Procedure for determining the specific activities of radionuclides in soil samples by gamma spectrometry

K-γ-SPEKT-BODEN-01

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1 Scope

The procedure described here serves to determine the specific activities of chiefly natural radionuclides in soils that are to be monitored in accordance with the Guideline for the Monitoring of Emissions and Immissions from Mining Operations (REI Bergbau).

2 Sampling

For sampling, reference is made to procedure F-γ-SPEKT-BODEN-01.

3 Analysis

3.1 Principle of the procedure

The sample material is generally coarsely fragmented and dried at a temperature of 105°C until its weight remains constant. The sample material is then further crushed to a grain size of less than 2 mm in a jaw crusher or suitable mill. Soil samples with a high content of organic materials should be ashed at a temperature of 400°C. The sample material will then need to be homogenised once more before it can be measured gamma spectrometrically with a semiconductor detector. The specific activities of the radionuclides always need to be stated relative to the dry mass (DM).

3.2 Sample preparation

3.2.1 Drying

The samples should be prepared according to procedure F-γ-SPEKT-BODEN-01. Drying the sample material to a constant weight may be effected at higher temperatures of up to 105°C, however. For drying soil samples with a high content of clay or loam, freeze-drying is recommended, as it will prevent the sample material from clogging.

3.2.2 Crushing and milling

The coarsely crushed and dried soil samples are milled with a suitable milling device to a grain size of less than 2 mm or crushed with a jaw crusher. If several milling processes are required as a result of a limited capacity of the milling vessel, the individual batches are to be combined and homogenised once milling has been completed.

3.2.3 Ashing

For ashing, reference is made to procedure F-γ-SPEKT-BODEN-01.

3.3 Radiochemical separation

No radiochemical separation is required.
4  Measuring the activity

The basics of gamma spectrometry are portrayed in chapters IV.1.1 through IV.1.4 of this procedures manual, with chapter IV.1.4 explicitly discussing particulars relevant to determining natural radionuclides in sample materials. These chapters also contain notes on summation and self-absorption corrections, which might need to be taken into consideration when measuring soil samples.

For measuring, preference should be given to an ultra-pure germanium-detector whose efficiency relative to a 3" x 3" NaI(Tl) crystal lies between 20 and 60 % and whose full width at half maximum is smaller than 2,0 keV relative to the 1332 keV-gamma line of Co-60. For measuring natural radionuclides, it will be of advantage to employ an ultra-low level measuring configuration (detector and shielding), because it ensures a very low background for analysing the required energy lines of a number of natural radionuclides (e. g., U-238, U-235, Ra-226, Pb-210, Ac-228).

Calibrating the gamma spectrometer is described in detail in procedure F-γ-SPEKT-MILCH-01.

5  Calculation of the results

For calculating the analysis results, industrial computers and high-performance software from a range of suppliers are available that comply with the requirements detailed in chapters IV.1.1 through IV.1.4 of this procedures manual.

Procedure C-γ-SPEKT-SEDIM-01 contains a portrait of how to calculate the specific activity of an individual nuclide, which may be applied analogously for calculating those of natural radionuclides, e. g., Pb-210 or K-40, too.

A problem in gamma spectrometrically determining natural radionuclides is the fact that some radionuclides have identical gamma lines or at least lines that are so close to each other that they cannot be analysed separately. These cases call for corrections by means of other gamma lines or by other methods.

If, for example, the specific activity of Ra-226 is determined on the basis of the singular gamma line with an energy of 186,1 keV, attention needs to be paid to the fact that U-235 has a line with an energy of 185,72 keV. Even though the specific activity of U-235 in soils accounts only for some 1/22 of the specific activity of Ra-226, the emission probability of the line of the U-235 is higher by a factor of 16 than the emission probability of the line of the Ra-226. This overlap does not present a problem if a radioactive equilibrium in the uranium-radon decay chain can be supposed, i. e., if the activity of U-238 equals that of Ra-226 and thus renders the activity of U-235 known. This does not necessarily apply to most soil samples, however, so that a correction is possible only if the activity of U-235 can be determined with the aid of other lines or derived from the activity of U-238. The specific activities of U-238 and U-235 in a sample may also be known from other measurements (e. g., determined by alpha spectrometry) or calculated from the results obtained for uranium analyses (e. g., by means of fluorimetry, phosphorimetry, X-ray fluorescence analysis, mass-spectrometry).
5.1 Equations

