BS ISO 13163:2013

BSI Standards Publication

Water quality — Lead-210 — Test method using liquid scintillation counting

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National foreword

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The UK participation in its preparation was entrusted to Technical Committee EH/3/8, Radioactivity measurements.

A list of organizations represented on this committee can be obtained on request to its secretary.

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Water quality — Lead-210 — Test method using liquid scintillation counting

Qualité de l'eau — Plomb 210 — Méthode d'essai par comptage des scintillations en milieu liquide

Reference number
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Foreword

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The committee responsible for this document is ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

Introduction

Radioactivity from several naturally occurring and anthropogenic sources is present throughout the environment. Thus, water bodies (e.g. surface water, groundwater, seawater) can contain the following radionuclides of natural or human-made origins:

— natural radionuclides, including potassium-40, and those originating from the thorium and uranium decay series, particularly radium-226, radium-228, uranium-234, uranium-238, and lead-210, can be found in water for natural reasons (e.g. desorption from the soil and wash-off by rain water) or can be released from technological processes involving naturally occurring radioactive materials (e.g. the mining and processing of mineral sands or the production and use of phosphate fertilizer);

— human-made radionuclides, such as transuranium elements (americium, plutonium, neptunium, curium), tritium, carbon-14, strontium-90, and gamma-emitting radionuclides, can also be found in natural waters as a result of authorized routine releases into the environment in small quantities of the effluent discharged from nuclear fuel cycle facilities. They are also released into the environment following their use in unsealed form for medical and industrial applications. They are also found in the water as a result of past fallout contamination resulting from the explosion in the atmosphere of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Drinking water may thus contain radionuclides at activity concentrations which could present a risk to human health. In order to assess the quality of drinking water (including mineral waters and spring waters) with respect to its radionuclide content and to provide guidance on reducing health risks by taking measures to decrease radionuclide activity concentrations, water resources (groundwater, river, lake, sea, etc.) and drinking water are monitored for their radioactivity content as recommended by the World Health Organization [WHO] and required by some national authorities.

An International Standard on a test method for lead-210 activity concentrations in water samples is justified for test laboratories carrying out these measurements, required sometimes by national authorities, as laboratories may have to obtain a specific accreditation for radionuclide measurement in drinking water samples.

Lead-210 activity concentration can vary according to local geological and climatic characteristics and usually ranges from 2 $mBq \cdot l^{-1}$ to 300 $mBq \cdot l^{-1}$ (References [12][13]). The guidance level for lead-210 in drinking water, as recommended by WHO, is 100 $mBq \cdot l^{-1}$ (Reference [14]).

NOTE The guidance level is the activity concentration with an intake of 2 $l \cdot day^{-1}$ of drinking water for 1 year that results in an effective dose of 0,1 $mSv \cdot year^{-1}$ for members of the public, an effective dose that represents a very low level of risk that is not expected to give rise to any detectable adverse health effect.

INTERNATIONAL STANDARD **ISO 13163:2013(E)**

Water quality — Lead-210 — Test method using liquid scintillation counting

WARNING — Persons using ISO 13163 should be familiar with normal laboratory practice. ISO 13163 does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to ISO 13163 be carried out by suitably trained staff.

1 Scope

ISO 13163 specifies the determination of lead-210 (^{210}Pb) activity concentration in samples of all types of water using liquid scintillation counting (LSC). For raw and drinking water, the sample should be degassed in order to minimize the ingrowth of ^{210}Pb from radon-222 (^{222}Rn).

Using currently available liquid scintillation counters, this test method can measure the ^{210}Pb activity concentrations in the range of less than 20 mBq·l^{-1} to 50 mBq·l^{-1}. These values can be achieved with a counting time between 180 min and 720 min for a sample volume from 0,5 l to 1,5 l.

Higher ^{210}Pb activity concentrations can be measured by either diluting the sample or using smaller sample aliquots or both.

It is the laboratory's responsibility to ensure the suitability of this test method for the water samples tested.

2 Normative references

The following documents, in whole or in part, are normatively referenced in this document and are indispensable for its application. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO/IEC Guide 98-3, *Uncertainty of measurement — Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

ISO/IEC Guide 99, *International vocabulary of metrology — Basic and general concepts and associated terms (VIM)*

ISO/IEC 17025, *General requirements for the competence of testing and calibration laboratories*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 11929, *Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation — Fundamentals and application*

ISO 80000-10, *Quantities and units — Part 10: Atomic and nuclear physics*

3 Symbols

For the purposes of this document, the symbols and designations given in ISO 80000-10, ISO 11929, ISO/IEC Guide 98-3, and ISO/IEC Guide 99 and the following apply.

C_{coeff}	coefficient of ^{210}Bi ingrowth to equilibrium in the sample between the end of bismuth elution and time of counting
c_A	activity concentration in the sample, in becquerel per litre
c_{A0}	activity concentration of the standard, in becquerel per litre
c_A^*	decision threshold, in becquerel per litre
$c_A^\#$	detection limit, in becquerel per litre
$c_A^\triangleleft, c_A^\triangleright$	lower and upper limits of the confidence interval, in becquerel per litre
R_{c}	chemical yield
r_{b}	count rate of the reagent blank, in reciprocal second
r_{g}	sample count rate, in reciprocal second
r_{s}	calibration count rate, in reciprocal second
r_0	background count rate, in reciprocal second
S1	eluted solution containing lead
t_{g}	sample counting time, in second
t_{s}	calibration counting time, in second
t_0	background counting time, in second
U	expanded uncertainty, calculated by $U = ku(c_A)$ with $k = 1, 2\ldots$, in becquerel per litre
$u(c_A)$	standard uncertainty associated with the measurement result, in becquerel per litre
V	volume of the eluted phase, in litre
V_{e}	total volume of the test sample plus the carrier, in litre
V_{s}	volume of the standard test sample, in litre
V_{sample}	volume of the sample, in litre
V_1	volume of the aliquot from S1 for ^{210}Pb counting, in litre
V_2	volume of the aliquot from S1 for the determination of the chemical yield of lead, in litre
ε	detection efficiency related to ^{210}Pb
ρ	concentration of lead of the eluate, in milligram per litre
ρ_{e}	concentration of lead in the sample after the addition of the carrier, in milligram per litre

4 Principle

^{210}Pb is a natural beta-emitting radionuclide with a maximum beta-energy of 63,9 keV and a half-life of 22,23 years (References [15][16]). It appears in the ^{238}U decay series ($4n$+2) as a long-lived decay product of ^{222}Rn (see Figure 1).

