Procedure for determining the activity concentration of radium-226 in drinking and ground water

K-Ra-226-TWASS-01

Authors:
M. Beyermann
B. Höfs
U.-K. Schkade
K. Schmidt

Federal coordinating office for questions of monitoring of the radioactivity at enhanced natural radioactivity (ENORM)
(Leitstelle für Fragen der Radioaktivitätsüberwachung bei erhöhter natürlicher Radioaktivität (ENORM))
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1 Scope

Ra-226 is a radionuclide of the U-238 decay chain that occurs naturally. The procedure described here serves to determine the activity concentration of Ra-226 in drinking and ground water. It is fit for detecting activity concentrations of Ra-226 in excess of 0,01 Bq∙l⁻¹. The procedure thus conforms to the requirements stipulated by the Guideline for the Monitoring of Emissions and Immissions from Mining Operations (REI Bergbau).

2 Sampling

For sampling of drinking water, reference is made to procedure H-γ-SPEKT-TWASS-01 and the hints given in (1).

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

3 Analysis
3.1 Principle of the procedure

For the principle of the procedure, see procedure H-Ra-226-TWASS-01. The procedure is based upon recording the alpha emissions of Rn-222 and its decay nuclides Po-218 and Po-214 following the transfer of Rn-222 from an adequately prepared sample to a scintillation measuring chamber, also known as a Lucas cell (Figure 1); this procedure is also referred to as emanometry. The main steps of the procedure are:

— Co-precipitating Ra-226 while barium carrier solution and sulphuric acid are added to barium sulphate;
— Dissolving the precipitate tetra-sodium ethylene diamine tetra-acetate solution (Na₄EDTA-solution) and transferring it to an emanation vessel;
— Ingrowth of the daughter nuclide Rn-222 over a period of about 14 days;
— Transferring the Rn-222 to a Lucas cell;
— Ingrowth of the short-lived Rn-222 decay products over a period of about 3 hours;
— Recording the alpha emission.
Fig. 1: Lucas cell (dimensions in mm)

3.2 Interferences

The procedure is specific to determining the activity concentration of Ra-226; interferences by other radium isotopes or radionuclides have not been observed.

3.3 Sample preparation

To stabilise and avoid adsorption effects on the walls of the vessel, all water samples are acidified with about 10 ml of nitric acid (14 mol·l⁻¹) per litre (pH ≈ 1) on site. Although samples of drinking and ground water would normally be clear, they are nevertheless filtered in the laboratory in order to remove possibly present pollutants that might interfere with the analysis. It may be supposed here that any radioactive substances attached to particles will already have dissolved since the acid was added so that their contribution will be duly recorded.

3.4 Radiochemical separation

3.4.1 In a 2-l-glass beaker, 1 litre of the water sample to be analysed is fortified with 5 ml of citric acid solution (1 mol·l⁻¹), 10 drops of methyl-red solution, and concentrated ammoniac solution (13 mol·l⁻¹) to the indicator's point of transition to yellow (ca. 2,5 ml). Then, 3 ml of barium nitrate solution (0,043 mol·l⁻¹) are added. The solution is heated to a soft boil, and barium (radium) sulphate is precipitated from the hot solution with 2,5 ml of sulphuric acid (9 mol·l⁻¹). The supernatant solution is decanted and discarded.

3.4.2 The precipitate is transferred to a 100-ml-centrifuge glass, centrifuged, and the supernatant solution is decanted and discarded.

3.4.3 The precipitate is purified twice with 50 ml of distilled water each and centrifuged. The purification solutions are decanted and discarded.
3.4.4 The precipitate is warmed in a water bath and dissolved in 5 ml of Na$_2$EDTA solution (0.5 mol·l$^{-1}$), upon which the solution is transferred quantitatively to an emanation vessel, with the centrifuge glass being flushed several times with a few millilitres of distilled water each. The solution in the emanation vessel is replenished with distilled water to a total volume of 25 ml (about two thirds of the vessel’s volume).