The following example is meant to illustrate this problem. The net count rate of the 186 keV-line is calculated according to equation (1), in which the radioactive decay need not be considered due to the long half-lives of U-235 ($t_r = 7,037 \cdot 10^8$ years) and Ra-226 ($t_r = 1,600 \cdot 10^3$ years).

$$R_n = (a_{Ra-226} \cdot p_{Ra-226} + a_{U-235} \cdot p_{U-235}) \cdot \varepsilon \cdot m_{DM}$$  \hspace{1cm} (1)

From this follows equation (2) for determining the specific activity of Ra-226, $a_{Ra-226}$, as:

$$a_{Ra-226} = \frac{R_n}{\varepsilon \cdot p_{Ra-226} \cdot m_{DM}} - \frac{a_{U-235} \cdot p_{U-235}}{p_{Ra-226}} = \frac{R_{Ra-226}}{\varepsilon \cdot p_{Ra-226} \cdot m_{DM}}$$  \hspace{1cm} (2)

with

$$R_n = R_g - R_T;$$
$$R_{Ra-226} = R_n - R_{U-235};$$
$$R_{U-235} = a_{U-235} \cdot \varepsilon \cdot m_{DM} \cdot p_{U-235}.$$  

In equations (1) and (2):

- $a_{Ra-226}$ specific activity of Ra-226, in Bq·kg⁻¹ (DM);
- $a_{U-235}$ specific activity of U-235, in Bq·kg⁻¹ (DM);
- $R_n$ net count rate, in s⁻¹;
- $R_g$ gross count rate, in s⁻¹;
- $R_T$ background count rate determined by the trapezoidal method, in s⁻¹;
- $R_{Ra-226}$ net count rate of Ra-226, in s⁻¹;
- $R_{U-235}$ calculated net count rate of U-235, in s⁻¹;
- $\varepsilon$ detection efficiency at 186 keV, in Bq⁻¹·s⁻¹;
- $p_{Ra-226}$ emission probability per disintegration for Ra-226;
- $p_{U-235}$ emission probability per disintegration for U-235;
- $m_{DM}$ dry mass (DM), in kg.

If the activity is measured with an ultra-low level measuring configuration, the contribution to the measuring effect by the background line at the gamma energy of 186 keV will be so small that it can be neglected. The standard uncertainty of the net count rate of Ra-226 is calculated according to chapter IV.5, section 4.7 of this procedures manual, applying equation (3) as follows:

$$s(R_{Ra-226}) = \sqrt{\frac{R_{Ra-226}}{t_m} + \frac{1}{t_m} \left[ R_T \cdot \left( 1 + \frac{b}{2 \cdot L} \right) + R_{U-235} + t_m \cdot s^2(R_{U-235}) \right]}$$  \hspace{1cm} (3)

in which:

$$s^2(R_{U-235}) = (R_{U-235})^2 \cdot \left( \frac{s^2(a_{U-235})}{a_{U-235}^2} + \frac{s^2(\varepsilon)}{\varepsilon^2} \right)$$  \hspace{1cm} (4)
For the standard uncertainty of the specific activity of Ra-226, equation (5) applies:

\[ s(a_{Ra-226}) = s(R_{Ra-226}) \cdot \frac{a_{Ra-226}}{R_{Ra-226}} \]  

(5)

Aside from the symbols already defined, in equations (3) through (5):
- \( s(R_{Ra-226}) \): standard uncertainty of the net count rate of Ra-226, in s\(^{-1}\);
- \( s(R_{U-235}) \): standard uncertainty of \( R_{U-235} \), in s\(^{-1}\);
- \( t_m \): duration of sample measurement, in s;
- \( b \): base width of the gamma line in channels;
- \( L \): number of channels for determining the background.

