Procedure for determining radium-226 in drinking water and groundwater

H-Ra-226-TWASS-01

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1   Scope

Being an element in the decay chain of U-238, Ra-226 is a radionuclide that occurs naturally. As a constituent of soil Ra-226 is in contact with, ground and spring waters, and can therefore be found at varying concentrations in drinking water and mineral water in particular.

The procedure described here for the determination of Ra-226 activity concentrations is suitable for analysing samples of drinking and mineral waters irrespective of their origin, but also for well, ground or spring waters.

2   Sampling

A sample volume of 1 l will usually be sufficient for the determination of the Ra-226 content present. Drinking water to be analysed is sampled from a regular water supply point. If water is taken from a water supply pipe, well or another point of sampling, the stagnating water in the piping system has to be pumped off or left to drain for a sufficiently long period prior to taking the sample.

Note
A good indicator for whether the period of draining stagnating water is sufficient is the water temperature or its electrical conductivity having reached a constant value.
Hints on the continuous collecting of water samples are given in the procedure H-γ-SPEKT-TWASS-01. After a water sample has been collected, it is acidified with 1 ml of hydrochloric acid (8 mol·l^{-1}) to prepare it for storage in polyethylene containers until it is processed further.

3   Analysis

3.1   Principle of the procedure

The Ra-226 content is determined by measuring the alpha radiation emitted by the daughter nuclide Rn-222. This radon-emanation method is extraordinarily selective and sensitive. The radium contained in the sample is co-precipitated with barium sulphate from a hydrochloric solution. The barium sulphate precipitate is then dissolved in ammoniacal ethylenediaminetetraacetate and transferred to a particular vessel (see Figure 1). The radon is removed by purging the sample with nitrogen, which will "de-emanate" the sample. The daughter nuclide radon will then regrow within a known storage period. Thereafter, the regrown radon is transferred with the aid of nitrogen to an evacuated special type of scintillation chamber (Lucas cell, see Figure 3) in which the alpha radiation of Rn-222 and its short-lived decay products can be detected.

The chemical yield of this method averages 95 % for drinking water. It may be verified by measuring the gamma radiation of Ba-133 that has been added as a tracer.

3.2   Sample preparation

2 ml of barium carrier solution and 10 ml of hydrochloric acid (8 mol·l^{-1}) is added to 1 l of the water to be analysed. If the chemical yield is to be determined, ca. 1000 Bq of Ba-133 tracer are added, too.

3.3   Radiochemical separation

For increased work efficiency, it is recommended to process several samples simultaneously.

3.3.1   The samples are heated under stirring in 2-l-beakers almost to boiling point (80 °C to 90 ºC). Stirring them vigorously, 5 ml of sulphuric acid (18 mol·l^{-1}) are added. Stirring is then continued for about another 5 minutes, after which 3 drops of barium carrier solution are added for seeding. It will be at this point at the latest that barium sulphate starts precipitating as a fine white precipitate. The stirring rods are removed under rinsing. The beakers are covered with watch glasses and the contained precipitates left to mature and cool down to room temperature over night.

3.3.2   The supernatant is scooped off and discarded. The barium sulphate precipitates are washed with as little sulphuric acid (0,1 mol·l^{-1}) as possible in 80 ml-centrifuge beakers and then centrifuged. The centrifugates are discarded. The precipitates are washed twice more with sulphuric acid (0,1 mol·l^{-1}) under stirring. The wash solutions are discarded.

3.3.3   The precipitates are dissolved under warming in 15 ml of EDTA solution (0,25 mol·l^{-1}) and 5 ml of ammoniac (13 mol·l^{-1}) in centrifuge beakers for 4 to 5 hours. If there is still a residue left after this period, a little more ammoniac (13 mol·l^{-1}) is added. The solution is then reduced to about 20 ml.

