On the determination of ^{228}Ra, ^{210}Po, ^{234}U and ^{238}U in mineral waters
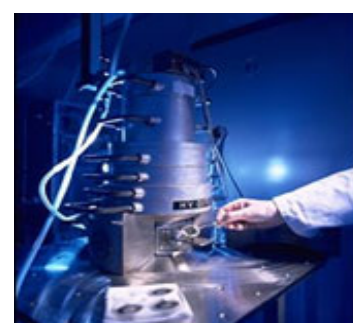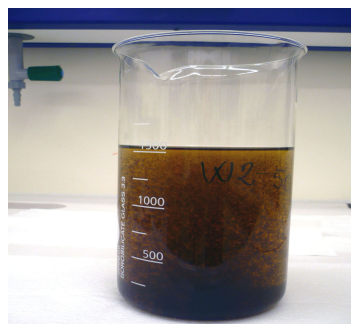
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I. INTRODUCTION

I.1. Background

The determination of uranium, radium and polonium isotopes is important in environmental studies and for the protection of public health. The 'Drinking Water Directive' sets standards for the most common substances (so-called parameters) that can be found in drinking water.

Among many other parameters (microbiological, chemical), radium and uranium isotopes have to be regularly monitored in drinking waters. As a basis for the standards in the 'Drinking Water Directive', the WHO guidelines are used.

The approach taken in those guidelines has two steps:

- screening for alpha and/or beta activity to determine if the activity concentration is below the levels at which no further action has to be taken,

- if these screening levels are exceeded, investigation of the concentrations of individual radionuclides and comparison with specific guidance levels is required (WHO, 2006).

According to the European Council Directive 98/83/EC, those screening methods may be used to monitor for the parametric value for total indicative dose (TID), excluding tritium, potassium, radon and radon decay products (Council Directive 98/83/EC).

According to a European Commission Recommendation in preparation, which will refine the presently valid Council Directive 98/83/EC ("drinking water directive"), the activity concentration limits of detection for ^{228}Ra, ^{234}U and ^{238}U which a laboratory must be capable to determine in water intended for human consumption are 80, 20 and 20 mBq·L^{-1}, respectively. Whereas the reference concentrations are 0.2 Bq·L^{-1} for ^{228}Ra, 2.8 Bq·L^{-1} for ^{234}U and 3.0 Bq·L^{-1} for ^{238}U, respectively. The term "reference concentration" refers to the radionuclide concentration which is used in the calculation of the Total Indicative Dose (TID). The ratio between observed concentration and reference concentration of the radionuclide has to be lower than one and then it may be assumed that the TID is less than the parametric indicator value of 0.1 mSv/year.

For radon and its decay products, ^{210}Pb and ^{210}Po, the reference values are proposed by another European Commission Recommendation (EURATOM, 2001). The reference concentrations for ^{210}Pb and ^{210}Po are 0.2 Bq·L^{-1} and 0.1 Bq·L^{-1}, respectively.

I.2. Aim of the study

In this work, the activity concentration of ^{228}Ra, ^{210}Po ^{234}U and ^{238}U radioisotopes are determined in mineral waters by beta and alpha-particle spectrometry, respectively. The activity concentration of ^{228}Ra was determined via its daughter ^{228}Ac and measured by a liquid scintillation counter, Wallac Quantulus 1220^{TM}. Uranium and polonium radioisotopes were sequentially determined using two different pre-concentration methods and two separation procedures. A comparison between the iron(III) hydroxide and manganese dioxide preconcentration methods for uranium and polonium radioisotopes from water will be described as well as the comparison between the two radiochemical separation procedures of the investigated radionuclides.

II. THEORETICAL PART

Radium has similar chemical behaviour to that of calcium and ingestion of radium isotopes through water consumption can accumulate radium in bones and cause local radiation damage. ^{226}Ra ($T_{1/2}$ = 1600 a) and ^{228}Ra ($T_{1/2}$ = 5.75 a) are the most radiotoxic isotopes of radium due to their long half-lives. ^{228}Ra is the decay product of ^{232}Th and is a low-energy beta-particle emitter. The maximum beta-particle energy of ^{228}Ra is 0.039 MeV and for this reason, the most suitable method for its activity determination is measurement of ^{228}Ac, its daughter product, which emits both beta-particles and gamma-rays. The disadvantage of using ^{228}Ac is its short half-life of 6.14 h, but on the other hand it has a beta-particle maximum energy of 2.1 MeV. In table 1 the half-lives and the main alpha- and gamma-energies of the naturally occuring radium isotopes are presented.

Table 1.   The half-lives and the main alpha-particle and gamma-ray energies of the
                 selected radium isotopes [Table of Isotopes, Browne et al., 1978]

Nuclide	Half-life	Decay mode	Energy (keV)	Abundance (%)
^{223}Ra	11.43d	α	5607	24.2
			5716	52.5
			5748	9.5
^{224}Ra	3.66d	α	5685	94
			5449	5.5
^{226}Ra	1600y	α	4784	94.45
		α	4601	5.55
		γ	186.1	3.3
^{228}Ra	**5.76y**	**β**	**39**	**60**
			14.5	**40**

Uranium is a naturally occurring radioactive element and is widely distributed in nature. It has three natural isotopes: ^{238}U (99.27% abundance), ^{235}U (0.72% abundance) and ^{234}U (0.0054% abundance). All of these isotopes emit alpha radiation and produce a long decay series of progeny. Uranium present in rocks can pass into solution during the weathering process. In natural waters and sediments disequilibrium between ^{238}U and ^{234}U is found; the

activity ratio of $^{234}U/^{238}U$ is observed to be greater than one. One of the reasons for this disequilibrium can be the alpha-recoil mechanism (Ivanovich and Harmon, 1982). The half-lives, the main alpha- and gamma-energies and the abundance of the selected uranium isotopes are presented in table 2.

Table 2. The half-lives and main alpha- and gamma-energies of the selected uranium isotopes [Table of Radioactive Isotopes, Browne and Firestone, 1986]

Nuclide	Half-life	Decay mode	Energy (keV)	Abundance (%)
^{232}U	68.9y	α	5320	68.6
			5263	31.2
^{234}U	$2.45*10^5$y	α	4773	72.5
			4723	27.5
^{235}U	$7.037*10^8$y	α	4395	55
		γ	185.7	53
^{238}U	$4.468*10^9$y	α	4196	77
		α	4147	23

Polonium-210 is a decay product of ^{238}U and due to its short half-life of 138.3 days is one of the radionuclides with the highest radiotoxicity. In the hydrological cycle ^{210}Po generally follows its precursor ^{210}Pb. In marine sediments it was found that ^{210}Po is not in equilibrium with ^{210}Pb, because polonium-210 is more readily adsorbed than lead-210 onto particulate matter (e.g. phytoplankton) (Ivanovich and Harmon, 1982). The half-lives and the main alpha-particle energies of polonium isotopes are presented in table 3.