^{210}Pb is separated from its daughters, bismuth-210 and polonium-210, by extraction chromatography and its activity is measured by liquid scintillation counting, either directly after its separation or indirectly after ingrowth of its progeny bismuth-210. Other separation methods exist (Reference [17]).

To avoid the possible interferences of the isotopes lead-211 and lead-214 and their progenies during the liquid scintillation counting, it is recommended to wait at least 3 h between elution of lead and the sample counting to allow these radionuclides to fully decay.

For radioisotopes with longer half-lives such as lead-212 and its progenies, their interferences are avoided by choosing appropriate counting windows as their energies are much higher than the energy of ^{210}Pb (see 7.4.2).

For samples with high activity concentration, dilution of the sample is required to avoid resin and detector saturation during the separation and counting steps, respectively.

Suspended material is removed prior to analysis by filtration using 0,45 µm filters. The analysis of the insoluble fraction requires a mineralization step that is not covered by ISO 13163.

NOTE A suitable mineralization step is specified in ISO 18589-2.[10]

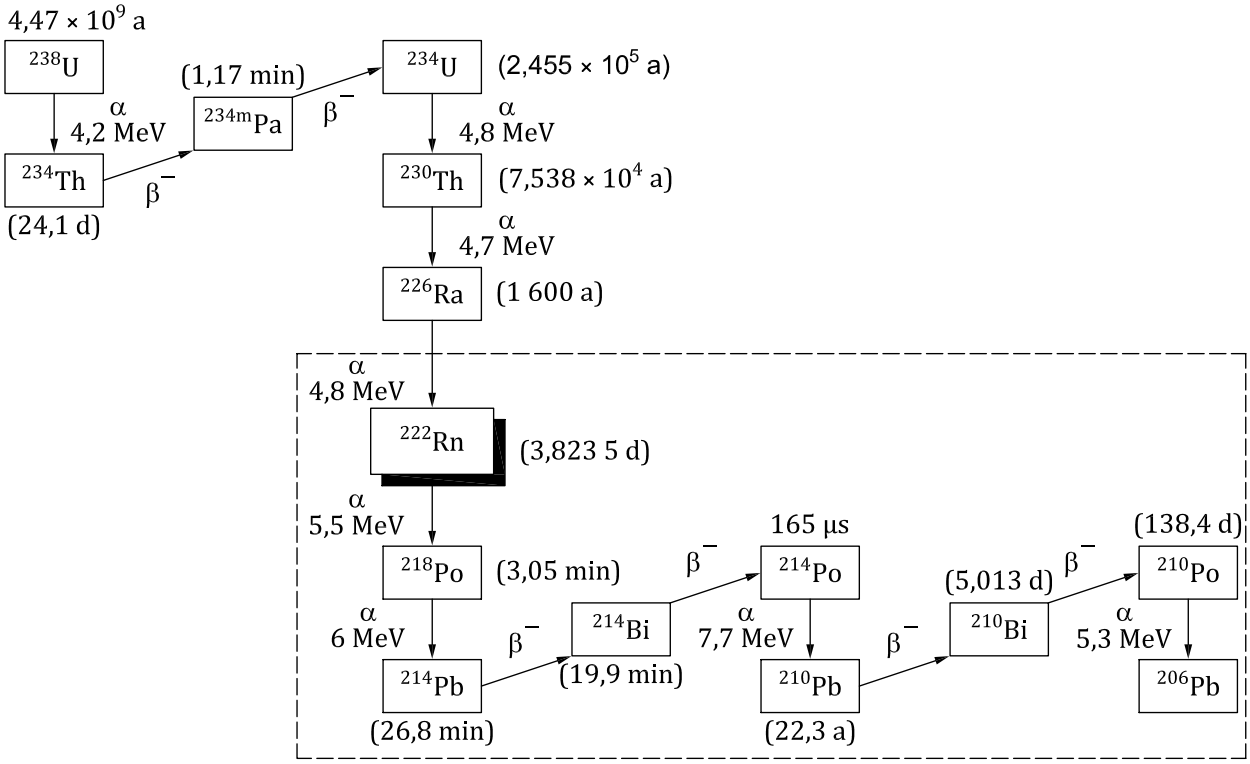

Figure 1 — Uranium-238 and its decay products (see ISO 13164-1)

It is necessary to know the concentration of the stable lead in the sample in order to determine the mass of the lead carrier to add and to calculate the chemical yield for the separation of ^{210}Pb.

It is possible to confirm the radiopurity of the ^{210}Pb fraction by monitoring ^{210}Bi ingrowth activity up to equilibration via repeated counting over an appropriate period of time.

5 Reagents and equipment

Use only reagents of recognized analytical grade.

5.1 Reagents

5.1.1 Nitric acid, HNO_3, concentrated, i.e. 700 $g \cdot l^{-1}$.

5.1.2 Hydrochloric acid, HCl, concentrated, i.e. 370 $g \cdot l^{-1}$.

5.1.3 Hydrochloric acid solution, 2 $mol \cdot l^{-1}$ HCl.

5.1.4 Nitric acid solution, 1 $mol \cdot l^{-1}$ HNO_3.

5.1.5 Nitric acid solution, 0,1 $mol \cdot l^{-1}$ HNO_3.

5.1.6 Solution of Fe(III), approximately 1 $g \cdot l^{-1}$ in 0,1 $mol \cdot l^{-1}$ HNO_3 or 0,5 $mol \cdot l^{-1}$ HCl.

5.1.7 Standard solution of Pb(II), approximately 1 $g \cdot l^{-1}$ in 0,1 $mol \cdot l^{-1}$ HNO_3 or 2 $mol \cdot l^{-1}$ HCl.

5.1.8 Ammonia, NH_4OH, concentrated, e.g. 280 $g \cdot l^{-1}$.

5.1.9 Ammonium citrate or **citric acid solution**, 0,01 $mol \cdot l^{-1}$ to 0,1 $mol \cdot l^{-1}$ or **EDTA solution**, 0,01 $mol \cdot l^{-1}$.

5.1.10 Chromatographic extraction resin, e.g. a crown ether 18C6-type resin.

5.1.11 Liquid scintillation cocktail, chosen according to the characteristics of the sample to be analysed and the properties of the detection equipment. The characteristics of the scintillation cocktail shall allow the mixture to be homogeneous and stable.

