_{\text{Po-210},t_1}^{-1}$  and the waiting period after sampling,  $t_B$ , increase (cf. Table 1 and Figure 2).

## 5.2 Worked examples

In the following, one calculation example each is provided for the calibration of the low-level anti-coincidence measuring station and for determining the activity concentration of Pb-210 and the activity concentration of Po-210 at the point of time of sampling,  $t_1$ .

### 5.2.1 Calibration

The following data are available after a calibration carried out according to section 4.2:

$$R_{gK} = 1,600 \text{ s}^{-1}; \quad R_0 = 0,004 \text{ s}^{-1};$$

$$A_K = 5,083 \text{ Bq}; \quad t_{mK} = 60000 \text{ s}.$$

The detection efficiency is calculated according to equation (1):

$$\varepsilon_{\text{Bi-210}} = \frac{1,600 - 0,004}{5,083} \text{ Bq}^{-1} \cdot \text{s}^{-1} = 0,314 \text{ Bq}^{-1} \cdot \text{s}^{-1}$$

The relative standard measurement uncertainty,  $s(A_K) \cdot A_K^{-1}$ , of the calibration source manufactured from the certified activity standards has been estimated to be 0,05. This supposed, the relative standard measurement uncertainty of the detection efficiency is calculated according to equation (2):

$$\frac{s(\varepsilon_{\text{Bi-210}})}{\varepsilon_{\text{Bi-210}}} = \sqrt{\frac{\frac{1,600}{60000} + \frac{0,004}{60000}}{(1,600 - 0,004)^2} + (0,05)^2} = 0,05$$

### 5.2.2 Determining the activity concentration of Pb-210

This calculation example is based upon the following numerical values:

$$t_{A,\text{Bi-210}} = 5,04 \cdot 10^4 \text{ s (14 h)}; \quad V = 1,0 \text{ l};$$

$$t_{\text{Bi-210}} = 4,33 \cdot 10^5 \text{ s (5,01 d)}; \quad \eta_{\text{Bi-210}} = 0,92;$$

$$f_{3,\text{Bi-210}} = 1,084; \quad \varepsilon_{\text{Bi-210}} = 0,314 \text{ Bq}^{-1} \cdot \text{s}^{-1}$$

$$R_{g,\text{Bi-210}} = 0,011 \text{ s}^{-1}; \quad t_m = 60000 \text{ s};$$

$$R_{0,\text{Bi-210}} = 0,004 \text{ s}^{-1}; \quad t_0 = 60000 \text{ s}.$$

Applying equation (3), the following activity concentration for Pb-210 is calculated:

$$c_{\text{Pb-210}} = \frac{(0,011 - 0,004) \cdot 1,084}{1,0 \cdot 0,314 \cdot 0,92} \text{ Bq} \cdot \text{l}^{-1} = 0,026 \text{ Bq} \cdot \text{l}^{-1}$$

Inserting the above values, equation (8) will show the relative standard measurement uncertainty of the activity concentration of Pb-210 to be:

$$\frac{s(c_{\text{Pb-210}})}{c_{\text{Pb-210}}} = \sqrt{\frac{\frac{0,004}{60000} + \frac{0,011}{60000}}{(0,011 - 0,004)^2} + (0,05)^2 + (0,07)^2} = 0,11$$

### 5.2.3 Determining the Po-210 activity concentration relative to the date of sampling

The Po-210 activity of the sample at the point of time of deposition,  $t_2$ , is calculated according to equations (3) and (4), using the following values:

$$\begin{array}{ll}
 A_{\text{Po-209}} = 0,08 \text{ Bq}; & t_m = 100000 \text{ s}; \\
 V = 1,0 \text{ l}; & t_0 = 300000 \text{ s}; \\
 t_{\text{Po-210}} = 1,196 \cdot 10^7 \text{ s (138,4 d)}; & R_{0,\text{Po-210}} = 6,67 \cdot 10^{-6} \text{ s}^{-1}; \\
 t_{A,\text{Po-210}} = 1,296 \cdot 10^5 \text{ s (36 h)}; & R_{g,\text{Po-210}} = 3,03 \cdot 10^{-3} \text{ s}^{-1}; \\
 f_{3,\text{Po-210}} = 1,008; & R_{0,\text{Po-209}} = 4,67 \cdot 10^{-5} \text{ s}^{-1}; \\
 \varepsilon_{\text{Po-210}} = 0,26 \text{ Bq}^{-1} \cdot \text{s}^{-1}; & R_{g,\text{Po-209}} = 2,06 \cdot 10^{-2} \text{ s}^{-1}; \\
 \eta_{\text{Po-210}} = 0,92. &
 \end{array}$$

$$A_{\text{Po-210},t_2} = \frac{(3,03 \cdot 10^{-3} - 6,67 \cdot 10^{-6}) \cdot 1,008}{0,92 \cdot 0,26} \text{ Bq} = 0,013 \text{ Bq}$$

