IAEA/AQ/34

IAEA Analytical Quality in Nuclear Applications Series No. 34

A Procedure for the Sequential Determination of Radionuclides in Phosphogypsum

Liquid Scintillation Counting and Alpha Spectrometry for ^{210}Po, ^{210}Pb, ^{226}Ra, Th and U Radioisotopes

IAEA

International Atomic Energy Agency

A PROCEDURE FOR THE SEQUENTIAL DETERMINATION OF RADIONUCLIDES IN PHOSPHOGYPSUM

The following States are Members of the International Atomic Energy Agency:

AFGHANISTAN
ALBANIA
ALGERIA
ANGOLA
ARGENTINA
ARMENIA
AUSTRALIA
AUSTRIA
AZERBAIJAN
BAHAMAS
BAHRAIN
BANGLADESH
BELARUS
BELGIUM
BELIZE
BENIN
BOLIVIA
BOSNIA AND HERZEGOVINA
BOTSWANA
BRAZIL
BRUNEI DARUSSALAM
BULGARIA
BURKINA FASO
BURUNDI
CAMBODIA
CAMEROON
CANADA
CENTRAL AFRICAN REPUBLIC
CHAD
CHILE
CHINA
COLOMBIA
CONGO
COSTA RICA
CÔTE D’IVOIRE
CROATIA
CUBA
CYPRUS
CZECH REPUBLIC
DEMOCRATIC REPUBLIC OF THE CONGO
DENMARK
DOMINICA
DOMINICAN REPUBLIC
ECUADOR
EGYPT
EL SALVADOR
ERITREA
ESTONIA
ETHIOPIA
FIJI
FINLAND
FRANCE
GABON
GEORGIA
GERMANY
GHANA
GREECE
GUATEMALA
HAITI
HOLY SEE
HONDURAS
HUNGARY
ICELAND
INDIA
INDONESIA
IRAN, ISLAMIC REPUBLIC OF
IRAQ
IRELAND
ISRAEL
ITALY
JAMAICA
JAPAN
JORDAN
KAZAKHSTAN
KENYA
KOREA, REPUBLIC OF
KUWAIT
KYRGYZSTAN
LAO PEOPLE’S DEMOCRATIC REPUBLIC
LATVIA
LEBANON
LESOTHO
LIBERIA
LIBYA
LIECHTENSTEIN
LITHUANIA
LUXEMBOURG
MADAGASCAR
MALAWI
MALAYSIA
MALI
MALTA
MARSHALL ISLANDS
MAURITANIA
MAURITIUS
MEXICO
MONACO
MONGOLIA
MONTENEGRO
MOROCCO
MOZAMBIQUE
MYANMAR
NAMIBIA
NEPAL
NETHERLANDS
NEW ZEALAND
NICARAGUA
NIGER
NIGERIA
NORWAY
OMAN
PAKISTAN
PALAU
PANAMA
PAPUA NEW GUINEA
PARAGUAY
PERU
PHILIPPINES
POLAND
PORTUGAL
QATAR
REPUBLIC OF MOLDOVA
ROMANIA
RUSSIAN FEDERATION
RWANDA
SAN MARINO
SAUDI ARABIA
SENEGAL
SERBIA
SEYCHELLES
SIERRA LEONE
SINGAPORE
SLOVAKIA
SLOVENIA
SOUTH AFRICA
SPAIN
SRI LANKA
SUDAN
SWAZILAND
SWEDEN
SWITZERLAND
SYRIAN ARAB REPUBLIC
TAJIKISTAN
THAILAND
THE FORMER YUGOSLAV REPUBLIC OF MACEDONIA
TOGO
TRINIDAD AND TOBAGO
TUNISIA
TURKEY
UGANDA
UKRAINE
UNITED ARAB EMIRATES
UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
UNITED REPUBLIC OF TANZANIA
UNITED STATES OF AMERICA
URUGUAY
UZBEKISTAN
VENEZUELA
VIET NAM
YEMEN
ZAMBIA
ZIMBABWE

The Agency’s Statute was approved on 23 October 1956 by the Conference on the Statute of the IAEA held at United Nations Headquarters, New York; it entered into force on 29 July 1957. The Headquarters of the Agency are situated in Vienna. Its principal objective is “to accelerate and enlarge the contribution of atomic energy to peace, health and prosperity throughout the world’’.

IAEA Analytical Quality in Nuclear Applications No. IAEA/AQ/34

A PROCEDURE FOR THE SEQUENTIAL DETERMINATION OF RADIONUCLIDES IN PHOSPHOGYPSUM

LIQUID SCINTILLATION COUNTING AND ALPHA SPECTROMETRY FOR ^{210}Po, ^{210}Pb, ^{226}Ra, Th AND U RADIOISOTOPES

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2014

COPYRIGHT NOTICE

All IAEA scientific and technical publications are protected by the terms of the Universal Copyright Convention as adopted in 1952 (Berne) and as revised in 1972 (Paris). The copyright has since been extended by the World Intellectual Property Organization (Geneva) to include electronic and virtual intellectual property. Permission to use whole or parts of texts contained in IAEA publications in printed or electronic form must be obtained and is usually subject to royalty agreements. Proposals for non-commercial reproductions and translations are welcomed and considered on a case-by-case basis. Enquiries should be addressed to the IAEA Publishing Section at:

Marketing and Sales Unit, Publishing Section
International Atomic Energy Agency
Vienna International Centre
PO Box 100
1400 Vienna, Austria
fax: +43 1 2600 29302
tel.: +43 1 2600 22417
email: sales.publications@iaea.org
http://www.iaea.org/books

For further information on this publication, please contact:

Terrestrial Environment Laboratory, Seibersdorf
International Atomic Energy Agency
2444 Seibersdorf
Austria
Email: Official.Mail@iaea.org

A PROCEDURE FOR THE SEQUENTIAL DETERMINATION OF RADIONUCLIDES IN PHOSPHOGYPSUM:
LIQUID SCINTILLATION COUNTING AND ALPHA SPECTROMETRY FOR ^{210}Po, ^{210}Pb, ^{226}Ra, Th AND U RADIOISOTOPES
IAEA, VIENNA, 2014
IAEA/AQ/34
ISSN 2074–7659
© IAEA, 2014
Printed by the IAEA in Austria
April 2014

FOREWORD

Since 2004, the Environment Programme of the IAEA has included activities aimed at the development of a set of procedures for the determination of radionuclides in terrestrial environmental samples. Reliable, comparable and ‘fit for purpose’ results are essential requirements for any decision based on analytical measurements. For the analyst, tested and validated analytical procedures are extremely important tools for the production of such analytical data. For maximum utility, such procedures should be comprehensive, clearly formulated, and readily available to both the analyst and the customer for reference.

In this publication, a combined procedure for the sequential determination of ^{210}Po, ^{210}Pb, ^{226}Ra, Th and U radioisotopes in phosphogypsum is described. The method is based on the dissolution of small amounts of phosphogypsum by microwave digestion, followed by sequential separation of ^{210}Po, ^{210}Pb, Th and U radioisotopes by selective extraction chromatography using Sr, TEVA and UTEVA resins. Radium-226 is separated from interfering elements using $Ba(Ra)SO_4$ co-precipitation. Lead-210 is determined by liquid scintillation counting. The alpha source of ^{210}Po is prepared by autodeposition on a silver plate. The alpha sources of Th and U are prepared by electrodeposition on a stainless steel plate. A comprehensive methodology for the calculation of results, including the quantification of measurement uncertainty, was also developed.

The procedure is introduced as a recommended procedure and validated in terms of trueness, repeatability and reproducibility in accordance with ISO guidelines.

The IAEA wishes to thank all the participants for their valuable contributions in developing the procedure and reviewing the publication, especially B. Varga (Hungary) who assisted in drafting. The IAEA officer responsible for this publication was A. Pitois of the IAEA Environment Laboratories.

EDITORIAL NOTE

This publication has been prepared from the original material as submitted by the contributors and has not been edited by the editorial staff of the IAEA. The views expressed remain the responsibility of the contributors and do not necessarily reflect those of the IAEA or the governments of its Member States.

This publication has not been edited by the editorial staff of the IAEA. It does not address questions of responsibility, legal or otherwise, for acts or omissions on the part of any person.

The use of particular designations of countries or territories does not imply any judgement by the publisher, the IAEA, as to the legal status of such countries or territories, of their authorities and institutions or of the delimitation of their boundaries.

The mention of names of specific companies or products (whether or not indicated as registered) does not imply any intention to infringe proprietary rights, nor should it be construed as an endorsement or recommendation on the part of the IAEA.

The contributors are responsible for having obtained the necessary permission for the IAEA to reproduce, translate or use material from sources already protected by copyrights.

The IAEA has no responsibility for the persistence or accuracy of URLs for external or third party Internet web sites referred to in this publication and does not guarantee that any content on such web sites is, or will remain, accurate or appropriate.

CONTENTS

1. INTRODUCTION

Phosphogypsum is a by-product derived from the wet process production of phosphoric acid by reacting phosphate rock with sulfuric acid, and represents one of the most serious problems facing the phosphate industry today. Very large quantities of phosphogypsum have been produced worldwide since the 1950s because of the high demand for phosphate fertilizer, and because the wet phosphoric acid process produces about 5 t of phosphogypsum for every tonne of phosphoric acid manufactured. Most of the phosphogypsum produced worldwide is stockpiled. There has been high interest in finding uses for this by-product, for example, as a building material or a soil amendment for the remediation of soils. Both the liquid wastes from the acidic process and the phosphogypsum itself are potential sources of contamination. The main problem associated with this material concerns the relatively high levels of natural radionuclides of the thorium and uranium decay series and non radioactive contaminants which could have an impact on the environment. The uranium and thorium decay series are shown on Fig. 1 and 2 in Appendix I. There is concern related to the possible contamination of groundwater under phosphogypsum stacks, and to radon exhalation which may pose a health risk to people working and living close to a stack.

The presence of radionuclides puts restrictions on the use of phosphogypsum in building materials and in soil amendments. The United States Environmental Protection Agency (US EPA) ruled that phosphogypsum would only be permitted for use in agriculture if the average concentration of ^{226}Ra in the phosphogypsum does not exceed 370 Bq kg^{-1} [1, 2]. National Council of Radiation Protection [3] guideline recommends ^{226}Ra content of 1.5 Bq g^{-1} in soil above which growing human food crops on it is restricted. In addition, the US EPA adopted an average 0.74 Bq m^{-2} s^{-1} upper limit on ^{222}Rn emission from phosphogypsum stacks. The phosphogypsum currently produced is stockpiled near the production site. Due to considerable demand for provision of a reference material with a phosphogypsum matrix from IAEA Member State laboratories which have phosphate industry, IAEA prepared and released a phosphogypsum reference material (IAEA-434) after performing the necessary homogeneity and characterization tests [4].

The procedure described in this report was developed as part of this work. Alpha emitters such as ^{210}Po, ^{226}Ra, Th and U radioisotopes, are generally measured by alpha spectrometry after radiochemical separation, while ^{210}Pb being a beta emitter is determined by liquid scintillation counting [5]. The nuclear data of relevant radionuclides and decay chains of the thorium and uranium decay series are given in Table 2 in Appendix II.

The purpose of this work was to develop a sequential separation method combining the extraction chromatography with Sr, TEVA and UTEVA resins, and Ba(Ra)SO_4 coprecipitation for sequential determination of ^{210}Po, ^{210}Pb, ^{226}Ra, Th and U radioisotopes in phosphogypsum. The method validation of the procedure was carried out in terms of trueness, repeatability and reproducibility with the IAEA-434 reference material.

2. SCOPE

The sequential separation method is described for the determination of ^{210}Po, ^{210}Pb, ^{226}Ra, Th and U radioisotopes in phosphogypsum by isotope dilution alpha spectrometry and liquid scintillation counting (LSC).

The mass of the sample required for the radiochemical analysis is typically 0.5 g. The method validation was carried out on the IAEA-434 reference material [4]. The typical chemical recovery and detection limits of relevant radionuclides in the proposed procedure are summarised in the Table 1.

TABLE 1. TYPICAL CHEMICAL RECOVERIES AND DETECTION LIMITS OF RELEVANT RADIONUCLIDES IN THE PROPOSED PROCEDURE

Isotope	Counting method	Source preparation	Typical recovery (%)	Typical detection limit (Bq kg^{-1}, as dry mass)
^{210}Pb	LSC	precipitation	80-90	24
^{210}Po	α-spectrometry	auto-deposition	40-70	1.2
^{234}U	α-spectrometry	electrodeposition	70-80	0.52
^{238}U				0.19
^{230}Th	α-spectrometry	electrodeposition	70-80	0.18
^{232}Th				0.19
^{226}Ra	α-spectrometry	electrodeposition	60-80	4.3

3. NORMATIVE REFERENCES

The principles of the normative references which have been applied to this document can be found in the list below.

- ISO 11929:2010. Determination of the characteristic limits (decision threshold, detection limit and limits of the confidence interval) for measurements of ionizing radiation – Fundamentals and application;
- ISO 17025:2005. General requirements for the competence of testing and calibration laboratories;
- ISO/TS 21748:2004, Guidance for the use of repeatability, reproducibility and trueness estimates in measurement uncertainty estimation;
- ISO/IEC Guide 98-3:2008. Uncertainty of measurement – Part 3: Guide to expression of uncertainty in measurement;
- ISO 7870-1:2007. Control charts – Part 1: General guidelines.

4. RESPONSIBILITIES

It is the responsibility of the analyst to follow this procedure and to establish appropriate safety and health practices. Compliance with national and/or internal safety rules or chemical and radioactive safety is obligatory. Although the method has been carefully tested each laboratory should perform an individual validation procedure.

5. TERMS AND DEFINITIONS, SYMBOLS AND ABBREVIATIONS

In the following, $u(x)$ indicates the uncertainty in quantity x and generally the relevant isotope is indicated as subscript:

a^* : Decision threshold (Bq kg^{-1}).

$a^\#$: Detection limit (Bq kg^{-1}).

a_0 : Activity of the analyte on the sampling date (Bq kg^{-1}).

a_{std} : Activity of the calibration standard (Bq g^{-1}).

a_s : Activity of the analyte on the separation date (Bq kg^{-1}).

A_T: Activity of ^{225}Ra tracer (Bq).

C : Certified activity of the analyte in the reference material (Bq kg^{-1}).

$C_{Pb\text{-}c}$: Mass fraction of Pb carrier solution.

$C_{Pb\text{-}s}$: Mass fraction of Pb already present in the sample.

C_T : Certified activity of tracer on the reference date (Bq g^{-1}).

$f_{A/B}$: Tailing factor, correction of interfered windows A and B.

f_g : Mass ratio of atomic mass of Pb to molar mass of PbC_2O_4.

f_T : Correction factor for the decay of the tracer during elapsed time between the reference date of tracer and the beginning of the measurement.

f_2: Correction factor for decay of the analyte during elapsed time between the separation and the beginning of the measurement.

f_3 : Correction factor for decay of the analyte over the counting time.

m_C : Mass of the carrier taken (in case of lead, mass of carrier solution) (g).

m_f : Mass of the filter used (g).

$m_{f,cal}$: Mass of the filter used in calibration (g).

m_{of} : Total mass of PbC_2O_4 and the filter used (g).

$m_{of,cal}$: Total mass of PbC_2O_4 and the filter used in the calibration (g).

m_s : Mass of the sample (kg).

m_T : Mass of the tracer taken (g).

$m_{T,Pb}$: Mass of the ^{210}Pb standard solution added (g).

M_{Pb} : Atomic mass of Pb (g mol^{-1}).

$M_{Pb\text{-}oxalate}$: Molar mass of PbC_2O_4 (g mol^{-1}).

n : Net counts in ROI of analyte (counts).

n_T: Net counts in ROI of tracer (counts).

n_0 : Blank or background counts in ROI of analyte (counts).

n_{0T} : Blank or background counts in ROI of tracer (counts).

P_α: Probability of α decay.

P_γ: Probability of γ decay.

r_0 : Blank or background count rate in ROI of analyte (counts s^{-1}).

r_{0T} : Blank or background count rates in ROI of tracer (counts s^{-1}).

r_{cal} : Count rates during the calibration (counts s^{-1}).

r_n : Net count rates in ROI of analyte (counts s^{-1}).

r_{nT}: Net count rates in ROI of tracer (counts s^{-1}).

r_g : Gross count rates in ROI of analyte (counts s^{-1}).

r_{gT}: Gross count rates in ROI of tracer (counts s^{-1}).

r_{nTmax}: Maximum detectable count rate (counts s^{-1}).

r_{0A}, r_{0B} : Count rates in windows A and B of the blank spectrum (counts s^{-1}).

r_{gA}, r_{gB} and $u(r_{gA})$, $u(r_{gB})$: Gross count rates in windows A and B of ^{210}Pb spectrum (counts s^{-1}).

r_{nA}, r_{nB} : Net count rates in windows A and B of ^{210}Pb spectrum (counts s^{-1}).

R : Chemical recovery of the analyte.

R_{cal} : Chemical recovery of making the calibration source.

R_L : Reproducibility limit (Bq kg^{-1}).

r_L : Repeatability limit (Bq kg^{-1}).

S_R : Standard deviation of reproducibility (Bq kg^{-1}).

S_r : Standard deviation of repeatability (Bq kg^{-1}).

t : Time interval between the sampling date and the measurement date (s).

t_0 : Counting time of the blank or background (s).

$t_{T,s}$: Time interval between the reference date of the tracer/standard and the separation date (s).

t_1 : Time interval between the sampling date and the separation date (s).

t_2 : Time interval between the separation date and the start of the measurement (s).

t_3 : Counting time of the sample (s).

t_T : Counting time of the tracer (s).

t_{Ac-225} : Time of build up of ^{225}Ac (s).

t_s : Time of the separation noted (s).

t_m : Time of the starting of the measurement (s).

t_{em} : Time of the end of the measurement (s).

$u(0)$: Uncertainty of non-negative measurand.

$\overline{X}$: Mean value of measurement results of the analyte in reference material (Bq kg^{-1}).

δ : Relative bias of the test result (%).

ε : Counting efficiency of the detector.

λ : Decay constant of the isotope (counts s^{-1}).

λ_T : Decay constant of the tracer (counts s^{-1}).

FWHM : Full width at half maximum.

LSC: Liquid scintillation counting .

NNDC: National Nuclear Data Center, Brookhaven National Laboratory.

ROI: Region of interest.

PSA: Pulse shape analysis.

$T_{1/2}$: Half-life of any isotope.

6. PRINCIPLE

The sample is digested in a microwave digestion system. ^{210}Po, ^{210}Pb, ^{226}Ra, U and Th radioisotopes are separated from interfering elements with a sequential chemical procedure, using extraction chromatographic resins and Ba(Pb)SO_4 co-precipitation. The most important features of the Sr, TEVA and UTEVA resins are shown on Fig. 3-6 in Appendix III. U and Th are electrodeposited on a polished stainless steel plate. The polonium source is prepared on a silver plate by auto-deposition. The ^{226}Ra source is prepared by Ba(Ra)SO_4 microcoprecipitation. The ^{210}Pb source is prepared with Pb-oxalate precipitation. ^{210}Po, ^{226}Ra, U and Th radioisotopes are determined by isotope dilution alpha spectrometry, and ^{210}Pb is determined by liquid scintillation counting. The flow chart of the combined procedure is given in Fig. 7 in Appendix IV.

