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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

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT), see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 3, *Radioactivity measurements*.

This second edition cancels and replaces the first edition (ISO 13163:2013), which has been technically revised.

The main changes compared to the previous edition are as follows:

— addition of the common introduction;

— transfer of separation processes to an annex.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

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

— natural radionuclides, including ^{40}K, ^{3}H, ^{14}C, and those originating from the thorium and uranium decay series, in particular ^{226}Ra, ^{228}Ra, ^{234}U, ^{238}U, ^{210}Po and ^{210}Pb can be found in water for natural reasons (e.g. desorption from the soil and washoff 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 phosphate fertilizers production and use);

— human-made radionuclides such as transuranium elements (americium, plutonium, neptunium, curium), ^{3}H, ^{14}C, ^{90}Sr, and gamma emitting radionuclides can also be found in natural waters. Small quantities of these radionuclides are discharged from nuclear fuel cycle facilities into the environment as a result of authorized routine releases. Some of these radionuclides used for medical and industrial applications are also released into the environment after use. Anthropogenic radionuclides are also found in waters as a result of past fallout contaminations resulting from the explosion in the atmosphere of nuclear devices and accidents such as those that occurred in Chernobyl and Fukushima.

Radionuclide activity concentration in water bodies can vary according to local geological characteristics and climatic conditions and can be locally and temporally enhanced by releases from nuclear installation during planned, existing, and emergency exposure situations.[1][2] Drinking-water can thus contain radionuclides at activity concentrations that could present a risk to human health.

The radionuclides present in liquid effluents are usually controlled before being discharged into the environment[3] and water bodies. Drinking waters are monitored for their radioactivity as recommended by the World Health Organization (WHO)[4] so that proper actions can be taken to ensure that there is no adverse health effect to the public. Following these international recommendations, national regulations usually specify radionuclide authorized concentration limits for liquid effluent discharged to the environment and radionuclide guidance levels for waterbodies and drinking waters for planned, existing, and emergency exposure situations. Compliance with these limits can be assessed using measurement results with their associated uncertainties as specified by ISO/IEC Guide 98-3 and ISO 5667-20[5].

Depending on the exposure situation, there are different limits and guidance levels that would result in an action to reduce health risk. As an example, during a planned or existing situation, the WHO guidelines[4] for guidance level in drinking water is 0,1 $Bq \cdot l^{-1}$ for ^{210}Pb activity concentration.

NOTE 1 The guidance level is the activity concentration with an intake of 2 $l \cdot d^{-1}$ of drinking water for one year that results in an effective dose of 0,1 $mSv \cdot a^{-1}$ for members of the public. This is an effective dose that represents a very low level of risk and which is not expected to give rise to any detectable adverse health effects[4].

In the event of a nuclear emergency, the WHO Codex Guideline Levels[6] mention that the activity concentration might not be greater than 0,1 $Bq \cdot l^{-1}$ for ^{210}Pb.

NOTE 2 The Codex guidelines levels (GLs) apply to radionuclides contained in foods destined for human consumption and traded internationally, which have been contaminated following a nuclear or radiological emergency. These GLs apply to food after reconstitution or as prepared for consumption, i.e., not to dried or concentrated foods, and are based on an intervention exemption level of 1 mSv in a year for members of the public (infant and adult)[6].

Thus, the test method can be adapted so that the characteristic limits, decision threshold, detection limit and uncertainties ensure that the radionuclide activity concentrations test results can be verified to be below the guidance levels required by a national authority for either planned/existing situations or for an emergency situation[2][6][7].

Usually, the test methods can be adjusted to measure the activity concentration of the radionuclide(s) in either wastewaters before storage or in liquid effluents before being discharged to the environment.

The test results will enable the plant/installation operator to verify that, before their discharge, wastewaters/liquid effluent radioactive activity concentrations do not exceed authorized limits.

The test method(s) described in this document may be used during planned, existing and emergency exposure situations as well as for wastewaters and liquid effluents with specific modifications that can increase the overall uncertainty, detection limit, and threshold.

The test method(s) may be used for water samples after proper sampling, sample handling, and test sample preparation (see the relevant part of the ISO 5667 series).

This document has been developed to answer the need of test laboratories carrying out these measurements, that are sometimes required by national authorities, as they might need to obtain a specific accreditation for radionuclide measurement in drinking water samples.

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

WARNING — Persons using this document should be familiar with normal laboratory practices. This document 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 determine the applicability of any other restrictions.

IMPORTANT — It is essential that tests conducted according to this document be carried out by suitably trained staff.

1 Scope

This document specifies a method for the measurement of ^{210}Pb in all types of waters by liquid scintillation counting (LSC).

The method is applicable to test samples of supply/drinking water, rainwater, surface and ground water, as well as cooling water, industrial water, domestic, and industrial wastewater after proper sampling and handling, and test sample preparation. Filtration of the test sample is necessary. Lead-210 activity concentration in the environment can vary and usually ranges from 2 mBq l^{-1} to 300 mBq l^{-1} [27][28].

Using currently available liquid scintillation counters, the limit of detection of this method for ^{210}Pb is generally of the order of 20 mBq l^{-1} to 50 mBq l^{-1}, which is lower than the WHO criteria for safe consumption of drinking water (100 mBq l^{-1}).[4][6] 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 activity concentrations can be measured by either diluting the sample or using smaller sample aliquots or both. The method presented in this document is not intended for the determination of an ultra-trace amount of ^{210}Pb.

The range of application depends on the amount of dissolved material in the water and on the performance characteristics of the measurement equipment (background count rate and counting efficiency).