Table 3. The half-lives and main alpha-energies of ^{208}Po, ^{209}Po and ^{210}Po [Table of Isotopes, Browne et al., 1978]

Nuclide	Half-life	Decay mode	Energy (keV)	Abundance (%)
^{208}Po	2.897y	α	5110	99
			4220	2.4E-4
^{209}Po	102y	α	4877	99.26
			4617	0.48
^{210}Po	138.4d	α	5304	100

II.1. SAMPLE PREPARATION TECHNIQUES

II.1.1. Pre-concentration techniques of radium isotopes

II.1.1.1 Barium sulphate co-precipitation method

Pre-concentration of radium from water by co-precipitation with barium sulphate was used by Kahn et al. (1990) and Chalupnik and Lebecka (1992), but they used different measurement techniques for the determination of ^{228}Ra. Kahn et al. used the daughter nuclide ^{228}Ac measuring the filter with the precipitate by gamma-ray spectrometry. Chalupnik and Lebecka co-precipitated Ra from the water sample with Ba carrier and Pb, and then the precipitate was dissolved in EDTA. Radium was separated from lead by co-precipitation of Ra and Ba as sulphates at pH = 4.5 and then the precipitate was transferred into a liquid scintillation vial, mixed with water and scintillation cocktail and measured by a low-level liquid scintillation counter.

II.1.1.2. Methods using manganese dioxide co-precipitation, manganese dioxide resin and manganese dioxide coated discs

Another co-precipitation method for pre-concentration of radium isotopes from waters is using manganese dioxide. The principle of this method is that after the acidification of the sample with concentrated HCl to pH=2, $KMnO_4$ is added, the pH is adjusted to $8 - 9$ with NaOH, then $MnCl_2$ is added and MnO_2 precipitate starts to form. The determination of ^{228}Ra is done via measurements of its daughter ^{228}Ac which is separated after the equilibrium is reached and measured by liquid scintillation counting (Nour et al., 2004).

The pre-concentration of radium isotopes can also be done using manganese dioxide resin (Moon et al., 2003) or by manganese dioxide coated discs (Eikenberg et al., 2001). In the first case, ^{228}Ra is quantified via its daughter ^{228}Ac, measured by liquid scintillation counting and in the second case, the ^{228}Ra was determined by alpha-particle spectrometry measurement of its granddaughter ^{228}Th.

II.1.1.3. Empore^{TM} Radium Rad Disks

Radium can be separated from water by using 3M Empore^{TM} Radium Rad Disks. Ďurecová (1997) determined ^{228}Ra by filtering the sample through the Radium Rad Disks. ^{228}Ra was

counted via its daughter ^{228}Ac which was eluted from the disc with di-ammonium hydrogen citrate.

The same type of discs was used by Matthews et al. (2000) who isolated radium on Empore^{TM} Radium Rad Disk, then the discs were stored to allow ^{228}Ac to grow in and measurement of ^{228}Ac at 911 keV and 969 keV gamma-rays was done.

II.1.2. Pre-concentration techniques of uranium isotopes

For the determination of uranium isotopes in water samples, pre-concentration with iron (III) hydroxide is a widely used method. After acidification of the water sample, iron (III) is added to the sample and the iron (III) hydroxide precipitation is achieved by increasing the pH to 9 – 10 with concentrated ammonia. Co-precipitation with manganese dioxide is another technique which was used by Skwarzec et al. (2001). Yet another method for pre-concentration of uranium isotopes consists of evaporation of water in order to reduce the sample volume; this was applied by Kovács et al. (2004) and also Tosheva et al. (2004).

II.1.3. Pre-concentration techniques of polonium isotopes

Co-precipitation using manganese dioxide (Minczewski et al., 1982) and iron (III) hydroxide are the most applied pre-concentration techniques for determination of polonium isotopes in water samples. When manganese oxide is used as precipitant, $MnCl_2$ and $KMnO_4$ solutions are added to the solution and the pH is adjusted to 8 – 9. The MnO_2 precipitate with co-precipitated polonium is dissolved in hydrochloric acid and H_2O_2. When iron hydroxide is used, iron (III) carrier is added and the pH is adjusted to 9 – 10 with concentrated ammonia solution.

II.2. RADIOCHEMICAL SEPARATION TECHNIQUES

II.2.1. Radiochemical separation of ^{228}Ra

Since the decay of ^{228}Ra by beta-particle emission produces daughter nuclides, ^{228}Ac which is a β-particle and γ-ray emitter and ^{228}Th which is an α-particle emitter, several separation and measurement procedures have been developed. For measurement of ^{228}Ra, Burnett et al.