5.1.12 Laboratory water, distilled or deionized, complying with ISO 3696,[1] grade 3.

Deionized water can contain detectable amounts of ^{222}Rn and its short-lived daughters. It is therefore strongly recommended that water be boiled under vigorous stirring and allowed to stand for 1 day before use; otherwise, degassing with nitrogen for about 1 h per 2 l is recommended.

All reagents shall be of high purity (containing no detectable lead) or with certified lead content. This is validated by performing regular reagent blank checks.

5.1.13 Radioactive solution, ^{210}Pb standard solution in equilibrium with ^{210}Bi for the determination of the counting yield in liquid scintillation.

5.1.14 Quenching agent, e.g. nitric acid, acetone, organochlorine compounds (e.g. chloroform), nitromethane. Any one of these quenching agents can be used.

CAUTION — Some quenching agents are dangerous or toxic.

5.2 Equipment

Usual laboratory equipment and in particular the following.

5.2.1 Centrifuge or **vacuum filtration system**.

5.2.2 Membrane filter, of pore size 0,45 µm.

5.2.3 Analytical balance, accuracy 0,1 mg.

5.2.4 Equipment for the measurement of stable lead, e.g. atomic absorption spectroscopy, ICP-MS, ICP-OES.

5.2.5 Beta-counter, liquid scintillation counter provided with a display system and facility for recording spectra.

5.2.6 Scintillation vials, e.g. of polyethylene, adapted to the liquid scintillation counter.

6 Sampling and storage

6.1 Sampling

It is important that the laboratory receive a representative sample, unmodified during transport or storage and in an undamaged container (see ISO 5667-3).

6.2 Sample storage

Samples shall be stored according to the general requirements of ISO 5667-3.

^{222}Rn in a sample at 100 Bq·l^{-1} will generate approximately 40 mBq·l^{-1} of ^{210}Pb for a storage time of 10 days. Thus, the storage time for ^{210}Pb shall be taken into consideration when the sample contains radon.

7 Procedure

The measurement is realized in the following three stages:

— stage 1: preconcentration of lead by co-precipitation with $Fe(OH)_3$ prepared *in situ* (Reference [18]);

— stage 2: separation of lead on the extraction chromatographic resin (References [17][18][19][20][21][22][23]);

— stage 3: determination of the beta-activity of ^{210}Pb or its progeny, ^{210}Bi (Reference [24]).

The chemical yield of the separation is obtained by measuring the yield of the stable lead used as a carrier. It is thus necessary to take the following steps.

— Measure the original lead content in the sample to determine the quantity of the carrier to add.

— Measure the lead content of the aliquot loaded with the carrier before chemical separation.

— Measure the lead content in the final eluate to be used for the counting of ^{210}Pb in order to calculate the chemical yield.

The measurement of the stable lead for the determination of the chemical yield can be carried out according to various protocols already described in other International Standards. These protocols include the following:

— ICP-OES according to ISO 11885;[5]

— ICP-MS according to ISO 17294-2;[9]

— AAS according to ISO 15586.[8]

The beta-activity of ^{210}Pb is measured by liquid scintillation counting.

7.1 Sample preparation

The preparation of the sample is to be adapted according to the detection limit required. Usually, the sample volume ranges from 0,5 l to 1,5 l.

If necessary, perform filtration before acidification using a filtering membrane of mesh size 0,45 µm. It is recommended that a single-use filtration device be used.

Acidify the filtrate with concentrated nitric acid and ensure that the pH of the sample filtrate is less than or equal to 2.

Acidification of the water sample minimizes the loss of radioactive material from the solution by adsorption. If filtration of the sample is required, acidification is performed afterwards; otherwise, radioactive material already adsorbed on to the particulate material can be desorbed.

NOTE For raw water, the percolation of such water sample through the resin can be reduced depending on its suspended material and salinity content.

It is recommended that all operations be performed under a ventilated hood.

7.2 Preconcentration

Add a known quantity of lead standard solution (e.g. corresponding to approximately 1 mg to 10 mg of Pb) to the sample for the determination of the chemical yield and mix well.

The concentrations of Ca, Ba, K, Na, and Sr in the sample can impact the chemical yield (see Clause 8).

An Fe(III) co-precipitation allows the greater part of alkaline and alkaline-earth elements to be eliminated. Add 10 mg to 20 mg of the Fe(III) solution to the sample. Mix to homogenize and warm the solution to approximately 50 °C to 60 °C.

Add concentrated ammonia to pH about 9: $Fe(OH)_3$ precipitates.

Allow the solution to settle and cool for at least 2 h, and then separate both phases by filtration or by centrifugation.

The $Fe(OH)_3$ precipitate is isolated and dissolved in a minimum volume of 2 $mol \cdot l^{-1}$ HCl (for method 1) or 1 $mol \cdot l^{-1}$ HNO_3 (for method 2). A small amount of acid (about 5 ml to 10 ml) should be used.

The preconcentration can be also performed with a sulfonic-type cation exchange resin (References [17] [25]). An example of a preconcentration procedure is described hereafter.

If suspended material is present, filter the sample (approximately 0,2 kg) under vacuum (0,45 µm).

Acidify with nitric acid, approximately to a concentration of 0,01 $mol \cdot l^{-1}$ (0,2 ml of concentrated nitric acid in 0,2 kg sample).

Add the stable lead carrier (e.g. 0,5 ml of a 10 000 mg l^{-1} lead standard solution, corresponding to 5 mg of lead).

Add 50 ml of strong cation exchange resin in H^+ form (i.e. Dowex 50W X8[1)]) and stir for 2 h.

Transfer to a chromatographic column and wash with 150 ml of water. Discard the washings.

Elute with 250 ml of 3 $mol \cdot l^{-1}$ HNO_3 and then 100 ml of water.

Evaporate the eluate until dry.

The residue is dissolved in a minimum volume of 2 $mol \cdot l^{-1}$ HCl (for method 1) or 1 $mol \cdot l^{-1}$ HNO_3 (for method 2). A small amount of acid (about 5 ml to 10 ml) should be used.

1) This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this supplier.

The quantity of the cation exchange resin should be established on the basis of its exchange capacity and the amount of cationic species in the sample. A large excess of resin is normally employed.

7.3 Separation of ^{210}Pb

7.3.1 General

The volumes of the solutions for the preconditioning, elution, and rinsing steps are sized for a volume of extraction chromatographic resin of 2 ml (i.e. approximately 0,7 g of dry resin). The volume of resin used shall take into account the salinity of the sample (see Clause 8).