3.5 De-emanation of the emanation vessel after sample preparation

3.5.1 The emanation vessel is connected via a hose that in turn is connected via valve 2 to an adjustable vacuum pump (Figure 2). The vacuum pump is then switched on and typically adjusted to a pressure of 800 mbar.

3.5.2 In order to obtain a defined starting point for the ingrowth of Rn-222, the Rn-222 that may be present needs to be removed from the emanation vessel. Valves 1 and 2 on the emanation vessel are opened to channel a homogeneous gas flow through the emanation vessel for a period of ca. 15 minutes.

Note
The solution must be kept from frothing.

3.5.3 Valve 1 on the emanation vessel is then closed to facilitate evacuation for a period of ca. 5 minutes.

3.5.4 Finally, valve 2 is also closed and the vacuum pump switched off. The point of time of completion of the de-emanation process and the beginning of the ingrowth of Rn-222 ($t_1$) is recorded.

Fig. 2: Setup for the de-emanation of the emanation vessel
3.6  Transfer of the Rn-222 from the emanation vessel to the Lucas cell

3.6.1  About 14 days later, the emanation vessel is connected via a drying tube filled with calcium chloride (Figure 3).

![Diagram of setup for transferring Rn-222 from the emanation vessel to the Lucas cell]

Fig. 3: Setup for transferring Rn-222 from the emanation vessel to the Lucas cell

3.6.2  The Lucas cell is connected to a radium-emanation device. Using a vacuum pump, the Lucas cell is evacuated. Valves 1 and 2 are closed during this process while valves 3, 4 and 5 will be open.

3.6.3  The integrity of the system is to be verified by checking that the pressure in the system will not rise when valve 3 is closed.
3.6.4 The following needs to be done to channel the Rn-222 from the emanation vessel to the Lucas cell:
- Valves 1, 2 and 3 are closed;
- Valve 2 is carefully opened so that no liquid or froth can enter the drying tube;
- Valve 1 is opened far enough to allow an unvarying airflow to be sucked through the sample solution. It takes about 20 minutes for the de-emanation process to be completed. The point of time of transferring the Rn-222 to the Lucas cell \( t_2 \) is recorded.

Notes
- In order to prevent aerosol particles from entering the Lucas cell, glass wool is inserted and compressed between the measuring chamber and the emanation vessel in the calcium chloride-filled drying tube.
- If the concentration of Rn-222 in the air of the laboratory cannot be neglected it is recommended that the inlet of valve 1 be fitted with a drying tube filled with activated charcoal.

3.6.5 Once radioactive equilibrium has established itself between the Rn-222 and its short-lived progeny (ca. 3 hours), the count rate is determined on the basis of the alpha emission in the Lucas cell. The point of time of the middle of the measuring period \( t_3 \) is recorded.

4 Measuring the activity

4.1 General

Following the ingrowth of the short-lived decay products of Rn-222 to almost perfect radioactive balance, the count rate resulting from the alpha emission by Rn-222, Po-218 and Po-214 is measured. The measuring period depends on the activity to be expected, respectively on the required detection limit for Ra-226. Typical measuring periods range from 100 to 200 minutes.

Note

Once measuring is completed, the Lucas cell needs to be flushed with air in order to prevent its becoming permanently contaminated with decay products of Rn-222. The background count rate produced by the Lucas cell needs to be checked for possible contamination.

4.2 Calibration

A calibration factor, \( \varphi_i \), is determined for each Lucas cell, \( i \), using a calibration solution produced from a Ra-226 activity standard. To this end, an aliquot of the calibration solution is filled into the emanation vessel and calibrated according to section 3.5 of this procedures manual. The calibration factor, \( \varphi_i \), for the Lucas cell, \( i \), is calculated according to equation (1):

\[
\varphi_i = \frac{A_{K,i}}{\left( R_{K,i} - R_{0,i} \right)} \cdot \frac{f_1}{f_2}
\]

(1)

in which:

\( \varphi_i \) calibration factor for the Lucas cell \( i \), in Bq·s;

\( A_{K,i} \) activity of the aliquot \( i \) of the calibration solution, in Bq;

\( R_{K,i} \) gross count rate of the Lucas cell \( i \), in s\(^{-1}\);

\( R_{0,i} \) background count rate of the Lucas cell \( i \), in s\(^{-1}\);
Correction factor for the ingrowth of the short-lived Rn-222 decay products during the period from the completion of the de-emanation process, respectively the start of the ingrowth of the Rn-222 ($t_1$), and the transfer of the ingrown Rn-222 to the Lucas cell ($t_2$);

Correction factor that allows for the decrease in activity of the Rn-222 during the period from completing the transfer to the Lucas cell ($t_2$) and the point of time of the middle of the measuring period ($t_3$).