3.4   Transfer

3.4.1   The solution is decanted quantitatively into a radon bubbler (Fig. 1). Since the activity concentration of Ra-226 is inferred from its daughter nuclide Rn-222 (half-life: 3,82 days), it is important that the time between the regeneration of radon and the transfer of the radon to the Lucas cell, as well as the time between the transfer to the Lucas cell and the start of the measurement be known with precision if the measurement takes place before radon and radium have reached equilibrium (after about 4 weeks). The ingrowth of Rn-222 from Ra-226 with respect to time is illustrated in Figure 2.

3.4.2   In order to get a defined starting point for the ingrowth of radon, nitrogen is purged through the sample in the bubbler for about 20 minutes (de-emanation). Thereafter, the two valves on the bubbler are closed and the sample is left standing to facilitate the ingrowth of Rn-222. The activity of the regenerated Rn-222 will have reached 80 % of the radioactive equilibrium value after 9 days. Samples with higher activities may also be measured following a shorter period of ingrowth. Samples with count rates in the order of magnitude of the background effect should preferably be measured when they are in equilibrium.
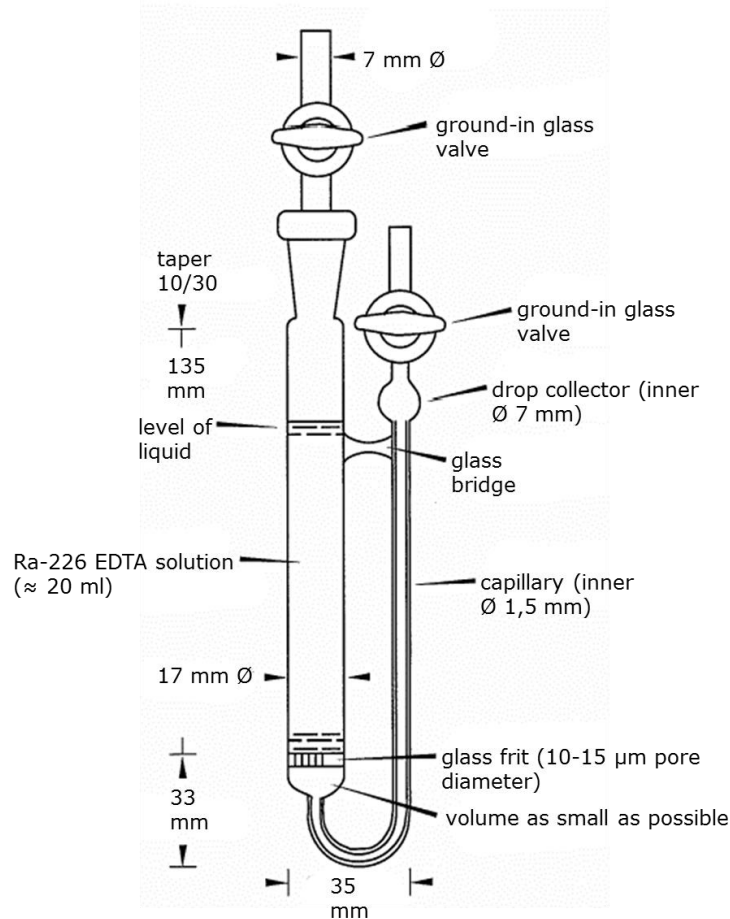
Fig. 1:   Radon Bubbler

3.4.3   The radon that has been generated in the bubbler is transferred to the Lucas cell (Figure 3) by means of a pump array that will also be employed for flushing the Lucas cell after the measurement has been completed (cf. Figures 4 and 5). In order to facilitate a transfer that is as quantitative as possible, the dead volumes of the connections between bubbler and Lucas cell have to be as small as possible. Capillaries must therefore be used as supply pipes. The drying tube (filled with magnesium perchlorate and soda lime) should be 100 mm in length with an inner diameter of 10 mm. The ends of the drying tube are blocked with glass wool.

Note
The drying agents have to be replaced at regular intervals.