7. EQUIPMENT AND CHEMICALS

7.1. EQUIPMENT

- Standard laboratory equipment, fume hood;
- Microwave oven;
- Alpha spectrometer with Si semiconductor detector;
- Vacuum pump;
- Liquid scintillation counting system;
- Auto-deposition system;
- Silver disk: fitted to the auto-deposition cell, diameter is equal or less than the diameter of the detector used for alpha spectrometry;
- Electrodeposition apparatus (Pt wire anode) equipped with DC power supply to provide up to 1 A of regulated current to the electrolytic cell;
- Stainless steel disc: diameter is equal or less than the diameter of the detector used for alpha spectrometry;
- Analytical balances;

- Hot plate with magnetic stirrer;
- Burner;
- Centrifuge, plastic centrifuge tube (minimum 20 mL volume);
- Water bath with temperature controller;
- Filtering set with filter paper for fine precipitate;
- Chromatography columns;
- pH meter or pH papers;
- Teflon beakers with Teflon tops and clips;
- Dispensers: 5-50 mL and 10-100 mL;
- Micropipettes with dispensable tips;
- Timer;
- Liquid scintillation vial: 20 mL, plastic (polyethylene), inner surface coated with Teflon.

7.2. CHEMICALS

- 30 mg mL^{-1} Pb^{2+} solution (usually as $Pb(NO_3)_2$);
- 0.4 Bq of ^{209}Po tracer as a certified solution;
- 0.04 Bq of ^{232}U tracer as a certified solution;
- 0.05 Bq of ^{225}Ra in equilibrium with its parent ^{229}Th as a certified solution;
- HNO_3 (65%);
- HF (40%);
- H_3BO_3;
- HCl (32%);
- Ultra pure water;
- DTPA (diethylenetriaminepentaacetic acid);
- Sr resin (100-150 μm);
- TEVA resin;
- UTEVA resin;
- Fine clean quartz crystals (analytical grade);
- $C_6H_8O_6$ (Ascorbic acid);
- NH_4SCN (ammonium thiocyanate);
- EDTA (ethylenediaminetetraacetic acid);
- $NH_3(aq)$ (ammonia);
- $(NH_4)_2SO_4$ (10%) (ammonium sulfate);
- $C_2O_4H_2 \cdot 2H_2O$ (oxalic acid);
- Methyl red solution (0.25%);
- Thymol blue solution (0.25%);
- Ba seeding solution [6];
- Sodium sulfate wash solution;
- CH_3CH_2OH (ethyl alcohol);
- Filter paper;
- Polypropylene filter (0.1 μm pore size, 25 mm diameter);
- Scintillation cocktail which forms a gel (for example, InstaGel Plus) or suitable for alpha/beta separation.

All the chemical reagents needed to carry out this procedure must be analytical grade. The preparation of specific chemical reagents is given in Appendix V. Information related to tracers and carriers are given in Appendix VI.

8. PROCEDURE

This procedure consists of the sample dissolution, the sequential separation of ^{210}Po, ^{210}Pb, Th and U isotopes, and ^{226}Ra from interfering elements and the source preparation for alpha spectrometry and liquid scintillation counting. The flowchart of this procedure is given in Appendix IV. Precautions to be followed for this procedure are given in Appendix VII.

8.1. SAMPLE DISSOLUTION USING MICROWAVE DIGESTION SYSTEM

(1) Weigh 0.5 g of phosphogypsum into a microwave container.
(2) Add about 30 mg of Pb^{2+} (usually as $Pb(NO_3)_2$ solution), about 0.4 Bq of ^{209}Po and 0.04 Bq of ^{232}U tracer and 0.05 Bq of ^{225}Ra in equilibrium with its parent ^{229}Th.
(3) Add 15 mL of 65% HNO_3.
(4) Consecutively digest the sample in the microwave oven at 120°C for 15 min and at 150°C for 25 min at 1000 W.
(5) Transfer the sample solution into a plastic centrifuge tube and centrifuge for 10 min.
(6) Transfer the supernatant into a Teflon beaker. The residue is transferred back into the microwave container with 3 mL of 65% HNO_3 and add 2 mL of 40% HF.
(7) Digest the residue in the microwave oven using the same conditions as mentioned above.
(8) Combine the solution with the supernatant from step (6).
(9) Add 0.1 g of H_3BO_3 and evaporate repeatedly to dryness with three portions of 5 mL of 65% HNO_3 to remove HF.
(10) Dissolve the residue in 30 mL of 2M HCl.

8.2. RADIOCHEMICAL SEPARATION PROCEDURES

8.2.1. Polonium and lead separation

(1) Prepare the Sr resin column with volume of approximately 8 mL (diameter: 10 mm, length: 100 mm) as follows: soak the resin in ultra pure water for at least 1 hour before use, then fill the column with resin and put a quartz crystal layer of approximately 10 mm on the top avoiding disturbance of the resin. The elution steps should be finished on the same working day.
(2) Load the sample solution onto the Sr resin column preconditioned in advance with 100 mL of 2M HCl, flow rate 5–6 drop/min, rinse the beaker several times with 1 mL of 2M HCl.
(3) Wash the column with 100 mL of 2M HCl followed by 25 mL of 6M HNO_3 to remove the non-retained ions.
(4) Combine the effluent and the washing solution into the same beaker and use it for the analysis of uranium and thorium.
(5) Strip Po with 60 mL of 6M HNO_3, flow rate 5–10 drops/min.
(6) Elute Pb with 60 mL of 6M HCl into the centrifuge tube, flow rate 5–10 drops/min.
(7) Sr resin columns can be reused several times. Regenerate with 50 mL of ultra pure water, wash it with 10 mL of 0.1M EDTA (pH adjusted to pH 7 with $NH_3(aq)$) then wash with 50 mL of ultra pure water, and before use load it with 100 mL of 2M HCl.

8.2.2. Thorium separation

(1) Prepare the TEVA column with a volume of 1.4 mL (diameter: 8 mm, length: 28 mm) as follows: soak the resin in ultra pure water for at least 1 hour before use, then fill the column with resin and put a quartz crystal layer of approximately 3 mm on the top avoiding disturbance of the resin.
(2) Evaporate the combined effluent and washing solutions from Sr resin column (8.2.1., step (4)).
(3) Dissolve the residue in 20 mL of 3M HNO_3
(4) Load the sample on the TEVA column preconditioned in advance with 20 mL of 3M HNO_3.
(5) Wash the column with 10 mL of 3M HNO_3.
(6) Combine the effluent and the washing solution into the same beaker and use it for analysis of uranium.
(7) Additionally wash the column with 20 mL of 3M HNO_3, this fraction is discarded.
(8) Elute Th with 20 mL of 8M HCl.
(9) Note the time of the separation of Th for recovery calculation of ^{226}Ra.

8.2.3. Uranium separation

(1) Prepare the UTEVA column with volume 1.4 mL (diameter: 8 mm, length: 28 mm) as follows: soak the resin in ultra pure water for at least 1 hour before use, then fill the column with the resin and put a quartz crystal layer of approximately 3 mm on the top avoiding the disturbance of the resin.
(2) Load the combined effluent and the washing solution from the TEVA column (8.2.2., step (6)) onto UTEVA column preconditioned in advance with 20 mL of 3M HNO_3.
(3) Wash the column with 20 mL of 3M HNO_3.
(4) Combine the effluent and the washing solution into the same beaker and use it for Ra analysis.
(5) Wash the column with 5 mL of 9M HCl and 15 mL of 6M HCl to remove small amounts of Po and Th remained on the column.
(6) Elute U with 6 mL of ultra pure water.

8.2.4. Radium separation

(1) Combine the effluent (30 mL of 3M HNO_3) and the washing solution (20 mL of 3M HNO_3) from the UTEVA column in a 200 mL volume of beaker (8.2.3, step (2) and (3)).
(2) Add 4 mL of concentrated H_2SO_4 and 20 mL of 20% Na_2SO_4 to the solution.
(3) Slowly add 5 mL of Pb^{2+} carrier (10 mg mL^{-1}) to form a $Pb(Ra,Ba)SO_4$ co-precipitate while stirring for 1–2 minutes.
(4) Remove the stirrer bar, wash it with a small amount of 0.1M HCl and ultra pure water.
(5) Allow to sit for 3–4 hours.
(6) Decant supernatant liquor to a volume as low as possible.
(7) Transfer the precipitate into a 50 mL conical centrifuge tube using 80% ethanol and centrifuge at 3000 revolutions min^{-1} for 10 minutes.
(8) Wash the precipitate with 20 mL of 80% ethanol and decant the supernatant.
(9) Wash the sides of the centrifuge tube with 5–10 mL of sodium sulfate wash solution and vortex to mix thoroughly, then add a further 5–10 mL to wash down the walls and then re-centrifuge at 3000 revolutions min^{-1} for 10 minutes.

(10) Pour out the supernatant, then invert the tube and wash the walls with ultra pure water to remove excess acid and sulfate (take care not to disturb the precipitate).
(11) Add 10 mL of 0.2M DTPA (diethylenetriaminepentaacetic acid) and 1 drop of 0.25% thymol blue. The solution should turn deep blue (if not, add 10M NaOH dropwise until a deep blue color is reached (pH>9)).
(12) Vortex to dissolve the precipitate.

8.3. SOURCE PREPARATION

8.3.1. Preparation of ^{210}Po source

(1) The Po solution is carefully evaporated to dryness at less than 150°C.
(2) Dissolve the residue in 10 mL of 0.5M HCl.
(3) Clean a silver disc with acetone, then with concentrated NH_3(aq), then with ultra pure water.
(4) Place the cleaned silver disc into the deposition cell (Teflon vial), with another disc placed underneath for support. Check if the cell is watertight.
(5) Add 0.05 g of ascorbic acid into the sample solution to reduce Fe^{3+} to Fe^{2+}, check the colour change after mixing one drop of sample solution and one drop of 0.1M NH_4SCN. Add ascorbic acid until the dark red colour disappears.
(6) Transfer the solution to the deposition cell.
(7) Rinse the beaker twice with 2 mL of 0.5M HCl and adjust the pH of the solution in the deposition cell to pH 2 with 6M NaOH.
(8) Place the deposition cell into a water bath at 90°C for 90 min with mechanical stirring or air bubbling.
(9) Remove the silver disc, wash with acetone or ultra pure water and dry it at room temperature.

8.3.2. Preparation of thorium and uranium sources

(1) The purified Th or U solution is evaporated to dryness three times with a few mL of 65% HNO_3, to destroy any existing organic matter.
(2) Dissolve the residues in 10 mL of 10% $(NH_4)_2SO_4$ solution at pH 2 (The pH of samples being deposited for thorium should be slightly more acidic, pH 1.5–pH 2).
(3) Transfer the solution into an electrodeposition cell.
(4) Electrodeposit Th or U onto polished stainless steel discs at 1 A for 90 minutes, respectively.
(5) At the end of the deposition time, fill the cell with 1.5M NH_4OH and continue the deposition for 1 min, then turn off the main power of deposition unit and disconnect the cathode.
(6) Rinse the cell twice with 1% NH_4OH, then three times with ultra pure water.
(7) Disassemble the cell, rinse the disc with ultra pure water and dry it.

8.3.3. Preparation of ^{226}Ra source

The ^{226}Ra source is prepared using $BaSO_4$ micro co-precipitation.
(1) Rapidly add 4 mL of a mixed solution of 5 parts of 20% Na_2SO_4 with 1 part of acetic acid to the solution from 8.2.4, step (12).
(2) Add 0.4 mL of Ba seeding solution as soon as possible.
(3) Adjust the pH to 4.8 with diluted H_2SO_4 as indicated by the colour change to a bright red.

(4) Allow to sit for at least 30 minutes.
(5) Filter the colloidal suspension of $Ba(Ra)SO_4$ through a pre-wetted with 80% ethanol 0.1 µm pore size polypropylene filter.
(6) Rinse the centrifuge tube walls with 4–5 mL of sodium sulfate wash solution and filter.
(7) Rinse the sides of the filter holder with 15–20 drops of 80% ethanol.
(8) Allow the filter to dry and place it into a 47 mm Petri dish. The time is recorded, which is considered as the time of $^{225}Ra/^{225}Ac$ separation or start of ^{225}Ac ingrowth.

The source preparation must be completed on the same day.

8.3.4. Preparation of ^{210}Pb source

(1) Evaporate the Pb solution, which was obtained from 8.2.1. step (6), and re-evaporate three times with 5 mL portions of 65% HNO_3.
(2) Dissolve the residue in 10 mL of 1M HNO_3.
(3) Add 40 mg of oxalic acid to the solution and adjust to pH 2–3 with 25% NH_4OH to prepare a Pb-oxalate precipitate.
(4) Let the solution cool down and filtrate the precipitate on a filter paper, wash the filter 3 times with 1 mL of ultra pure water and 2 mL of 80% ethanol.
(5) Dry the precipitate (40–50^{o}C) and cool down in a desiccator.
(6) Weigh the dried precipitate and calculate the chemical recovery using the gravimetric method.
(7) Quantitatively transfer the precipitate into a liquid scintillation vial together with the filter, and add 1 mL of 6M HNO_3 into the vial to dissolve the precipitate.
(8) Mix the solution with 15 mL of scintillation cocktail.

8.4. MEASUREMENT

8.4.1. Alpha spectrometry

(1) Introduce the source into the vacuum chamber and pump until a vacuum of about 0.5 Pa (5×10^{-3} mbar) is obtained. Then switch on the bias voltage button of the detector.
(2) Record the file name, sample information and measurement date in each detector log book, and start the measurement. A typical measuring time is about 1 day when using a 450 mm^2 area detector.
(3) Integrate the counts in the peaks corresponding to the alpha emitting tracers and analytes respectively. The alpha spectra should be similar to the spectra illustrated in Appendix VIII. The FWHM of alpha peaks should be in the range of 30–60 keV.
(4) Spectrum analysis: Integrate the channel counts in a region of interest (ROI) which has the width of about 4 × FWHM (about 3 × FWHM to the left and 1 × FWHM to the right when FWHM is about 30–60 keV). Integrate the channel counts in the same regions of interest (ROI) in the sample spectrum and in the blank spectrum then subtract them from the sample spectrum to give the net area of peaks for further calculation.

Performing a reliable measurement knowing the background of the chamber and detector is essential, moreover it is important to prepare a separate reagent blank. Therefore the set of measurement always has to involve above the samples a background and a reagent blank. If the quality of the determination has to be proved, a reference material also should be part of the preparation series.

Typical alpha spectra, obtained after radiochemical separation, of the Po, Ra, Th and U radioisotopes are shown on Fig. 8-11 in Appendix VIII. The interferences between some of the radioisotopes without radiochemical separation is illustrated on Fig. 12 (overlapping Po and U radioisotopes) and on Fig. 13 (overlapping Th and U radioisotopes) in Appendix VIII.

8.4.2. Liquid scintillation counting for ^{210}Pb determination

8.4.2.1. Source preparation for determination of counting efficiency of ^{210}Pb

(1) Take 10 mL of 2M HCl solution into a 50 mL beaker.
(2) Add the ^{210}Pb standard solution (10–15 Bq) and 30 mg of Pb^{2+} carrier to the solution.
(3) Load the solution onto a Sr resin column (3 g of Sr resin, 100–150 μm), which has been preconditioned in advance with 100 mL of 2M HCl.
(4) Wash the column with 80 mL of 2M HCl. Combine the washing solution with the effluent to get a pure ^{210}Bi fraction.
(5) Rinse the column with 20 mL of 2M HCl. This last portion of 20 mL of 2M HCl is discarded to avoid overlapping between the ^{210}Bi and ^{210}Po portions.
(6) Wash the column with 25 mL of 6M HNO_3.
(7) Elute Po with 60 mL of 6M HNO_3.
(8) Elute Pb with 60 mL of 6M HCl.
(9) Evaporate the Bi, Po and Pb fractions to dryness.
(10) Dissolve each portion of ^{210}Bi and ^{210}Po in 1 mL of 6M HNO_3, and then transfer each of them into 20 mL polyethylene vials coated with PTFE (polytetrafluoroethylene).
(11) Mix each of the solutions with 14 mL of scintillation cocktail.
(12) Evaporate Pb fraction three times with 2 mL of 65% HNO_3.
(13) Dissolve the residue in 20 mL of 1M HNO_3.
(14) Add 0.4 g of oxalic acid while warming and stirring.
(15) Adjust the pH to 3–5 with NH_4OH to form a Pb-oxalate precipitate.
(16) Filter the precipitate through a pre-weighed filter paper (diameter of 24 mm).
(17) Wash the precipitate three times with 1 mL of ultra pure water, then with 2 mL of 80% ethanol.
(18) Dry the precipitate in an oven at 40–50°C.
(19) Cool and weigh the precipitate to determine the chemical recovery of Pb.
(20) Carefully transfer the Pb-oxalate precipitate into a 20 mL liquid scintillation vial together with the filter.
(21) Add 1 mL of 6M HNO_3 to the vial to dissolve the precipitate.
(22) Mix with 14 mL of scintillation cocktail.
(23) Set up windows for ^{210}Pb and ^{210}Bi and count the three vials (for ^{210}Pb, ^{210}Bi and ^{210}Po) in a liquid scintillation counter until the counting statistic uncertainty is less than 1%.

8.4.2.2. Optimum window setting for ^{210}Pb

The activity concentration of ^{210}Pb is determined by LSC adjusted to the low energy mode and low bias with double energetic window method [7]. For the successful determination of this radionuclide two counting windows should be optimized, because of the overlapping of the beta spectra of ^{210}Pb and ^{210}Bi. The result of the optimization of counting region is shown on Fig. 14 in Appendix IX, where a typical liquid scintillation counting spectrum is presented. In this example the lower limit for the ^{210}Pb energy (window A) is set at channel 115 to avoid the counts caused by chemiluminescence in the cocktail, while the upper limit is set at channel 320, where the ^{210}Pb peak ends.

The lower limit for the ^{210}Bi energy region (window B) is set at channel 320, and the upper limit is set at channel 410 to avoid interference from the ^{210}Po peak.

The efficiency of liquid scintillation for beta particles depends on the energy of the beta decay. For most beta particles with a maximum beta energy above 100 keV, efficiency is high, more than 90%. For lower energy beta particles, the efficiency is usually less, and the real value depends on the degree of quenching in the sample.

To determine the efficiency, a known activity of ^{210}Pb in equilibrium with its daughters has to be measured several times (it is practical to choose more than 10 times of counting for getting a good estimate of the uncertainty in the efficiency).

9. EXPRESSION OF RESULTS

9.1. CALCULATION OF ACTIVITIES OF RELEVANT RADIONUCLIDES

9.1.1. Calculation of the activity of ^{210}Pb

9.1.1.1. Calculation of the counting efficiency of ^{210}Pb

The counting efficiency (ε) of ^{210}Pb can be calculated using equations (1) and (2).

$$\varepsilon = \frac{Z}{R_{cal} \cdot a_{std,\ Pb-210} \cdot m_{T,\ Pb-210} \cdot e^{-\lambda_{Pb-210} \cdot t_{Ts}}} \tag{1}$$

$$Z = r_{nA} - r_{nB} \cdot f_{A/B} \tag{2}$$

where:

$$r_{nA} = r_{gA} - r_{0A}, \qquad r_{nB} = r_{gB} - r_{0B},$$

$f_{A/B}$: Tailing factor (See *9.1.1.2.)*

R_{cal} : Chemical recovery of making the calibration source (see equation (4))

9.1.1.2. Calculation of the tailing factor

The ^{210}Pb energy region (window A) is interfered with counts from ingrown ^{210}Bi. The interference is compensated for by using the ratio of counts in window A to those in window B in a pure ^{210}Bi spectrum: the so-called "tailing factor": $f_{A/B}$. The tailing factor is independent of the activity level of ^{210}Bi in the sample, but is dependent on the quenching level of the sample. The quenching levels of the calibrant, the sample and the reagent blank are necessary to keep constant within ±2% relative standard deviation. The tailing factor can be calculated by the following formula:

$$f_{A/B} = \frac{r_{nA,std,Bi-210}}{r_{nB,std,Bi-210}} \tag{3}$$

where: $r_{nA,std,Bi-210} = r_{gA,std,Bi-210} - r_{0A}$, $\qquad r_{nB,std,Bi-210} = r_{gB,std,Bi-210} - r_{0B}$

9.1.1.3. Chemical recoveries of Pb in calibration source and sample

The chemical recovery of Pb in the calibration source preparation process is determined gravimetrically using equation (4).

$$R_{cal} = \frac{f_g \cdot (m_{of,\,cal} - m_{f,\,cal})}{C_{Pb-c} \cdot m_c} \tag{4}$$

When the amount of Pb in the sample is not negligible compared with that in the Pb carrier, the sample Pb content should be allowed for in calculation of the chemical recovery of Pb.