Method 1 is preferred when ^{210}Pb and ^{210}Po are measured. For the measurement of ^{210}Pb alone, either method is applicable.

7.3.2 Method 1

Precondition the extraction chromatographic resin with approximately 10 ml of 2 mol·l^{-1} HCl.

Load the sample solution in 2 mol·l^{-1} HCl (see 7.2) on to the resin.

Under these conditions, iron and bismuth are not fixed and are eluted with approximately 10 ml of 2 mol·l^{-1} HCl.

Note the date and the time of the end of the rinsing step (i.e. the beginning of the growth of ^{210}Bi).

Elute polonium by means of 5 ml of 1 mol·l^{-1} HNO_3 and 15 ml of 0,1 mol·l^{-1} HNO_3 (this fraction can be used to measure ^{210}Po, provided that a polonium tracer has previously been added to the sample during its preparation).

Finally, elute lead with 10 ml to 20 ml of a solution of ammonium citrate (0,1 mol·l^{-1}), or citric acid (0,1 mol·l^{-1}), or EDTA (0,01 mol·l^{-1}) to obtain solution S1 and make it up to a known volume, *V*.

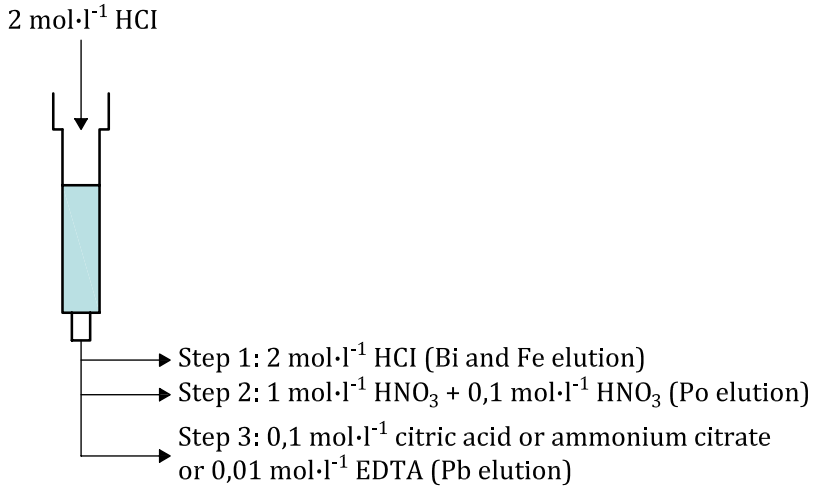

Figure 2 — Separation scheme of ^{210}Pb with HCl as starting solution

7.3.3 Method 2

Precondition the extraction chromatographic resin with approximately 10 ml of 1 mol·l^{-1} HNO_3.

Load the sample solution in 1 mol·l^{-1} HNO_3 (see 7.2) on to the resin.

Under these conditions, iron, bismuth, and a fraction of polonium are not fixed and are eluted by means of approximately 10 ml of 1 mol·l^{-1} HNO_3.

Note the date and the time of day of the end of the rinsing step (at the beginning of the growth of ^{210}Bi).

The fraction of fixed polonium is eluted by means of 2 × 10 ml of 0,1 mol·l^{-1} HNO_3.

Finally, elute the lead with 10 ml to 20 ml of a solution of ammonium citrate (0,1 mol·l^{-1}), or citric acid (0,1 mol·l^{-1}), or EDTA (0,01 mol·l^{-1}) to obtain solution S1 and make it up to a known volume, *V*.

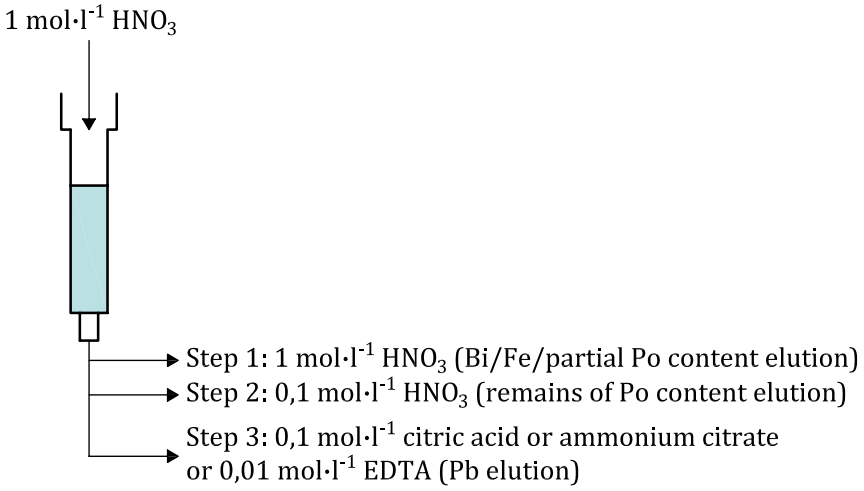

Figure 3 — Separation scheme of ^{210}Pb with HNO_3 as starting solution

7.3.4 Preparation for the counting and the determination of the chemical yield

Take an aliquot of volume, V_1, generally of the order of 10 ml, from solution S1 to measure ^{210}Pb by liquid scintillation counting.

Take an aliquot of volume, V_2, from solution S1 for the determination of the stable lead to estimate the chemical yield.

In a scintillation vial, mix volume V_1 with the scintillation cocktail. After closing, shake the vial to homogenize the mixture. The chemical yield can reach 80 % to 90 % if low salinity is present.

7.4 Measurement

7.4.1 Calibration

Periodically check the measurement performances of the instruments using sources of constant activity, covering the energy range to be measured.

The counting background of the system is measured for a period of at least equal to that of the counting time used for the test sample and standards.

The count rate of the reagent blank is denoted, r_b, which can be replaced by the appropriate background count rate value, r_0, if these values are equivalent.

The counting efficiency of ^{210}Pb is determined with a standard ^{210}Pb solution of known activity and purity. A volume of known activity is prepared in conditions similar to those of the sample, as in the following:

— lead carrier addition;

— determination of lead mass content before separation;

— separation on the resin of ^{210}Pb and its progenies;

— determination of lead mass content after separation and calculation of the chemical yield;

— liquid scintillation counting: measure the activity of ^{210}Pb as soon as possible to minimize the contribution due to the ingrowth of ^{210}Bi.

Repeated counting of the ^{210}Pb standard allows the ingrowth of ^{210}Bi and thus the separation efficiency to be verified.