Supposing a waiting period,  $t_B$ , of 60 days, a ratio of  $A_{\text{Pb-210},t_2} \cdot A_{\text{Po-210},t_2}^{-1}$ , and a Pb-210 activity,  $A_{\text{Pb-210},t_2}$ , of 0,026 Bq, the Po-210 activity concentration in the sample is calculated according to equations (10) and (12):

$$f_4 = e^{\frac{\ln 2 \cdot 60 \cdot 24 \cdot 60 \cdot 60}{138,4 \cdot 24 \cdot 60 \cdot 60}} = 1,35$$

$$c_{\text{Po-210},t_1} = \frac{0,026 \cdot (1 - 1,35) + (0,013 \cdot 1,35)}{1,0} \text{ Bq} \cdot \text{l}^{-1} = 0,00845 \text{ Bq} \cdot \text{l}^{-1}$$

The relative combined standard measurement uncertainty of the Po-210 activity concentration relative to the point of time of sampling is calculated according to equation (13), using the values given in sections 5.2.2 and 5.2.3:

$$\frac{s(c_{\text{Po-210},t_1})}{c_{\text{Po-210},t_1}} = \sqrt{(1 - 1,35)^2 \cdot 3,1^2 \cdot 0,11^2 + 0,05^2 + 1,35^2 \cdot 1,55^2 \cdot 0,09^2} = 0,23$$

## 5.3 Consideration of uncertainties

Procedure-related contributions to the combined standard measuring uncertainty, which need to be paid attention to in particular for the Po-210 determination, are explained in the following.

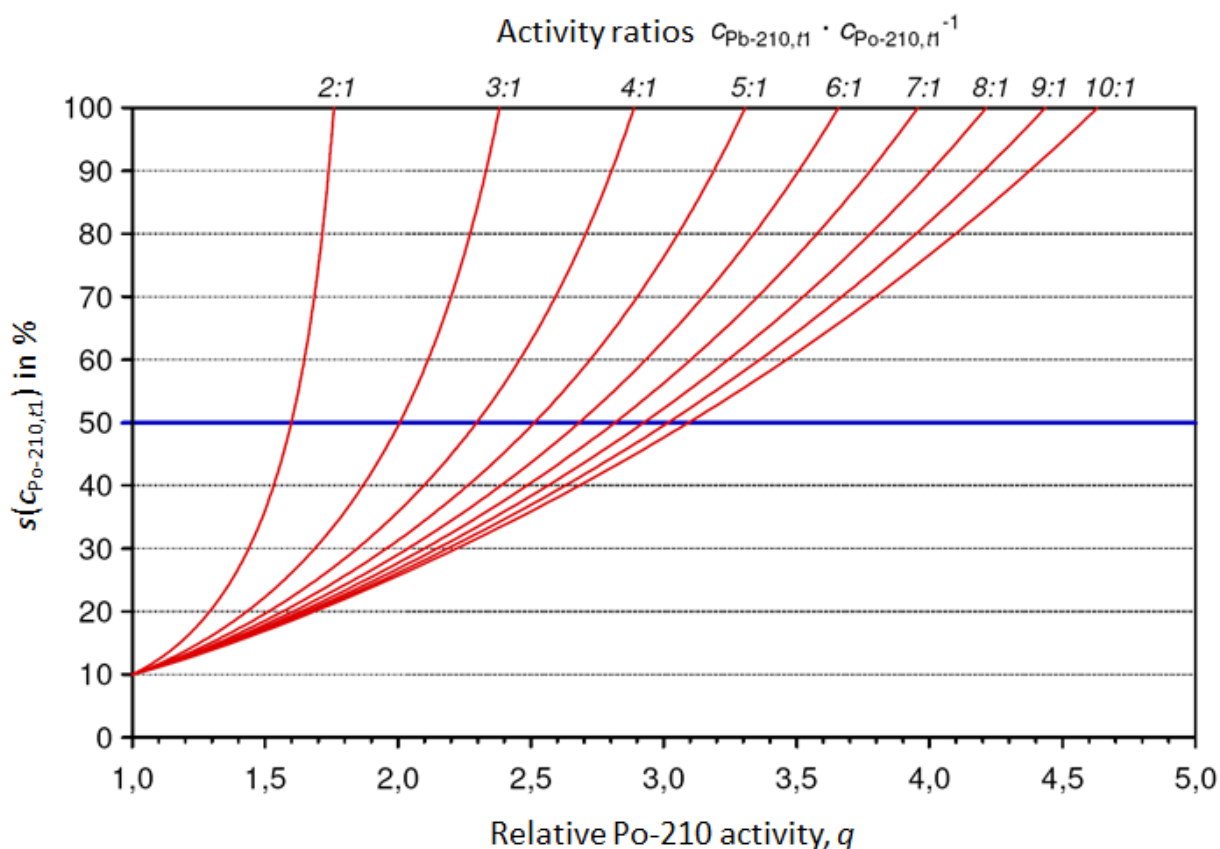
The combined standard measuring uncertainty of the activity concentration of Pb-210 is determined by the counting statistical measurement uncertainty, the measuring uncertainty of the calibration process, and the measurement uncertainty of the yield; it will typically lie in a range of 10 % to 20 %.