The method described in this document is applicable to an emergency situation.

The analysis of Pb adsorbed to suspended matter is not covered by this method.

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

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. 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 3696, *Water for analytical laboratory use — Specification and test methods*

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

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

ISO 5667-10, *Water quality — Sampling — Part 10: Guidance on sampling of waste water*

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

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

ISO 19361, *Measurement of radioactivity — Determination of beta emitters activities — Test method using liquid scintillation counting*

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

3 Terms, definitions and symbols

3.1 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 80000-10, the ISO 11929 series, ISO/IEC Guide 98-3 and ISO/IEC Guide 99 apply

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.2 Symbols and abbreviated terms

Symbol	Definition	Unit
c_A	Activity concentration in the sample	Bq l^{-1}
c_{A0}	Activity concentration of the standard	Bq l^{-1}
c_A^*	Decision threshold	Bq l^{-1}
$c_A^\#$	Detection limit	Bq l^{-1}
$c_A^\triangleleft, c_A^\triangleright$	Lower and upper limits of the probabilistically symmetric coverage interval	Bq l^{-1}
$c_A^<, c_A^>$	Lower and upper limits of the shortest coverage interval	Bq l^{-1}
C_{coeff}	Coefficient of ^{210}Bi ingrowth in the sample from the end of bismuth elution to time of counting	n/a
DPM	Disintegrations per minute	n/a
βmax	Maximum Beta particle energy	keV
R_c	Chemical recovery	n/a
r_b	count rate of reagent blanks	s^{-1} or counts s^{-1}
r_g	Sample count rates	s^{-1}
r_s	Calibration count rates	s^{-1}
r_0	Background count rate	s^{-1}
S	Eluted solution containing lead	n/a
SQPE	Spectral quench parameter of the external standard	n/a
TDCR	Triple to double counts ratio	n/a
t_g	Sample counting time	s
t_s	Calibration counting time	s
t_0	Background counting time	s
n/a Not applicable.		

Symbol	Definition	Unit
tSIE	Transformed spectral index of the external standard	n/a
U	Expanded uncertainty, calculated by $U = ku(c_A)$ with k = 1, 2...	Bq l^{-1}
$u(c_A)$	Standard uncertainty associated with the measurement result	Bq l^{-1}
V	Volume of the eluted phase S containing lead	l
V_e	Total volume of the test sample plus carrier	l
V_s	Volume of the standard test sample	l
V_{sample}	Volume of the sample	l
V_1	Volume of the aliquot from S for ^{210}Pb counting	l
V_2	Volume of the aliquot from S for determination of chemical recovery of lead	l
ε	General term for detection efficiency	s^{-1} Bq^{-1}
C_{Pb}	Concentration of lead in the eluted solution S	mg l^{-1}
$C_{Pb,e}$	Concentration of lead in the sample after addition of carrier	mg l^{-1}
n/a Not applicable.		

4 Principle

Lead-210 is a naturally occurring beta-emitting radionuclide with a maximum beta-energy of 63,5(5) keV and a half-life of 22,23(12) years [8][9]. It appears in the ^{238}U decay series (4n+2) as a long-lived decay product of ^{222}Rn (see Figure 1).

This document describes the measurement of ^{210}Pb after separation from its progeny, ^{210}Bi and ^{210}Po and its activity is measured by liquid scintillation counting, either immediately after its separation or indirectly after ingrowth of its progeny ^{210}Bi [10][26] to [34].

Lead-210 is chemically purified from potential interferents, which consist of any isotope that can make the liquid scintillator emits light in the region of interest (ROI) of ^{210}Pb. Different methods for the purification of ^{210}Pb are presented in Annex A.

After removal of the potential interferents, the chemical recovery of lead (R_c) is determined. The purified sample is mixed with the scintillation cocktail in a counting vial to obtain a homogenous medium. The vial is counted by LSC.

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 (Table 1).

To avoid the possible interferences of the isotopes with short half-lives such as ^{211}Pb and ^{214}Pb and their progeny during the liquid scintillation counting, it is recommended to wait at least 3 h between elution of lead and sample counting to allow these radionuclides to substantially decay.

The beta-energies of ^{211}Pb, ^{212}Pb and ^{214}Pb and their progeny are higher than the maximum energy of ^{210}Pb. The 3 h delay time before counting can be reduced by setting appropriate counting windows different from the one set for ^{210}Pb to eliminate these interferences. In this approach, it is possible to start counting without a 3 h delay to neglect ^{210}Bi ingrowth during counting.

It is necessary to know the content of stable lead in the sample in order to adjust the quantity of the lead carrier to add to avoid resin saturation and to allow for the chemical recovery of ^{210}Pb. Total content of stable lead in samples should not exceed 10 mg Pb per gram of extraction chromatographic resin 18C6 to be used for the lead separation.

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

Suspended material is removed prior to analysis by filtration through a 0,45 µm filter membrane. The analysis of the insoluble fraction requires a mineralization step that is not covered by this document.

NOTE A suitable mineralization step is specified in ISO 18589-2 [11].