For the liquid scintillation cocktail, verify the stability of the mixture over time.

Also check the lead carrier solution regarding its stability over time.

The samples collected after the chromatographic separation should show similar quenching index (e.g. tSIE) for a specific type of matrix as the chemical medium is always the same. However, a quench calibration curve can be constructed to cover the quenching index value range encountered. This curve is made by adding a known amount of ^{210}Pb tracer and varying concentrations of a quenching agent (5.1.14) to blank aliquots. A quench curve can be obtained by plotting detection efficiency against quenching index value.

7.4.2 Liquid scintillation counting

The beta-emission of ^{210}Pb is measured in a counting window with a maximum energy equivalent to 64 keV. It is advisable to establish several counting windows to check for the presence of potential interfering beta- or alpha-emitters, as well as chemiluminescence. If the LSC spectrum shows the presence of an interference, an additional purification step may be implemented.

The detection efficiency of ^{210}Pb is in the range of 30 % to 60 %, depending on the performance of the beta counter, the counting mode (low background noise), the counting window, the counting vial, the scintillation cocktail, and its mixing ratio to the sample volume.

Depending on the origin of the sample, it is recommended that the sample LSC vial be cooled and kept in the dark for 3 h prior to counting. Possible interferences from the decay chains of ^{238}U, ^{235}U, and ^{232}Th can be avoided either due to their short half-lives or because they are not retained on the resin (^{212}Bi, ^{214}Bi, ^{211}Bi, ^{207}Tl, and ^{208}Tl). Because of their identical separation behaviour in the extraction chromatographic procedure and their half-lives, ^{214}Pb, ^{211}Pb, and ^{212}Pb are potential interferences. However, their beta-energies are much higher than the maximum energy of ^{210}Pb. Therefore, if present, they should be observable in counting windows different from the one set for ^{210}Pb.

Usually, start counting of the ^{210}Pb samples within 12 h following separation to maintain ^{210}Bi ingrowth at a negligible level (^{210}Bi represents about 6,5 % of the total activity after 12 h [26]). The duration of the counting period is determined according to the detection limit required and the evaluation of the ingrowth yield of the ^{210}Bi daughter.

8 Quality assurance and quality control programme

8.1 General

Quality control operations should meet the requirements of ISO/IEC 17025.

8.2 Influencing variables

Some variables may have diverse degrees of influence on the measurement. Special care shall be taken in order to limit as much as possible the influence of parameters that may bias the measurement and lead to a non-representative result of the investigation situation. Failure to take sufficient precautions may require corrective factors to be applied to the measured result.

The variables affecting each measurement method are discussed in ISO 13164-2[6] and ISO 13164-3.[7]

Influencing variables can affect the following stages of the measurement process: sampling, transportation and storage of the sample, reagents, transfer and the measurement of the lead activity.

An Fe(III) co-precipitation allows elimination of alkaline elements such as K and Na. The crown ether-18C6 type has very low affinity for alkaline-earth elements. If these elements are present at high concentrations, the volume of the crown ether-18C6 type resin column can be increased to overcome lower separation yields resulting from column saturation given that the working Pb capacity of the crown ether-18C6 type resin is about 20 $mg \cdot g^{-1}$ of dry resin.

If a cation exchange resin is used for the preconditioning step, the quantity of resin is determined according to the salinity of the sample, given that the cation exchange capacity is about 1,1 $mEq.ml^{-1}$ to 1,7 $mEq.ml^{-1}$ in hydrogen or sodium form for standard strong cation exchangers (Reference [27]).

8.3 Instrument verification

Major instrument parameters (efficiency, background) shall be periodically checked within a quality assurance programme established by the laboratory and in accordance with the manufacturer's instructions.

NOTE Appropriate vials (e.g. flame-sealed vials of tritium, carbon-14, and "background") for instrument control are usually supplied by the manufacturer.

8.4 Contamination

Check for contamination of the reagents through the periodic performance of reagent blank analyses (see 7.4).

8.5 Method verification

A periodic verification of method accuracy should be run. This may be accomplished by

— participating in intercomparison exercises,

— analysing reference materials, and

— analysing spiked materials.

Method repeatability should also be checked, e.g. by replicate measurements. For this method, laboratories have experienced for 1,5 l sample uncertainties of less than 10 % at 0,2 $Bq \cdot l^{-1}$. A 5 % reproducibility and a 3 % repeatability were obtained. The accuracy of the method was about 5 % for activity concentrations in the range of 0,2 $Bq \cdot l^{-1}$ to 1 $Bq \cdot l^{-1}$.

8.6 Demonstration of analyst capability

If an analyst has not performed this procedure before, a precision and bias test should be performed by running a duplicate measurement of a reference or spiked material. Acceptance limits should be defined by the laboratory.

A similar evaluation should be performed by the analysts who routinely apply this procedure, with a periodicity defined by the laboratory. Acceptance limits should be defined.

9 Expression of results

9.1 General

In the particular case of the measurement by liquid scintillation, only the elementary uncertainties of the following parameters are retained:

— test and blank samples counts;

— detection efficiency in the considered energy window for a given quench indicator parameter;

— volume or mass of test sample.

The other uncertainties may be neglected in the first approximation (scintillation liquid volume or mass, counting time, etc.).

The calculation approach presented in 9.2 to 9.6 is based on an immediate counting (within 12 h of ^{210}Bi separation) to limit the ingrowth of ^{210}Bi during the counting time.

9.2 Yield determination

The chemical yield for lead separation is determined as follows for the two calculation methods:

$$R_c = \frac{\rho V}{(\rho_e V_e)} \tag{1}$$

$$R_c = \frac{\rho V}{(\rho_e V_e)} \cdot 100\ \% \tag{2}$$

The beta-counting efficiency is determined from a ^{210}Pb solution of known activity, $c_{A,0}$, prepared following ISO 13163 and defined as follows:

$$\varepsilon = \frac{(r_s - r_0) \cdot C_{coeff}}{c_{A,0} \cdot R_c \cdot V_s} \cdot \frac{V}{V_1} \tag{3}$$

where C_{coeff} is the correction coefficient of the ingrowth of ^{210}Bi in the sample with respect to time, given by

$$C_{coeff} = \frac{1}{2 - \exp\left(\frac{-\ln 2}{T_{1/2}} \Delta t\right)} \tag{4}$$

where

$T_{1/2}$ is the half-life of ^{210}Bi in days (i.e. 5,013 days);

Δt is the time delay, in days, between the start of bismuth rinsing and the mid-point counting duration.