The chemical recovery of Pb in the sample can be calculated using equations (5) and (6).

$$R = \frac{f_g \cdot (m_{of} - m_f)}{(C_{Pb-c} \cdot m_c + C_{Pb-s} \cdot m_s)} \tag{5}$$

Mass ratio *(f_g)* of atomic mass of Pb to molar mass of Pb-oxalate:

$$f_g = \frac{M_{Pb}}{M_{Pb-oxalate}} \tag{6}$$

9.1.1.4. Calculation of the activity of ^{210}Pb

The activity of ^{210}Pb on the separation date can be calculated from the LSC measurement, using the following equations:

$$a_{Pb\text{-}210,\,s} = \frac{Z \cdot f_{2-Pb} \cdot f_{3-Pb}}{m_s \cdot \varepsilon \cdot R} \tag{7}$$

$$f_{2-Pb} = e^{-\lambda_{Pb-210} \cdot t_2} \tag{8}$$

$$f_{3-Pb} = \frac{\lambda_{Pb-210} \cdot t_3}{1 - e^{\lambda_{Pb-210} \cdot t_3}} \tag{9}$$

However, if the time interval (t_2) between the separation of ^{210}Pb and the beginning of the measurement and the counting time of the sample (t_3) are much smaller than the half-life of ^{210}Pb (22.2 y), f_{2-Pb}, f_{3-Pb}, $u(f_{2-Pb})$ and $u(f_{3-Pb})$ are negligible.

9.1.2. Calculation of the activity of ^{210}Po

The activity of ^{210}Po on the separation date is calculated according to the procedure detailed in IAEA/AQ/12 [8].

9.1.3. Calculation of the activities of the U and Th radioisotopes

The ratio of the net counts of the tracer and analyte peak is used to calculate the activity of the analyte in the sample on the date of chemical separation, taking into account the activity of the tracer solution, the masses of the sample and the tracer used. The activity of the analyte (a_s, Bq·kg^{-1}, dry mass) at the separation time is calculated by the following formula:

$$a_s = \frac{C_T \cdot r_n}{m_s \cdot r_{nT}} \cdot m_T \cdot f_T = \frac{C_T \cdot m_T \cdot f_T}{m_s} \cdot \frac{r_g - r_0}{r_{gT} - r_{0T}} \tag{10}$$

The decay of the tracer between its reference date (from the certificate) and counting is taken into correction by f_T as follows:

$$f_T = e^{-\lambda_T \cdot t_{T,s}} \tag{11}$$

The activity of analyte in the sample should be calculated back to the date of sample collection:

$$a_0 = a \cdot e^{-\lambda \cdot t} \tag{12}$$

The detector efficiency is not needed in isotope dilution alpha spectrometry for calculation of the activity of the analyte, but is needed for calculation of the chemical recovery. It is determined from the activity of the tracer added and the net counts in the corresponding peak as follows:

$$R = \frac{r_{nT}}{C_T \cdot m_T \cdot \varepsilon} \cdot e^{-\lambda_T \cdot t_{T,s}} \tag{13}$$

The detector efficiency is determined by the calibration source prepared in a similar way as the analytes and using the same measurement conditions. For analytes, which are co-precipitated, the calibration source also should be co-precipitated using the same conditions including filter diameter. For analytes, which are electrodeposited, the calibration source should also be prepared by electrodeposition. Efficiency determinations are typically performed and regularly checked in the frame of the analytical quality control. The efficiency can be calculated according to the following equation:

$$\varepsilon = \frac{r_{n,cal}}{A_{cal}} \tag{14}$$

Where:
$r_{n,\,cal}$: net count rate of calibration source in respective ROI
A_{cal}: certified activity of the calibration source

9.1.4. Calculation of the activity of ^{226}Ra

9.1.4.1. Calculation of the chemical recovery of Ra

The chemical recovery is determined by using the peak of ^{217}At at 7066.9 keV (P_α: 0.99932) [9]. The ingrowth of ^{225}Ac ($T_{1/2}$: 10.0 d), the daughter of ^{225}Ra, is directly associated with the short lived progenies ^{221}Fr ($T_{1/2}$: 4.8 min), ^{217}At ($T_{1/2}$: 32.3 ms) and ^{213}Po ($T_{1/2}$: 3.7 µs). When the daughters are in equilibrium with ^{225}Ra, the ^{217}At peak shows no overlap with descendants of natural isotopes of radium in the alpha spectrum (^{225}Ac interferes with ^{224}Ra, ^{221}Fr interferes with ^{220}Rn). From the initial tracer activity, A_T (added ^{229}Th/^{225}Ra), the maximum detectable count rate, r_{nTmax}, is calculated by taking into account the decay of unsupported ^{225}Ra after its separation from Th ($t_{sTh-229}$), as well as the build-up of ^{225}Ac ($t_{sRa-225}$) in the following equation:

$$r_{nT\max} = \varepsilon \cdot A_T \cdot e^{-\lambda_{Ra-225}\cdot(t_{sRa-225}-t_{sTh-229})} \cdot \frac{\lambda_{Ac-225}}{\lambda_{Ac-225}-\lambda_{Ra-225}} \tag{15}$$

The chemical recovery R is calculated as ratio of the measured count rate r_{nT} and theoretical value r_{nTmax}:

$$R = \frac{r_{nT}}{r_{nT\max}} \tag{16}$$

9.1.4.2. Calculation of activity of ^{226}Ra

While A_T is the activity of the ^{225}Ra tracer after the separation from ^{229}Th, its activity at the beginning of the build-up of ^{225}Ac is yielded as follows:

$$A_{Ra-225} = A_T \cdot e^{-\lambda_{Ra-225}\cdot(t_{Ac-225}-t_s)} \tag{17}$$

The activity of ^{225}Ac at any time is given by:

$$A_{Ac-225} = \frac{\lambda_{Ac-225}\cdot A_{Ra-225}\cdot\left(e^{-\lambda_{Ra-225}\cdot(t-t_{Ac-225})} - e^{-\lambda_{Ac-225}\cdot(t-t_{Ac-225})}\right)}{\lambda_{Ac-225}-\lambda_{Ra-225}} \tag{18}$$

Integrating over the counting period with t_m as the start and t_{em} as the end of the measurement results into the activity of ^{225}Ac at t_{em}:

$$A_{Ac-225}(t_m, t_{em}) = A_{Ra-225}\cdot\frac{\lambda_{Ac-225}}{(\lambda_{Ac-225}-\lambda_{Ra-225})\cdot(t_{em}-t_m)}\cdot\left\{\frac{1}{\lambda_{Ra-225}}\cdot\left(e^{-\lambda_{Ra-225}\cdot(t_m-t_{Ac-225})} - e^{-\lambda_{Ra-225}\cdot(t_{em}-t_{Ac-225})}\right)\right.$$

$$\left. - \frac{1}{\lambda_{Ac-225}}\cdot\left(e^{-\lambda_{Ac-225}\cdot(t_m-t_{Ac-225})} - e^{-\lambda_{Ac-225}\cdot(t_{em}-t_{Ac-225})}\right)\right\} \tag{19}$$

Finally the activity concentration of ^{226}Ra is the following:

$$A_{Ra-226} = A_{Ac-225}(t_{m,}t_{em}) \cdot \frac{r_{Ra-226}}{r_{At-217}} \tag{20}$$

where:

$$r_{Ra-226} = \frac{n_{Ra-226}}{t_{em} - t_m} - \frac{n_{Ra-226,0}}{t_0} \quad \text{and} \quad r_{At-217} = \frac{n_{At-217}}{t_{em} - t_m} - \frac{n_{At-217,0}}{t_0}$$

9.2. EXPRESSION OF COMBINED UNCERTAINTIES OF RELEVANT RADIONUCLIDES

According to the Guide to Expression of Uncertainty in Measurement [10–12], the method for calculating standard uncertainty and combined uncertainty for the relevant radioisotopes is described in detail in Appendix X. An example is calculated for each relevant radionuclide in Appendix XI. The detailed study about the usual contributors of uncertainty in the nuclear analytical techniques could be found in the IAEA-TECDOC-1401 [11].

9.3. DECISION THRESHOLD

In accordance with ISO 11929:2010, the decision threshold gives a decision on whether or not the physical effect quantified by the measurand is present.

The decision threshold, a^*, is the non-negative measurand quantifying the physical effect of interest. If the result, a, is below the decision threshold, the result can not be attributed to the physical effect, nevertheless it can not be concluded that it is absent. If the physical effect is really absent, the probability of taking the wrong decision, that the effect is present, is equal to the specified probability of α (the error of first kind, often chosen 0.05 and moreover $\alpha=\beta$, where β is the error of second kind; then $k_{1-\alpha}=k_{1-\beta}=1.65$). Any of the determined primary measurement result is only significant for the true value of the measurand to differ from zero, if it is larger than the decision threshold given here:

$$a^*=k_{1-\alpha} \cdot u(0),$$

where $u(0)$ is the uncertainty associated to the non-negative measurand, uncertainty of decision threshold itself (with other words: it can be estimated as uncertainty associated to slightly higher values than background or reagent blank depending on the procedure) and can be quantified here as:

$$u(0) = \frac{1}{m_s \cdot \varepsilon \cdot R} \cdot \sqrt{\frac{n_0}{t_3 \cdot t_0} + \frac{n_0}{t_0^2}} \tag{21}$$

The decision threshold of the isotopes in the applied procedure is given in Table 12 in Appendix XII.

9.4. DETECTION LIMIT

In accordance with ISO 11929:2010, the detection limit indicates the smallest true value of the measurand, which can be still detected with the applied procedure; this gives a decision on whether or not the measurement procedure satisfies the requirements and is therefore suitable for the intended measurement purpose. In order to find out whether a procedure is suitable for the purpose, the detection limit is compared with the specified guideline value of the measurand.

The detection limit, $a^{\#}$, is the smallest true value of the measurand, for which the probability of the wrong assumption that the physical effect is absent does not exceed the probability β (error of the second kind). The detection limit is obtained as the smallest solution of the following equation:

$a^{\#}=a^{*}+k_{1-\beta}\cdot(a^{\#})$, where $a^{\#} \geq a^{*}$ (22)

Equation (22) is an implicit equation which can be calculated by iteration. As a starting approximation $a_1=3\cdot a^{*}$ can be chosen; in most cases the iteration converges and the linear interpolation with approximation of $a^{\#}=(k_{1-\alpha}+k_{1-\beta})\cdot u(a)$ leads to the approximation:

$$a^{\#} = q + \sqrt{q^2 + (k_{1-\beta}^2 - k_{1-\alpha}^2)\cdot u^2(0)} \qquad (23)$$

$$\text{with } q = k_{1-a}\cdot u(0) + \frac{1}{2}\cdot\left\{\frac{k_{1-\beta}^2}{a_1}\cdot\left[u^2(a_1) - u^2(0)\right]\right\} \qquad (24)$$

If $\alpha=\beta$, than $k_{1-\alpha}=k_{1-\beta}=k$, $a^{\#}=2\cdot q$ follows:

$$a^{\#} = 2k\cdot u(0) + \frac{k^2}{a_1}\cdot\left[u^2(a_1) - u^2(0)\right] \qquad (25)$$

Where, α is the probability of the error of first kind; the probability of rejecting a hypothesis if it is true, and β is the probability of the error of second kind; the probability of accepting an hypothesis if it is false.

The detection limit of the isotopes in the applied procedure is given in Table 12 in Appendix XII.

The difference between using the decision threshold and using the detection limit is that the measured values are to be compared with the decision threshold, whereas the detection limit is to be compared with the guideline value (guideline value corresponds to scientific, legal or other requirements for which the measuring procedure intended to assess).

10. VALIDATION OF THE PROCEDURE

The validation of the procedure was carried out using the IAEA Reference Material: IAEA-434 Phosphogypsum [4, 12]. The results of the validation procedure were evaluated in terms of relative bias, repeatability and reproducibility. The control charts showing the results for the individual radionuclides with their associated uncertainties are presented in Fig. 16-22 in Appendix XIII. The analysis of variance using ANOVA for the relevant radionuclides is given in Table 13 in Appendix XIII.

The validation results of the procedure and the method performance parameters (trueness, precision, repeatability and reproducibility) are shown in Table 14 in Appendix XIV for the relevant radioisotopes.

10.1. TRUENESS OF THE METHOD

The relative bias of the method is calculated by the following formula:

$$\delta(\%) = \frac{\overline{X} - C}{C} \times 100 \qquad (26)$$

10.2. PRECISION OF THE METHOD

The precision index (*PI(%)*) is calculated according to the following formula:

$$PI(\%) = \sqrt{\frac{u(C)^2}{C^2} + \frac{u(\overline{X})^2}{\overline{X}^2}} \times 100 \qquad (27)$$

10.3. REPEATABILITY

The repeatability limit is estimated by analyzing five subsamples from the same bottle of the IAEA-434 reference material for the relevant radionuclides in repeatability conditions: instrument, analyst, shortest time, etc. The repeatability limit is calculated by the following formula:

$$r_L = 2.8 S_r \qquad (28)$$

10.4. REPRODUCIBILITY

The reproducibility limit is also estimated by analyzing the IAEA-434 reference material from ten duplicates. Samples were taken from ten randomly selected packing unit, with at least one parameter being changed in the analytical system (analyst, analysis date, instrument, etc.). The reproducibility limit is calculated by the following formula:

$$R_L = 2.8 S_R \qquad (29)$$

10.5. OUTLIER TEST

The presence of individual values that appear to be inconsistent with all other laboratories or values may cause some problems during the final evaluation of data. According to ISO 5725-2, an outlier test should be performed before the calculation of repeatability and reproducibility. The analysis includes a systematic application of a statistical test of outliers, a great variety are available, which could be used for the purposes of this part of ISO/IEC 17025. Usually the graphical consistency technique or the numerical outlier test is applied. Cochran's test of variabilities should be applied first, and then any necessary action should be taken. Grubb's test is primarily a test of in between laboratory variability.

10.6. ACCEPTANCE CRITERIA

The method can be accepted if

$$PI(\%) < 25\%$$

$$\left|\delta\right| < R_L \qquad (30)$$

According to these criteria the method performs well.

11. TEST REPORT

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

- A title (test report, calibration report, reference material production, etc.);
- The name and address of the laboratory, and location where any part of the test or calibration or production of reference material was carried out;
- Unique identification of the report on each page with numbering of pages;
- Analysis request code;
- Reference to the measurement method used;
- Sampling date (if available);
- Sample description;
- Sample code or identification number;
- Date of the separation of analyte;
- Applied tracers with their reference dates and activity values with the code of their certificate;
- The results with units of measurement and associated uncertainty value expressed in the same unit as the result;
- Date to which the test result has been corrected (corrected to the sampling date or separation time: dd-mm-yyyy);
- Responsible person.

12. CONCLUSION

A procedure was developed and tested for the sequential determination of ^{210}Po, ^{210}Pb, Th and U radioisotopes, and ^{226}Ra in phosphogypsum using liquid scintillation counting and alpha spectrometry. The radionuclides are radiochemically separated using sequential extraction chromatographies and co-precipitation operations.

According to the repeatability and reproducibility tests, the measurement process is considered to perform adequately.

The method is recommended for the analysis of technically enhanced radionuclides in phosphogypsum, a by-product derived from the wet process production of phosphoric acid.

APPENDIX I

U AND TH DECAY SERIES

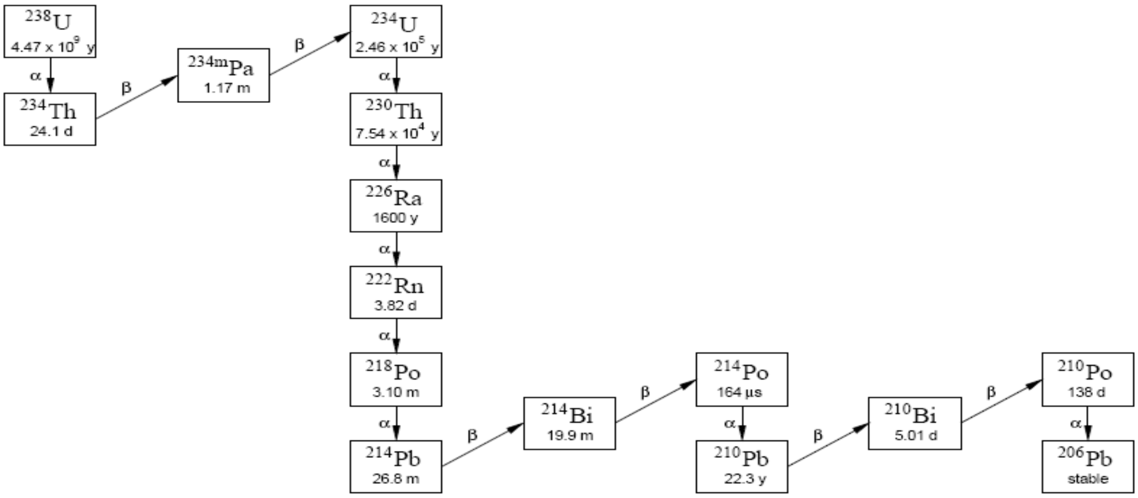


FIG. 1. Decay chain of ^{238}U. [5]

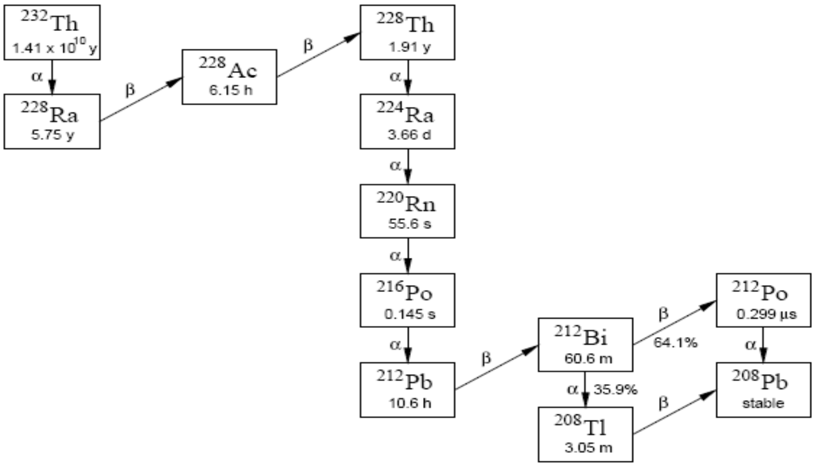


FIG. 2. Decay chain of ^{232}Th. [5]

APPENDIX II

NUCLEAR DATA OF RELEVANT RADIONUCLIDES AND DECAY CHAINS OF U AND TH SERIES

TABLE 2. NUCLEAR DATA OF RELEVANT RADIONUCLIDES [13]

Radionuclide	Half-life	Disintegration modes	E (MeV)*	Probability (%)
^{225}Ac	10.0(1) d	α	5.580 5(14)	0.95(4)
		α	5.599 3(14)	0.114(7)
		α	5.609 0(14)	1.09(5)
		α	5.637 3(14)	4.16(23)
		α	5.682 2(14)	1.31(4)
		α	5.686 4(14)	0.021(14)
		α	5.723 1(14)	2.03(23)
		α	5.730 5(14)	1.6(3)
		α	5.731 6(14)	1.24(10)
		α	5.731 9(17)	9.0(5)
		α	5.797 7(14)	6.2(9)
		α	5.793 1(21)	18.9(20)
		α	5.804 2(14)	0.3
		α	5.829 6(14)	52.4(24)
^{217}At	32.3(4) x 10^{-3} s	α	6.484 7(16)	0.016 7(8)
		α	6.813 8(16)	0.038 4(15)
		α	7.066 9(16)	99.932(3)
^{133}Ba	10.540(6) y	γ	0.053 162 2(6)	2.14(3)
		γ	0.079 614 2(12)	2.65(5)
		γ	0.080 997 9(11)	32.9(3)
		γ	0.276 398 9(12)	7.16(5)
		γ	0.302 850 8(5)	18.34(13)
		γ	0.356 012 9(7)	62.05(19)
		γ	0.383 848 5(12)	8.94(6)
^{210}Bi	5.012(5) d	β	1.162 1(8)	99.999 86(2)
^{212}Bi	60.54(6) min	β	0.633(2)	1.90(4)
		β	0.741(2)	1.45(29)
		β	1.527(2)	4.58(21)
		β	2.254(2)	55.23(21)
		α	6.050 92(4)	25.1(1)
		α	6.090 02(4)	9.7(1)
^{221}Fr	4.79(2) min	α	6.126 3(15)	15.1(2)
		α	6.243(2)	1.34(7)
		α	6.341 0(13)	82.8(2)

TABLE 2. NUCLEAR DATA OF RELEVANT RADIONUCLIDES [13] (Cont.)