The measurement of stable lead for the determination of the chemical recovery can be carried out according to protocols such as:

— ICP-AES according to ISO 11885 [12];

— ICP-MS according to ISO 17294-2 [13]; or

— AAS according to ISO 15586.[14][15]

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

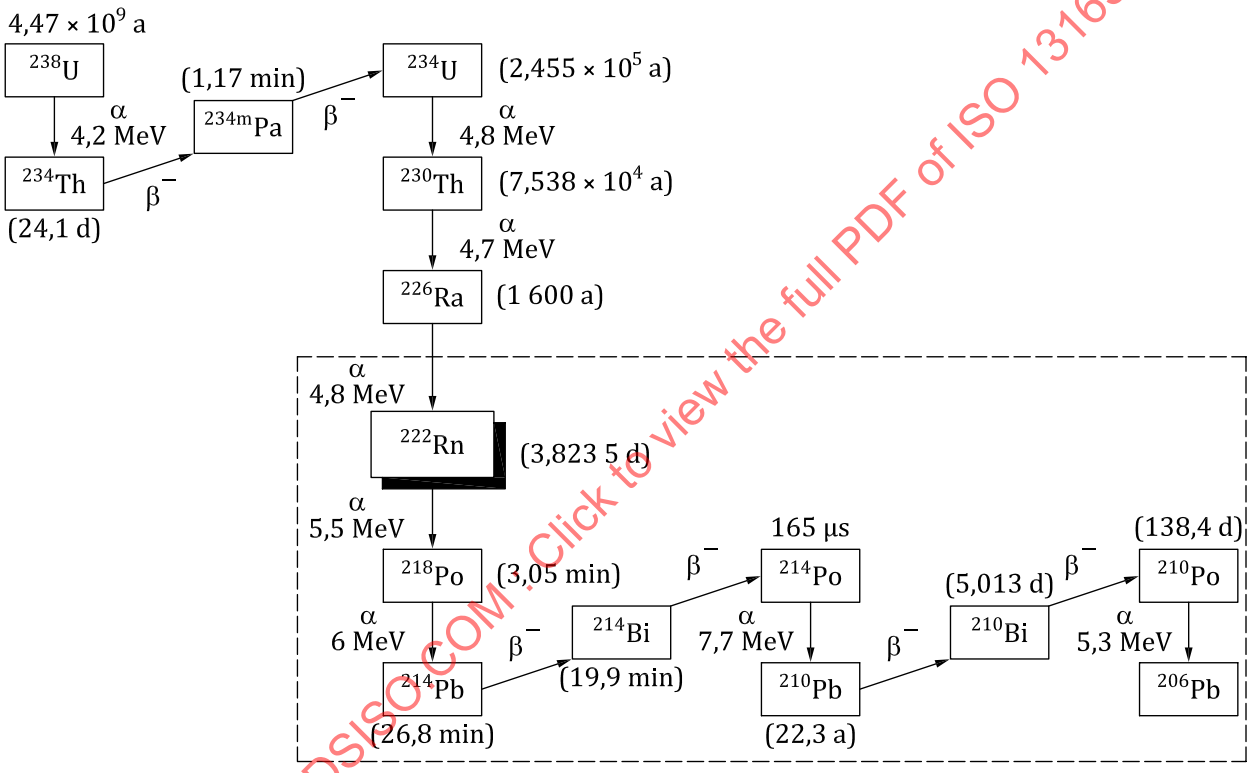


Figure 1 — Uranium-238 and its decay products

Table 1 — Decay data for lead radioisotopes and their progenies[9]

Lead radioisotopes	$T_{1/2}$	Decay mode	Emission energy (keV)	Emission probability (%)	Progeny
^{210}Pb	22,23(12) y	β-	63,5(5)	19,8(13) %	^{210}Bi
		β-	17,0(5)	80,2(13) %	^{210}Bi
		α	3792(20)	0,0000019(4) %	^{206}Hg
^{210}Bi	5,012(5) d	β-	1161,2(8)	99,99986(2) %	^{210}Po
		α	4778(4)	0,000056(6) %	^{206}Tl
		α	4740(4)	0,000084(9) %	^{206}Tl
^{210}Po	138,3763(17) d	α	5604,40(9)	0,00124(4) %	^{206}Pb (stable)
			5407,45(7)	99,99876(4) %	

Table 1 *(continued)*

Lead radioisotopes	$T_{1/2}$	Decay mode	Emission energy (keV)	Emission probability (%)	Progeny
^{206}Tl	4,202(11) min	β-	1532,4(6)	99,885(14) %	^{206}Pb (stable)
^{211}Pb	36,1(2) min	β-	1367(6) 962(6) 535(6) 257(6)	91,28(12) % 1,57(9) % 6,32(9) % 1,06(4) %	^{211}Bi
^{211}Bi	2,15(2) min	α α β-	6750,4(6) 6399,8(9) 574(5)	83,56(23) % 16,16(23) % 0,276(4) %	^{207}Tl ^{207}Tl ^{211}Po
^{207}Tl	4,774(12) min	β-	1418(5)	99,729(10) %	^{207}Pb (stable)
^{211}Po	0,516(3) s	α	7594,48(51)	100 %	^{207}Pb (stable)
^{212}Pb	10,64(1) h	β-	569,9(19) 331,3(19) 154,6(19)	13,3(11) % 81,7(11) % 4,99(21) %	^{212}Bi
^{212}Bi	60,54(6) min	β- α	2252 1(17) 6207 26(3)	64,07(7) % 35,93(7) %	^{208}Tl ^{212}Po
^{208}Tl	3,058(6) min	β-	1801,3(17) 1523,9(17) 1290,5(17)	49,2(6) % 22,1(5) % 24,1(2) %	^{208}Pb (stable)
^{212}Po	300(2) ns	α	8954 12(11)	100 %	^{208}Pb (stable)
^{214}Pb	26,916(44) min	β-	1019 (11) 729(11) 667(11) 485(11) 180(11)	9,2(7) % 41,09(39) % 46,52(37) % 1,047(17) % 2,762(22) %	^{214}Bi
^{214}Bi	19,8(1) min	β- α	3270(11) 5621(3)	99,979(13) % 0,0210(13) %	^{214}Po ^{210}Tl
^{214}Po	162,3(12) µs	α	7833,46(6)	99,9895(7) %	^{210}Pb

5 Sampling and storage

Sampling, handling, and storage of the water shall be done according to ISO 5667-1, ISO 5667-3 and ISO 5667-10 and guidance is given for the different types of water in Reference [16] to Reference [23]. It is important that the laboratory receives a sample that is representative of the material being tested and has not been damaged or modified during transportation or storage.

