Procedure for determining the specific activity of radium-226 in foodstuffs of plant origin

K-Ra-226-LEBM-01

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1 Scope

The procedure described here serves to determine the specific activity of Ra-226 in foodstuffs of plant origin. It facilitates recording specific activities of Ra-226 in excess of 0.05 Bq·kg⁻¹ fresh mass (FM) and thus conforms to the requirements stipulated in the Guideline for the Monitoring of Emissions and Immissions from Mining Operations (REI Bergbau).

Note
The procedure described here is also fit for use with processed soil and sediment samples.

2 Sampling

For sampling, reference is made to procedure E-γ-SPEKT-LEBM-01 and its section 2.2.1 in particular.

3 Analysis

3.1 Principle of the procedure

The principle of the procedure is described in procedure H-Ra-226-TWASS-01. It is based upon recording the alpha radiation of Rn-222 and its decay products 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:

— Ashing of the dried samples at 400 °C;
— Microwave-digestion with nitric acid and hydrofluoric acid;
— Adding barium carrier solution;
— Precipitating the sulphates;
— Dissolving the precipitates in 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.
3.2 Interferences
The procedure is specific to determining the activity concentration of Ra-226; interferences by other radium isotopes or radionuclides are not observed.

3.3 Sample preparation
Depending on the situation, the samples are washed and coarsely chopped, weighed (FM), laid out on metal trays, and dried in a fan-forced drying cabinet at 80 °C until their weight remains constant. The dry mass (DM) is determined. The sample material is dry-ashed at 400 °C for about 24 hours. The residue is then crushed further and ashed once more for ca. 24 hours. The mass of ash (AM) is determined.

3.4 Radiochemical separation
3.4.1 1 g to 2 g of the pre-treated sample are cautiously (an intensive reaction must be anticipated) infused with 3 ml to 4 ml of hydrogen peroxide solution (10 mol·l⁻¹) in a beaker made of polytetra-fluor-ethylene (PTFE) and left standing for ca. 5 minutes.

Note
The instructions given in the following steps refer to a mass of 1 g of ash.

3.4.2 Following the addition of 7 ml of concentrated nitric acid (14 mol·l⁻¹) and 1 ml of hydrofluoric acid (22.6 mol·l⁻¹), the PTFE-beaker is closed and exposed to microwave digestion at 210 °C (1000 Watt) over a period of ca. 1 hour. If the sample has been refracted completely, the resultant solution will be clear; if this is not the case, the decomposition process must be repeated after 5 ml of concentrated nitric acid (14 mol·l⁻¹) have been added.
3.4.3 The decomposed sample is quantitatively transferred to a glass beaker and the PTFE-beaker flushed with a little hot distilled water. Following the addition of 3 ml of barium nitrate solution (0.043 mol l⁻¹), the solution is desiccated on a sand bath to a dry extract. The residue is dissolved in 5 to 10 ml of concentrated nitric acid (14 mol l⁻¹) and the solution replenished with distilled water to a total volume of about 0.5 l.

3.4.4 The solution is fortified under stirring with 5 ml of citric acid solution (1 mol l⁻¹), a few drops of methyl-red solution, and ca. 2.5 ml of concentrated ammoniac solution (13 mol l⁻¹) to the indicator’s point of transition to yellow. The solution is then heated to boiling and its content of barium (radium) sulphate is precipitated from the hot solution using 2.5 ml of sulphuric acid (9 mol l⁻¹). Once the precipitates have sedimented (ca. 12 hours), the supernatant solution is decanted and discarded.

3.4.5 The precipitate is transferred together with distilled water to a 100-ml-centrifuge glass and centrifuged. The supernatant solution is decanted and discarded.

3.4.6 The precipitate is purified twice with 50 ml of distilled water each and centrifuged. The cleansing solutions are decanted and discarded.

3.4.7 The precipitate is warmed in a water bath and dissolved in 5 ml of Na₄EDTA solution (0.5 mol l⁻¹), upon which the solution is transferred quantitatively to an emanation vessel, whereas the latter is flushed several times with a few millilitres of distilled water. 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 by a hose that in turn is connected by 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 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 (t₁) is recorded.
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 to the Lucas cell via a drying tube filled with calcium chloride (Figure 3).

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 a constant 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 in the calcium chloride-filled drying tube located between the measuring chamber and the emanation vessel.
- If the concentration of Rn-222 in the room air 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 decay products (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.

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

## 4.1 General

Following the ingrowth of the short-lived decay products of Rn-222 to almost perfect radioactive equilibrium, 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 of Ra-226. Typical measuring periods range from 100 to 200 minutes.

**Note**

Once measuring is completed, the Lucas cell needs to be cleansed by an airstream in order to prevent it becoming permanently contaminated with decay products of Rn-222. The background count rate of 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 measuring instruction. The calibration factor, \( \varphi_i \), for the Lucas cell, \( i \), is calculated according to equation (1):

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

in which:
- \( \varphi_i \) calibration factor for the Lucas cell \( i \), in Bq·s⁻¹;
- \( A_{K,i} \) 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;
- \( f_1 \) correction factor that allows 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 (\( t_2 \));
- \( f_2 \) 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):

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

in which:

$\lambda_{\text{Rn-222}}$ decay constant of Rn-222, in $\text{h}^{-1}$;

$t_3 - t_2$ 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 $\text{h}$.