5.2 Worked example

Measuring the specific activity of Ra-226 from the gamma line shared by Ra-226 and U-235 at 186 keV produces the following data:

- \( a_{U-235} = 1,8 \text{ Bq kg}^{-1} \) (DM);
- \( R_T = 0,000954 \text{ s}^{-1} \);
- \( R_{Ra-226} = 0,0351 \);
- \( m_{DM} = 0,230 \text{ kg (DM)} \);
- \( R_{U-235} = 0,00616 \text{ s}^{-1} \);
- \( b = 2 \text{ L.} \)

According to equation (2), the specific activity of Ra-226 amounts to:

\[ a_{Ra-226} = \frac{0,01339}{0,351} \cdot \frac{1,8 \cdot 0,572}{0,0351} \cdot 34,5 \text{ Bq kg}^{-1} = 34,5 \text{ Bq kg}^{-1} \]  

The standard uncertainty of the net count rate of Ra-226 is calculated according to equation (3):

\[ s(R_{Ra-226}) = \sqrt{\frac{0,000954 \cdot 2 + 0,00616 + 60000 \cdot (1,5 \cdot 10^{-5})^2}{60000}} \cdot s^{-1} = 5,05 \cdot 10^{-4} \text{ s}^{-1} \]

and according to equation (5), the standard uncertainty of the specific activity is calculated as:

\[ s(a_{Ra-226}) = 5,05 \cdot 10^{-4} \cdot \frac{34,5}{0,00723} \cdot 2,4 \text{ Bq kg}^{-1} = 2,4 \text{ Bq kg}^{-1} \]  

5.3 Consideration of uncertainties

The uncertainty in determining the specific activity is mainly due to the uncertainty from counting statistics in the net count number and the uncertainty arising from determining the energy-dependent detection efficiency. The uncertainty in the U-235 count rate that has to be subtracted needs to be given particular attention. Other impact factors can be neglected. The total uncertainty must be expected to amount to ca. 10 %.
6 Characteristic limits of the procedure

6.1 Equations

The detection limit is calculated according to chapter IV.5 of this procedures manual, following equation (6):

\[
g = \frac{(k_{1-\alpha} + k_{1-\beta}) \cdot k_{1-\alpha}}{2 \cdot t_m \cdot \varepsilon \cdot m_{DM} \cdot p_{Ra-226}} \cdot \sqrt{1 + \frac{4 \cdot t_m}{k_{1-\alpha}^2} \cdot \left( R_T \cdot \left(1 + \frac{b}{2 \cdot L}\right) + R_{U-235} + t_m \cdot \frac{g}{2} (R_{U-235}) \right)} \tag{6}
\]

Aside from the symbols already defined:

- \( g \) detection limit of the specific activity of Ra-226, in Bq kg\(^{-1}\) (DM);
- \( k_{1-\alpha}, k_{1-\beta} \) quantile of the normal distribution for considering errors of the 1\(^{st}\) and 2\(^{nd}\) kind.

6.2 Worked example

Using the example given above and inserting values of \( k_{1-\alpha} = 3 \) and \( k_{1-\beta} = 1,645 \), the detection limit of the specific activity of Ra-226 amounts to:

\[
g = \frac{(3 + 1,645) \cdot 3}{2 \cdot 60000 \cdot 0,026 \cdot 0,23 \cdot 0,0351} \cdot \sqrt{1 + \frac{4 \cdot 60000}{3^2} \cdot \left[ \frac{0,000954 \cdot 2 + 0,00616 + 60000 \cdot \left(1,5 \cdot 10^{-5}\right)^2}{3} \right]} \text{Bq} \cdot \text{kg}^{-1} (\text{DM}) =
\]

\[
= 8.5 \text{ Bq} \cdot \text{kg}^{-1} (\text{DM})
\]

7 Catalogue of chemicals and equipment

7.1 Chemicals

No chemicals are required.

7.2 Equipment

- Gamma spectrometry measuring station consisting of:
  - Semiconductor made of ultra-pure germanium with a relative efficiency relative to a 3 x 3" NaI(Tl) crystal of preferentially between 20 and 60 % and a full width at half maximum of less than 2,0 keV relative to the 1332 keV-gamma line of Co-60.
  - Computer with software for analysing spectra;
  - Multi-channel analyser;
  - Measuring electronics;
- Drying cabinet;
- Ashing furnace;
- Freeze-drying installation;
- Jaw crusher or mill;
- Ring dishes or cans with screw-on lids;
- Basic laboratory equipment.