The yield is thus defined from the initial time of the separation of lead from other radionuclides in the natural decay series.

NOTE The coefficient of ingrowth of ^{210}Bi can be negligible if the measurements are done within the first 12 h from the separation time.

$$\varepsilon = \frac{(r_s - r_0)}{c_{A,0} \cdot R_c \cdot V_s} \cdot \frac{V}{V_1} \tag{5}$$

9.3 Calculation of activity concentration

The sample activity concentration c_A of ^{210}Pb in the sample is calculated using Formula (6):

$$c_A = \frac{(r_g - r_0)\cdot C_{coeff}}{\varepsilon \cdot R_c \cdot V_{sample}} \cdot \frac{V}{V_1} = (r_g - r_0)w \tag{6}$$

where

$$w = \frac{C_{coeff}}{\varepsilon \cdot R_c \cdot V_{sample}} \cdot \frac{V}{V_1} \tag{7}$$

If the conditions in 9.2 (see Note) are satisfied, the activity concentration is calculated according to

$$c_A = \frac{(r_g - r_0)}{\varepsilon \cdot R_c \cdot V_{sample}} \cdot \frac{V}{V_1} \tag{8}$$

It is recommended that a blank be measured at the beginning and at the end of each series of measurements.

The standard uncertainty is calculated using Formula (9):

$$u(c_A) = \sqrt{w^2 \cdot \left(u^2(r_g) + u^2(r_0)\right) + c_A^2 \cdot u_{rel}^2(w)} = \sqrt{w^2 \cdot \left(\frac{r_g}{t_g} + \frac{r_0}{t_0}\right) + c_A^2 \cdot u_{rel}^2(w)} \tag{9}$$

Uncertainties on counting times of the sample and the background are considered negligible. Relative uncertainty on w is calculated using Formula (10):

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(R_c) + u_{rel}^2\left(V_{sample}\right) + u_{rel}^2(V) + u_{rel}^2(V_1) + u_{rel}^2(C_{coeff}) \tag{10}$$

Uncertainties on counting time and half-life of ^{210}Bi are considered negligible. Relative uncertainty on w is calculated using Formula (11):

$$u_{rel}^2(w) = u_{rel}^2(\varepsilon) + u_{rel}^2(R_c) + u_{rel}^2\left(V_{sample}\right) + u_{rel}^2(V) + u_{rel}^2(V_1) \tag{11}$$

and the relative standard uncertainty of ε is calculated using Formula (12):

$$u_{rel}^2(\varepsilon) = u_{rel}^2(r_s - r_0) + u_{rel}^2(C_{coeff}) + u_{rel}^2(c_{A0}) + u_{rel}^2(R_c) + u_{rel}^2(V_s) + u_{rel}^2(V) + u_{rel}^2(V_1) \tag{12}$$

Uncertainties on counting time and half-life of ^{210}Bi are considered negligible. Relative uncertainty on w is calculated using Formula (13):

$$u_{rel}^2(\varepsilon) = u_{rel}^2(r_s - r_0) + u_{rel}^2(c_{A0}) + u_{rel}^2(R_c) + u_{rel}^2(V_s) + u_{rel}^2(V) + u_{rel}^2(V_1) \tag{13}$$

$$u_{rel}^2(\varepsilon) = \left(\frac{r_s}{t_s} + \frac{r_0}{t_0}\right) \Big/ (r_s - r_0) + u_{rel}^2(c_{A0}) + u_{rel}^2(R_c) + u_{rel}^2(V_s) + u_{rel}^2(V) + u_{rel}^2(V_1) \tag{14}$$

where

$u_{rel}^2(c_{A0})$ includes all the uncertainties related to the calibration source: i.e. in the standard solution and the preparation of the calibration source;

$u_{rel}^2(R_c)$ is the uncertainty on the chemical yield and it depends upon its evaluation method.

For the calculation of the characteristic limits, $\tilde{u}(\tilde{c}_A)$ is needed (see ISO 11929), i.e. the standard uncertainty of c_A as a function of its true value, calculated using Formula (15):

$$\tilde{u}(\tilde{c}_A)=\sqrt{w^2\cdot\left[\left(\frac{\tilde{c}_A}{w}+r_0\right)\Big/t_g+\frac{r_0}{t_0}\right]+\tilde{c}_A^2\cdot u_{rel}^2(w)} \tag{15}$$

9.4 Decision threshold

The decision threshold, c_A^*, is obtained from Formula (15) for $\tilde{c}_A=0$ (see ISO 11929). This yields:

$$c_A^*=k_{1-\alpha}\cdot\tilde{u}(0)=k_{1-\alpha}\cdot w\cdot\sqrt{\frac{r_0}{t_g}+\frac{r_0}{t_0}} \tag{16}$$

α = 0,05 with $k_{1-\alpha}$ = 1,65 are often chosen by default.

9.5 Detection limit

The detection limit, $c_A^\#$, is calculated using Formula (9) (see ISO 11929):

$$c_A^\#=c_A^*+k_{1-\beta}\cdot\tilde{u}(c_A^\#)=c_A^*+k_{1-\beta}\cdot\sqrt{w^2\cdot\left[\left(\frac{c_A^\#}{w}+r_0\right)\Big/t_g+\frac{r_0}{t_0}\right]+c_A^{\#2}\cdot u_{rel}^2(w)} \tag{17}$$

β = 0,05 with $k_{1-\beta}$ = 1,65 are often chosen by default.

The detection limit can be calculated by solving Formula (18) for $c_A^\#$ or, more simply, by iteration with a starting approximation $c_A^\#=2c_A^*$.

When taking $\alpha=\beta$ then $k_{1-\alpha}=k_{1-\beta}=k$, the solution of Formula (17) is given by Formula (18):

$$c_A^\#=\frac{2\cdot c_A^*+\left(k^2\cdot w/t_g\right)}{1-k^2\cdot u_{rel}^2(w)} \tag{18}$$

9.6 Confidence interval limits

The lower, $c_A^\triangleleft$, and upper, $c_A^\triangleright$, confidence limits are calculated using Formulae (19) and (20) (see ISO 11929):

$$c_A^\triangleleft=c_A-k_p\cdot u(c_A)\quad p=\omega\left(1-\frac{\gamma}{2}\right) \tag{19}$$

$$c_A^\triangleright=c_A-k_q\cdot u(c_A)\quad q=1-\frac{\omega\gamma}{2} \tag{20}$$

where

$$\omega=\Phi\left[\frac{y}{u(y)}\right] \tag{21}$$

Φ being the distribution function of the standardized normal distribution;

$1-\gamma$ is the probability for the confidence interval of the measurand.