Radionuclide	Half-life	Disintegration modes	E (MeV)*	Probability (%)
^{210}Pb	22.23(12) y	β	0.017 0(5)	80.2(13)
		β	0.063 5(5)	19.8(13)
		γ	0.046 539(1)	4.252(40)
^{208}Po**	2.898(2) y	α	5.114 9(14)	99.995 8(4)
		α	4.220(15)	2.4(7)x10^{-4}
^{209}Po	115(13) y	α	4.885(2)	19.8(32)
		α	4.883(2)	79.2(32)
		α	4.622(5)	0.548(7)
^{210}Po	138.376 3(17) d	α	5.304 33(7)	99.998 76
		α	4.516 66(9)	0.001 24(4)
^{213}Po	3.70(5) x 10^{-6} s	α	8.375 9(25)	99.995 0(5)
^{216}Po	0.150(5) s	α	6.778 6(5)	99.998 1(3)
		α	5.988 6(10)	0.001 9(3)
^{218}Po	3.094(6) min	α	6.002 35(9)	99.976 9(32)
^{223}Ra**	11.43(5) d	α	5.747 0(4)	9.00(20)
		α	5.716 23(29)	51.6(13)
		α	5.606 73(30)	25.2(5)
		α	5.539 80(90)	9.00(20)
^{224}Ra	3.627(7) d	α	5.448 81(16)	5.26(7)
		α	5.685 50(15)	94.72(7)
		γ	0.240 986(6)	4.12(4)
^{225}Ra	14.82(19)d	β	0.316(5)	68.8(20)
		β	0.356(5)	31.2(20)
		γ	0.040 09(5)	30.0(7)
^{226}Ra	1 600(7) y	α	4.601(1)	5.95(4)
		α	4.784 34(25)	94.038(40)
^{228}Ra	5.75(4) y	β	0.0127(7)	30(10)
		β	0.0256(7)	8.7(9)
		β	0.0391(7)	49(10)
		β	0.0395(7)	12(10)
^{220}Rn	55.8(3) s	α	5.748 46(14)	0.118(15)
		α	6.288 22(10)	99.882(15)
^{222}Rn	3.823 2(8) d	α	5.489 48(30)	99.92(1)
^{228} Th	698.60(23) d	α	5.176 89(23)	0.20(2)
		α	5.211 08(22)	0.38(3)
		α	5.340 38(22)	26.2(2)
		α	5.423 28(22)	73.2(2)

TABLE 2. NUCLEAR DATA OF RELEVANT RADIONUCLIDES [13] (Cont.)

Radionuclide	Half-life	Disintegration modes	E (MeV)*	Probability (%)
^{229}Th**	7 340(160) y	α	5.053(2)	6.60(10)
		α	4.978 5(12)	3.17(4)
		α	4.967 5(12)	5.97(6)
		α	4.901 0(12)	10.20(8)
		α	4.845 3(12)	56.20(20)
		α	4.814 6(12)	9.30(8)
^{230}Th**	7.538(30) x 10^4 y	α	4.687 0(15)	76.3(3)
		α	4.620 5(15)	23.4(10)
^{232}Th	14.02(6) x 10^9 y	α	3.810 0(14)	0.068(20)
		α	3.948 5(14)	21.0(13)
		α	4.011 2(14)	78.9(13)
^{234}Th	24.10(3) d	β	0.105(10)	6.5(7)
		β	0.106(10)	14.1(12)
		β	0.198(10)	77.8(15)
		γ	0.063 30(2)	3.75(8)
^{232}U	70.6(11) y	α	5.263 48(9)	30.6(6)
		α	5.320 24(9)	69.1(6)
^{233}U**	1.592(2) x 10^5 y	α	4.824 2(12)	84.3(6)
		α	4.783 5(12)	13.2
^{234}U	2.455(6) x 10^5 y	α	4.603 5(7)	0.210(2)
		α	4.722 4(7)	28.42(2)
		α	4.774 6(7)	71.37(2)
^{235}U	704(1) x 10^6 y	α	4.322(4)	3.33(6)
		α	4.397 8(13)	57.19(20)
		α	4.414 9(5)	3.01(16)
		α	4.502 4(7)	1.28(5)
		α	4.556 0(4)	3.79(6)
		α	4.596 4(13)	4.74(6)
^{236}U	2.343(6) x 10^7 y	α	4.445(5)	26.1(40)
		α	4.494(3)	73.8(40)
^{238}U	4.468(5) x 10^9 y	α	4.038(5)	0.13(3)
		α	4.151(5)	22.33(50)
		α	4.198(3)	77.54(50)

* E_{max} for beta emitting radioisotopes.

** Data were taken from [14]

APPENDIX III

PROPERTIES OF RESINS

Sr Resin:

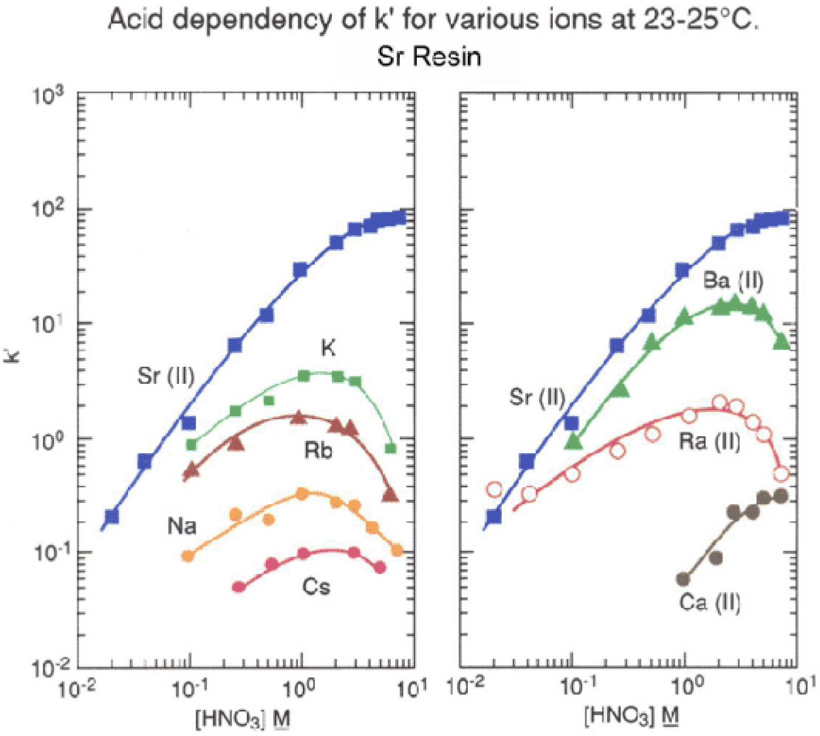


FIG. 3. Capacity factor of Sr resin in nitric acid (www.eichrom.com) [15].

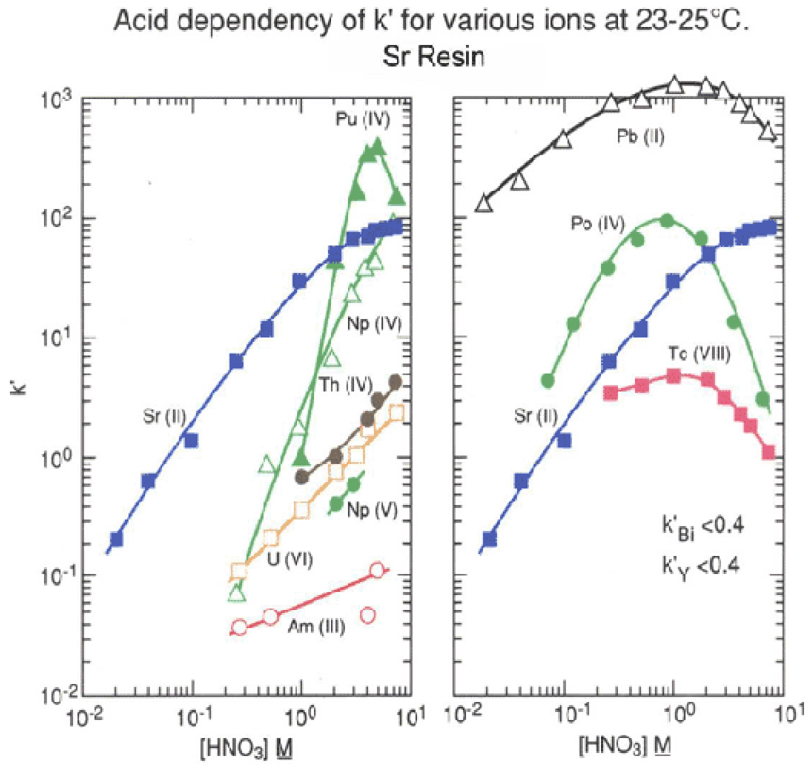


FIG. 4. Capacity factor of Sr resin in nitric acid (www.eichrom.com) [16].

TEVA resin

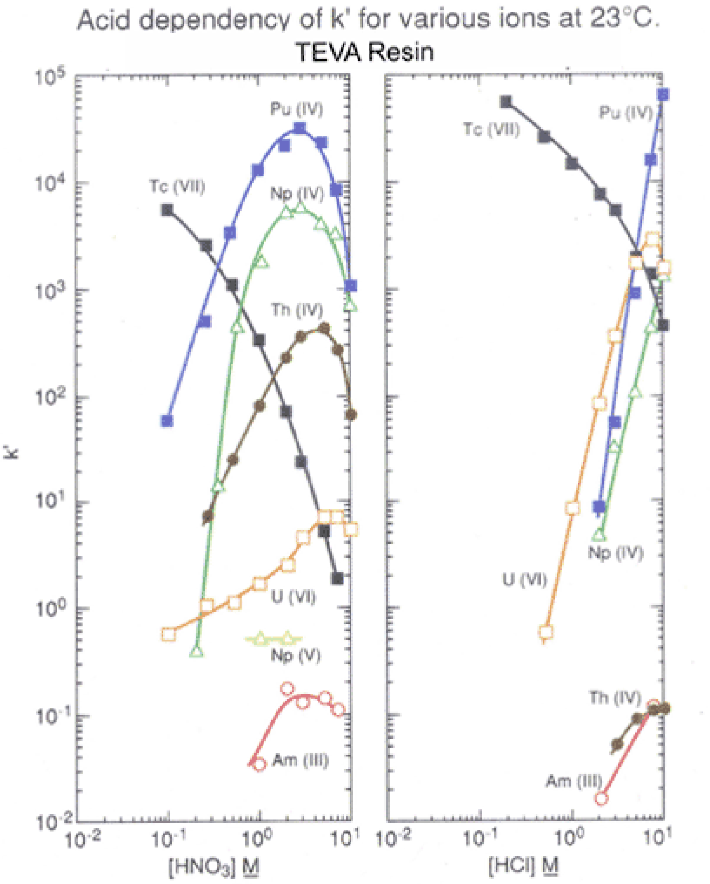


FIG. 5. Capacity factor of TEVA resin in nitric acid and hydrochloric acid (www.eichrom.com) [17].

UTEVA resin

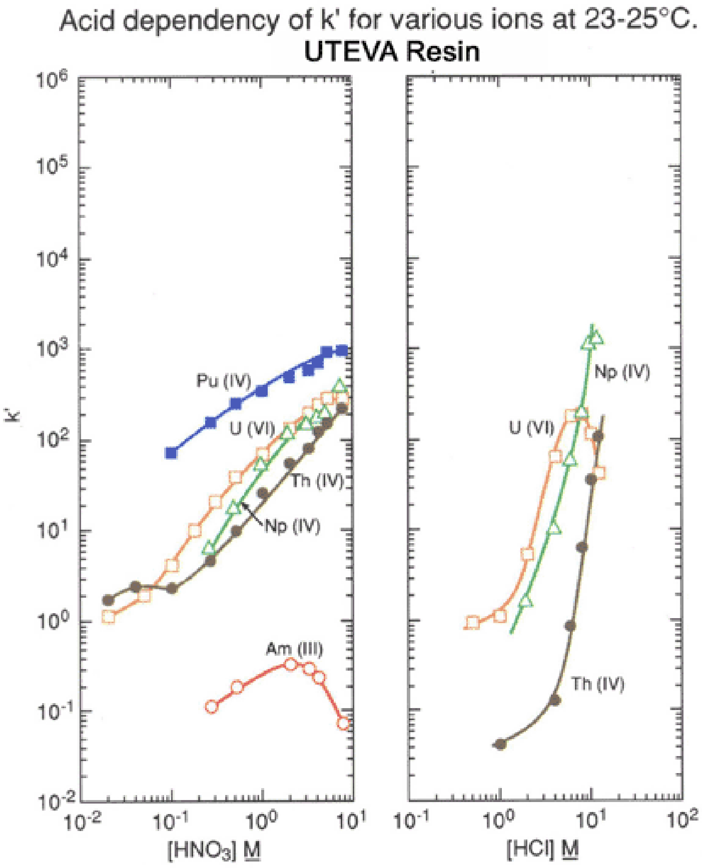


FIG. 6. Capacity factor of UTEVA resin in nitric acid and hydrochloric acid (www.eichrom.com) [18].

APPENDIX IV

FLOW CHART FOR SEQUENTIAL SEPARATION OF 210PO, 210PB, TH AND U RADIOISOTOPES, AND 226RA IN PHOSPHOGYPSUM

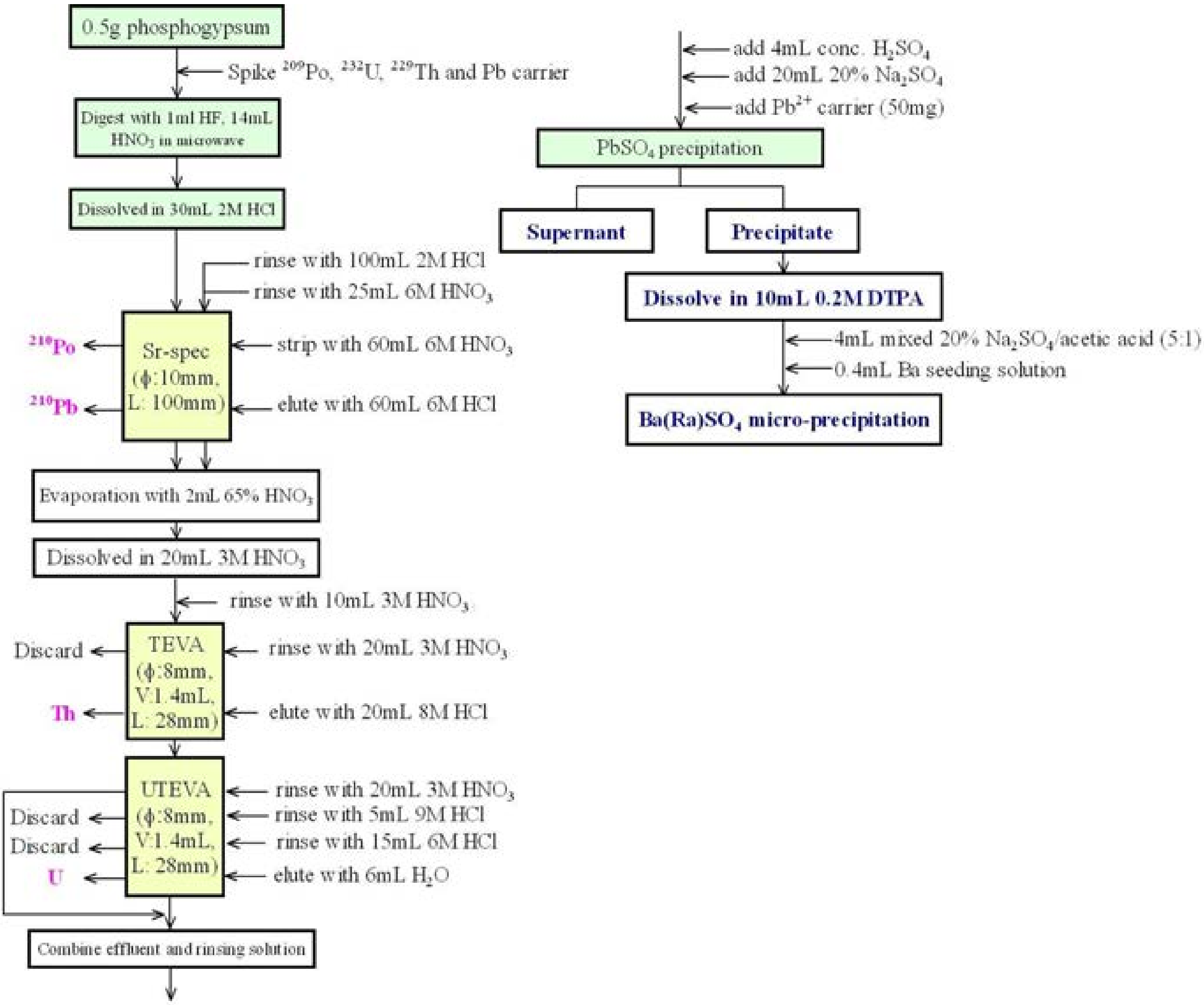


FIG. 7. Flow chart for sequential separation of ^{210}Po, ^{210}Pb, Th and U radioisotopes, and ^{226}Ra in phosphogypsum

APPENDIX V

PREPARATION OF SPECIFIC CHEMICALS

- Ba seeding solution [6]: Weigh between 0.012 g and 0.016 g of $BaCl_2 \cdot 2H_2O$ into a tall 150 mL quartz beaker. Add approximately 0.4 mL of ultra pure water to completely dissolve the $BaCl_2 \cdot 2H_2O$. In a fume hood add 10 mL of a 70% sodium hydrogen sulfate solution, and 2 drops of 72% $HClO_4$. Evaporate the solution on a hot plate or a burner at high heat with continuous swirling until most of the excess sulfuric acid has been expelled and a pyrosulfate fusion is obtained. Cool the beaker while rolling the melt around the sides so that the cake is deposited on the sides as uniformly as possible to facilitate rapid dissolution. Cool the beaker and contents to room temperature in a desiccating chamber. Add a solution of 50 mL of 20% Na_2SO_4 to the beaker. Swirl continuously until the cake is completely dissolved. Place it in an ultrasonic bath for 10 minutes before each use. If a build up of particulate matter occurs, then make a fresh solution.

- Sodium sulfate wash solution: Dissolve 100 g of anhydrous Na_2SO_4 in 2 L of 0.5% H_2SO_4. Filter through a 0.45 μm pore size membrane filter.