(1995) developed a procedure using extraction chromatographic resins (**Ln Spec^{TM}**) and later on in 2004 Nour et al. used another resin (**Diphonix** resin) to isolate the direct daughter ^{228}Ac. In figure 1 is presented the chart of radiochemical separation of ^{228}Ac using Ln resin. Ln resin is composed of di(2-ethylhexyl) orthophosphoric acid impregnated onto an inert support and Diphonix resin contains diphosphonic acid groups bound to a styrene-based polymer matrix (Figure 2).
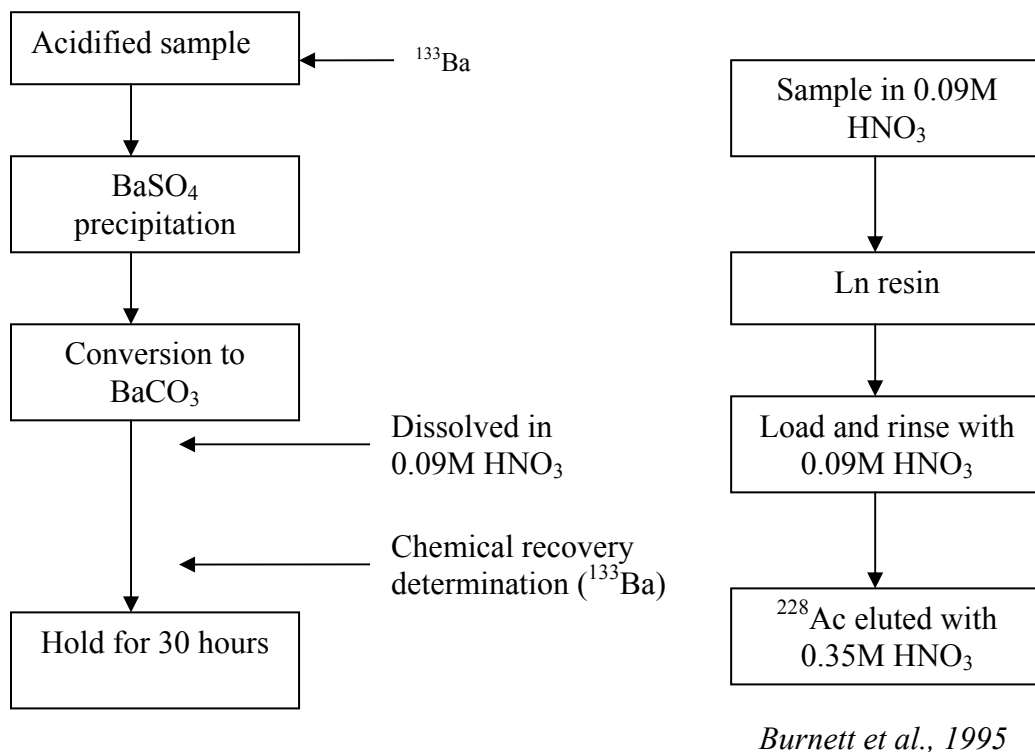

Burnett et al., 1995

Figure 1.   Flow chart of actinium separation using an Ln resin
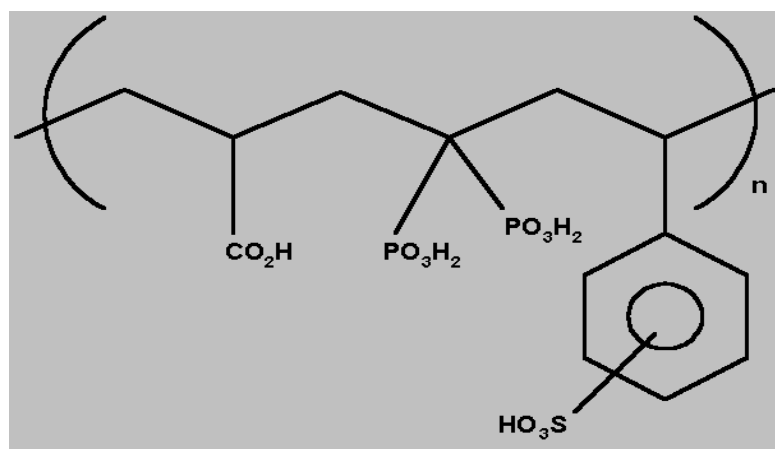
http://www.eichrom.com/products/info/diphonix_resin.cfm

Figure 2.   The chemical composition of diphonix resin

II.2.2. Radiochemical separation of uranium isotopes

Extraction chromatography is used for the **uranium isotopes** separation. UTEVA resin is one of the most popular extraction chromatographic resins used for uranium separation. The method was described by Horwitz et al. in 1992 and the resin consists of diamyl amylphosphonate sorbed on an inert polymeric support (Amberlite XAD-7). Uranium is eluted using diluted hydrochloric acid. The chemical structure of diamyl amyl phosphonate is shown in Figure 3.
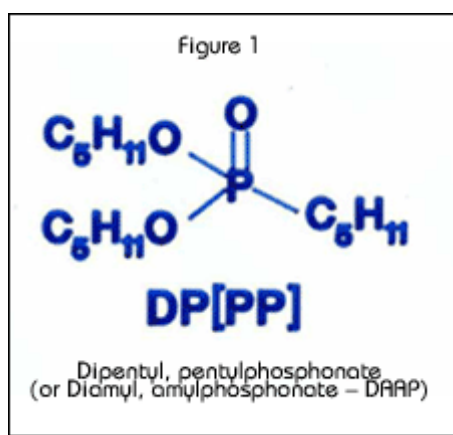
Figure 3. Chemical structure of diamyl amylphosphonate

Solvent extraction and anion exchange chromatography are also used for separation of uranium isotopes from environmental samples. The disadvantage of liquid – liquid extraction chromatography is the lengthy time needed, and for routine work - when a large number of samples have to be analysed - it can be difficult. When uranium isotopes have to be separated from thorium isotopes, anion exchange chromatography can also be used because of their different adsorbtion behaviour in nitric and hydrochloric acid on anion exchangers. Vera Tomé et al. (1994), separated uranium isotopes using Dowex anion exchange resin from 9M HCl medium.

II.2.3. Radiochemical separation of polonium isotopes

Polonium isotopes are also separated using extraction chromatography. The Sr-Spec resin is used for isolation of polonium isotopes from environmental samples. The extractant is a

crown ether (1M bis-4,4'(5'0-tbutyl- cyclohexano-18,6-crown ether) dissolved in 1-octanol. The structure of the extractant is shown in Figure 4.

Figure 1

4,4'(5')-di-t-butylcyclohexano
18-crown-6

Diluent: 1-octanol
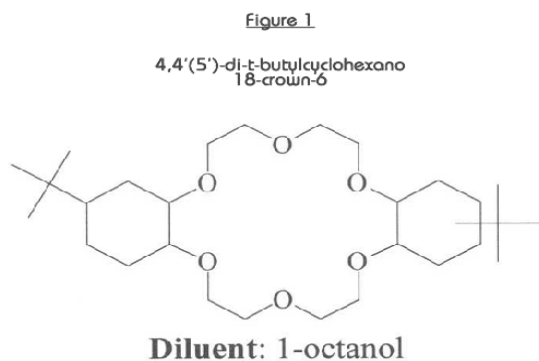
http://www.eichrom.com/products/info/sr_resin.cfm

Figure 4.   The Sr-resin structure

Samples were loaded on a Sr resin (Eichrom Industries Inc) column in 2M HCl. The non-retained ions were washed from the column with 2M HCl and polonium was stripped with 6M HNO_3 (Vajda et al., 1997).

Anion exchange chromatography and solvent extraction are also used for the separation of polonium isotopes. Pacer (1983) used Dowex anion exchange resin for the separation of [210]Po which was eluted with 8M HNO_3. Jia et al. (2004) showed that polonium isotopes can be extracted by 5% TOPO in toluene in a wide range of hydrochloric acid acidities (0.1 - 10M HCl).