The value of ω may be set to 1 if $c_A \geq 4u(c_A)$. In this case:

$$c_A^{\triangleleft} = c_A^{\triangleright} = c_A \pm k_{1-\gamma/2^{u(c_A)}} \tag{22}$$

γ = 0,05 and then, $k_{1-\gamma/2}$ = 1,96 is often chosen by default.

10 Test report

The test report shall conform to the requirements of ISO/IEC 17025 and shall contain at least the following information:

a) test method used, together with a reference to ISO 13163 (i.e. ISO 13163:2013);

b) evaluation procedure used;

c) identification of the sample;

d) date of separation and date of measurement;

e) units in which the results are expressed;

f) test result, $c_A \pm u(c_A)$ or $c_A \pm U$ with the associated k value.

Complementary information can be provided such as:

g) probabilities α, β, and $(1-\gamma)$;

h) decision threshold and the detection limit;

i) depending on customer requirements, there are different ways of presenting the result:

   — When the activity concentration c_A is compared with the decision threshold (see ISO 11929), the result of the measurement should be expressed as $\leq c_A^*$ when the result is less than or equal to the decision threshold.

   — When the activity concentration c_A is compared with the detection limit, the result of the measurement can be expressed as $\leq c_A^{\#}$ when the result is less than or equal to the detection limit. If the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose.

j) mention of any relevant information to explain or on influences likely to have affected the results.

Annex A
(informative)

Spectra examples

In these spectra examples, three windows were set as described in Table A.1.

Table A.1 — Windows set for LSC counting of ^{210}Pb

Window A	Window B	Window C
0 keV to 28 keV	2 keV to 28 keV	28 keV to 3 000 keV

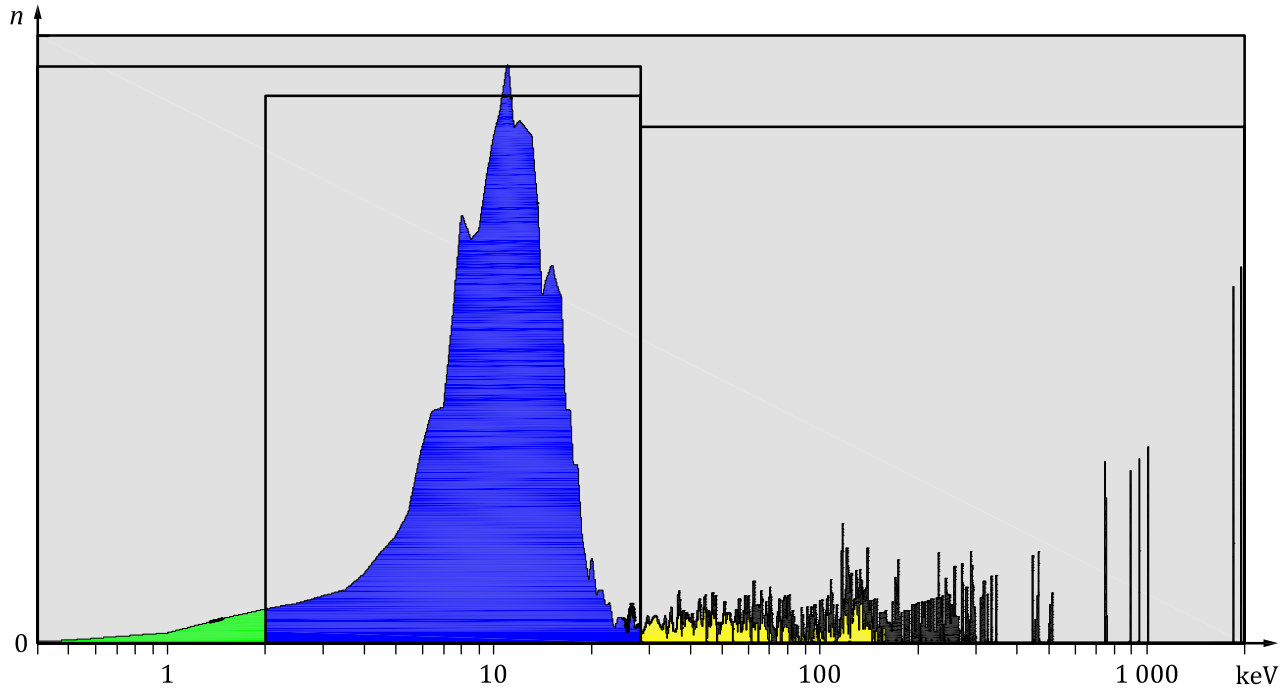

Figure A.1 — Example of LSC spectrum of ^{210}Pb fraction 24 h after separation on the crown-ether 18C6-type resin