Selected values for correction factors $f_1$ and $f_2$ are provided in Table 1.

The correction factor $f_1$ is calculated according to equation (2):

$$f_1 = 1 - e^{-\lambda_{Rn-222} \cdot (t_2 - t_1)}$$

in which:

- $\lambda_{Rn-222}$ decay constant of Rn-222, in d$^{-1}$;
- $t_2 - t_1$ period from the beginning of the ingrowth of Rn-222 (point of time $t_1$) to its transfer to the Lucas cell ($t_2$), in d.

The correction factor $f_2$ is calculated according to equation (3):

$$f_2 = 1 - e^{-\lambda_{Rn-222} \cdot (t_3 - t_2)}$$

in which:

- $\lambda_{Rn-222}$ decay constant of Rn-222, in h$^{-1}$;
- $t_3 - t_2$ period between the transfer of the Rn-222 to the Lucas cell ($t_2$) and the point of time of the middle of the measuring period ($t_3$), in h.

## 5 Calculation of the results

### 5.1 Equations

The activity concentration, $c$, of Ra-226 is calculated according to equation (4):

$$c = \frac{\varphi_i \cdot (R_b - R_{0,i})}{V \cdot \eta} \frac{f_2}{f_1}$$

and the relative standard measuring uncertainty of the activity concentration of the Ra-226 is calculated according to chapter IV.5 of this procedures manual, following equation (5):

$$s(c) = \sqrt{\left(\frac{R_b}{(R_b - R_{0,i})^2}\right)^2 + \left(\frac{s(\varphi_i)}{\varphi_i}\right)^2 + \left(\frac{s(\eta)}{\eta}\right)^2}$$

in which (equations 4 and 5):

- $c$ activity concentration of Ra-226, in Bq·l$^{-1}$;
- $R_b$ gross count rate, in s$^{-1}$;
- $R_{0,i}$ background count rate of the Lucas cell $i$, in s$^{-1}$;
\( V \) volume of the sample, in l;
\( \varphi_i \) calibration factor for the Lucas cell \( i \), in Bq·s;
\( \eta \) chemical yield;
\( f_1, f_2 \) correction factors according to Table 1;
\( t_m \) duration of sample measurement, in s;
\( t_0 \) duration of background measurement, in s.

**Notes**
- Experience shows that the chemical yield from precipitating Ra-226 with barium sulphate amounts to 95 % (\( \eta = 0.95 \)). The yield is determined by way of spot checks using Ba-133 as a tracer and gamma spectrometric measuring.
- Transferring the Rn-222 from the emanation vessel to the Lucas cell will be quantitative if the apparatus, valves and hose joints are properly sealed. It will be of advantage to keep all hoses as short as possible.

### 5.2 Worked example

#### 5.2.1 Determining the activity concentration of Ra-226

The following worked example supposes the following numerical values for typical waiting and measuring periods as well as for the background count rate and the calibration factor:

\[
\begin{align*}
t_2 - t_1 &= 14 \text{ d}; & R_0 &= 0.155 \text{ s}^{-1}; \\
t_3 - t_2 &= 3 \text{ h}; & R_{0,i} &= 0.006 \text{ s}^{-1}; \\
t_m &= 6000 \text{ s}; & \varphi_i &= 0.375 \text{ Bq·s}; \\
t_0 &= 6000 \text{ s}; & \lambda_{\text{Rn-222}} &= 0.1813 \text{ d}^{-1} (0.007554 \text{ h}^{-1}); \\
V &= 1.00 \text{ l}; & \eta &= 0.95.
\end{align*}
\]