II.3.   MEASUREMENT   TECHNIQUES   FOR   THE DETERMINATION OF [228]Ra, [210]Po, [234]U AND [238]U IN WATERS

II.3.1. Alpha-particle spectrometry

The activity concentration of [228]Ra can be determined using its granddaughter [228]Th. Eikenberg et al. (2001) determined the activity concentration of [228]Ra using MnO_2-coated polyamide discs for α-particle measurement of [228]Th. The MnO_2-coated discs were mounted in a teflon holder, and then immersed in a glass beaker containing the sample. Before immersion, the pH of the sample was adjusted to 7-8 and adsorption of radium onto disc was done over two days under continuous stirring. Evaluation of [228]Ra was done via measurement

of its daughter ^{228}Th after a standing time of about 6 – 12 months. The most important parameters which were investigated regarding the chemical recovery for radium on the MnO$_2$-coated discs were: pH, manganese layer density, temperature and salt concentrations of the sample.

Alpha-particle spectrometry is the measurement technique used for the determination of uranium and polonium isotopes in environmental samples. The advantage is the low background and the good resolution. For alpha-particle measurements, the prepared sources have to be thin in order to reduce the self-absorption.

II.3.2. Beta-particle spectrometry

The activity concentration of ^{228}Ra can be determined by beta-particle spectrometry. Being a low energy beta-particle emitter, $E_{\beta max} = 39$ keV, the most used methods for the determination of ^{228}Ra are based on measurement of its daughter ^{228}Ac after a standing time to reach equilibrium. ^{228}Ac is a high energy beta-particle emitter ($E_{\beta max} = 2.1$ MeV) but the disadvantage is its short half-life ($T_{1/2} = 6.14$ hours). Gas flow proportional counting and liquid scintillation counting are two measurement techniques which are used for measuring ^{228}Ac. For using a gas flow proportional counter the actinium source is prepared using Ce as carrier and co-precipitated as CeF$_3$ by addition of concentrated HF (Burnett et al., 1995). Liquid scintillation counting can be used for the measurement of the low energy beta-particle of ^{228}Ra and also for the measurement of its daughter ^{228}Ac. The activity concentration of ^{228}Ra was directly measured by Chalupnik and Lebecka (1992) while Nour et al. (2004) determined it via ^{228}Ac, both using liquid scintillation counting.

II.3.3. Gamma-ray spectrometry

As ^{228}Ra does not emit suitable gamma rays its determination is done through its daughter product ^{228}Ac, which has a gamma line of 911 keV with an emission probability of 29 %. Different radiochemical separation processes are applied to the sample in view of measurement by gamma-ray spectrometry. One of them is using barium sulphate precipitate (Kahn et al., 1990). Another method is to use Empore^{TM} Radium Rad Disks to measure ^{228}Ac by gamma spectrometry in order to determine ^{228}Ra. After the sample is filtered, the Rad

Disks are stored to allow ^{228}Ac to grow in and then measured using the gamma-ray emission of 911 keV (Matthews et al., 2000).

III. EXPERIMENTAL

III.1. REAGENTS, EQUIPMENT and SAMPLES

- Diphonix resin (100 – 200 mesh), Eichrom Industries Inc;

- TEVA resin, (100-150 μm, 2mL), (Eichrom Industries Inc);

- UTEVA resin (100-150 μm, 2mL), (Eichrom Industries Inc);

- Liquid scintillation cocktails: Packard Ultima Gold AB cocktail; InstaGel – Plus cocktail (Perkin Elmer);

- ^{133}Ba tracer;

- Thorium solution standard (1 mg/ml natural thorium, 2% HNO_3);

- ^{208}Po tracer: A calibrated solution, product code PMP10030, was purchased from AEA Technology, UK. The tracer contains impurities of ^{209}Po. A working solution with an activity of 1.172 (0.015) Bq/g on 15/04/2008 was used;

- ^{232}U: A working solution with an activity of 1.158 (0.016) Bq/g on 19/06/2007 was prepared from an IRMM standard solution with an activity of 0.734 kBq/g;

- Hydrochloric acid 32 %;

- Nitric acid 65 %;

- Hydrogen peroxide 27 %;

- Potassium permanganate, manganese chloride, sodium hydroxide;

- Centrifuge;

- HPGe detector;

- Liquid Scintillation Counter: Wallac Quantulus 1220^{TM};

- Canberra Model 7401 VR (Canberra, Meriden, CT, USA) alpha-particle spectrometer and PIPS detectors with 450 mm^2 sensitive areas.

SAMPLES

For this study we used three types of mineral water samples: water-1, water-2 and water-3. ^{228}Ra was determined in water-1 and water-2 and uranium and polonium isotopes were determined in water-1 and water-3. Water was purchased from different companies in Hungary and it was bottled in 1.5 L PET bottles.

III.2. SAMPLE PREPARATION

III.2.1. ^{228}Ra pre-concentration method

Two types of bottled mineral water were analysed, water-1 and water-2. For the chemical separation we used the procedure described by Nour et al. (2004). Because of the low activity concentration of ^{228}Ra in the waters under investigation, volumes of 1.5 L and 3 L were used for each single determination. Pre-concentration of ^{228}Ra was done using MnO_2 co-precipitation. The pH was adjusted to 2 with concentrated hydrochloric acid and then a known amount of ^{133}Ba tracer was added to be used for determination of the chemical yield of the radiochemical separation procedure. Depending on volume of the water taken for the analysis, precipitation of radium with MnO_2 was done by adding 0.375 or 0.75 mL of $KMnO_4$ and 0.75 or 1.5 mL of $MnCl_2$, and adjusting the pH to 8 - 9 with 2M NaOH. The sample was stirred for two hours and then left overnight to allow the precipitate to settle down. The supernatant was decanted, the MnO_2 precipitate was centrifuged for 5 minutes at 3500 rpm and the precipitate was dissolved in the mixture of concentrated HCl and H_2O_2.

III.2.2. Polonium and uranium isotopes pre-concentration methods

A volume of 1.5 L, 3 L or 4.5 L mineral water was used. The pre-concentration of uranium and polonium isotopes from mineral waters was done using two different methods: iron (III) hydroxide and manganese dioxide co-precipitation.