APPENDIX VI

TRACERS AND CARRIER

Tracer for Polonium determination:

The two tracers commonly used for ^{210}Po determination are ^{208}Po and ^{209}Po. ^{209}Po has a clear advantage over ^{208}Po in energy separation from the ^{210}Po peak and is the preferred tracer, if available. It should also be noted that ^{208}Po solutions normally contain traces of ^{209}Po.

Tracer for Thorium determination:

Naturally occurring thorium can be determined by the following tracers: ^{228}Th and ^{229}Th. Both of them have short lived daughters, which emit alpha particles, but as the energies of all their daughters are higher than 5.68 MeV, thus no spectral interference occurs from ingrowth of daughters of either ^{228}Th or ^{229}Th. The ^{228}Th daughter of ^{232}U can be used as a tracer for the determination of ^{230}Th and ^{232}Th. In this case, the natural ^{228}Th content in phosphogypsum should be measured or estimated separately to allow for this [4].

Tracer for Uranium determination:

Naturally occurring uranium can be determined by the following tracers: ^{232}U, ^{233}U or ^{236}U. Among them ^{232}U (containing ^{228}Th daughter in known ratio, close to 1) is applied most frequently. The amount of ^{232}U tracer to be added to the sample should be carefully calculated, because this is the highest-energy uranium peak in the uranium spectrum and hence its tailing might affect other peaks in low energy region if the added concentration is too high.

Tracer for Radium determination:

In the case of ^{226}Ra analysis several tracers such as ^{133}Ba, ^{223}Ra, ^{224}Ra, ^{225}Ra might be applied. ^{133}Ba is the most commonly used tracer for the determination of ^{226}Ra, since it can be measured by gamma-ray spectrometry. A disadvantage of this tracer is that, although its chemical behavior is very similar to that of Ra, their chemical behavior is not identical as they are different elements. An alternative is ^{225}Ra (daughter of ^{229}Th), which does not exist in nature, and its decay does not produce radon, which might escape from the source. ^{225}Ra is both a beta and gamma emitter, with a gamma line at 40.09 keV (P_γ: 0.300), which is well measurable with an n-type HPGe detector with carbon-epoxi or Be window. Alternatively, its descendants ^{225}Ac, ^{221}Fr, ^{217}At are alpha emitters and the determination of chemical recovery is possible via ^{217}At at 7.066 7 MeV (P_α: 0.999 32) using ingrowth decay equations [4].

Carrier:

If there is no suitable radioactive tracer available, the chemical recovery can be checked by using an inactive carrier, namely a stable isotope of the same element. In the present case, 30 mg of Pb^{2+} carrier is used as $Pb(NO_3)_2$ solution for checking the chemical recovery of ^{210}Pb determination gravimetrically.

APPENDIX VII

PRECAUTIONS

- Do not ash the sample if ^{210}Po determination is required, gentle drying is allowed, but not higher than 80^{o}C.

- During the handling of the ion exchange chromatography columns, always keep several mm of liquid above the surface of resin, do not allow it to become dry during the separation steps.

- Labeling of the different fractions is essential to avoid mixing solutions, this includes the different load solutions and chemicals.

- The complete separation of Po from U is important, because ^{210}Po (E_α: 5.263 MeV) can interfere with the alpha peak of ^{232}U (E_α: 5.320 MeV) and its activity is much higher than that of U in phosphogypsum. In addition ^{209}Po (E_α: 4.866 MeV) can interfere with the alpha peak of ^{234}U (E_α: 4.766 MeV).

- The complete separation of Th from U is also important, because several peaks in the spectra overlap.

- Applying ^{225}Ra as a yield tracer for the determination of ^{226}Ra in the radiochemical procedure needs to include steps to guarantee the complete separation of the parent/progeny couples, ^{229} Th/^{225}Ra and ^{225}Ra/^{225}Ac.

APPENDIX VIII

TYPICAL ALPHA SPECTRA OF ANALYTES

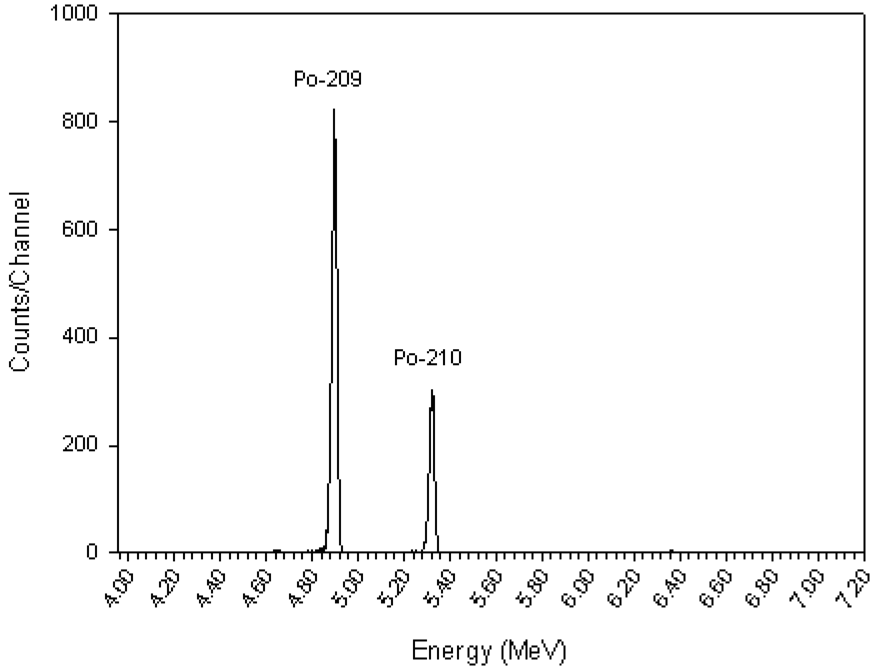


FIG. 8. Alpha spectrum of Po isotopes.

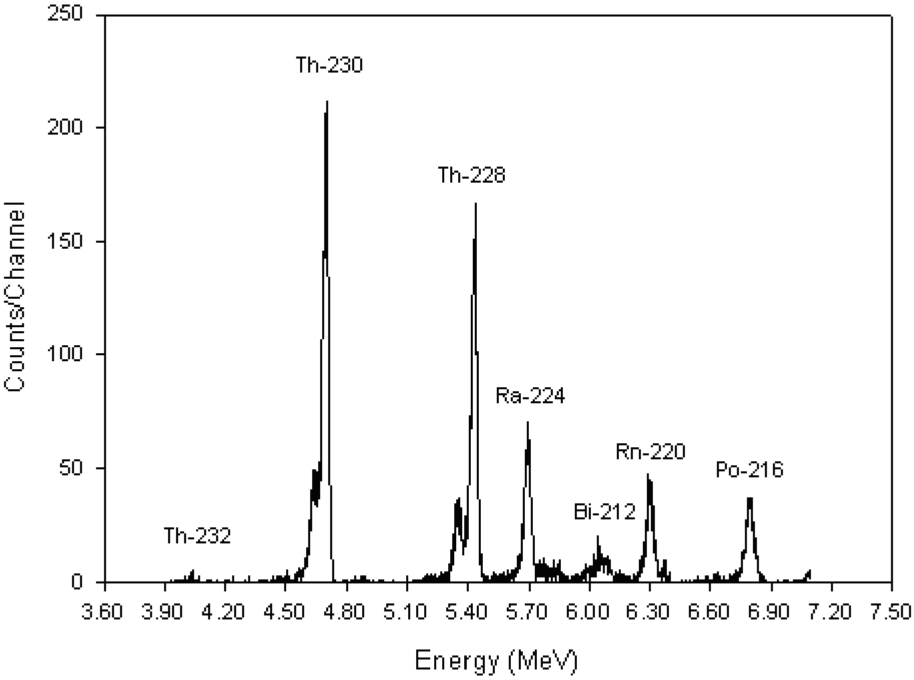


FIG. 9. Alpha spectrum of Th isotopes in phosphogypsum (with progenies), ^{228}Th is resulted from the ^{232}U tracer spiked in the sample.

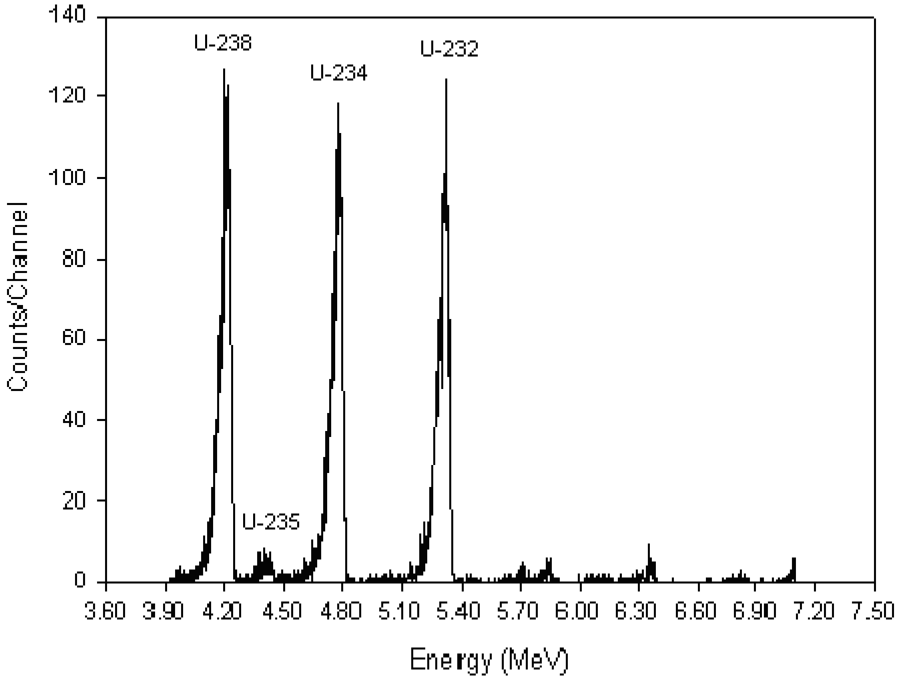


FIG. 10. Alpha spectrum of U isotopes.

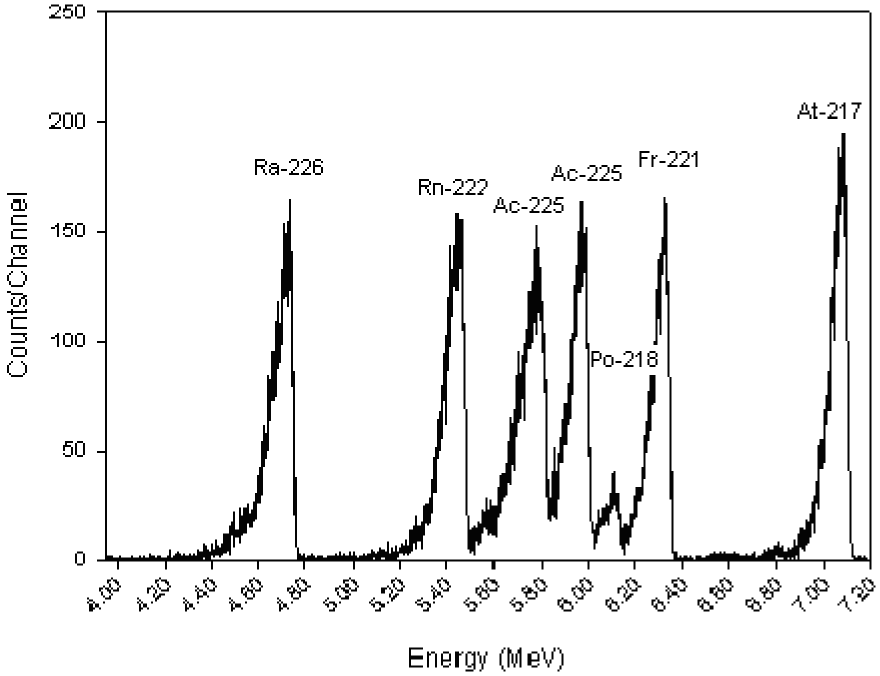


FIG. 11. Alpha spectrum of ^{226}Ra and its progenies (spiked with ^{225}Ra).

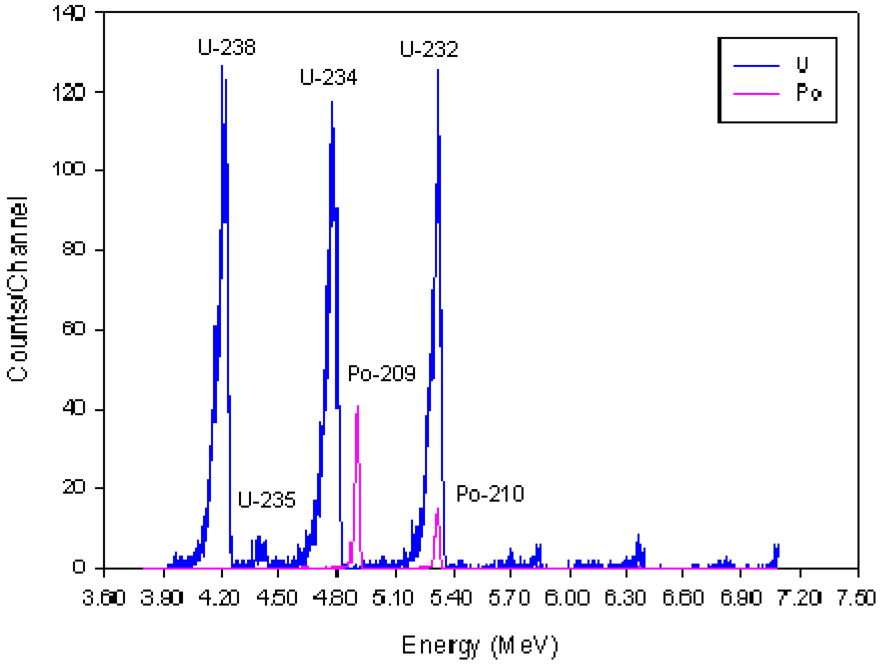


FIG. 12. Overlapping alpha spectra of U and Po isotopes.

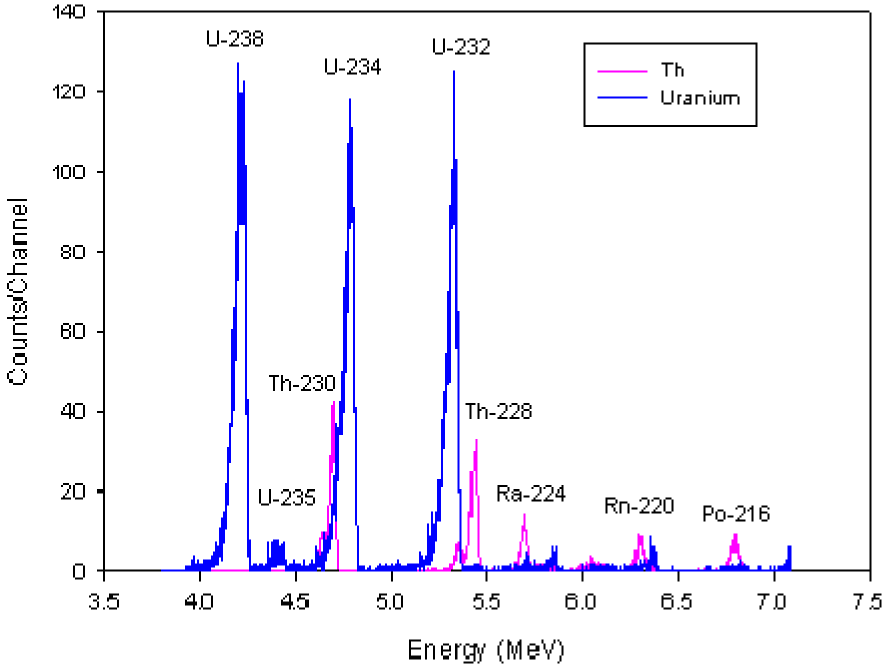


FIG. 13. Overlapping alpha spectra of U and Th (with progenies) isotopes.

APPENDIX IX

TYPICAL LIQUID SCINTILLATION SPECTRA

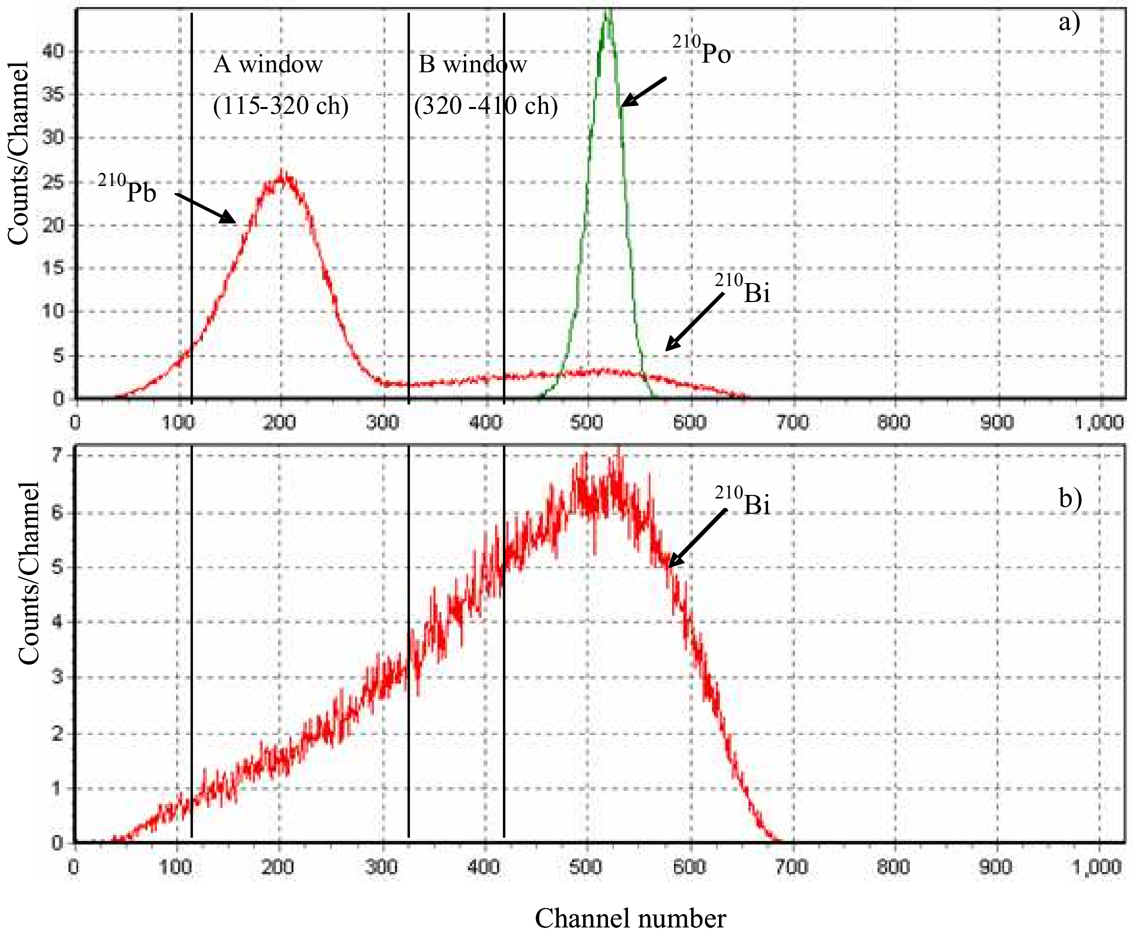


FIG. 14. Typical liquid scintillation spectra of beta emitting ^{210}Pb and ^{210}Bi and alpha emitting ^{210}Po (calibration sources) a) ^{210}Pb, ^{210}Bi and ^{210}Po spectra, b) pure ^{210}Bi spectrum.