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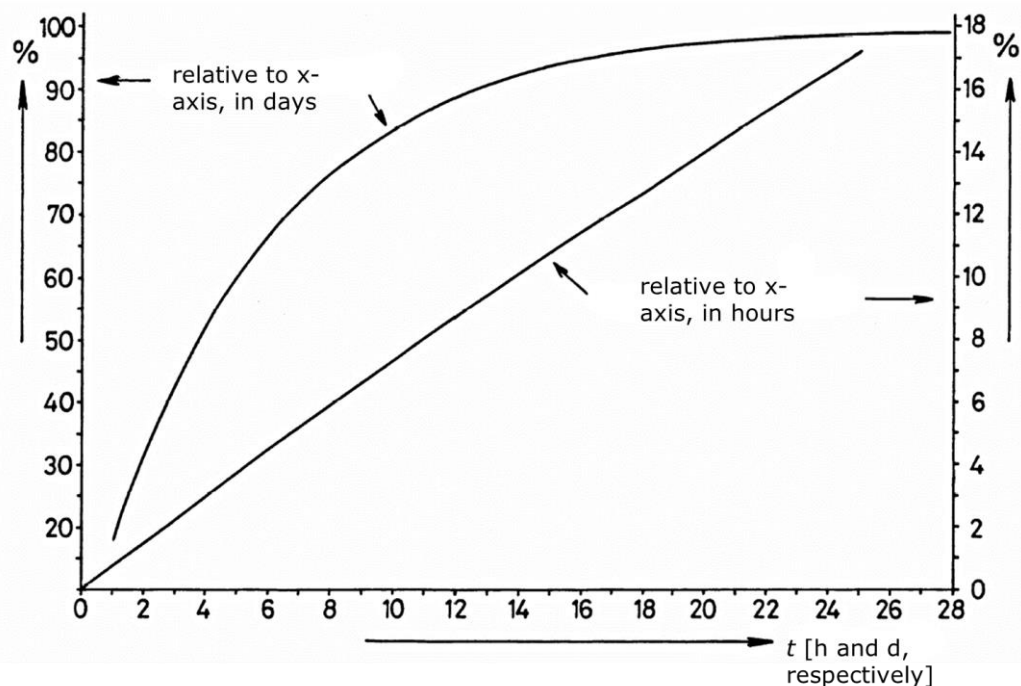
Fig. 2: Formation of radon-222 from radium-226. Percentage of the equilibrium value as a function of time in hours (right y-axis) and in days (left y-axis)
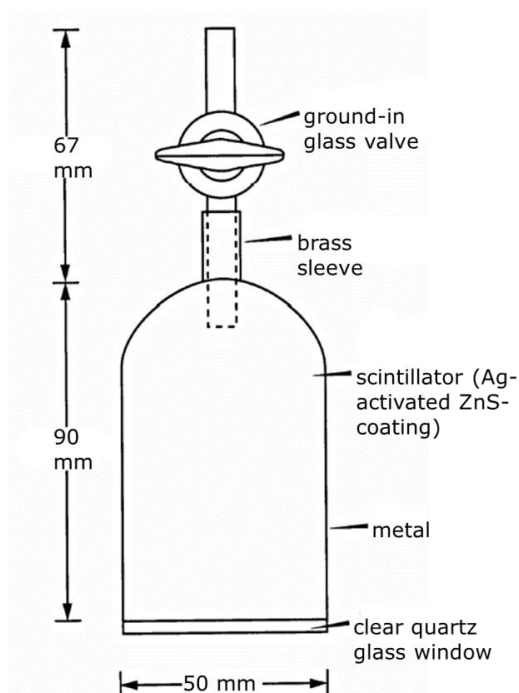

Fig. 3: Lucas cell

3.4.4 It is recommended to supply the radon-free carrier gas (matured compressed air, matured nitrogen or helium) not directly from the gas cylinder, but rather from a plastic bag under atmospheric pressure. This will prevent excess pressure as a result of inappropriately handling the control valve. The following individual steps need to be taken:

— Connect the Lucas cell on the pump array (Figure 4). The flange needs to be greased very lightly to ensure the connection is properly sealed, but no grease must enter the drill hole because grease is able to dissolve radon.

— Evacuate the Lucas cell (the mercury column of the manometer will rise).

— Close the valve to the Lucas cell. Filling the plastic bag with carrier gas (the mercury column will fall).