The combined standard measurement uncertainty of the activity concentration of Po-210 at the point of time of sampling is additionally influenced to a major extent by the Pb-210 activity present and furthermore, if Pb-210 activity is present, by a contribution stemming from the unknown Bi-210 activity concentration at the point of time of sampling. If the framework conditions of the procedure are adhered to (ratio  $c_{\text{Pb-210},t_1} \cdot c_{\text{Po-210},t_1}^{-1} < 10$ , waiting period,  $t_B$ , between sampling and deposition  $< 90$  d), the latter contribution may be estimated to be about 5 % (cf. Figure 3).

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While the relative standard measurement uncertainties of the measurands  $c_{\text{Pb-210}}$  and  $c_{\text{Po-210}, t_2}$  are decisive for the resultant measurement uncertainty of the Po-210 activity concentration at ratios of  $c_{\text{Pb-210}, t_1} \cdot c_{\text{Po-210}, t_1}^{-1} < 1$ , the impact of the waiting period,  $t_B$ , will increase as the value of the activity ratio increases.

Fig. 3 illustrates as an example the dependency of the combined standard measurement uncertainty of the Po-210 activity concentration at the point of time of sampling,  $t_1$ , on the ratio  $c_{\text{Pb-210}, t_1} \cdot c_{\text{Po-210}, t_1}^{-1}$  and on the variance of the measured Po-210 activity after various waiting periods,  $t_B$ . The relative standard measurement uncertainties of the determined Pb-210 and Po-210 activities at the point of time of deposition,  $t_2$ , are supposed to be 0,10 throughout.



**Fig. 3:** Scheme of the combined standard measurement uncertainty of the Po 210 activity concentration relative to the point of time of sampling; the relative Po-210 activity,  $q$ , is the ratio between the measured Po-210 activity at the point of time of deposition,  $t_2$ , and the activity of Po-210 in the sample relative to the point of time of sampling,  $t_1$ .

As Figure 3 illustrates, a ratio of  $c_{\text{Pb-210}, t_1} \cdot c_{\text{Po-210}, t_1}^{-1} = 5$  will come with a standard measurement uncertainty of the Po-210 activity concentration at the point of time of sampling,  $t_1$ , of about 30 %, if the relative Po-210 activity (ratio of the measured Po-210 activity at the point of time of deposition,  $t_2$ , to the activity of Po-210 in the sample at the point of time of sampling,  $t_1$ ) reaches a value of 1,9, for example. This value corresponds to a waiting period,  $t_B$ , of about 50 days.

For selected activity ratios and supposed relative standard measurement uncertainties of the determined Pb-210 and Po-210 activity concentrations,  $s(c_{r,t_2}) \cdot c_{r,t_2}^{-1}$ , at the point of time of deposition,  $t_2$ , the following resultant combined measuring uncertainties of the Po-210 activity concentration relative to the date of sampling,  $t_1$ , dependent on the waiting period,  $t_B$ , are tabulated.