APPENDIX X

CALCULATIONS OF STANDARD UNCERTAINTY AND COMBINED UNCERTAINTY

Uncertainty of the ^{210}Pb result

Uncertainty of counting efficiency of ^{210}Pb [19]

$$u(\varepsilon) = \sqrt{\left(\frac{\varepsilon}{Z}\right)^2 \cdot u(Z)^2 + (\varepsilon \cdot t_b)^2 \cdot u(\lambda_{Pb-210})^2 + \left(-\frac{\varepsilon}{a_{Pb-210,\,std}}\right)^2 \cdot u(a_{Pb-210,\,std})^2 + \left(-\frac{\varepsilon}{R_{cal}}\right)^2 \cdot u(R_{cal})^2 + \left(-\frac{\varepsilon}{m_{T,\,Pb}}\right)^2 \cdot u(m_{T,\,Pb})^2} \tag{31}$$

$$u\,(\mathrm{Z}) = \sqrt{u(r_{n\,A})^2 + (-f_{A/B})^2 \cdot u(r_{n\,B})^2 + (-r_{n\,B})^2 \cdot u(f_{A/B})^2} \tag{32}$$

$$u\,(r_{nA}) = \sqrt{u\,(r_{gA})^2 + u\,(r_{0A})^2} \tag{33}$$

$$u\,(r_{nB}) = \sqrt{u\,(r_{gB})^2 + u\,(r_{0B})^2} \tag{34}$$

Uncertainty of the tailing factor, $f_{A/B}$

The uncertainty of the tailing factor, $f_{A/B}$, is calculated according to the following equations:

$$u(f_{A/B}) = f_{A/B} \cdot \sqrt{\left(\frac{u\,(r_{nA,\ cal,\,Bi-210})}{r_{nA,\ cal,\,Bi-210}}\right)^2 + \left(\frac{u\,(r_{nB,\ cal,\,Bi-210})}{r_{nB,\ cal,\ Bi-210}}\right)^2} \tag{35}$$

$$u\,(r_{nA,\,cal,\,Bi-210}) = \sqrt{u\,(r_{gA,\,cal,\,Bi-210})^2 + u\,(r_{0A})^2} \tag{36}$$

$$u\,(r_{nB,\,cal,\,Bi-210}) = \sqrt{u\,(r_{gB,\,cal,\,Bi-210})^2 + u\,(r_{0B})^2} \tag{37}$$

The uncertainty of counting efficiency for ^{210}Pb can be calculated using equation (38).

$$u(\varepsilon) = \sqrt{\left(\frac{\varepsilon}{Z}\right)^2 \cdot u(Z)^2 + (\varepsilon \cdot t_b)^2 \cdot u(\lambda_{Pb-210})^2 + \left(-\frac{\varepsilon}{a_{Pb-210,\,std}}\right)^2 \cdot u(a_{Pb-210,\,std})^2 + \left(-\frac{\varepsilon}{R_{cal}}\right)^2 \cdot u(R_{cal})^2 + \left(-\frac{\varepsilon}{m_{T,\,Pb}}\right)^2 \cdot u(m_{T,\,Pb})^2} \tag{38}$$

$$u\,(\mathrm{Z}) = \sqrt{u(r_{n\,A})^2 + (-f_{A/B})^2 \cdot u(r_{n\,B})^2 + (-r_{n\,B})^2 \cdot u(f_{A/B})^2} \tag{39}$$

$$u(r_{nA}) = \sqrt{u(r_{gA})^2 + u(r_{0A})^2} \tag{40}$$

$$u(r_{nB}) = \sqrt{u(r_{gB})^2 + u(r_{0B})^2} \tag{41}$$

Uncertainty of chemical recovery of Pb

Uncertainty of chemical recoveries of Pb in the calibration source:

$$u\,(\mathrm{R}_{\mathrm{cal}}) = \left\{ \left(\frac{R_{cal}}{f_g} \right)^2 \cdot u(f_g)^2 + \left(\frac{R_{cal}}{(m_{of,cal} - m_{f,cal})} \right)^2 \cdot u(m_{of,cal})^2 + \left(-\frac{R_{cal}}{(m_{of,cal} - m_{f,cal})} \right)^2 \cdot u(m_{f,cal})^2 \right.$$

$$\left. + \left(-\frac{R_{cal} \cdot m_c}{(C_{Pb-c} \cdot m_c)} \right)^2 \cdot u(C_{Pb-c})^2 + \left(-\frac{R_{cal} \cdot C_{Pb-c}}{(C_{Pb-c} \cdot m_c)} \right)^2 \cdot u(m_c)^2 \right\}^{\frac{1}{2}} \tag{42}$$

The uncertainty of the chemical recovery of Pb in the sample can be calculated according to:

$$u\,(\mathrm{R}) = \left\{ \left(\frac{R}{f_g} \right)^2 \cdot u(f_g)^2 + \left(\frac{R}{(m_{of} - m_f)} \right)^2 \cdot u(m_{of})^2 + \left(-\frac{R}{(m_{of} - m_f)} \right)^2 \cdot u(m_f)^2 \right.$$

$$+ \left(-\frac{R \cdot m_c}{(C_{Pb-c} \cdot m_c + C_{Pb-s} \cdot m_s)} \right)^2 \cdot u(C_{Pb-c})^2 + \left(-\frac{R \cdot C_{Pb-c}}{(C_{Pb-c} \cdot m_c + C_{Pb-s} \cdot m_s)} \right)^2 \cdot u(m_c)^2$$

$$\left. + \left(-\frac{R \cdot m_s}{(C_{Pb-c} \cdot m_c + C_{Pb-s} \cdot m_s)} \right)^2 \cdot u\,(C_{Pb-s})^2 + \left(-\frac{R \cdot C_{Pb-s}}{(C_{Pb-c} \cdot m_c + C_{Pb-s} \cdot m_s)} \right)^2 \cdot u\,(m_s)^2 \right\}^{\frac{1}{2}} \tag{43}$$

Uncertainty of mass ratio

The uncertainty of the mass ratio *(f_g)* of atomic mass of Pb to molar mass of Pb-oxalate is calculated using the equations below:

$$u(f_g) = f_g \cdot \sqrt{ \left(\frac{u_{\mathrm{M}_{\mathrm{Pb}}}}{M_{Pb}} \right)^2 + \left(\frac{u_{M_{Pb\text{-}oxalate}}}{M_{Pb-oxalate}} \right)^2 } \tag{44}$$

The uncertainty of the molar mass of lead oxalate $u(M_{Pb\text{-}oxalate})$ can be derived by combining standard uncertainties in atomic masses of its constituents as shown in Table 3.

TABLE 3. STANDARD UNCERTAINTIES OF ATOMIC WEIGHT AND THE GRAVIMETRIC FACTOR f_g

Element	Atomic weight ($g{\cdot}mol^{-1}$)	Quoted uncertainty ($g{\cdot}mol^{-1}$)	Conversion factor	Standard uncertainty ($g{\cdot}mol^{-1}$)	Mass ratio of atomic mass of Pb to molar mass of Pb-oxalate	Uncertainty of atomic mass of Pb to molar mass of Pb-oxalate
Pb	207.2152	0.00015	$\sqrt{3}$	0.000087	0.7019	0.000002
C	12.0107	0.0008	$\sqrt{3}$	0.00046		
O	15.9994	0.0003	$\sqrt{3}$	0.00017		

Combined uncertainty of activity of ^{210}Pb

The combined uncertainty of the ^{210}Pb activity is calculated using equation (45).

$$u_c(a_{Pb,1}) = \left\{\left(\frac{a_{Pb-210,s}}{Z}\right)^2 \cdot u(r_{nA})^2 + \left(-f_{A/B}\cdot\frac{a_{Pb-210,s}}{Z}\right)^2 \cdot u(r_{nB})^2 + \left(-r_{nB}\cdot\frac{a_{Pb-210,s}}{Z}\right)^2 \cdot u(f_{A/B})^2 + \left(-\frac{a_{Pb-210,s}}{m_d}\right)^2 \cdot u(m_s)^2 \right.$$
$$\left. + \left(-\frac{a_{Pb-210,s}}{\varepsilon}\right)^2 \cdot u(\varepsilon)^2 + \left(-\frac{a_{Pb-210,s}}{R}\right)^2 \cdot u(R)^2 + \left(\frac{a_{Pb-210,s}}{f_{2-Pb}}\right)^2 \cdot u(f_{2-Pb})^2 + \left(\frac{a_{Pb-210,s}}{f_{3-Pb}}\right)^2 \cdot u(f_{3-Pb})^2 \right\}^{\frac{1}{2}} \quad (45)$$

$$u(f_{2-Pb}) = f_{2-Pb}\cdot t_2 \cdot u(\lambda_{Pb-210}) \quad (46)$$

$$u(f_{3-Pb}) = f_{3-Pb}\cdot\left\{1-\lambda_{Pb-210}\cdot t_3\cdot\frac{e^{-\lambda_{Pb-210}\cdot t_3}}{1-e^{-\lambda_{Pb-210}\cdot t_3}}\right\}\cdot\frac{u(\lambda_{Pb-210})}{\lambda_{Pb-210}} \quad (47)$$

However, if the time interval (t_2) between the separation of ^{210}Pb and the beginning of the measurement and the counting time of the sample (t_3) are much smaller than the half-life of ^{210}Pb, f_{2-Pb}, f_{3-Pb}, $u(f_{2-Pb})$ and $u(f_{3-Pb})$ are negligible. The uncertainties associated to components mentioned above can be calculated as follows:

$$u(r_n) = \sqrt{\frac{r_g}{t_{3-Po}}+\frac{r_0}{t_0}} \quad (48)$$

$$u(r_{nt}) = \sqrt{\frac{r_{gt}}{t_{3-Po}}+\frac{r_{0t}}{t_0}} \quad (49)$$

$$u\,(a_{Po-210,s}) = \left\{ \left(\frac{a_{Po-210,s}}{A_T} \right)^2 \cdot u(A_T)^2 + \left(\frac{a_{Po-210,s}}{r_n} \right)^2 \cdot u(r_n)^2 + \left(-\frac{a_{Po-210,s}}{r_{nt}} \right)^2 \cdot u(r_{nt})^2 \right.$$

$$+ \left(-\frac{a_{Po-210,s}}{m_s} \right)^2 \cdot u(m_s)^2 + \left(\frac{a_{Po-210,s}}{m_T} \right)^2 \cdot u(m_T)^2 + \left(\frac{a_{Po-210,s}}{f_{2-Po}} \right)^2 \cdot u(f_{2-Po})^2 + \left(\frac{a_{Po-210,s}}{f_T} \right)^2 \cdot u(f_T)^2$$

$$\left. + \left(\frac{a_{Po-210,s}}{f_{3-Po}} \right)^2 \cdot u(f_{3-Po}) \right\}^{\frac{1}{2}} \tag{50}$$

$$u\,(f_t) = f_T \cdot t_T \cdot u\,(\lambda_T) \tag{51}$$

$$u\,(f_{2-Po}) = f_{2-Po} \cdot t_{2-Po} \cdot u\,(\lambda_{Po-210}) \tag{52}$$

$$u\,(f_{3-Po}) = f_{3-Po} \cdot \left\{ 1 - \lambda_{Po-210} \cdot t_3 \frac{e^{-\lambda_{Po-210} \cdot t_3}}{1 - e^{-\lambda_{Po-210} \cdot t_3}} \right\} \cdot \frac{u\,(\lambda_{Po-210})}{\lambda_{Po-210}} \tag{53}$$

Combined uncertainty of activity of ^{210}Po

The uncertainty of the activity of ^{210}Po on the separation date is calculated according to IAEA/AQ/12 procedure [8].

Uncertainty of other alpha emitting isotopes

The same formulas are used to calculate the combined uncertainties of the activity of alpha emitting analytes at the separation time and the sampling date as well as the chemical recovery and counting efficiency. These formulas have to be applied in the spreadsheet approach for calculating the combined uncertainties, knowing the standard uncertainty of each component.

Spreadsheet approach

For quantifying the uncertainties the spreadsheet technique [20] was used, which could be summarised as follows and showed in Fig. 15.

- Calculate function, y, using parameter x_j:

$$y = f(x_1, x_2, \ldots x_j, \ldots x_n) \tag{54}$$

- Recalculate the same function n times, increasing x_j to $x_j + dx_j$ (dx_j, standard deviation) and keeping the remaining parameters constant:

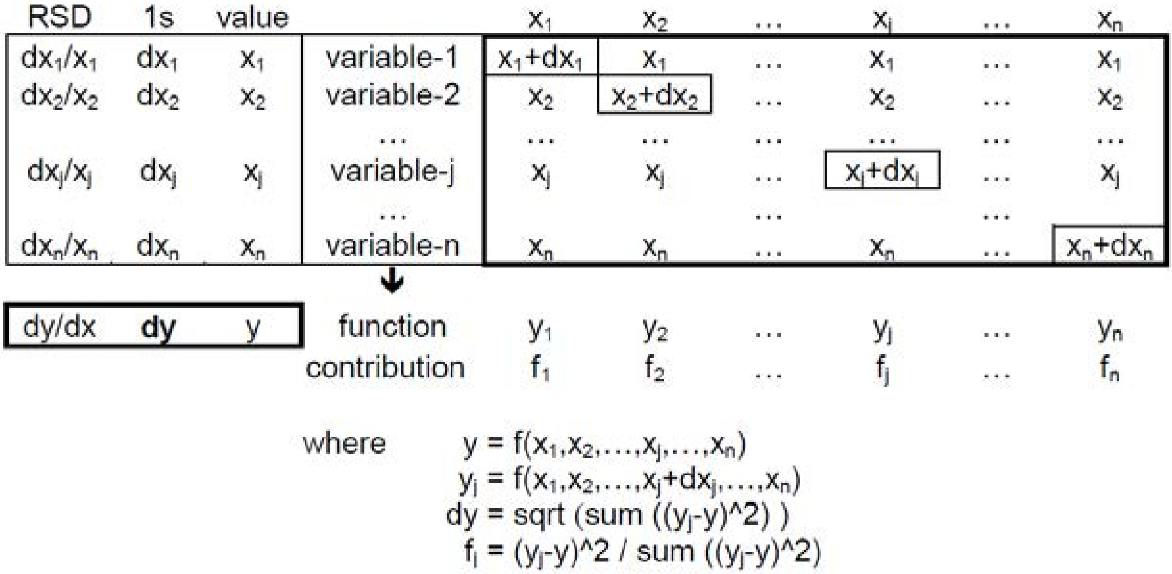
$$y = f(x_1, x_2, \ldots x_j + dx_j, \ldots x_n) \tag{55}$$

- The uncertainty on the function, *dy*, is the square root of the sum of squares :

$$dy = \sqrt{\sum_{1}^{n} (y - y_j)^2} \tag{56}$$

- The individual variance contribution, f_j, is:

$$f_j = \frac{(y - y_j)^2}{\sum_{1}^{n} (y - y_j)^2} \tag{57}$$



RSD	1s	value		x_1	x_2	…	x_j	…	x_n
dx_1/x_1	dx_1	x_1	variable-1	x_1+dx_1	x_1	…	x_1	…	x_1
dx_2/x_2	dx_2	x_2	variable-2	x_2	x_2+dx_2	…	x_2	…	x_2
			…	…	…	…	…	…	…
dx_j/x_j	dx_j	x_j	variable-j	x_j	x_j	…	x_j+dx_j	…	x_j
			…			…		…	
dx_n/x_n	dx_n	x_n	variable-n	x_n	x_n	…	x_n	…	x_n+dx_n
dy/dx	**dy**	y	function	y_1	y_2	…	y_j	…	y_n
			contribution	f_1	f_2	…	f_j	…	f_n

where $y = f(x_1,x_2,\ldots,x_j,\ldots,x_n)$

$y_j = f(x_1,x_2,\ldots,x_j+dx_j,\ldots,x_n)$

dy = sqrt (sum ((y_j-y)^2))

f_j = (y_j-y)^2 / sum ((y_j-y)^2)

FIG. 15. Spreadsheet approach for quantifying the uncertainty of the measurement.

APPENDIX XI

QUANTIFYING UNCERTAINTY FOR THE RELEVANT RADIONUCLIDES

TABLE 4. AN EXAMPLE OF QUANTIFYING UNCERTAINTIES OF ^{210}Po RESULT

Symbol, unit	Value of variable	Uncertainty	Conversion factor to standard uncertainty	Standard uncertainty	Contribution to combined uncertainty (%)
m, g	0.5089	0.0073	$\sqrt{3}$	0.0042	0.10
r_{gt}, s^{-1}	0.197	0.075	1	0.075	36.1
r_{0t}, s^{-1}	0.000017	0.000034	1	0.000034	0.000014
r_g, s^{-1}	0.081	0.029	1	0.029	63.52
r_0, s^{-1}	0.000034	0.000033	1	0.000033	0.00008
a_t, Bq	0.829	0.019	1	0.019	0.252
λ_t, d^{-1}	0.000019	0.000013	1	0.000013	negligible*
λ_{Po}, d^{-1}	0.005	7.2×10^{-9}	1	7.2×10^{-9}	negligible*
f_t	0.98214	0.00043	1	0.00043	0.000091
$f_{2\text{-}Po}$	1.005	7.3×10^{-9}	1	7.3×10^{-9}	negligible*
$f_{3\text{-}Po}$	1.0055	1.8×10^{-8}	1	1.8×10^{-8}	negligible*
a_{Po}, Bq·kg^{-1}	672	94			

* contribution is less than 1×10^{-5}%

TABLE 5. AN EXAMPLE OF QUANTIFYING UNCERTAINTIES OF EFFICIENCY OF ^{210}Pb

Symbol, unit	Value of variable	Uncertainty	Conversion factor to standard uncertainty	Standard uncertainty	Contribution to combined uncertainty (%)
m_{vial}, g	14.93635	0.0001	$\sqrt{3}$	0.00017	0.0048
$m_{vial+carr.sol}$, g	16.03654	0.0001	$\sqrt{3}$	0.00017	0.0048
c_{Pb}, g g^{-1}	0.02742	0.000021	1	0.000021	0.11
m_{vial}, g	16.03672	0.00010	$\sqrt{3}$	0.00017	0.0048
$m_{vial+std}$, g	17.1326	0.00010	$\sqrt{3}$	0.00017	0.0048
a_{std}, Bq	12.45	0.189	1	0.189	80.5
$f_{gravimetry}$	0.70185	0.00041	1	0.00041	0.066
m_{filter}, g	0.03654	0.00010	$\sqrt{3}$	0.00017	4.2
$m_{filter+Pb\text{-}precipitate}$, g	0.07377	0.00010	$\sqrt{3}$	0.00017	4.1
r_A, s^{-1}	7.362	0.041	1	0.041	7.6
r_{A0}, s^{-1}	0.0295	0.003	1	0.0027	0.035
r_B, s^{-1}	0.4160	0.011	1	0.011	0.60
r_{B0}, s^{-1}	0.0117	0.002	1	0.0022	0.024
$f_{A/B}$	1.049	0.023	1	0.023	0.40
$t_{1/2\ Pb}$, d	8145.08	73.05	1	73.1	2.3
$t_{meas\text{-}ref}$, d	4 532	-			
ε	0.8597	0.0153			

TABLE 6. AN EXAMPLE OF QUANTIFYING UNCERTAINTIES OF ^{210}Pb RESULT

Symbol, unit	Value of variable	Uncertainty	Conversion factor to standard uncertainty	Standard uncertainty	Contribution to combined uncertainty (%)
m_s, g	0.5089	0.0073	$\sqrt{3}$	0.0042	0.3
r_{gA}, s^{-1}	0.283	0.035	1	0.035	88.3
r_{0A}, s^{-1}	0.0117	0.0022	1	0.0022	0.3
r_{gB}, s^{-1}	0.031	0.009	1	0.009	5.8
r_{0B}, s^{-1}	0.0056	0.0023	1	0.0023	0.4
Z, s^{-1}	0.2451	0.0327	1	0.0327	-
$f_{A/B}$	1.0153	0.0129	1	0.0129	0.01
ε	0.8597	0.0153	1	0.0153	1.3
R	0.8588	0.0253	1	0.0772	3.5
a_{Pb}, Bq·kg^{-1}	652	12			