— Disconnect the plastic bag from the gas cylinder and pump. Connecting the bubbler to the lower end of the drying tube (Figure 5).

— Open the valve to the Lucas cell (causing diminished pressure that makes the mercury column rise once more). Test for leaks in the array.

— Open the exit valve of the bubbler. Bubbles will rise for a short while until pressure is equalised.

— Open the supply valve of the bubbler slowly, so that the carrier gas can enter the system. One bubble per second should rise below the frit. As the filling of the Lucas cell increases, the mercury column will fall until it reaches atmospheric pressure. The transfer process should not take less than about 15 minutes.

— Close the valve to the Lucas cell. Detaching the Lucas cell and allow it to equilibrate for about 3 hours prior to starting the measurement to facilitate the ingrowth of the short-lived radon decay products.

Note

The sample in the bubbler may be "milked" again following the regeneration of radon. In this case, the two valves need to be closed after the transfer is complete. The point of time of the radon transfer to the Lucas cell marks point zero of the radon ingrowth.
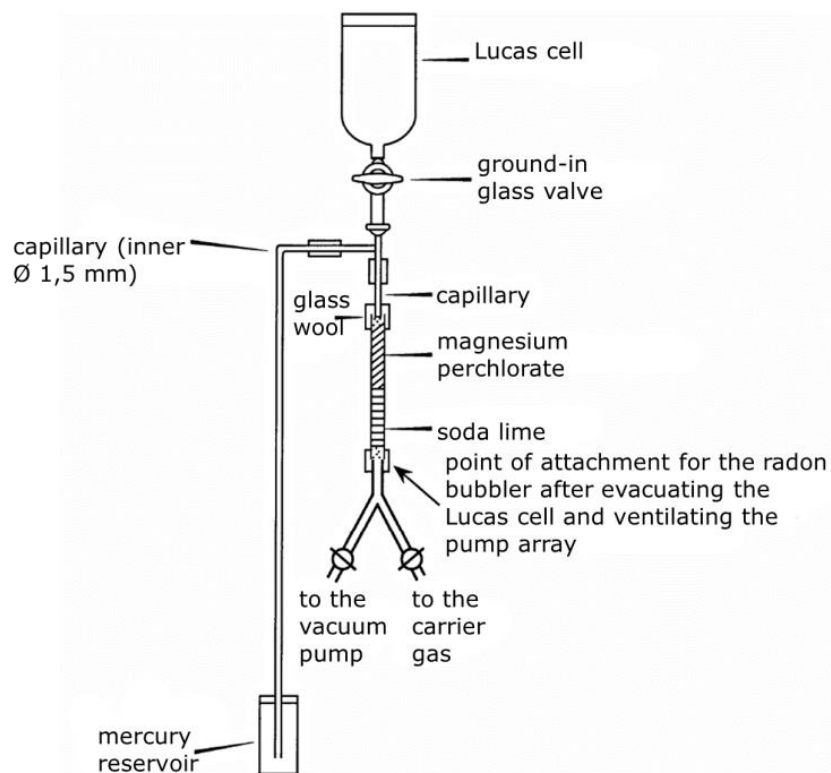