III.2.2.1. Iron(III) hydroxide co-precipitation

After the samples were aliquoted and acidified to pH=1 with concentrated nitric acid, 0.1 g of each ^{232}U and ^{208}Po tracer solutions was added and mixed for 3 hours. After addition of 30mg iron(III) the pH was adjusted to $9 - 10$ with ammonium hydroxide and mixed for another 6 hours. Then, the samples were let over night to allow the precipitate to settle down. The next day the supernatant was discarded and the remaining suspension was centrifuged for 5 minutes at 3500 rpm; the precipitate was dissolved in nitric acid or hydrochloric acid, depending on the applied procedure.

III.2.2.2. **Manganese dioxide co-precipitation**

After the samples were aliquoted, the pH was adjusted to 2 with concentrated hydrochloric acid, 0.1 g of each ^{232}U and ^{208}Po tracer solutions were added and then the samples were stirred for 3 hours. After addition of 0.375 mL of $KMnO_4$, the pH was adjusted to $8-9$ with 2M NaOH, 0.750 mL of $MnCl_2$ was added and MnO_2 precipitate started to form and the sample was stirred for another 6 hours. The next day the supernatant was discarded and the remaining suspension was centrifuged for 5 minutes at 3500 rpm. The precipitate was dissolved in hydrochloric or nitric acid and H_2O_2, depending on the used procedure.

III.3. RADIOCHEMICAL SEPARATION METHODS

III.3.1. Radiochemical separation of ^{228}Ra from mineral waters

After the pre-concentration of radium isotopes from the mineral water samples with MnO_2, ^{228}Ra is separated applying the following procedure.

After dissolving the precipitate with concentrated HCl and H_2O_2, de-ionised water was added to adjust to 2M HCl and the sample was ready to be loaded onto the first Diphonix resin column. The resin column (0.5 cm i.d., 15 cm long) was conditioned with 10 mL of 2M HCl, then the sample was loaded onto the column and the non-retained ions (Ra, Ba) were eluted with 15 mL of 2M HCl. The eluted fractions were collected and stored for approximately two days to allow ^{228}Ac to reach equilibrium with its parent ^{228}Ra. A second Diphonix resin column (0.8 cm i.d., 2.3 cm long), conditioned with 10 mL 2M HCl was used for the separation of ^{228}Ac, which was eluted with 5 mL of 1M of 1-hydroxyethane-1,1-diphosphonic acid (HEDPA) in a polyethylene liquid scintillation vial. A blank was prepared in the same way as the samples using the same reagents and deionised water.

A schematic representation of the procedure is presented in figure 5.

A year earlier, the radium isotopes from aliquots of the same water samples were co-precipitated as $Ra(Ba)SO_4$ following the method of Lozano et al. (1997) and the sources were stored such that ^{228}Th, the grand-daughter of ^{228}Ra, would grow in. After dissolving the precipitate in EDTA, ^{229}Th was added. Thorium isotopes were separated using a TEVA resin and measured using a Canberra Model 7401 VR alpha-particle spectrometer.

Figure 5. **Radiochemical separation of radium and ²²⁸Ac from mineral waters**

The flowchart contains:

MnO$_2$ pre-concentration of Ra isotopes ^{133}Ba added

Centrifugation

Precipitate dissolved in conc.HCl+few drops of H$_2$O$_2$ and deionised water was added to adjust the conc. to 2M HCl

Diphonix ion exchange resin The possible interferences from actinides and lanthanides are eliminated

^{133}Ba- recovery determination **^{228}Ra** (load and wash)

Allow ~2 days for **^{228}Ac** to grow in

^{228}Ra, ^{228}Ac

^{228}Ac Diphonix ion exchange resin

1M HEDPA

^{228}Ac

MnO$_2$ pre-concentration
of Ra isotopes
^{133}Ba added

Centrifugation

Precipitate dissolved in conc.HCl+few drops of H$_2$O$_2$ and deionised water was added to adjust the conc. to 2M HCl

Diphonix ion exchange resin
The possible interferences from actinides and lanthanides are eliminated

^{133}Ba- recovery determination
^{228}Ra (load and wash)