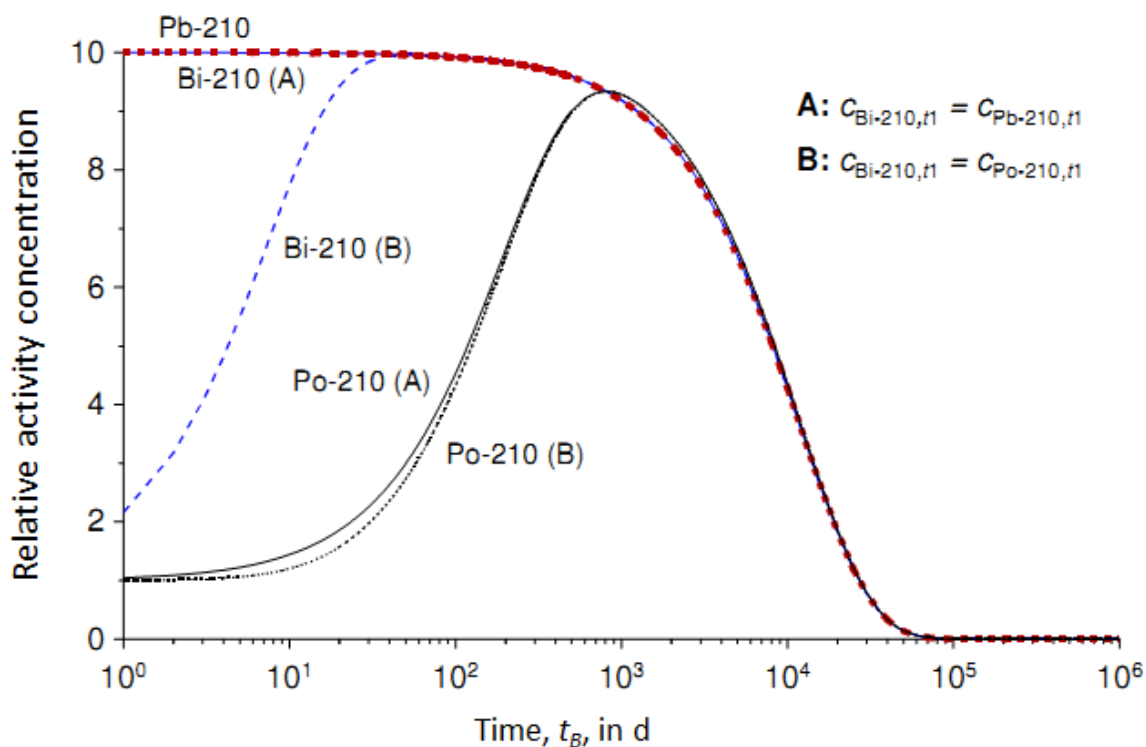
In order to obtain a standard measurement uncertainty of the Po-210 activity concentration that will still be acceptable at ratios of  $c_{Pb-210,t_1} \cdot c_{Po-210,t_1}^{-1} > 5$  and waiting periods,  $t_B$ , of more than 30 days, the relative standard measurement uncertainties in column 2 must not exceed about 10 %. The values provided in Table 1 furthermore indicate that the applicability of the procedure is limited by extensive waiting periods,  $t_B$ .

**Tab. 1:** Combined standard measurement uncertainty of the Po-210 activity concentration depending on the ratio  $c_{Pb-210,t_1} \cdot c_{Po-210,t_1}^{-1}$  and the waiting period,  $t_B$

$\frac{c_{Pb-210}}{c_{Pb-210,t_1}}$	$\frac{s(c_{r,t_2})}{c_{r,t_2}}$ in %	$\frac{s(c_{Po-210,t_1})}{c_{Po-210,t_1}}$ in % after n days of waiting			
		n = 30	n = 45	n = 60	n = 90
0,5	10	11	11	14	17
	30	33	34	36	39
	10	15	17	19	25
2	20	28	32	37	49
	30	41	48	≥ 50	
	10	20	26	33	48
5	20	40	≥ 50		
	10	31	44	≥ 50	
10	20	≥ 50			

The impact of the unknown activity ratio between Pb-210 and Bi-210 at the point of time of sampling,  $t_1$ , is illustrated as an example in Figure 4. It shows the attainment of the radioactive equilibrium between Pb-210, Bi-210 and Po-210 in the shape of two borderline cases by supposing a ratio of  $c_{Pb-210,t_1} \cdot c_{Po-210,t_1}^{-1} = 10$ . In case A, the Bi-210 activity concentration corresponds to that of Pb-210, while in case B, it equals the Po-210 activity concentration. This outlines the maximum and minimum Bi-210 activity concentrations that may occur at the point of time of sampling.