Fig. 4: Pump array for transferring radon-222 from the bubbler to the Lucas cell and flushing the Lucas cell.
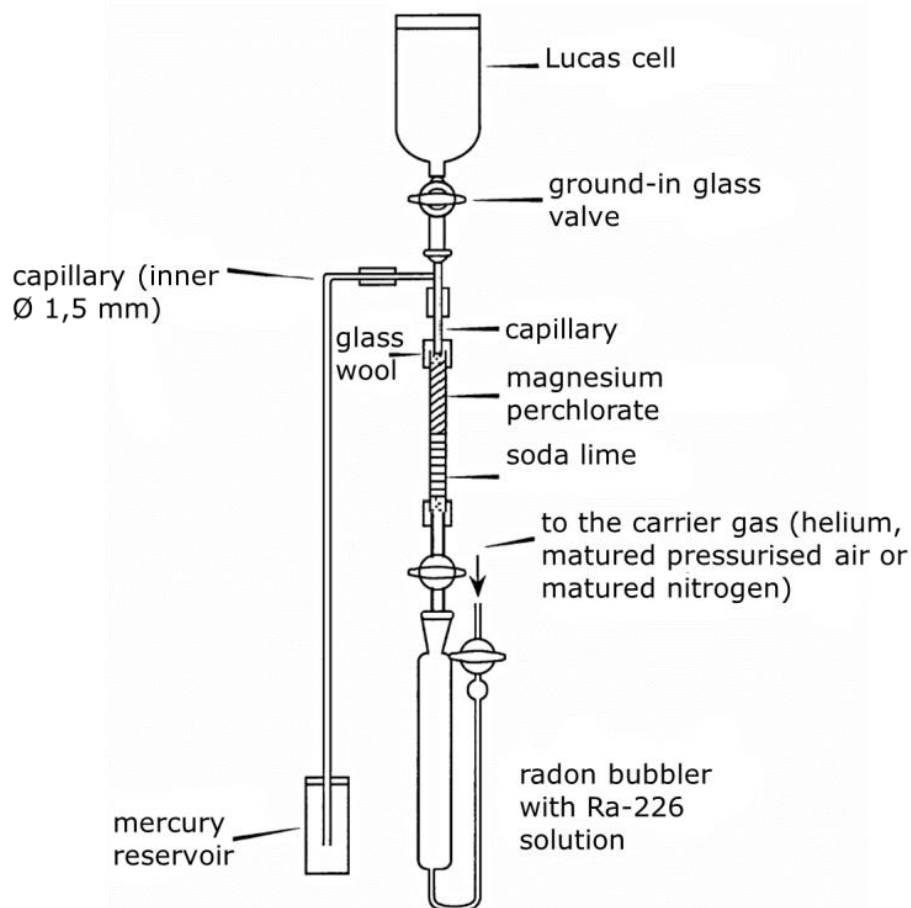
Fig. 5: Transfer of radon-222 from the bubbler to the Lucas cell.

4 Measuring the activity

4.1 Instrumentation

A workstation for radon measurements consists of a Lucas cell, a photo-multiplier with amplifier, a high-voltage power supply unit, a counter, and a recording device. The photo-multiplier is mounted in a perfectly opaque casing and aligned thus that the Lucas cell can be placed vertically on top of it for measuring through the window. A block diagram is shown in Figure 6.

4.2 Measurement

After a waiting period of 3 hours, the alpha radiation of the radon, including its short-lived daughter nuclides, is measured. The duration of measurement depends on the expected activity and the required detection limit.

Note
In the case of a sample with a higher activity, there is a risk of contaminating the Lucas cells with long-lived decay products such as Pb-210. To avoid this, such samples should be measured only briefly.
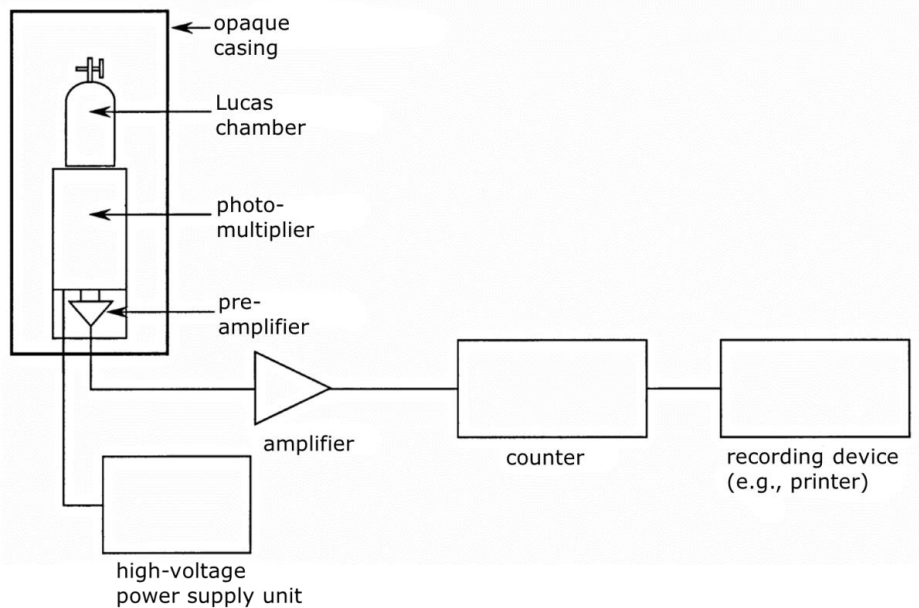
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Fig. 6:   Block diagram of a workstation for radon-222 measurements