The sample is filtered to remove suspended matter using a 0,45 µm filter membrane. A smaller pore size filter can also be used, but the filtration might be more time consuming. After filtration, the sample is acidified with nitric acid (HNO_3) to 0,01 mol·l^{-1} HNO_3.

An activity concentration of 100 Bq l $^{-1}$ of ^{222}Rn in a sealed water sample with no airspace generates approximately 40 mBq·l^{-1} of ^{210}Pb for a storage time of 10 days. Thus, the storage time of samples dedicated to ^{210}Pb measurement shall be taken into consideration when the sample contains radon.

6 Procedure

6.1 Sample preparation for measurement

Filter and acidify the samples and a blank sample prepared with ultrapure water as specified in Clause 5.

A minimum of 1 blank sample per batch is required. However, the average of several blanks can be used. Measuring blank samples at regular interval enables to rapidly detect a background issue when measuring the samples (see quality assurance and quality control program in Clause 7).

Purify the sample from potential interferents. Examples of purification methods are described in Annex A.

Determine the chemical recovery.

6.2 Sample measurement

Measure ^{210}Pb in the samples by LSC by following the instructions provided by the instrument manufacturer and the steps described in ISO 19361.

7 Quality assurance and quality control program

7.1 General

Quality control operations shall meet the requirements of ISO/IEC 17025. Measurement methods shall be performed by suitably skilled staff under a quality assurance program.

7.2 Variables that could influence the measurement

Special care shall be taken in order to limit as much as possible the influence of parameters that can bias the measurement and lead to a non-representative result. Failure to take sufficient precautions can require corrective factors to be applied to the measured result.

Sampling, transportation and storage, reagents, transfer, measurement of stable lead, and the activity measurement of ^{210}Pb are all subject to potential interference or variability.

The presence of chemiluminescence prevents the accurate measurement of the samples. To reduce the chemiluminescence, the samples are left in the dark for a few hours before counting them. This delay can be the same as used for progeny decay as mentioned in Clause 4. If a chemiluminescence peak is observed, wait until the chemiluminescence has decayed and re-count the samples.

Preconcentration step of lead is performed using an Fe(III) co-precipitation, which allows the elimination of Group 1 elements such as K and Na. The chromatographic extraction resin, e.g. an 18C6 crown ether-type resin, has very low affinity for Group 2 elements when choosing appropriate chemical conditions. If these elements are present at high concentrations, the volume of the 18C6 crown ether-type resin column can be revised to cope with their interferences given that the working lead capacity of the 18C6 crown ether-type resin is about 20 mg Pb·g^{-1} of dry resin.

If a cation exchange resin is used for the preconcentration step instead of the Fe(III) co-precipitation, the quantity of cation exchange resin should be determined based on its exchange capacity and amount of cationic species in the sample.[26] An excess of resin is usually employed.

7.3 Instrument quality control

The main instrument parameters such as efficiency and background shall be periodically checked within a quality assurance program established by the laboratory and in accordance with the manufacturer's instructions.

7.4 Reagent interferents

The periodic performance of reagent blank analysis provides a check for interferents in laboratory reagents. Laboratory procedures shall ensure that laboratory and equipment contamination as well as sample cross contamination is avoided.

7.5 Interference control

It is the user's responsibility to ensure that all potential interferences have been removed or accounted for. The removal of potential interferents is limited by the decontamination factor of the method and the instrumental capabilities.

7.6 Method verification

A periodic verification of the method accuracy should be performed. This may be accomplished by some or all of the following:

— participating in intercomparison exercises;

— analysing reference materials;

— analysing spiked samples.

The repeatability of the method should be verified (for example, by replicate measurements).

Using this method, laboratories have reported uncertainties of 10% for a water sample size of 1,5 litres containing ^{210}Pb at a level of 0.2 Bq l^{-1}. A 5 % reproducibility and a 3 % repeatability were obtained. The robustness of the method was about 5 % for activity concentrations in the range 0,2 Bq l^{-1} to 1 Bq l^{-1}.

7.7 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.

7.8 Calibration

Periodically, verify 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:

— determination of lead mass content before separation;

— lead carrier addition, if required, depending on the initial determination of lead mass content (see above);

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

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

— liquid scintillation counting: measurement of the activity of ^{210}Pb as soon as possible, but after decay period given in Clause 4, 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.

Check the lead carrier solution regarding its stability over time.

The samples collected after the chromatographic separation should show a similar quenching index (such as tSIE, SQPE, TDCR, direct DPM) for a specific type of matrix as the chemical medium is very similar. 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 and varying concentrations of a quenching agent to blank aliquots. A quench curve can be obtained by plotting detection efficiency against quenching index value.

The beta-emission of ^{210}Pb is measured in a counting window with a maximum energy equivalent to 64 keV. It is advisable to monitor other suitable 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 any interference, an additional purification step may be implemented.

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

The duration of the counting period is determined according to the detection limit required and the evaluation of the ingrowth yield of the daughter.