TABLE 7. AN EXAMPLE OF QUANTIFYING UNCERTAINTIES OF ^{234}U RESULT

Symbol, unit	Value of variable	Uncertainty	Conversion factor to standard uncertainty	Standard uncertainty	Contribution to combined uncertainty (%)
m_s, g	0.5089	0.0073	$\sqrt{3}$	0.0042	0.03
r_{gt}, s^{-1}	0.02178	0.00801	1	0.008	36.9
r_{0t}, s^{-1}	0.000030	0.000022	1	0.000022	0.0005
r_g, s^{-1}	0.01615	0.00590	1	0.006	62.8
r_0, s^{-1}	0.000016	0.000022	1	0.000022	0.0001
a_t, Bq	0.08835	0.00210	1	0.00201	0.29
a_{U-234}, $Bq \cdot kg^{-1}$	129	3			

TABLE 8. AN EXAMPLE OF QUANTIFYING UNCERTAINTIES OF ^{238}U RESULT

Symbol, unit	Value of variable	Uncertainty	Conversion factor to standard uncertainty	Standard uncertainty	Contribution to combined uncertainty (%)
m_s, g	0.5089	0.0073	$\sqrt{3}$	0.0042	0.03
r_{gt}, s^{-1}	0.02178	0.00801	1	0.008	35.3
r_{0t}, s^{-1}	0.000030	0.000022	1	0.000022	0.0005
r_g, s^{-1}	0.01561	0.00567	1	0.006	64.4
r_0, s^{-1}	0.000009	0.000008	1	0.000008	0.0001
a_t, Bq	0.08835	0.00210	1	0.0021	0.28
a_{U-238}, $Bq \cdot kg^{-1}$	124	3			

TABLE 9. AN EXAMPLE OF QUANTIFYING UNCERTAINTIES OF ^{230}Th RESULT

Symbol, unit	Value of variable	Uncertainty	Conversion factor to standard uncertainty	Standard uncertainty	Contribution to combined uncertainty (%)
m_s, g	0.5089	0.0073	$\sqrt{3}$	0.0042	0.05
r_{gt}, s^{-1}	0.02263	0.00644	1	0.006	38.7
r_{0t}, s^{-1}	0.000077	0.000063	1	0.000063	0.0061
r_g, s^{-1}	0.02838	0.00790	1	0.008	60.8
r_0, s^{-1}	0.000012	0.000010	1	0.000010	0.0001
a_t, Bq	0.09003	0.00230	1	0.002303	0.51
$a_{Th\text{-}230}$, $Bq \cdot kg^{-1}$	223	9			

TABLE 10. AN EXAMPLE OF QUANTIFYING UNCERTAINTIES OF ^{232}Th RESULT

Symbol, unit	Value of variable	Uncertainty	Conversion factor to standard uncertainty	Standard uncertainty	Contribution to combined uncertainty (%)
m_s, g	0.5089	0.0073	$\sqrt{3}$	0.0042	0.04
r_{gt}, s^{-1}	0.02263	0.00644	1	0.006	26.5
r_{0t}, s^{-1}	0.000077	0.000063	1	0.000063	0.0042
r_g, s^{-1}	0.00028	0.00010	1	0.0001	72.7
r_0, s^{-1}	0.000011	0.000008	1	0.000008	0.48
a_t, Bq	0.09003	0.00230	1	0.0023	0.35
$a_{Th\text{-}232}$, $Bq \cdot kg^{-1}$	2.1	0.09			

TABLE 11. AN EXAMPLE OF QUANTIFYING UNCERTAINTIES OF ^{226}Ra RESULT

Symbol, unit	Value of variable	Uncertainty	Conversion factor to standard uncertainty	Standard uncertainty	Contribution to combined uncertainty (%)
m_s, g	0.5089	0.0073	$\sqrt{3}$	0.0042	0.03
r_{gt}, s^{-1}	0.04310	0.02505	1	0.02505	60.3
r_{0t}, s^{-1}	0.000111	0.000128	1	0.000128	0.004
r_g, s^{-1}	0.06332	0.01878	1	0.01878	39.3
r_0, s^{-1}	0.000070015	0.000070013	1	0.000070013	0.0005
$a_{t\ Ra\text{-}225}$, Bq	0.77950	0.02253	1	0.02253	0.4
λ_{Ac225}, d^{-1}	0.069315	0.000624	1	0.000624	0.00002
λ_{Ra225}, d^{-1}	0.046520	0.000693	1	0.000693	0.08
t_1-t_0, d	33.7				
$a_{Ra\text{-}226}$, Bq·kg^{-1}	766	39			

APPENDIX XII

DECISION THRESHOLD AND DETECTION LIMIT

TABLE 12. TYPICAL DECISION THRESHOLD AND DETECTION LIMIT FOR RELEVANT ISOTOPES

Symbol, unit	^{210}Pb	^{210}Po	^{234}U	^{238}U	^{230} Th	^{232} Th	^{226}Ra
k	1.65	1.65	1.65	1.65	1.65	1.65	1.65
m, kg	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005	0.0005
ε	0.86	0.31	0.26	0.26	0.35	0.35	0.25
R	0.86	0.73	0.94	0.94	0.68	0.68	0.61
n_0	52	16	4	4	6	6	28
T_g, s	36000	98899	343024	343024	277345	277345	124984
t_0, s	35542	548190	512901	512901	559286	559286	446755
a^*, Bq·kg^{-1}	**1.3**	**0.36**	**0.09**	**0.09**	**0.12**	**0.12**	**0.68**
a_1, Bq·kg^{-1}	3.8	1.1	0.28	028	0.36	0.36	2.05
$u^2(0)$, Bq^2·kg^{-2}	2.9	0.15	0.0084	0.0084	0.0065	0.0047	0.78
$u^2(a_1)$, Bq^2·kg^{-2}	23	0.41	0.059	0.025	0.028	0.052	2.04
$a^\#$, Bq·kg^{-1}	**24**	**1.2**	**0.52**	**0.19**	**0.18**	**0.19**	**4.3**

APPENDIX XIII

CONTROL CHARTS OF THE INDIVIDUAL RADIONUCLIDES RESULTS WITH ASSOCIATED UNCERTAINTIES AND ANALYSIS OF VARIANCE

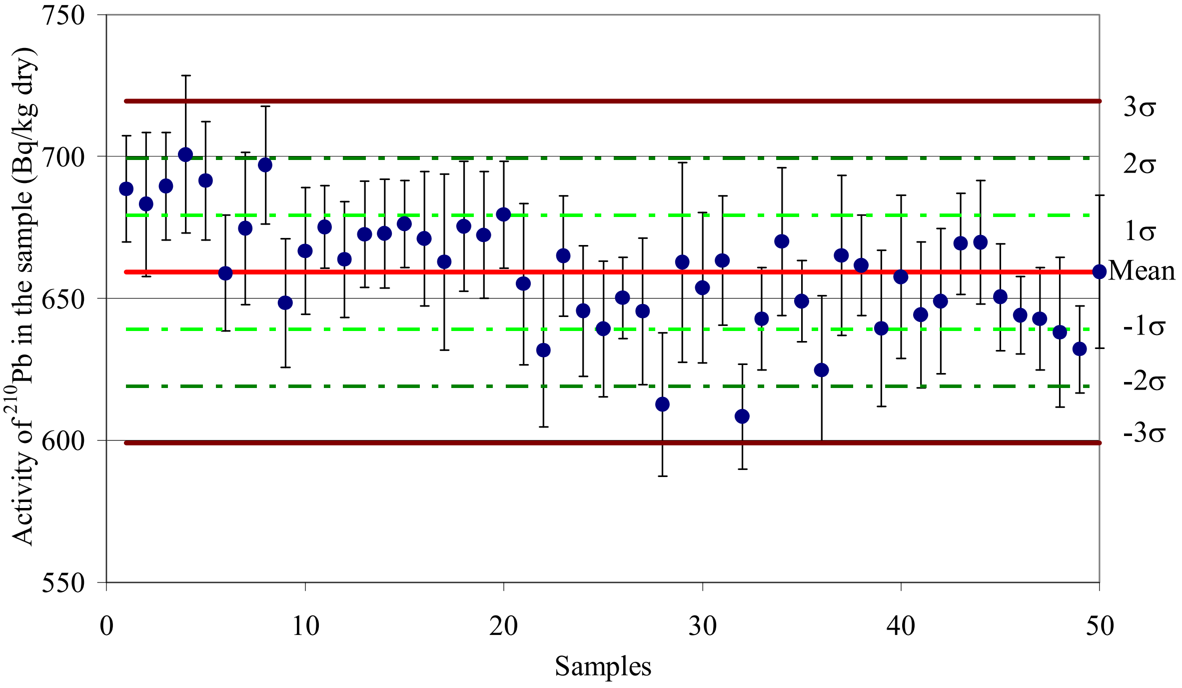


FIG. 16. ^{210}Pb results with associated uncertainties.

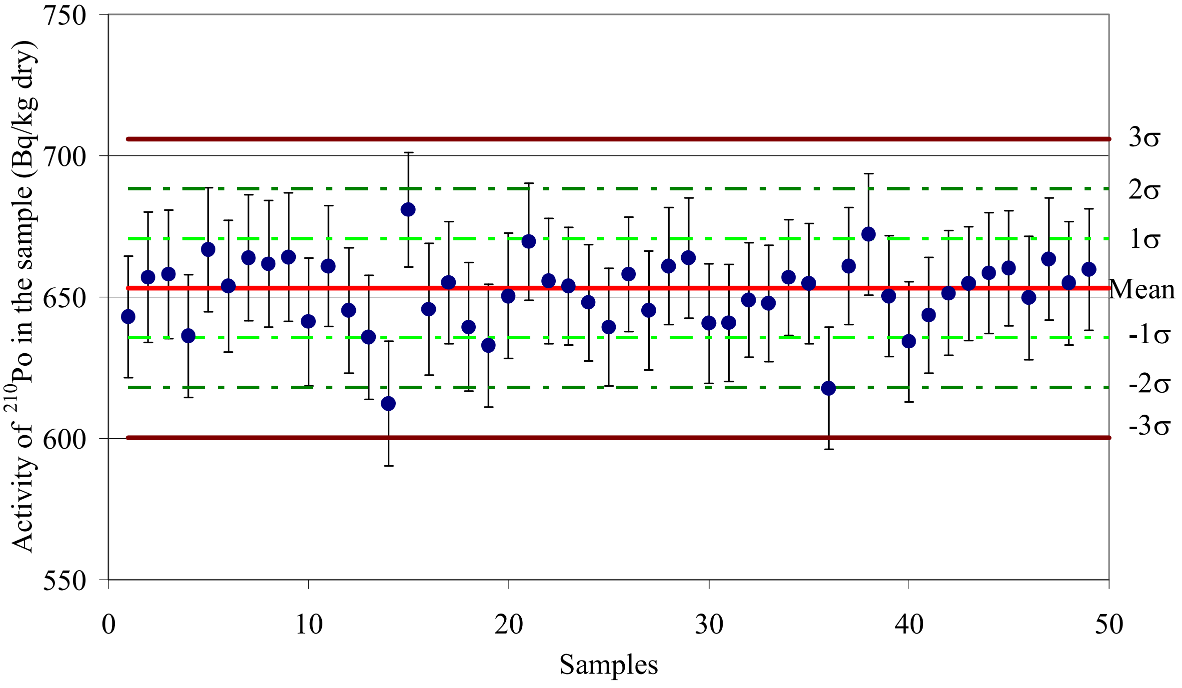


FIG. 17. ^{210}Po results with associated uncertainties.