Allow ~2 days for
^{228}Ac to grow in

^{228}Ra, ^{228}Ac

^{228}Ac
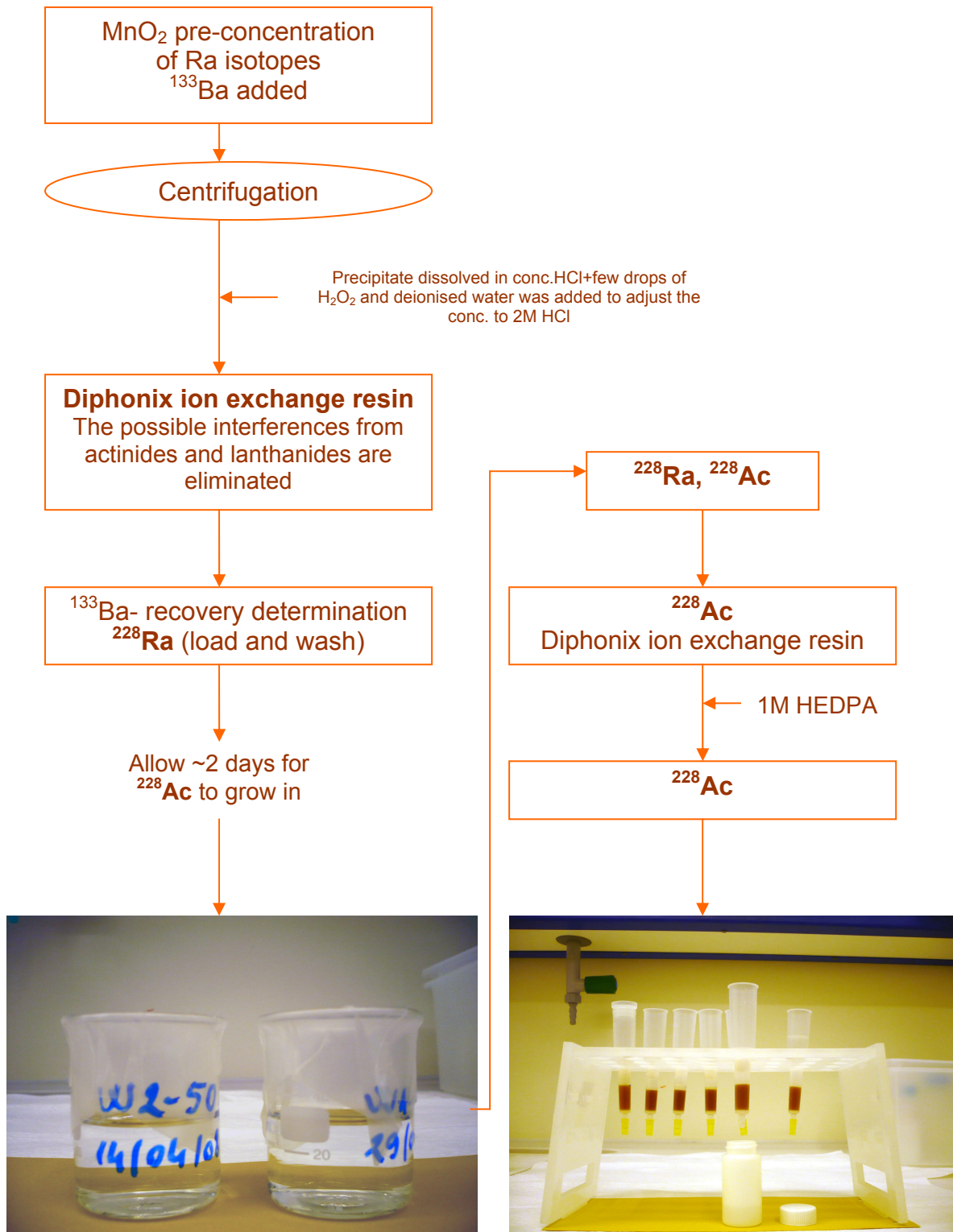Diphonix ion exchange resin

1M HEDPA

^{228}Ac

Figure 5. **Radiochemical separation of radium and ^{228}Ac from mineral waters**

III.3.2. Radiochemical separation of polonium and uranium isotopes from mineral waters

For the radiochemical separation of polonium and uranium isotopes from mineral waters, we used two pre-concentration methods and two procedures (procedure-1 and procedure-2). Iron(III) hydroxide and manganese dioxide co-precipitation were the pre-concentration methods. In the case of procedure-1, we separate first uranium isotopes using UTEVA resin and then polonium isotopes by self-deposition on copper disks. In procedure-2, first polonium isotopes were separated by self-deposition and then uranium isotopes using UTEVA resin.

III.3.2.1. Procedure-1

The MnO_2 or $Fe(OH)_3$ precipitate was dissolved in concentrated nitric acid and H_2O_2 or concentrated nitric acid, respectively. Then de-ionised water was added to adjust to 3M HNO_3 and the samples were then passed through UTEVA resin column which was pre-conditioned with 15 mL of 3M HNO_3. Then the column was washed with 10 mL of 3M HNO_3, 5 mL of 9M HCl and 20 mL of 5M HCl + 0.05M oxalic acid to remove Th, Np, Pu. Uranium isotopes were eluted with 10 mL of 1M HCl, micro co-precipitated with CeF_3 and measured by alpha-particle spectrometry. Before co-precipitation, U(VI) must be reduced to U(IV) with 1mL 15 % of $TiCl_3$. Uranium radioisotopes were co-precipitated with 1 mL of 48 % HF and 0.1mL of 0.5 mg·mL^{-1} of Ce^{3+} as carrier. The solution was shaken and allowed to stay in the fridge for one hour. Precipitated uranium radioisotopes on CeF_3 were filtered through 0.1μm, 25 mm polypropylene filter (Resolve filter, Eichrom). After filtration of the precipitate, the filter was washed with 5 mL of de-ionised water and 5 mL of 80 % ethanol solution. The filter was air dried, mounted on a stainless steel disc and covered with 6 % VYNS foil.

The collected 3M HNO_3 solution is used for determination of polonium isotopes. The solution is evaporated avoiding temperatures higher than 100°C (to prevent the evaporation of polonium isotopes) close to dryness. The wet residue is dissolved in concentrated hydrochloric acid and H_2O_2, the pH is adjusted to 1.5 with de-ionised water and 0.5 g ascorbic acid is added to eliminate the interferences from other ions, like Fe^{3+}, Mn^{6+}. A teflon holder is used to keep the copper disc. After 4 hours at 90°C, the copper disc is removed and it is washed with de-ionised water and acetone. The disc is air dried, mounted on a stainless steel disc and covered with 6 % VYNS foil. A schematic presentation of the procedure-1 is presented in Figure 6.