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 separated during the analysis (^{212}Bi, ^{214}Bi, ^{211}Bi, ^{207}Tl, and ^{208}Tl).

Start counting of the ^{210}Pb samples as soon as possible after lead elution and within 12 h following its separation to maintain ^{210}Bi ingrowth at a negligible level (^{210}Bi represents about 6,5 % of the total activity after 12 h [25]).

8 Expression of results

8.1 General

For measurement by liquid scintillation, only the uncertainties of the following parameters are considered:

— test and blank samples counts;

— counting efficiency;

— volume or mass of test sample.

Other uncertainties such as scintillation liquid volume or mass, counting time, may be neglected in the first approximation.

The calculation approach presented in 8.2 to 8.6 is based on an immediate counting (within 12 h of ^{210}Bi separation) to limit the ingrowth of ^{210}Bi during the counting time.

For counting where ^{210}Bi ingrowth is not negligible, a method using the contribution of ^{210}Bi in the ^{210}Pb window can be used [33], but is not covered in this document.

8.2 Sample recovery, activity and uncertainties

The chemical recovery for lead separation is determined using Formula (1):

$$R_c = \frac{C_{Pb} \cdot V}{\left(C_{Pb,e} \cdot V_e\right)} \tag{1}$$

The beta-counting efficiency is determined from a ^{210}Pb solution of known activity, $c_{A,0}$, prepared following this document and defined using Formula (2):

$$\varepsilon = \frac{\left(r_s - r_0\right) \cdot C_{coeff}}{c_{A,0} \cdot R_c \cdot V_s} \cdot \frac{V}{V_1} \tag{2}$$

where C_{coeff} is the correction coefficient of the ingrowth of ^{210}Bi in the sample with respect to time, given by Formula (3):

$$C_{coeff} = \frac{1}{2 - \exp\left(\frac{-ln2}{T_{\frac{1}{2}}} \Delta t\right)} \tag{3}$$

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 average counting duration.

C_{coeff} If the sample is counted within 12 h after ^{210}Pb separation, then C_{coeff} can be assumed as equal to 1

The yield is thus defined from the initial time of the separation of lead from its progeny.

The sample activity concentration c_A of ^{210}Pb in the sample is calculated using Formulae (4):

$$c_A = \frac{\left(r_g - r_0\right) \cdot C_{Coeff}}{\varepsilon \cdot R_c \cdot V_{sample}} \cdot \frac{V}{V_1} = \left(r_g - r_0\right) \cdot w \tag{4}$$

where

$$w = \frac{C_{Coeff}}{\varepsilon \cdot R_c \cdot V_{sample}} \cdot \frac{V}{V_1}$$

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

The standard uncertainty on activity concentration is calculated using Formula (5):

$$u_{[c_A]} = \sqrt{w^2 \cdot \left(u^2\left(r_g\right) + u^2\left(r_0\right)\right) \cdot c_A^2 \cdot u_{rel}^2(w)} = \sqrt{w^2 \cdot \left(\frac{r_g}{t_g} + \frac{r_0}{t_0}\right) \cdot c_A^2 \cdot u_{rel}^2(w)} \tag{5}$$

Uncertainties on counting times of the sample and the background are considered negligible.

Relative uncertainty on w is calculated using Formula (6):

$$u_{\mathrm{rel}}^2(w)=u_{\mathrm{rel}}^2(\varepsilon)+u_{\mathrm{rel}}^2(R_{\mathrm{c}})+u_{\mathrm{rel}}^2(V_{\mathrm{sample}})+u_{\mathrm{rel}}^2(V_1)+u_{\mathrm{rel}}^2(V)+u_{\mathrm{rel}}^2(C_{\mathrm{Coeff}}) \tag{6}$$

Uncertainties on counting time and half-life of ^{210}Bi are considered negligible. Relative uncertainty on w is calculated using Formula (7):

$$u_{\mathrm{rel}}^2(w)=u_{\mathrm{rel}}^2(\varepsilon)+u_{\mathrm{rel}}^2(R_{\mathrm{c}})+u_{\mathrm{rel}}^2(V_{\mathrm{sample}})+u_{\mathrm{rel}}^2(V_1)+u_{\mathrm{rel}}^2(V) \tag{7}$$

Relative standard uncertainty of ε is calculated using the following:

$$u_{\mathrm{rel}}^2(\varepsilon)=u_{\mathrm{rel}}^2(r_{\mathrm{s}}-r_0)+u_{\mathrm{rel}}^2(C_{\mathrm{coeff}})+u_{\mathrm{rel}}^2(c_{\mathrm{A0}})+u_{\mathrm{rel}}^2(R_{\mathrm{C}})+u_{\mathrm{rel}}^2(V_{\mathrm{s}})+u_{\mathrm{rel}}^2(V_1)+u_{\mathrm{rel}}^2(V)$$

$$u_{\mathrm{rel}}^2(\varepsilon)=\left(\frac{r_{\mathrm{s}}}{t_{\mathrm{s}}}+\frac{r_0}{t_0}\right)/(r_{\mathrm{s}}-r_0)^2+u_{\mathrm{rel}}^2(C_{\mathrm{coeff}})+u_{\mathrm{rel}}^2(c_{\mathrm{A0}})+u_{\mathrm{rel}}^2(R_{\mathrm{C}})+u_{\mathrm{rel}}^2(V_{\mathrm{s}})+u_{\mathrm{rel}}^2(V_1)+u_{\mathrm{rel}}^2(V)$$