At waiting periods,  $t_B$ , of at least 30 days and ratios of  $c_{Pb-210,t_1} \cdot c_{Po-210,t_1}^{-1} < 8$  that may be expected in natural waters (2), deviations in the calculated Po-210 activity concentrations of about 5 % will be noted in both scenario A ( $c_{Bi-210,t_1} = c_{Pb-210,t_1}$ ) and scenario B ( $c_{Bi-210,t_1} = c_{Po-210,t_1}$ ).



**Fig. 4:** Attainment of the equilibria between the activity concentrations of Pb-210, Bi-210 and Po-210; here, the relative activity concentration is the ratio between the time-dependent activity concentration of the radionuclides mentioned above and the activity concentration of Po-210 at the point of time of sampling

## 6 Characteristic limits of the procedure

### 6.1 Equations

#### 6.1.1 Equation for calculating the detection limit of the Pb-210 activity concentration

Characteristic limits are calculated according to chapter IV.5 of this procedures manual.

The detection limit of the activity concentration,  $g$ , of Pb-210 is calculated according to equation (14), provided that the measuring period of the sample,  $t_m$ , equals that of the background effect,  $t_0$ :

$$g_{\text{Pb-210}} = \frac{k_{1-\alpha} + k_{1-\beta}}{V \cdot \varepsilon_{\text{Bi-210}} \cdot \eta_{\text{Bi-210}}} \cdot f_{3,\text{Bi-210}} \cdot \sqrt{\frac{2 \cdot R_{0,\text{Bi-210}}}{t_0}} \quad (14)$$

In addition to the variables already defined:

- $g_{\text{Pb-210}}$  detection limit of the Pb-210 activity concentration, in  $\text{Bq} \cdot \text{l}^{-1}$ ;
- $k_{1-\alpha}, k_{1-\beta}$  quantiles of the normal distribution for taking into consideration errors of first and second kind.

### 6.1.2 Equations for calculating the detection limit of the Po-210 activity concentration

The detection limit of the activity concentration of Po-210 in waters with different activity concentrations of Pb-210 and Po-210 is calculated with a preset time, small background counts number, and different measuring periods for the counting source produced from the sample and the background in approximation according to equation (15) while incorporating equation (16):

$$g_{\text{Po-210}} = \frac{f_{3,\text{Po-210}} \cdot f_4}{\eta_{\text{Po-210}} \cdot V \cdot \varepsilon_{\text{Po-210}}} \cdot \left[ (k_{1-\alpha} + k_{1-\beta}) \cdot \sqrt{(R_0 + f_6) \cdot \left( \frac{1}{t_0} + \frac{1}{t_m} \right) + s^2(f_6) + 0,25 \cdot (k_{1-\alpha} + k_{1-\beta})^2 \cdot \left( \frac{1}{t_0} + \frac{1}{t_m} \right)} \right] \quad (15)$$

By including correction factor  $f_6$ , Po-210 is taken into account that will have ingrown during the waiting period,  $t_B$ , if Pb-210 activity is present; in this way, a sample-specific background count rate is calculated for each measurement. The correction factor  $f_6$  increases with the waiting period and is calculated according to equation (16). The uncertainty of correction factor  $f_6$  is taken into consideration with the term  $s^2(f_6)$  and is calculated according to equation (17).

$$f_6 = \frac{A_{\text{Pb-210},t_2} \cdot f_5}{V} \cdot \frac{\eta_{\text{Po-210}} \cdot V \cdot \varepsilon_{\text{Po-210}}}{f_{3,\text{Po-210}}} \quad (16)$$

$$s^2(f_6) = f_6^2 \cdot \left( \left( \frac{s(\varepsilon_{\text{Po-210}})}{\varepsilon_{\text{Po-210}}} \right)^2 + \left( \frac{s(\eta_{\text{Po-210}})}{\eta_{\text{Po-210}}} \right)^2 + \left( \frac{s(A_{\text{Pb-210},t_1})}{A_{\text{Pb-210},t_1}} \right)^2 \right) \quad (17)$$