III.3.2.2. Procedure-2

Applying procedure-2, polonium isotopes were determined first and then uranium isotopes. The sample is dissolved in 1 mL of concentrated hydrochloric acid and H_2O_2, and then the pH is adjusted with de-ionised water to pH=1.5. To eliminate the possible interferences, 0.5 g of ascorbic acid is added. A teflon holder which contains a copper disc is immersed in the solution and the self-deposition of polonium isotopes is done for 4 hours at 90°C. The remaining solution is evaporated to dryness and the residue is treated with concentrated nitric acid and H_2O_2 to destroy the ascorbic acid. The final medium of the sample is 3M HNO_3 and it is then loaded on an UTEVA resin column which is pre-conditioned with 10 mL 3M HNO_3. After the column is washed with 10 mL of 3M HNO_3, 5 mL of 9M HCl and 20 mL of 5M HCl + 0.05M $H_2C_2O_4$, the uranium isotopes are eluted with 10 mL of 1M HCl. The micro co-precipitation of the uranium isotopes is done with CeF_3. Before co-precipitation, U(VI) must be reduced to U(IV) with 1 mL of 15 % of $TiCl_3$. Uranium radioisotopes are co-precipitated with 1 mL of 48 % HF and 0.1 mL of 0.5 mg·mL^{-1} of Ce^{3+} as carrier. The solution is shaken and allowed to stay in the fridge for one hour. Precipitated uranium radioisotopes on CeF_3 are filtered through 0.1μm, 25 mm polypropylene filter (Resolve filter, Eichrom). After filtration of the precipitate, the filter is washed with 5 mL of de-ionised water and 5 mL of 80 % ethanol solution. The filter is air dried, mounted on a stainless steel disc and covered with 6 % VYNS foil. A schematic presentation of procedure-2 is presented in Figure 7.
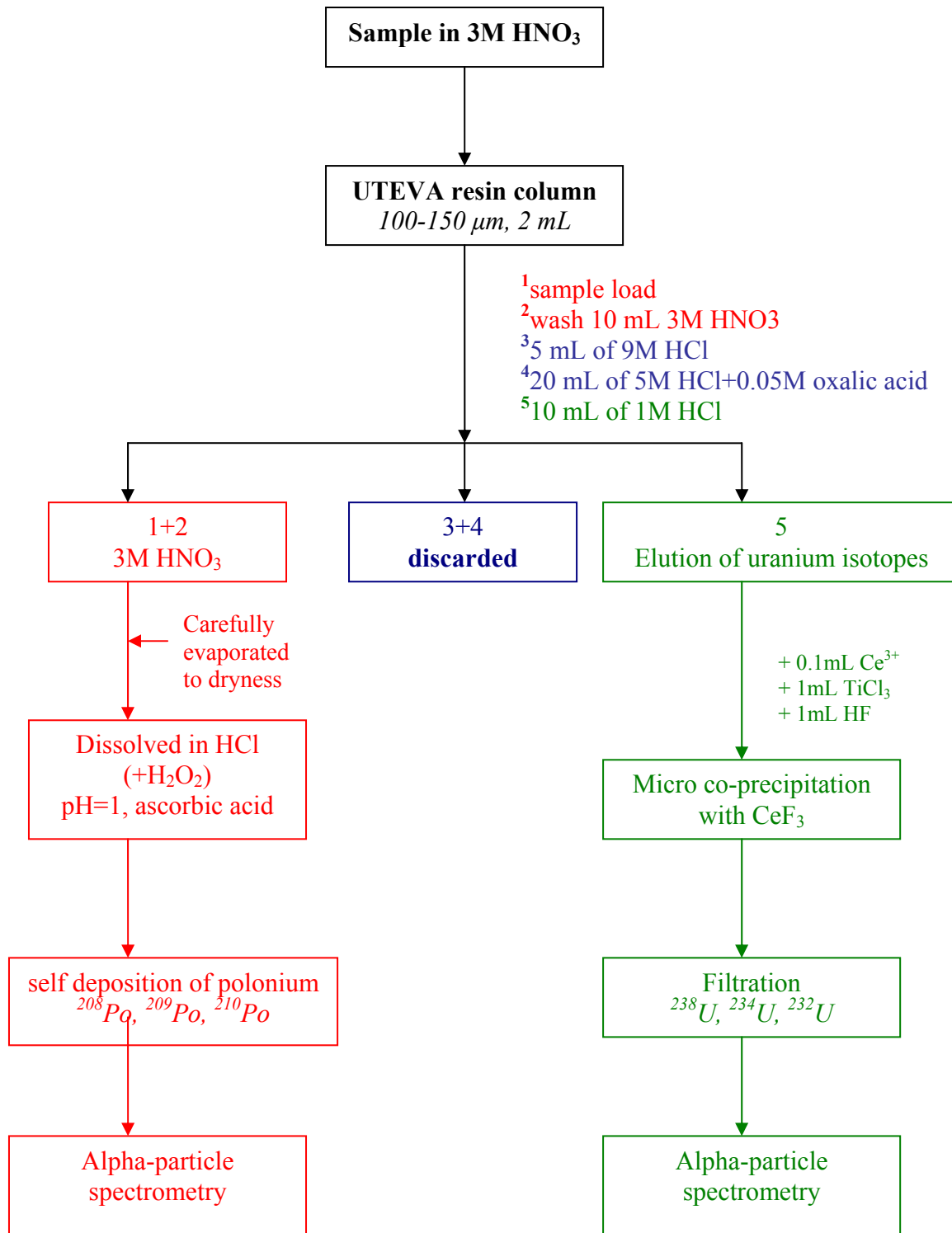
```
                        ┌─────────────────────────┐
                        │   Sample in 3M HNO₃      │
                        └─────────────────────────┘
                                    │
                                    ▼
                        ┌─────────────────────────┐
                        │   UTEVA resin column     │
                        │   100-150 μm, 2 mL       │
                        └─────────────────────────┘
                                    │
```
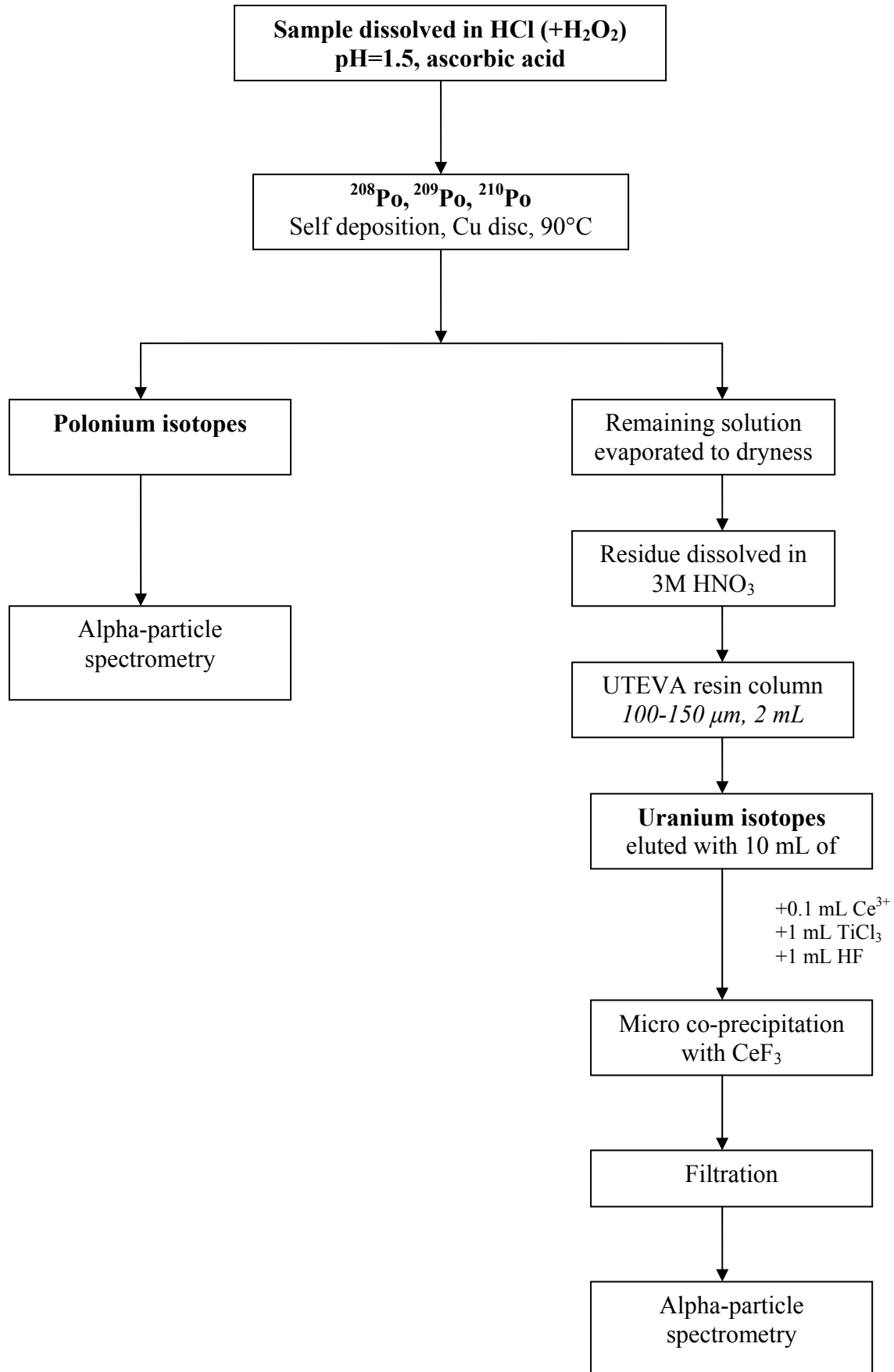
¹sample load
²wash 10 mL 3M HNO3
³5 mL of 9M HCl
⁴20 mL of 5M HCl+0.05M oxalic acid
⁵10 mL of 1M HCl

```
        ┌──────────────┐   ┌──────────────┐   ┌───────────────────────────┐
        │    1+2       │   │    3+4       │   │    5                      │
        │   3M HNO₃    │   │  discarded   │   │  Elution of uranium       │
        │              │   │              │   │  isotopes                 │
        └──────────────┘   └──────────────┘   └───────────────────────────┘
             │                                       │
       Carefully                              + 0.1mL Ce³⁺
       evaporated                             + 1mL TiCl₃
       to dryness                             + 1mL HF
             │                                       │
             ▼                                       ▼
        ┌──────────────┐                      ┌───────────────────────────┐
        │ Dissolved in │                      │  Micro co-precipitation   │
        │ HCl (+H₂O₂)  │                      │  with CeF₃                │
        │ pH=1,        │                      └───────────────────────────┘
        │ ascorbic acid│                             │
        └──────────────┘                             ▼
             │                               ┌───────────────────────────┐
             ▼                               │  Filtration               │
        ┌──────────────────────┐             │  ²³⁸U, ²³⁴U, ²³²U          │
        │ self deposition of   │             └───────────────────────────┘
        │ polonium             │                     │
        │ ²⁰⁸Po, ²⁰⁹Po, ²¹⁰Po  │                     ▼
        └──────────────────────┘             ┌───────────────────────────┐
             │                               │  Alpha-particle           │
             ▼                               │  spectrometry             │
        ┌──────────────┐                     └───────────────────────────┘
        │ Alpha-particle│
        │ spectrometry  │
        └──────────────┘
```