Uncertainties on counting time and half-life of ^{210}Bi are considered negligible. Relative uncertainty on ε is calculated using Formula (8):

$$u_{\mathrm{rel}}^2(\varepsilon)=\left(\frac{r_{\mathrm{s}}}{t_{\mathrm{s}}}+\frac{r_0}{t_0}\right)/(r_{\mathrm{s}}-r_0)^2+u_{\mathrm{rel}}^2(c_{\mathrm{A0}})+u_{\mathrm{rel}}^2(R_{\mathrm{C}})+u_{\mathrm{rel}}^2(V_{\mathrm{s}})+u_{\mathrm{rel}}^2(V_1)+u_{\mathrm{rel}}^2(V) \tag{8}$$

where

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

$u_{\mathrm{rel}}^2(R_{\mathrm{C}})$ is the uncertainty on the chemical recovery and it depends upon its evaluation method.

If needed, the characteristic limits, $\tilde{u}(\tilde{c}_{\mathrm{A}})$, can be calculated using Formula (9) as explained in ISO 11929-1:

$$\tilde{u}_{[\tilde{c}_{\mathrm{A}}]}=\sqrt{w^2\cdot\left[\frac{(\tilde{C}_{\mathrm{A}}/w)+r_0}{t_{\mathrm{g}}}+\frac{r_0}{t_0}\right]+c_{\mathrm{A}}^2\cdot u_{\mathrm{rel}}^2(w)} \tag{9}$$

8.3 Decision threshold

The decision threshold, c_{A}^*, is obtained from Formula (10) for $\tilde{c}_{\mathrm{A}}=0$ (see ISO 11929-1). This yields:

$$c_{\mathrm{A}}^*=k_{1-\alpha}\cdot w\cdot\sqrt{\frac{r_0}{t_{\mathrm{g}}}+\frac{r_0}{t_0}} \tag{10}$$

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

8.4 Detection limit

The detection limit, $c_{\mathrm{A}}^{\#}$, is calculated using Formula (11) (see ISO 11929-1):

$$c_{\mathrm{A}}^{\#}=c_{\mathrm{A}}^*+k_{1-\beta}\cdot\tilde{u}(c_{\mathrm{A}}^{\#})=c_{\mathrm{A}}^*+k_{1-\beta}\cdot\sqrt{w^2\cdot\left(\left[(c_{\mathrm{A}}^{\#}/w)+r_0\right]/t_{\mathrm{g}}+(r_0/t_0)\right)+c_{\mathrm{A}}^{\#2}\cdot u_{\mathrm{rel}}^2(w)} \tag{11}$$

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

The detection limit can be calculated by solving the previous formula 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 the detection limit is given by Formula (12):

$$c_A^{\#} = \left(2 \cdot c_A^* + \left(\left(w \cdot k^2\right)/t_g\right)\right)/\left(1 - k^2 \cdot u_{rel}^2(w)\right) \tag{12}$$

8.5 Limits of the coverage intervals

8.5.1 Limits of the probabilistically symmetric coverage interval

The lower, $c_A^{\triangleleft}$, and upper, $c_A^{\triangleright}$, coverage limits are calculated using Formulae (13) and (14), according to ISO 11929-1:

$$c_A^{\triangleleft} = c_A - k_p \cdot u(c_A); p = \cdot\omega \cdot (1 - \gamma/2) \tag{13}$$

$$c_A^{\triangleright} = c_A - k_q \cdot u(c_A); q = 1 - \omega \cdot \gamma/2 \tag{14}$$

where

$\omega = \Phi(y/u(y))$, Φ being the distribution function of the standardized normal distribution;

$1\text{-}\gamma$ is the probability for the coverage interval of the measurand;

ω = 1 may be set if $c_A \geq 4\,u(c_A)$. In this case:

$$c_A^{\triangleleft}, c_A^{\triangleright} = c_A \pm k_{1-\gamma/2} \cdot u\left(c_A\right) \tag{15}$$

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

8.5.2 The shortest coverage interval

As described in detail in ISO 11929-1, the lower limit of the shortest coverage interval, $c_A{}^{<}$, and the upper limit of the shortest coverage interval, $c_A{}^{>}$, are calculated from a primary measurement result, c_A, of the measurand and the standard uncertainty, $u(c_A)$, associated with c_A, either by

$$c_A{}^{<}, c_A{}^{>} = c_A \pm k_p \cdot u(c_A); p = (1 + \omega \cdot (1 - \gamma))/2$$

or if $C_A{}^{<} < 0$, by :

$$c_A{}^{<} = 0; c_A{}^{>} = c_A \pm k_q \cdot u\left(c_A\right); q = 1 - \omega \cdot \gamma$$

$\omega = \Phi[y/u(y)]$, Φ being the distribution function of the standardized normal distribution;

The relation $0 \leq c_A{}^{<} < c_A{}^{>}$ applies and the approximation of Formula (15) is valid.

9 Test report

The test report shall conform to ISO/IEC 17025 requirements. It shall contain the following information:

a) reference to this document, i.e. (ISO 13163:2021);

b) identification of the sample;

c) units in which the results are expressed;

d) the test result:

1) when the activity concentration, c_A is compared with the decision threshold (see the ISO 11929 series);

— if the result is less than the decision threshold, the result of the measurement is expressed as $\leq c_A^*$;

— if the result is greater than the decision threshold, the result of the measurement is expressed as $c_A \pm u_c(c_A)$ or $c_A \pm U$ with the associated k value.