### 5 Calculation of the results

#### 5.1 Equations

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

$$a = \frac{\phi_i \cdot (R_b - R_{0,i})}{m_A \cdot \eta \cdot q_1 \cdot q_2 \cdot f_1}$$

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

$$\frac{s(a)}{a} = \sqrt{\frac{R_b}{t_m} + \frac{R_{0,i}}{t_0} + \left(\frac{s(\phi_i)}{\phi_i}\right)^2 + \left(\frac{s(\eta)}{\eta}\right)^2}$$

in which (equations 4 and 5):

$c$ specific activity of Ra-226 relative to FM, in $\text{Bq kg}^{-1}$;

$R_b$ gross count rate, in $\text{s}^{-1}$;

$R_{0,i}$ background count rate of the Lucas cell $i$, in $\text{s}^{-1}$;

$m_A$ mass of ash (AM) used, in $\text{kg}$;

$q_1$ ratio DM/AM;

$q_2$ ratio FM/DM;

$\phi_i$ calibration factor for the Lucas cell $i$, in $\text{Bq} \cdot \text{s}$;

$\eta$ chemical yield;

$f_1, f_2$ correction factors according to Table 1;

$t_m$ duration of sample measurement, in $\text{s}$;

$t_0$ duration of background measurement, in $\text{s}$.

#### 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 specific activity 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:

\[ t_2 - t_1 = 19 \text{ d}; \quad R_b = 0,155 \text{ s}^{-1}; \]
\[ t_3 - t_2 = 4 \text{ h}; \quad R_{0,i} = 0,006 \text{ s}^{-1}; \]
\[ t_m = 6000 \text{ s}; \quad \varphi_i = 0,505 \text{ Bq.s}; \]
\[ t_0 = 6000 \text{ s}; \quad \lambda_{\text{Ra-222}} = 0,1813 \text{ d}^{-1} (0,007554 \text{ h}^{-1}); \]
\[ m_A = 0,001 \text{ kg}; \quad q_1 = 30; \]
\[ \eta = 0,90; \quad q_2 = 6,0. \]

According to equation (4), the specific activity of Ra-226 relative to the fresh mass (FM) amounts to:

\[
a = \frac{0,505 \cdot (0,155 - 0,006)}{0,001 \cdot 0,90 \cdot 30 \cdot 6} \cdot \frac{1,0307}{0,9617} \cdot \text{Bq} \cdot \text{kg}^{-1} = 0,50 \text{ Bq} \cdot \text{kg}^{-1}
\]

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

\[
s(a) = \sqrt{\frac{0,155 + 0,006}{6000 + 6000} + (0,1)^2 + (0,1)^2} = 0,15
\]

5.3 Consideration of uncertainties

The combined standard measuring uncertainty of the specific activity of Ra-226 is determined mainly by the uncertainty arising from the count statistics and the uncertainties attached to the calibration factors and the chemical yield. It amounts to about 10 % to 20 %.

6 Characteristic limits of the procedure

6.1 Equations

Calculating the detection limit is performed according to chapter IV.5 of 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 (\( t_0 \)):

\[
g = \frac{(k_{1-\alpha} + k_{1-\beta}) \cdot \varphi_i \cdot f_2 \cdot \sqrt{2 \cdot R_{0,i}}}{m_A \cdot \eta \cdot q_1 \cdot q_2 \cdot f_1 \cdot \frac{t_m}{t_0}}
\]

(6)
Aside from the symbols already defined:

\( g \) detection limit of the activity concentration, in Bq\( \cdot \)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 specific activity of Ra-226 relative to the fresh mass (FM) is obtained according to equation (6):

\[
g = \left(3,0 + 1,645\right) \cdot 0,505 \cdot \frac{1,0307}{0,9617} \cdot \sqrt{\frac{2 \cdot 0,006}{6000}} \text{ Bq} \cdot \text{kg}^{-1} = 2,2 \cdot 10^{-2} \text{ Bq} \cdot \text{kg}^{-1}
\]

### 7 Catalogue of chemicals and equipment

#### 7.1 Chemicals

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

- Ammonic solution, NH\(_3\): 13 mol\( \cdot \)l\(^{-1}\) (25 %);
- Barium nitrate solution, Ba(NO\(_3\))\(_2\): 0,043 mol\( \cdot \)l\(^{-1}\) (11,2 g\( \cdot \)l\(^{-1}\));
- Calcium chloride, CaCl\(_2\): free of water;
- Citric acid solution: 1,0 mol\( \cdot \)l\(^{-1}\) (210,15 g\( \cdot \)l\(^{-1}\));
- Hydrofluoric acid, HF: 22,6 mol\( \cdot \)l\(^{-1}\);
- Methyl-red solution: 0,1 %;
- Na\(_4\)EDTA-solution: 0,5 mol\( \cdot \)l\(^{-1}\) (186,0 g of Na\(_2\)EDTA\( \cdot \)2H\(_2\)O and 40 g of NaOH are dissolved in deionised water to form 1 litre);
- Nitric acid, HNO\(_3\): 14 mol\( \cdot \)l\(^{-1}\);
- Sulphuric acid, H\(_2\)SO\(_4\): 9 mol\( \cdot \)l\(^{-1}\);
- Hydrogen peroxide solution, H\(_2\)O\(_2\): ca. 10 mol\( \cdot \)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.
Tab. 1: Correction factors $f_1$ and $f_2$

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

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

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