## 6.2 Worked examples

### 6.2.1 Example for calculating the detection limit of the Pb-210 activity concentration

Applying a measuring period of the sample of 60000 seconds,  $k_{1-\alpha} = 3,0$ ,  $k_{1-\beta} = 1,645$ , and the values given in section 5.2 for the detection efficiency, the background count rate, the volume of the sample, the chemical yield, and the correction factor for the decay of Bi-210, equation (16) will give the following detection limit of the activity concentration of Pb-210:

$$g_{\text{Pb-210}} = \frac{3,0 + 1,645}{1,0 \cdot 0,314 \cdot 0,92} \cdot 1,084 \cdot \sqrt{\frac{2 \cdot 0,004}{60000}} \text{ Bq} \cdot \text{l}^{-1} = 6,4 \cdot 10^{-3} \text{ Bq} \cdot \text{l}^{-1}$$

### 6.2.2 Example for calculating the detection limit of the Po-210 activity concentration

Applying the analytic data:

$$\begin{array}{ll} V & = 1,0 \text{ l}; & \eta_{\text{Po-210}} & = 0,9; \\ t_{A,\text{Po-210}} & = 1,296 \cdot 10^5 \text{ s (36 h)}; & t_0 & = 300000 \text{ s}; \\ t_B & = 60 \text{ d}; & t_m & = 100000 \text{ s}; \\ \varepsilon_{\text{Po-210}} & = 0,2 \text{ Bq}^{-1} \cdot \text{s}^{-1}; & R_{0,\text{Po-210}} & = 6,67 \cdot 10^{-6} \text{ s}^{-1}; \\ A_{\text{Pb-210},t_2} & = 0,02 \text{ Bq} \cdot \text{l}^{-1}. \end{array}$$



and an estimated value of 3 % for the relative standard measurement uncertainty of the detection efficiency  $s(\varepsilon_{\text{Po-210}}) \cdot \varepsilon_{\text{Po-210}}^{-1}$ , and a chemical yield of  $s(\eta_{\text{Po-210}}) \cdot \eta_{\text{Po-210}}^{-1}$ , equations (15), (16) and (17) will show the detection limit of the Po-210 activity concentration relative to the date of sampling as follows:

$$f_6 = \frac{0,026 \cdot 0,259}{1,0} \cdot \frac{0,92 \cdot 1,0 \cdot 0,26}{1,008} \text{ s}^{-1} = 1,60 \cdot 10^{-3} \text{ s}^{-1}$$

$$s^2(f_6) = (1,6 \cdot 10^{-3})^2 \cdot (0,03^2 + 0,03^2 + 0,11^2) \text{ s}^{-2} = 3,56 \cdot 10^{-8} \text{ s}^{-2}$$

$$g = \frac{1,008 \cdot 1,35}{0,9 \cdot 1,0 \cdot 0,26}$$

$$\cdot \left[ 4,645 \cdot \sqrt{(6,67 \cdot 10^{-6} + 1,6 \cdot 10^{-3}) \cdot \left( \frac{1}{3 \cdot 10^5} + \frac{1}{10^5} \right) + 3,56 \cdot 10^{-8} + 0,25 \cdot (4,645)^2 \cdot \left( \frac{1}{3 \cdot 10^5} + \frac{1}{10^5} \right)} \right] \text{ Bq} \cdot \text{l}^{-1}$$

$$= 6,9 \cdot 10^{-3} \text{ Bq} \cdot \text{l}^{-1}$$

## 7 Catalogue of chemicals and equipment

### 7.1 Chemicals

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

- Ascorbic acid;
- Perchloric acid, HClO<sub>4</sub>: 12 mol·l<sup>-1</sup>;
- Nitric acid, HNO<sub>3</sub>: 14 mol·l<sup>-1</sup>;
- Hydrochloric acid, HCl: 1 mol·l<sup>-1</sup>.

### 7.2 Equipment

- Low-level anti-coincidence measuring station;
- Alpha spectrometry measuring station;
- Hotplate with magnetic stirrer;
- Sand bath;
- Nickel discs for electrochemical deposition;
- Holding bracket for the nickel disc made of PTFE ([www.tracerlab.com](http://www.tracerlab.com));
- Water bath with thermostat;
- Aluminium foil (area-related mass about 7 mg·cm<sup>-2</sup>).

## References

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