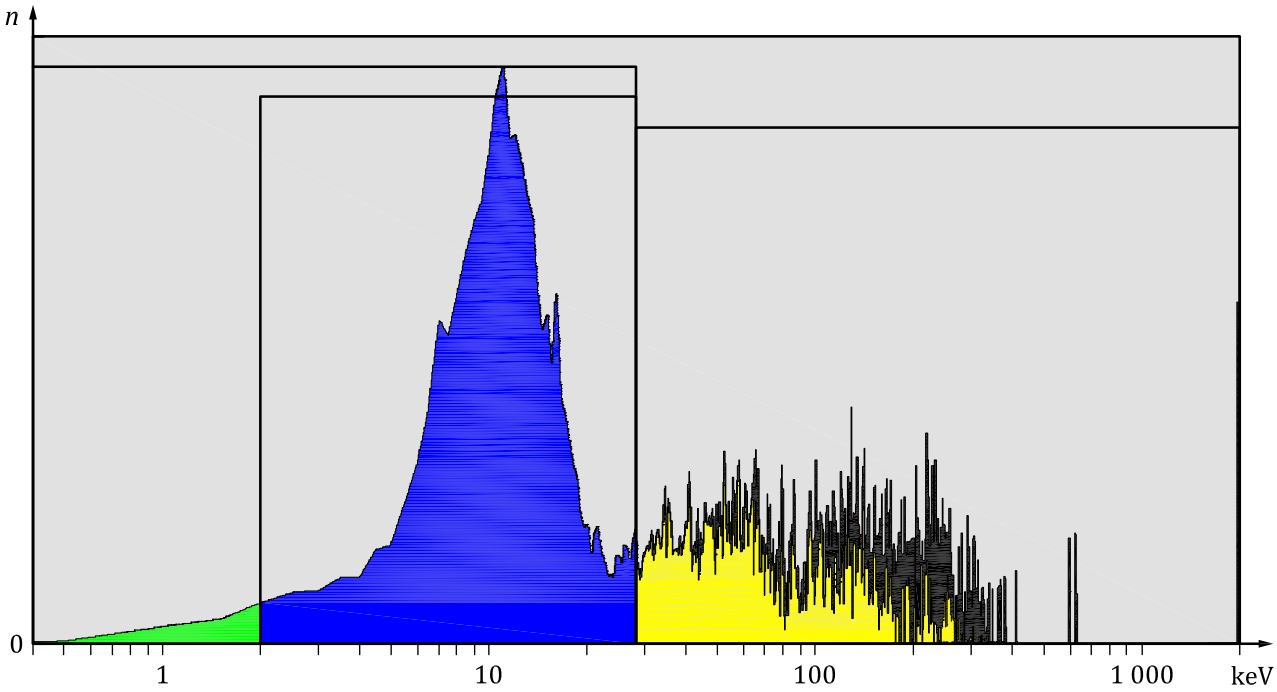

Figure A.2 — Example of LSC spectrum of ^{210}Pb fraction 25 days after separation on the crown-ether 18C6-type resin, showing ^{210}Bi ingrowth

Bibliography

[1] ISO 3696, *Water for analytical laboratory use — Specification and test methods*

[2] ISO 5667-1, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes and sampling techniques*

[3] ISO 5667-14, *Water quality — Sampling — Part 14: Guidance on quality assurance of environmental water sampling and handling*

[4] ISO 6107-2, *Water quality — Vocabulary*

[5] ISO 11885, *Water quality — Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)*

[6] ISO/CD 13164-2, *Water quality — Measurement of the activity concentration of radon-222 — Part 2: Gamma spectrometry method*

[7] ISO/CD 13164-3, *Water quality — Measurement of the activity concentration of radon-222 — Part 3: Emanometric method*

[8] ISO 15586, *Water quality — Determination of trace elements using atomic absorption spectrometry with graphite furnace*

[9] ISO 17294-2, *Water quality — Application of inductively coupled plasma mass spectrometry (ICP-MS) — Part 2: Determination of 62 elements*

[10] ISO 18589-2, *Measurement of radioactivity in the environment — Soil — Part 2: Guidance for the selection of the sampling strategy, sampling and pre-treatment of samples*

[11] FD T90-112, Qualité de l'eau— Dosage de huit éléments métalliques (Mn, Fe, Co, Ni, Cu, Zn, Ag, Pb) par spectrométrie d'absorption atomique dans la flamme [Water quality — Determination of eight metallic elements (Mn, Fe, Co, Ni, Cu, Zn, Ag, Pb) by flame atomic absorption spectrometry]

[12] Kratzlberger C., Wallner G., Irlweck K. Determination of 210Pb, 210Bi and 210Po in Natural Drinking Water. *J. Radioanal. Nucl. Chem.* 2001, **249** (1) pp. 191–196

[13] Persson B.R., & Holm E. Polonium-210 and Lead-210 in the Terrestrial Environment: A Review. *J. Environ. Radioact.* 2011, **102** (5) pp. 420–429

[14] *WHO-Guidelines for Drinking-Water Quality*. Geneva, 2011

[15] United Nations Scientific Committee on the Effects of Atomic Radiations. Annex B: Exposures from natural radiation sources. In:Report to the General Assembly, sources and effects of ionizing radiation, Vol. 1, pp. 84–156. Vienna: UNSCEAR, 2000. Available (viewed 2012-05-10) at: http://www.unscear.org/docs/reports/annexb.pdf

[16] Laboratoire Henri Becquerel. Recommended data [Internet]: Nuclear data base — Decay data evaluation project. Available (viewed 2012-11-08) at: http://www.nucleide.org/DDEP_WG/DDEPdata.htm

[17] Letho J., & Hou X. eds. Chemistry and Analysis of Radionuclides, Laboratory Techniques and Methodology. Weinheim, Germany: Wiley-VCH Verlag GmBH & Co. KGaA, 2011. 406p

[18] RP 280, Determination of lead-210 in water using extraction chromatography. In: *DOE Methods Compendium*. Battelle Press, Columbus, OH, 1997

[19] Seki T., Hirano Y., Oguma K. On-line Preconcentration and Determination of Traces of Lead in River-water and Seawater by Flow Injection – Flame Atomic Absorption Spectroscopy and ICP-MS Spectroscopy. *Anal. Sci.* 2002, **18** pp. 351–354

[20] Letho J., Kelokaski P., Vaaramaa K., Jaakkola T. Soluble and particle-bound 210Po and 210Pb in groundwaters. *Radiochim. Acta.* 1999, **85** pp. 149–155

[21] Vajda N., La Rosa J., Zeisler R., Danesi P., Kis-Benedek G. A novel technique for the simultaneous determination of Pb-210 and Po-210 using a crown ether. *J. Environ. Radioact.* 1997, **37** pp. 355–372

[22] Horwitz E.P., Dietz M.L., Rhoads S., Felinto C., Gale N.H., Houghton J. A lead-selective extraction chromatographic resin and its application to the isolation of lead from geological samples. *Anal. Chim. Acta*. 1994, **292** pp. 263–273

[23] Kim C.K., Paul M., Aleš F. Quantification of measurement uncertainty in the sequential determination of 210Pb and 210Po by liquid scintillation counting and alpha-particle spectrometry. *Accredit. Qual. Assur.* 2008, **13** (12) pp. 691–702

[24] L'Annunziata M.F. *Handbook of radioactivity analysis*. Academic Press, San Diego, CA, Second Edition, 2003, 1273 p.

[25] Analytical Procedures, Lead-210 and Polonium-210 in water, Eichrom Technologies LLC, OTW01, July 28, 2009

[26] Loveland W.D., Morrissey D.J., Seaborg G.T., eds. *Modern nuclear chemistry*. Wiley-Interscience, Hoboken, NJ, 2006

[27] Lenntech – Water Treatment Solutions. Ion Exchange Resins. Available (viewed 2012-11-09) at: http://www.lenntech.com/products/resins/dowex/dowex-ionexchange-resin.htm

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