After the measurement, the Lucas cells are flushed at least three times with carrier gas, i. e., by alternately evacuating them with the aid of the pump array and refilling (Figure 4).

Prior to the determination of the background effect of the Lucas cells again, the short-lived decay products of radon must have been left to decay. This will be the case after a waiting period of 24 hours.

4.3   Calibration

The calibration factor, φ_i, needs to be determined with the help of a standard solution of known Ra-226 activity concentration for each Lucas cell separately. This involves transferring the radon as described in section 3.4.

It is advisable to verify the values of the background effect and calibration factor, φ_i, for each Lucas cell at regular intervals and record the results in logs. This will help to spot irregularities and remove contaminated cells or those with notoriously poor count yields.

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5 Calculation of the results

5.1 Calculation of the calibration factor

The calibration factor, φ_i, for the Lucas cell i is calculated according to equation (1):

$$\varphi_i = \frac{A_{\mathrm{S}}}{R_{\mathrm{S}i} - R_{0i}} \cdot f_1 \cdot f_2 \cdot f_3 \tag{1}$$

where

A_{s} activity of the Ra-226 standard, in Bq;
$R_{\mathrm{S}i}$ gross count rate of the Ra-226 standard in cell i, in s^{-1};
R_{0i} background count rate of cell i, in s^{-1}.

The correction factor f_1 takes into consideration the period of time between de-emanating the Ra-226 solution in the bubbler and transferring the ingrown radon to the Lucas cell. Equation (2) applies:

$$f_1 = \left[1 - \exp\left(-\ln 2 \cdot \frac{t_1}{t_{\mathrm{Rn\text{-}222}}} \right) \right]^{-1} \tag{2}$$

where
t_1 time between the radon regeneration and the transfer to the Lucas cell, in s;

$t_{\mathrm{Rn\text{-}222}}$ half-life of Rn-222, in s.

For its part, correction factor f_2 takes into consideration the decay of the Rn-222 in the Lucas cell during the period from its transfer to the start of the measurement. Equation (3) applies:

$$f_2 = \exp\left(\ln 2 \cdot \frac{t_2}{t_{\mathrm{Rn\text{-}222}}} \right) \tag{3}$$

where

t_2 the period of time between the completion of the transfer and start of the measurement, in s

The factor f_3 takes into account the decay of the Rn-222 during the measurement itself. Equation (4) applies:

$$f_3 = \ln 2 \cdot \frac{t_{\mathrm{m}}}{t_{\mathrm{Rn\text{-}222}}} \cdot \left[1 - \exp\left(-\ln 2 \cdot \frac{t_{\mathrm{m}}}{t_{\mathrm{Rn\text{-}222}}} \right) \right]^{-1} \tag{4}$$

where

t_{m} duration of measurement, in s

If the duration of measurement is less than 21600 s (6 h), f_3 may be set to unity.

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5.2 Calculation of the Ra-226 activity concentration

The activity concentration, *c*, of Ra-226 is obtained according to equation (5):

$$c_{\text{Ra-226}} = \frac{\varphi_i \cdot (R_g - R_0)}{V \cdot \eta} \cdot f_1 \cdot f_2 \cdot f_3 \tag{5}$$

where

R_0 background count rate, in s^{-1};

R_g gross count rate of the sample, in s^{-1};

φ_i calibration factor, in Bq·s;

V volume of the sample, in l;

η chemical yield, < 1,0;

The correction factors f_1, f_2, and f_3 are calculated according to equation (2), (3), and (4).