2) when the activity concentration, c_A is compared with the detection limit;

— if the result is less than the detection limit, the result of the measurement is expressed as $\leq c_A^\#$;

— if the result is greater than the detection limit, the result of the measurement is expressed as $c_A \pm u_c(c_A)$ or $c_A \pm U$ with the associated k value.

Complementary information can be provided such as:

e) the uncertainty can also be expressed as the limits of the probabilistically symmetric coverage interval $c_A^\triangleleft, c_A^\triangleright$ and/or the limits of the shortest coverage interval $c_A^<, c_A^>$;

f) probabilities α, β and (1 - γ);

g) decision threshold and the detection limit;

h) if the detection limit exceeds the guideline value, it shall be documented that the method is not suitable for the measurement purpose;

i) mention of any relevant information likely to affect the results.

NOTE Occasionally, it is requested by the customer or regulator to compare the primary measurement result, c_A, with the detection limit, $c_A^\#$, in order to decide whether the physical effect is recognized or not. Such stipulations are not in accordance with the ISO 11929 series. They have the consequence that it is decided too frequently that the physical effect is absent when in fact it is not absent.

Annex A
(informative)

Separation and purification of ^{210}Pb

A.1 Principle

The sample is filtered and acidified as described in Clause 5. The lead carrier is added. Lead is preconcentrated. The solution of Pb obtained after the preconcentration step forms the load solution to next step. This can be either 2 mol. l^{-1} HCl (A.3) or 1 mol. l^{-1} HNO_3 (A.4). The load solution of 2 mol.l^{-1} HCl is preferred when both ^{210}Pb and ^{210}Po are measured. For the measurement of ^{210}Pb alone, either load solution medium (2mol.l^{-1} HCl or 1mol.l^{-1} HNO_3) is applicable.

The solution is further purified from potential interferents by passing it through a crown-ether based resin that selectively extracts Pb. After elution, the ^{210}Pb is measured by LSC.

A.2 Reagents and apparatus

A.2.1 Reagents

All reagents shall be of recognized analytical grade and shall not contain, as far as possible, any detectable alpha and beta activity, except for radioactive standard solutions.

A.2.1.1 Lead-210 standard solutions

The Pb-210 standard solutions should be traceable to national or international measurement standards, and can be obtained from a number of commercial suppliers and national measurement institutes.

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

A.2.1.2 Standard solution of Pb(II)

These can be obtained from a number of commercial suppliers at a range of concentrations. Approximately 1 $g{\cdot}l^{-1}$ in acidic medium (for example, 0,5 $mol{\cdot}l^{-1}$ HNO_3).

A.2.1.3 Quenching agent

A suitable chemical should be used, such as nitromethane (CH_3NO_2). Nitric acid, acetone or organochlorine compounds (e.g. chloroform), can also be used.

CAUTION — Some quenching agents are dangerous or toxic.

A.2.1.4 Laboratory water, distilled or deionized, complying with grade 3 of ISO 3696

Deionized water can contain detectable amounts of ^{222}Rn and short-lived progeny. It is therefore strongly recommended that water be boiled with vigorous stirring and allowed to stand for 1 d before use. Otherwise, degas it with nitrogen for about 1 h per 2 l.

A.2.1.5 Solution of stable iron carrier, approximately 1 $g \cdot l^{-1}$ (for example in 0,5 $mol \cdot l^{-1}$ HNO_3).

A.2.1.6 Cationic exchange resin, e.g. sulfonic type 8 % cross-linking.

A.2.1.7 Hydrochloric acid solution, $c(HCl) = 2\ mol \cdot l^{-1}$.

A.2.1.8 Nitric acid solution, $c(HNO_3) = 1\ mol \cdot l^{-1}$.

A.2.1.9 Nitric acid solution, $c(HNO_3) = 0{,}1\ mol \cdot l^{-1}$.

A.2.1.10 ammonium hydroxide solution, $c(NH_4OH)$ concentrated = 280 $g \cdot l^{-1}$.

A.2.1.11 Ammonium citrate or citric acid solution, $c(C_6H_{11}NO_7)$ or $c(C_6H_8O_7) = 0{,}01\ mol \cdot l^{-1}$ to 0,1 $mol \cdot l^{-1}$

A.2.1.12 EDTA solution, $c(C_{10}H_{16}N_2O_8) = 0{,}01\ mol \cdot l^{-1}$.

A.2.1.13 Chromatographic extraction resin, 18C6 Crown ether-type resins.

A.2.1.14 Liquid scintillation cocktail

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

A.2.2 Apparatus

Usual laboratory equipment and in particular the following.

A.2.2.1 Centrifuge or vacuum filtration system.

A.2.2.2 Membrane filter, of pore size 0,45 µm.

A.2.2.3 Analytical balance, accuracy 0,1 mg.

A.2.2.4 Equipment for the measurement of stable lead.

e.g. AAS, ICP-MS, ICP-OES.

A.2.2.5 Measurement equipment: Liquid scintillation counter

^{210}Pb may be counted with a commercial liquid scintillation counter. These may include:

— “conventional” twin photomultiplier tube systems with CIEMAT-NIST efficiency tracing routines (CIEMAT/NIST measurements require additional software for data analysis); and

— triple-to-double coincidence ratio systems (TDCR measurements require additional software for data analysis).

— Liquid scintillation counters should be used in accordance with ISO 19361.

A.2.2.6 Scintillation vials

Glass or plastic (PTFE or PE) vials, suitable for the selected liquid scintillation counter.