According to equation (4), the activity concentration of Ra-226 amounts to:

\[
c = \frac{0.375 \cdot (0.155 \cdot 0.006)}{1.0 \cdot 0.95} \cdot \frac{1.0229}{0.9210} \text{ Bq · l}^{-1} = 0.065 \text{ Bq · l}^{-1}
\]

Applying the above values according to equation (5), the relative standard measuring uncertainty of the activity concentration of Ra-226 amounts to:

\[
s(c) = \sqrt{\left(\frac{0.155}{6000} - \frac{0.006}{6000}\right)^2 + (0.1)^2 + (0.05)^2} = 0.12
\]

### 5.3 Considerations of uncertainties

The combined standard measuring uncertainty of the activity concentration of Ra-226 is determined mainly by the uncertainty arising from the counting statistics and the uncertainties attached to the calibration factors and the chemical yield. It amounts to about 7 % to 14 %.
6 Characteristic limits of the procedure

6.1 Equations

Calculating the detection limit is performed according to chapter IV.5 of this procedures manual.

The detection limit of the activity concentration, \( g \), is calculated according to equation (6), given that the measuring period applied to the sample (\( t_m \)) equals that for the background effect (\( t_0 \)):

\[
g = \frac{(k_{1-\alpha} + k_{1-\beta}) \cdot \varphi_f}{V \cdot \eta} \cdot \frac{f_2}{f_1} \sqrt{\frac{2 \cdot R_{0,f}}{t_0}}
\]

(6)

Aside from the symbols already defined:

- \( g \) detection limit of the activity concentration, in Bq\text{∙m}^{-3};
- \( k_{1-\alpha}, k_{1-\beta} \) quantile of the normal distribution for considering type I and type II errors.

6.2 Worked example

Applying the values given in section 5.2 as well as the values of the quantiles of the normal distribution, \( k_{1-\alpha} = 3,0 \) and \( k_{1-\beta} = 1,645 \), the following detection limit for the activity concentration of Ra-226 is obtained according to equation (6):

\[
g = \frac{(3,0 + 1,645) \cdot 0,375}{1,0 \cdot 0,95} \cdot \frac{1,0229}{0,921} \cdot \frac{2 \cdot 0,006}{6000} \text{Bq} \cdot \text{m}^{-1} = 2,9 \cdot 10^{-3} \text{Bq} \cdot \text{m}^{-1}
\]

7 Catalogue of chemicals and equipment

7.1 Chemicals

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

- Ammoniac solution, NH\(_3\): 13 mol\text{∙l}^{-1} (25 %);
- Barium nitrate solution, Ba(NO\(_3\))\(_2\): 0,043 mol\text{∙l}^{-1} (11,2 g\text{∙l}^{-1});
- Calcium chloride, CaCl\(_2\): free of water;
- Citric acid solution: 1,0 mol\text{∙l}^{-1} (210,15 g\text{∙l}^{-1});
- Na\(_4\)EDTA-solution: 0,5 mol\text{∙l}^{-1} (186,0 g of Na\(_2\)EDTA∙2H\(_2\)O and 40 g of NaOH are dissolved in deionised water to form 1 litre);
- Methyl-red solution: 0,1 %;
- Nitric acid, HNO\(_3\): 14 mol\text{∙l}^{-1};
- Sulphuric acid, H\(_2\)SO\(_4\): 9 mol\text{∙l}^{-1}.

7.2 Equipment

- Scintillation measuring chamber (Lucas cell);
- Emanation device with emanation vessel;
- Measuring station consisting of: photo-multiplier, amplifier, high-voltage power supply unit, counter, registration device;
— Heated stirrer;
— Basic equipment of a radiochemical laboratory.

References

(1) Norm DIN 38402 Teil 14 Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung; Allgemeine Angaben (Gruppe A); Probenahme von Rohwasser und Trinkwasser (A14), 1986-03

Tab. 1: Correction factors $f_1$ and $f_2$

$\lambda_{Rn-222} = 0,1813 \text{ d}^{-1}$

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$\lambda_{Rn-222} = 0,007554 \text{ h}^{-1}$

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