5.3 Worked example

Inserting the following numerical values:

t_1 = 1,21·10⁶ s (14 d); t_2 = 1,08·10⁴ s (3 h);

$t_{\text{Rn-222}}$ = 3,305·10⁵ s (3,825 d); t_m = 1,44·10⁴ s (4 h);

f_1 = 1,09; f_2 = 1,02;

f_3 = 1,02; V = 1 l;

φ_i = 0,6 Bq·s; η = 0,95 (95 %);

R_b = 0,010 s^{-1}; R_0 = 0,003 s^{-1}.

the activity concentration, *c*, of Ra-226 amounts to:

$$c_{\text{Ra-226}} = 5,0 \cdot 10^{-3} \text{ Bq·l}^{-1}$$

5.4 Consideration of uncertainties

The total relative statistical uncertainty, $s(c)/c$, of the measurement is calculated according to equation (6):

$$\frac{s(c)}{c} = \sqrt{\frac{\dfrac{R_{gi}}{t_m} + \dfrac{R_{0i}}{t_0}}{(R_{gi} - R_{0i})^2} + \left(\frac{s(\varphi)}{\varphi}\right)^2 + \left(\frac{s(\eta)}{\eta}\right)^2} \tag{6}$$

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

t_0 duration of background measurement, in s;

$s(c)$ total standard deviation of the radium concentration, in Bq·l⁻¹;

$s(\varphi_i)$ standard deviation of the calibration factor of Lucas cell *i*, in Bq·s;

$s(\eta)$ standard deviation of the chemical yield η.

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Inserting the values given in section 5.3 and:

$$s(\eta)/\eta = 0,05$$

$$s(\varphi_i)/\varphi_i = 0,1$$

the relative uncertainty of the radium concentration amounts to:

$$s(c)/c = 0,17$$

The result of the activity measurement therefore reads:

$$c = (5,0 \pm 0,8) \text{ mBq} \cdot \text{l}^{-1}$$

6 Characteristic limits of the procedure

For the calculation of the the detection limit of the activity, G, reference is made to chapter IV.5 of this procedures manual and to equation (2.5) in particular. Calculating the detection limit of the activity concentration, g, follows equation (7):

$$g = \frac{G}{V \cdot \eta} \cdot f_1 \cdot f_2 \cdot f_3 \qquad (7)$$

Inserting the values given above and a measuring period for the background effect of 14400 s (4 h), a background effect of the measuring configuration of 0,003 s^{-1}, and $k_{1-\alpha} + k_{1-\beta} = 4,645$, the detection limit of the activity concentration, g, amounts to:

$$g = 2 \cdot 10^{-3} \text{ Bq} \cdot \text{l}^{-1}$$

7 Catalogue of chemicals and equipment

7.1 Chemicals

All chemicals used should be of the purity grade "*pro analysi*", if possible.

— Ammoniac solution, NH_3: 13 mol·l^{-1};
— Barium carrier solution, 16 mg·ml^{-1} Ba^{2+} (28,4 g of $BaCl_2 \cdot 2H_2O$ in 1000 ml of distilled water);
— EDTA, ethylene diamine tetra-acetate: 0,25 mol·l^{-1} (7,4448 g l^{-1});
— Magnesium perchlorate, $MgClO_4$, anhydrous;
— Soda lime, $NaOH + Ca(OH)_2$ anhydrous;
— Ra-226 standard solution (about 1 Bq·ml^{-1}) ;
— Hydrochloric acid, HCl: 8 mol·l^{-1};
— Sulphuric acid, H_2SO_4: 0,1 mol·l^{-1} and 18 mol·l^{-1};
— Carrier gas, helium or matured nitrogen (free of radon);
— Mercury, Hg.

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7.2　Equipment

— Hotplate with magnetic stirrer;

— Radon bubbler (Figure 1);

— Measuring workstation (Figure 6), consisting of a Lucas cell (Figure 3), photo-multiplier, amplifier, high-voltage power supply unit, counter, and recording device;

— Basic equipment of a radiochemical laboratory.

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