A.3 Procedure with 2 mol.l^{-1} HCl loading medium

A.3.1 Preconcentration

A.3.1.1 Preparation

Add a known quantity of lead carrier solution (A.2.1.2) (e.g. corresponding to approximately 1 mg to 10 mg of Pb) to the sample (obtained from Clause 5) for the determination of the chemical recovery and shake. The presence of Ca, Ba, K, Na and Sr in the sample can impact the chemical recovery (see 7.2).

The sample solution is preconcentrated either by iron hydroxide precipitation (A.3.1.2) or by cation exchange resin (A.3.1.3).

A.3.1.2 Preconcentration by iron (III) hydroxide co-precipitation

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 (A.2.1.5) to the sample obtained in A.3.1.1. Shake to homogenize and warm the solution to approximately 50 °C to 60 °C.

Add concentrated ammonium hydroxide solution (A.2.1.10) to about pH 9 until brown $Fe(OH)_3$ precipitates.

Allow to settle and cool for at least 2 h, then separate the iron hydroxide precipitate by filtration or by centrifugation.

The iron hydroxide precipitate is isolated and dissolved in a minimum volume (about 5 ml to 10 ml) of 2 mol·l^{-1} HCl (A.2.1.7).

A.3.1.3 Preconcentration with cation exchange resin [10]

The water sample obtained in A.3.1.1 is loaded onto the cation exchange resin (A.2.1.6). The eluate is evaporated to almost dryness and dissolved in a minimum volume (about 5 ml to 10 ml) of 2 mol.l^{-1} HCl (A.2.1.7).

If polonium is also to be determined, the temperature of evaporation has to be below 85 °C to prevent loss of polonium.

A.3.2 Separation of ^{210}Pb - Method with 2 mol.l^{-1} HCl loading medium (see Figure A.1)

A.3.2.1 General

The volumes of the solutions for the preconditioning, the elution and rinsing steps are given 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 7.2).

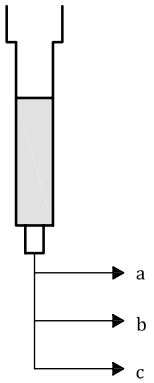
Precondition the extraction chromatographic resin (A.2.1.13) with approximately 10 ml of 2 mol·l^{-1} HCl (A.2.1.7).

Step 1: Load the sample solution (A.3.1.2) or (A.3.1.3) on to the resin. An additional volume of 5 ml of 2 mol.l^{-1} HCl (A.2.1.7) is used to rinse Bi and Fe (in case $Fe(OH)_3$ preconcentration is used) from the resin.

Step 2: Elute polonium with 5 ml of 1 mol·l^{-1} HNO_3 (A.2.1.8) followed by 15 ml of 0,1 mol·l^{-1} HNO_3 (A.2.1.9). The 0,1 mol·l^{-1} HNO_3 fraction can be used for the determination of ^{210}Po, provided that a polonium tracer has previously been added to the sample during its preparation.

Note the date and the time of the end of the rinsing (beginning of the ingrowth of ^{210}Bi).

Step 3: Elute lead with 10 ml to 20 ml of a solution of ammonium citrate or citric acid (A.2.1.11) or EDTA (A.2.1.12) to obtain solution *S* and make it up to a known volume, *V*.



Key

a step 1: Load and rinse in 2 mol.l^{-1} HCl (A.2.1.7) (Bi and Fe elution)

b step 2: Rinses with 1 mol·l^{-1} HNO_3 (A.2.1.8) + 0,1 mol·l^{-1} HNO_3 (A.2.1.9) (Po elution)

c step 3: Rinse with or 0,1 mol·l^{-1} citric acid or ammonium citrate (A.2.1.11) or 0,01 mol·l^{-1} EDTA (A.2.1.12) (Pb elution)

Figure A.1 — Separation scheme of ^{210}Pb with 2 mol·l^{-1} HCl as loading medium

A.3.2.2 Preparation for the counting and the determination of the chemical recovery

In a 20 ml vial, take an aliquot of volume, V_1, generally of the order of 10 ml, from solution S, complete to 20 ml with LSC cocktail (A.2.1.14) and mix the sample to measure ^{210}Pb by liquid scintillation.

Take an aliquot of volume, V_2, of solution S for the determination of the stable lead to estimate the chemical recovery. The chemical recovery can reach 80 % to 90 % if the sample has low salinity.

A.3.2.3 Measurement

Measure ^{210}Pb in the samples by LSC as indicated in 6.2 and 7.8.

Measure the stable Pb concentration in the samples by AAS, ICP-OES or ICP-MS for chemical recovery (R_c).

A.4 Procedure with 1 mol.l^{-1} HNO_3 loading medium

A.4.1 Preparation

Apply the procedure described in A.3.1.1.

A.4.2 Preconcentration

Apply the same procedure as described in A.3.1.2 or A.3.1.3 but replace the final dissolution step and preparation of load solution with 1 mol·l^{-1} HNO_3 (A.2.1.8) instead of 2 mol·l^{-1} HCl (A.2.1.7).

A.4.3 Separation of ^{210}Pb - Method with 1mol.l^{-1} HNO_3 loading medium (see Figure A.2)

Precondition the extraction chromatographic resin (A.2.1.13) with approximately 10 ml of 1 mol·l^{-1} HNO_3 (A.2.1.8) and not 2mol.l^{-1} HCl.

Step 1: Load the sample solution (A.4.2) on to the resin.

NOTE In 1 mol.l^{-1} HNO_3 medium, bismuth and iron are not retained on the resin. Polonium is only partly retained.

Step 2: Elute remaining polonium by means of 15 ml of 0,1 mol·l^{-1} HNO_3 (A.2.1.9).