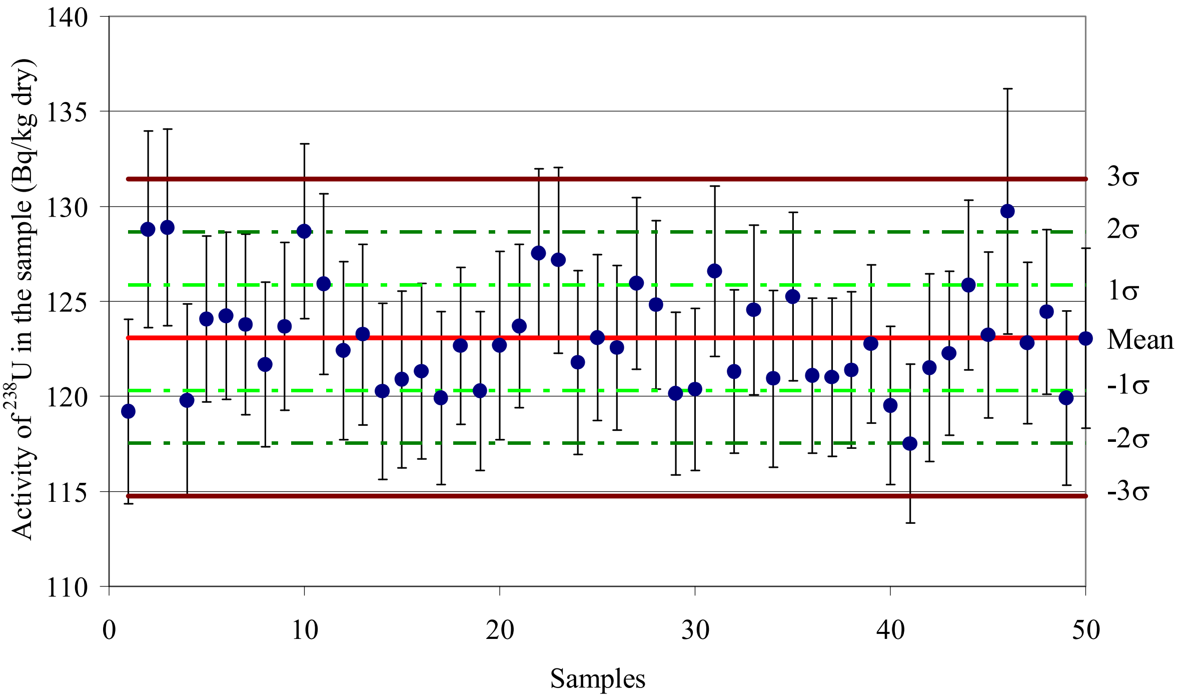


FIG. 18. ^{238}*U results with associated uncertainties.*

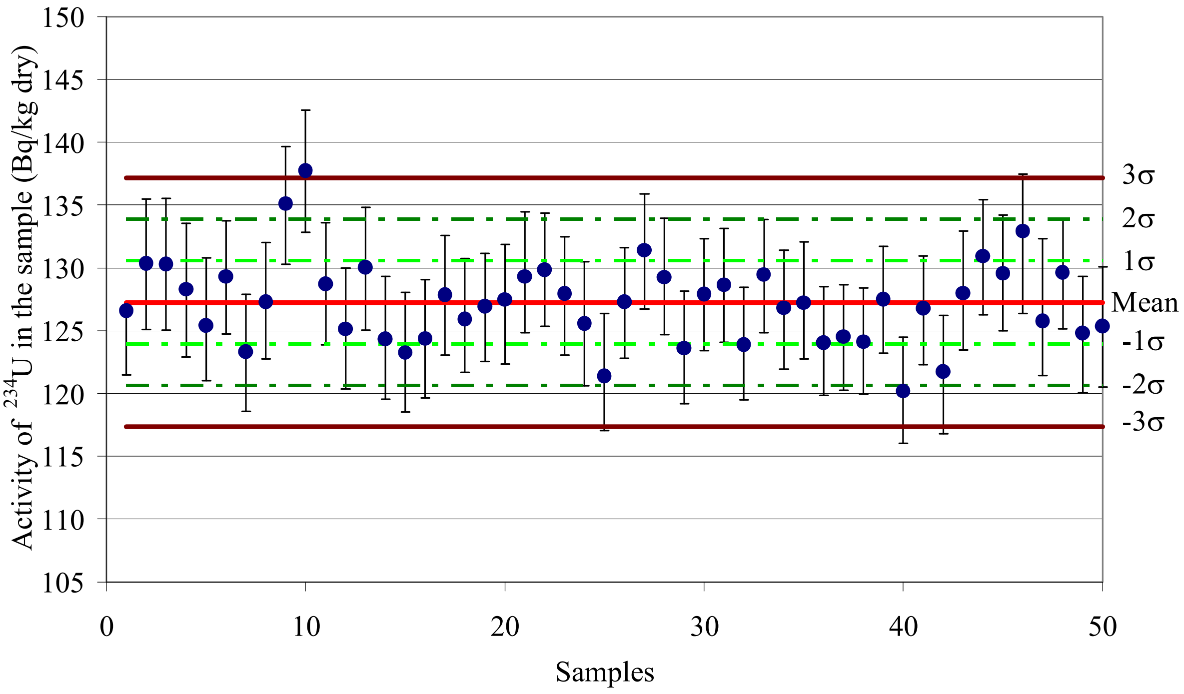


FIG. 19. ^{234}*U results with associated uncertainties.*

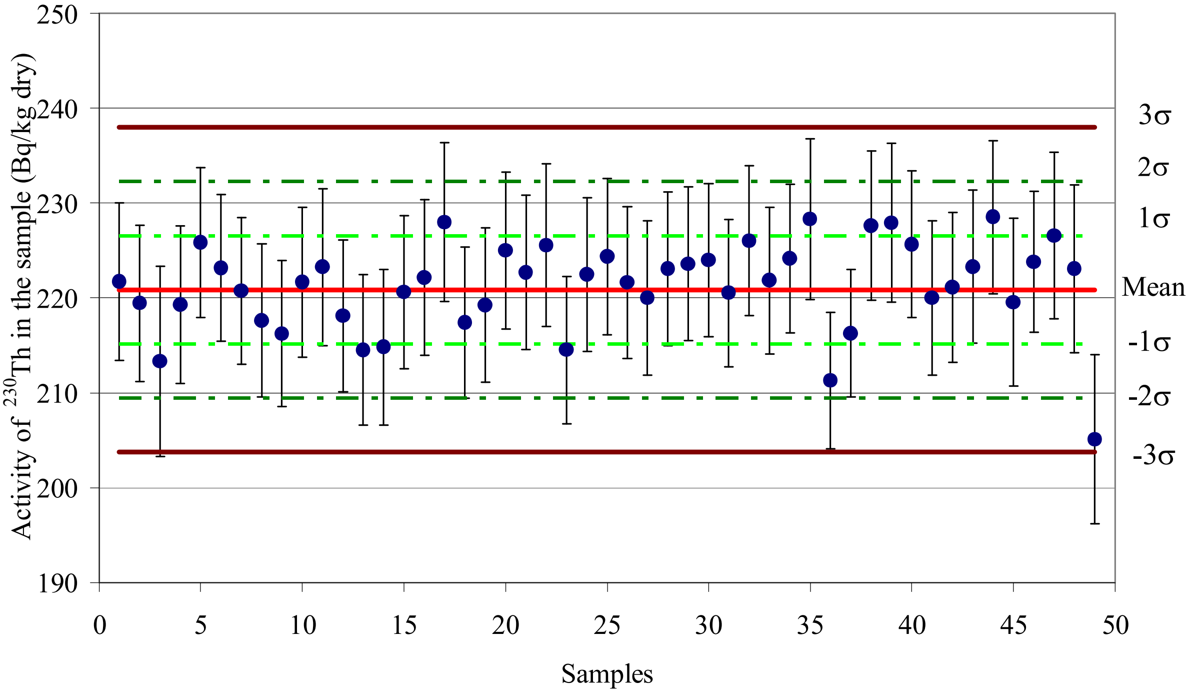


FIG. 20. ^{230}*Th results with associated uncertainties.*

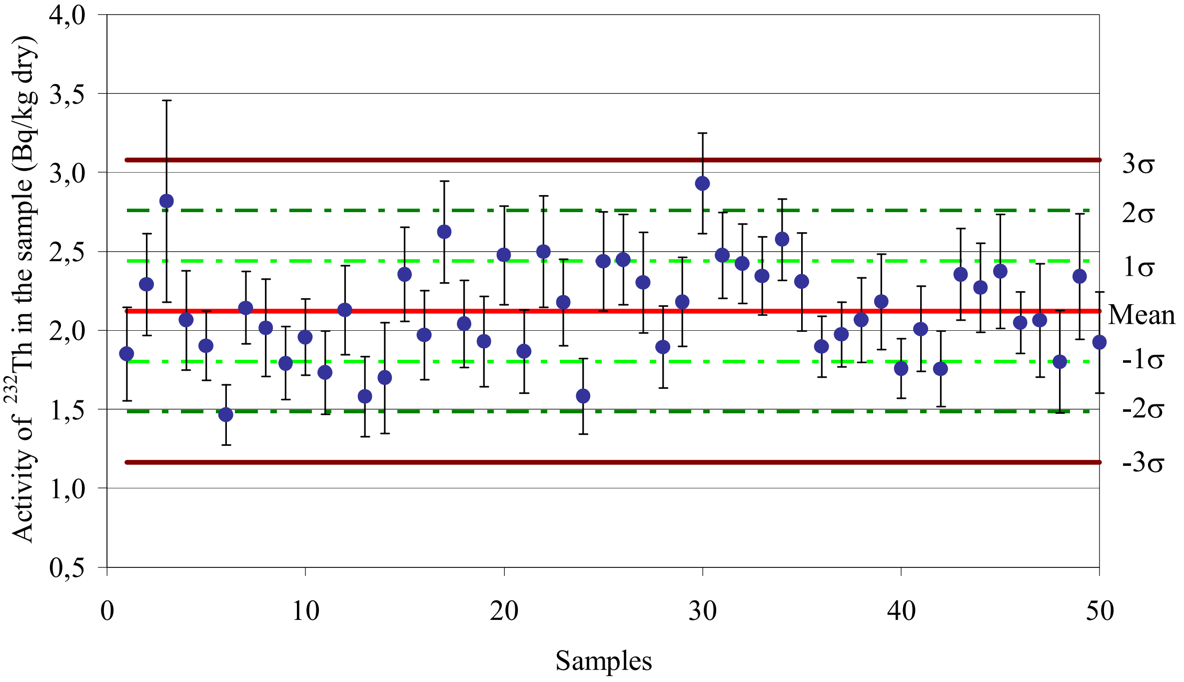


FIG. 21. ^{232}*Th results with associated uncertainties.*

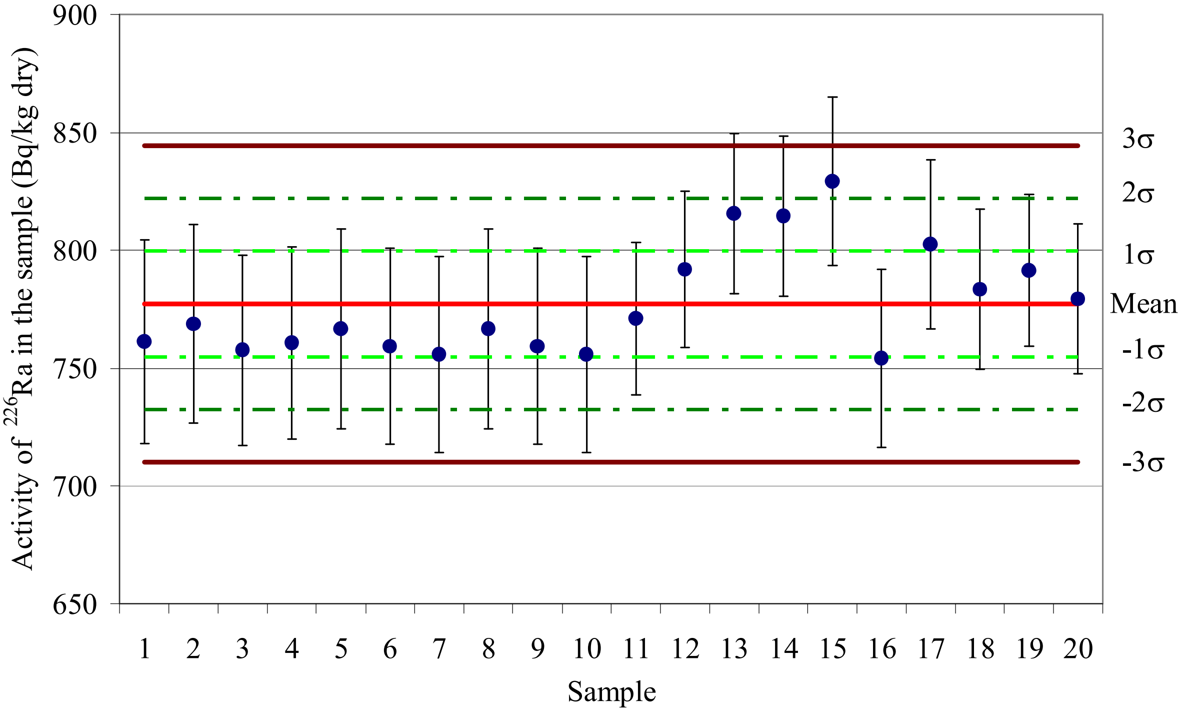


FIG. 22. ^{226}Ra results with associated uncertainties.

TABLE 13. ANALYSIS OF VARIANCE (ANOVA) FOR ^{210}Po, ^{210}Pb, ^{238}U, ^{230}Th AND ^{226}Ra IN PHOSPHOGYPSUM

Nuclide	SS_{wb}	SS_{bb}	MS_{wb}	MS_{bb}	S_{wb} (as CV%)	S_{bb} (as CV%)
^{210}Po	12462	15179	312	1687	2.71	2.54
^{210}Pb	8385	19754	210	2195	2.20	3.02
^{238}U	314	386	7.85	42.9	2.27	2.15
^{230}Th	2176	1598	54.4	178	3.34	2.25
^{226}Ra	412	686	137	85.8	1.21	0.54

SS_{wb}: sum of squares within bottles

SS_{bb}: sum of squares between bottles

MS_{wb}: mean of squares within bottles

MS_{bb}: mean of squares between bottles

S_{wb}: standard deviation as percent of covalent variance within bottles

S_{bb}: standard deviation as percent of covalent variance between bottles

APPENDIX XIV

VALIDATION RESULTS OF THE PROCEDURE AND PERFORMANCE PARAMETERS

TABLE 14. VALIDATION RESULTS OF THE PROCEDURE AND PERFORMANCE PARAMETERS

Parameters	^{210}Po	^{210}Pb	^{234}U	^{238}U	^{230}Th	^{226}Ra
C, Bq kg^{-1}	680	680	120	120	211	780
$\bar{x}$, Bq kg^{-1}	653	659	127	123	221	793
u(C), Bq kg^{-1}	58	58	9	11	9	62
u($\bar{x}$), Bq kg^{-1}	23	22	5	5	10	35
δ(%)	-4.0	-3.1	5.8	2.5	4.7	1.7
r_L, Bq kg^{-1}	10.6	10.2	4.8	4.7	6.2	49.8
R_L, Bq kg^{-1}	23.7	45.4	5.9	5.3	8.9	70.7
PI(%)	9.2	9.2	8.5	10.0	6.2	9.1

REFERENCES

[1] FEDERAL REGISTER, National emission standards for hazardous air pollutants **57** 107 (1992) 23305-23320.

[2] RUTHERFORD, P.M., DUDAS, M.J., AROCENA, J.M., Heterogeneous distribution of radionuclides, barium and strontium in phosphogypsum by-product, Sci. Total Environ., **180** (1996) 201–209.

[3] NATIONAL COUNCIL ON RADIATION PROTECTION AND MEASUREMENTS, Evaluation of Occupational and Environmental Exposures to Radon and Radon Daughters in the United States, NCRP Report 78 (1984).

[4] INTERNATIONAL ATOMIC ENERGY AGENCY, Reference Material IAEA-434: Naturally Occurring Radionuclides in Phosphogypsum, IAEA Analytical Quality in Nuclear Applications Series No. 17, IAEA/AQ/17, IAEA, Vienna (2010).

[5] MARTIN, P., HANCOCK, G.J., Routine analysis of naturally occurring radionuclides in environmental samples by alpha-particle spectrometry, Supervising Scientist Report 180, (2004). http://www.environment.gov.au/ssd/publications/ssr/180.html

[6] MEDLEY, P., BOLLHÖFER, A., ILES, M., RYAN, B., MARTIN, P., Barium sulfate method for radium-226 analysis by alpha spectrometry, Environmental Research Institute of the Supervising Scientist, internal report 501, (2005).

[7] VAJDA, N., LAROSA, J., ZEISLER, R., DANESI, P., KIS-BENEDEK, G., A Novel Technique for the Simultaneous Determination of ^{210}Pb and ^{210}Po using a Crown Ether, J. Environ. Radioactivity **37** (1997) 355–372.

[8] INTERNATIONAL ATOMIC ENERGY AGENCY, A Procedure for the Determination of Po-210 in Water Samples by Alpha Spectrometry, IAEA Analytical Quality in Nuclear Applications Series No. 12, IAEA/AQ/12, IAEA, Vienna (2009).

[9] GUOGANG J., TORRI G., INNOCENZI P., OZONE R., Di LULLO A., Determination of radium isotopes in mineral and environmental water samples by alpha-spectrometry, J. Radioanal. Nucl. Chem., **267** 3 (2005) 505–514.

[10] EURACHEM/CITAC Guide, Quantifying uncertainty in analytical measurement, 2nd Ed.(2000).

[11] INTERNATIONAL ATOMIC ENERGY AGENCY, Quantifying Uncertainty in Nuclear Analytical Measurements, IAEA-TECDOC-1401, IAEA, Vienna (2004).

[12] SHAKHASHIRO, A., SANSONE, U., Technically Enhanced Naturally Occurring Radionuclides (TENORM) in Phosphogypsum: The Interlaboratory Comparison, CCRI(II)07-35, Metrologia (2009).

[13] Monographie BIPM-5 Vol. 1–Monographie BIPM-5 Vol. 5, http://www.nucleide.org: Decay Data Evaluation Project (DDEP) accessed in October 2010.

[14] NuDat 2.5 (Database at the US NNDC), http://www-nds.iaea.org, accessed in October 2010.

[15] HORWITZ, E.P., et al., A Novel Strontium-Selective Extraction Chromatographic Resin, Solvent Extraction & Ion Exchange, **10** (1992) 313.

[16] HORWITZ, E.P., et al., Extraction Chromatography of Actinides and Selected Fission Products: Principles and Achievement of Selectivity, presented at International Workshop on the Application of Extraction Chromatography in Radionuclide Measurement, IRMM, Geel, 1998.

[17] HORWITZ, E.P., et al., Separation and Preconcentration of Actinides by Extraction Chromatography Using a Supported Liquid Anion Exchanger: Application to the Characterization of High-Level Nuclear Waste Solutions, Anal. Chim. Acta, **310** (1995) 63–78.

[18] HORWITZ, E.P., et al., Separation and Preconcentration of Uranium from Acidic Media by Extraction Chromatography, Anal. Chim. Acta, **266** (1992) 25–37.

[19] KIM, C-K., MARTIN, P., FAJGELJ A., Quantification of measurement uncertainty in the sequential determination of ^{210}Pb and ^{210}Po by liquid scintillation counting and alpha particle spectrometry, Accredit. Qual. Assurance **13** 12 (2008) 691–702.

[20] KRAGTEN, J., Calculating Standard Deviation and Confidence Intervals with a Universally Applicable Spreadsheet Technique, Analyst **119** (1994) 2161–2165.

CONTRIBUTORS TO DRAFTING AND REVIEW

Gaigl, F.A.	International Atomic Energy Agency
Hampe, D.	Verein für Kernverfahrenstechnik und Analytik Rossendorf e.V., Dresden, Germany
Kim, C.-K.	International Atomic Energy Agency
Kis-Benedek, G.	International Atomic Energy Agency
Martin, P.	International Atomic Energy Agency
Mietelski, J.W.	The Henryk Niewodniczanski Institute of Nuclear Physics, Polish Academy of Sciences, Poland
Pitois, A.	International Atomic Energy Agency
Sansone, U.	International Atomic Energy Agency
Varga, B.	National Food Chain Safety Office, Food and Feed Safety Directorate, Hungary

ORDERING LOCALLY

In the following countries, IAEA priced publications may be purchased from the sources listed below or from major local booksellers.

Orders for unpriced publications should be made directly to the IAEA. The contact details are given at the end of this list.

AUSTRALIA
DA Information Services
648 Whitehorse Road, Mitcham, VIC 3132, AUSTRALIA
Telephone: +61 3 9210 7777 • Fax: +61 3 9210 7788
Email: books@dadirect.com.au • Web site: http://www.dadirect.com.au

BELGIUM
Jean de Lannoy
Avenue du Roi 202, 1190 Brussels, BELGIUM
Telephone: +32 2 5384 308 • Fax: +32 2 5380 841
Email: jean.de.lannoy@euronet.be • Web site: http://www.jean-de-lannoy.be

CANADA
Renouf Publishing Co. Ltd.
5369 Canotek Road, Ottawa, ON K1J 9J3, CANADA
Telephone: +1 613 745 2665 • Fax: +1 643 745 7660
Email: order@renoufbooks.com • Web site: http://www.renoufbooks.com

Bernan Associates
4501 Forbes Blvd., Suite 200, Lanham, MD 20706-4391, USA
Telephone: +1 800 865 3457 • Fax: +1 800 865 3450
Email: orders@bernan.com • Web site: http://www.bernan.com

CZECH REPUBLIC
Suweco CZ, spol. S.r.o.
Klecakova 347, 180 21 Prague 9, CZECH REPUBLIC
Telephone: +420 242 459 202 • Fax: +420 242 459 203
Email: nakup@suweco.cz • Web site: http://www.suweco.cz

FINLAND
Akateeminen Kirjakauppa
PO Box 128 (Keskuskatu 1), 00101 Helsinki, FINLAND
Telephone: +358 9 121 41 • Fax: +358 9 121 4450
Email: akatilaus@akateeminen.com • Web site: http://www.akateeminen.com

FRANCE
Form-Edit
5 rue Janssen, PO Box 25, 75921 Paris CEDEX, FRANCE
Telephone: +33 1 42 01 49 49 • Fax: +33 1 42 01 90 90
Email: fabien.boucard@formedit.fr • Web site: http://www.formedit.fr

Lavoisier SAS
14 rue de Provigny, 94236 Cachan CEDEX, FRANCE
Telephone: +33 1 47 40 67 00 • Fax: +33 1 47 40 67 02
Email: livres@lavoisier.fr • Web site: http://www.lavoisier.fr

L'Appel du livre
99 rue de Charonne, 75011 Paris, FRANCE
Telephone: +33 1 43 07 50 80 • Fax: +33 1 43 07 50 80
Email: livres@appeldulivre.fr • Web site: http://www.appeldulivre.fr

GERMANY
Goethe Buchhandlung Teubig GmbH
Schweitzer Fachinformationen
Willstätterstrasse 15, 40549 Düsseldorf, GERMANY
Telephone: +49 (0) 211 49 8740 • Fax: +49 (0) 211 49 87428
Email: s.dehaan@schweitzer-online.de • Web site: http://www.goethebuch.de

HUNGARY
Librotade Ltd., Book Import
PF 126, 1656 Budapest, HUNGARY
Telephone: +36 1 257 7777 • Fax: +36 1 257 7472
Email: books@librotade.hu • Web site: http://www.librotade.hu

INDIA
Allied Publishers
1st Floor, Dubash House, 15, J.N. Heredi Marg, Ballard Estate, Mumbai 400001, INDIA
Telephone: +91 22 2261 7926/27 • Fax: +91 22 2261 7928
Email: alliedpl@vsnl.com • Web site: http://www.alliedpublishers.com

Bookwell
3/79 Nirankari, Delhi 110009, INDIA
Telephone: +91 11 2760 1283/4536
Email: bkwell@nde.vsnl.net.in • Web site: http://www.bookwellindia.com

ITALY
Libreria Scientifica "AEIOU"
Via Vincenzo Maria Coronelli 6, 20146 Milan, ITALY
Telephone: +39 02 48 95 45 52 • Fax: +39 02 48 95 45 48
Email: info@libreriaaeiou.eu • Web site: http://www.libreriaaeiou.eu

JAPAN
Maruzen Co., Ltd.
1-9-18 Kaigan, Minato-ku, Tokyo 105-0022, JAPAN
Telephone: +81 3 6367 6047 • Fax: +81 3 6367 6160
Email: journal@maruzen.co.jp • Web site: http://maruzen.co.jp

NETHERLANDS
Martinus Nijhoff International
Koraalrood 50, Postbus 1853, 2700 CZ Zoetermeer, NETHERLANDS
Telephone: +31 793 684 400 • Fax: +31 793 615 698
Email: info@nijhoff.nl • Web site: http://www.nijhoff.nl

Swets Information Services Ltd.
PO Box 26, 2300 AA Leiden
Dellaertweg 9b, 2316 WZ Leiden, NETHERLANDS
Telephone: +31 88 4679 387 • Fax: +31 88 4679 388
Email: tbeysens@nl.swets.com • Web site: http://www.swets.com

SLOVENIA
Cankarjeva Zalozba dd
Kopitarjeva 2, 1515 Ljubljana, SLOVENIA
Telephone: +386 1 432 31 44 • Fax: +386 1 230 14 35
Email: import.books@cankarjeva-z.si • Web site: http://www.mladinska.com/cankarjeva_zalozba

SPAIN
Diaz de Santos, S.A.
Librerias Bookshop • Departamento de pedidos
Calle Albasanz 2, esquina Hermanos Garcia Noblejas 21, 28037 Madrid, SPAIN
Telephone: +34 917 43 48 90 • Fax: +34 917 43 4023
Email: compras@diazdesantos.es • Web site: http://www.diazdesantos.es

UNITED KINGDOM
The Stationery Office Ltd. (TSO)
PO Box 29, Norwich, Norfolk, NR3 1PD, UNITED KINGDOM
Telephone: +44 870 600 5552
Email (orders): books.orders@tso.co.uk • (enquiries): book.enquiries@tso.co.uk • Web site: http://www.tso.co.uk

UNITED STATES OF AMERICA
Bernan Associates
4501 Forbes Blvd., Suite 200, Lanham, MD 20706-4391, USA
Telephone: +1 800 865 3457 • Fax: +1 800 865 3450
Email: orders@bernan.com • Web site: http://www.bernan.com

Renouf Publishing Co. Ltd.
812 Proctor Avenue, Ogdensburg, NY 13669, USA
Telephone: +1 888 551 7470 • Fax: +1 888 551 7471
Email: orders@renoufbooks.com • Web site: http://www.renoufbooks.com

United Nations
300 East 42nd Street, IN-919J, New York, NY 1001, USA
Telephone: +1 212 963 8302 • Fax: 1 212 963 3489
Email: publications@un.org • Web site: http://www.unp.un.org

Orders for both priced and unpriced publications may be addressed directly to:

IAEA Publishing Section, Marketing and Sales Unit, International Atomic Energy Agency
Vienna International Centre, PO Box 100, 1400 Vienna, Austria
Telephone: +43 1 2600 22529 or 22488 • Fax: +43 1 2600 29302
Email: sales.publications@iaea.org • Web site: http://www.iaea.org/books

14-08081

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA
ISSN 2074–7659