Figure 6.   Procedure-1

```
┌─────────────────────────────────┐
│  Sample dissolved in HCl (+H₂O₂) │
│      pH=1.5, ascorbic acid       │
└─────────────────────────────────┘
                 │
                 ▼
┌─────────────────────────────────┐
│      ²⁰⁸Po, ²⁰⁹Po, ²¹⁰Po         │
│   Self deposition, Cu disc, 90°C │
└─────────────────────────────────┘
```

$$^{208}\text{Po, }^{209}\text{Po, }^{210}\text{Po}$$

Self deposition, Cu disc, 90°C

Polonium isotopes

Alpha-particle spectrometry

Remaining solution evaporated to dryness

Residue dissolved in 3M HNO_3

UTEVA resin column *100-150 μm, 2 mL*

Uranium isotopes eluted with 10 mL of

+0.1 mL Ce^{3+}
+1 mL $TiCl_3$
+1 mL HF

Micro co-precipitation with CeF_3

Filtration

Alpha-particle spectrometry

Figure 7.   Procedure-2

III.4. RESULTS AND DISCUSSIONS

III.4.1 ^{228}Ra results

The activity concentration of ^{228}Ra and therefore that of the resulting ^{228}Ac in the mineral waters studied was very low. In addition, the decay of ^{228}Ac occurs very fast ($T_{1/2} = 6.14$ h), too fast to allow for lengthy measurements. The background contribution is very significant and any means to reduce it must be employed. Different liquid scintillation (LS) cocktails present different levels of background due to their inherent radioactivity. Salonen et al. (1997) observed in the β-spectrum of Ultima Gold AB (Perkin Elmer) ^{40}K impurities. We also observed higher background count rates in the region from channel 700 to 900, interfering with the ^{228}Ac beta-particle spectrum.

Using 15 mL of Ultima Gold AB, a count rate of 6 cpm for the range from channel 1 to 1024 and 3.7 cpm for channels 350 – 850 was observed. For 15 mL Insta-Gel Plus (Perkin Elmer) the count rate was 3.5 cpm from channel 1 to 1024 and 1.7 cpm (channels 350 – 850). In Figure 8 (a) and (b), respectively, the beta-particle spectra of 15 mL Ultima Gold AB and 15 mL Insta-Gel Plus cocktails measured with a Wallac Quantulus 1220^{TM} for 120 minutes are presented. Different volumes of Insta-Gel Plus cocktail (6, 7, 8, 10, 12 and 15 mL) were measured. A volume of 7 mL of Insta-Gel Plus cocktail was enough to assure a homogeneous single phase mixture with the sample and at the same time obtain a low background in the measurement window from 350 to 850 channels. To compensate for fluctuations the blank was measured for 120 minutes each time before and after each sample.

The chemical recovery of radium was determined using the 356 keV gamma-ray line of ^{133}Ba. The chemical recovery $\mathbf{R_{chem}}$ was calculated according to equation (1):

$$R_{chem} = \left(\frac{A_{sample}}{t_{sample} \cdot m_{sample}} \right) \cdot \left(\frac{t_{Std} \cdot m_{Std}}{A_{Std}} \right), \qquad (1)$$

where:

A_{sample}, A_{Std}	are the net areas of ^{133}Ba peak from the sample and the standard sample, respectively;
t_{sample}, t_{Std}	are the counting times of sample and standard sample, respectively;
m_{sample}, m_{Std}	are the masses of added ^{133}Ba in the sample and of ^{133}Ba in the standard sample respectively.
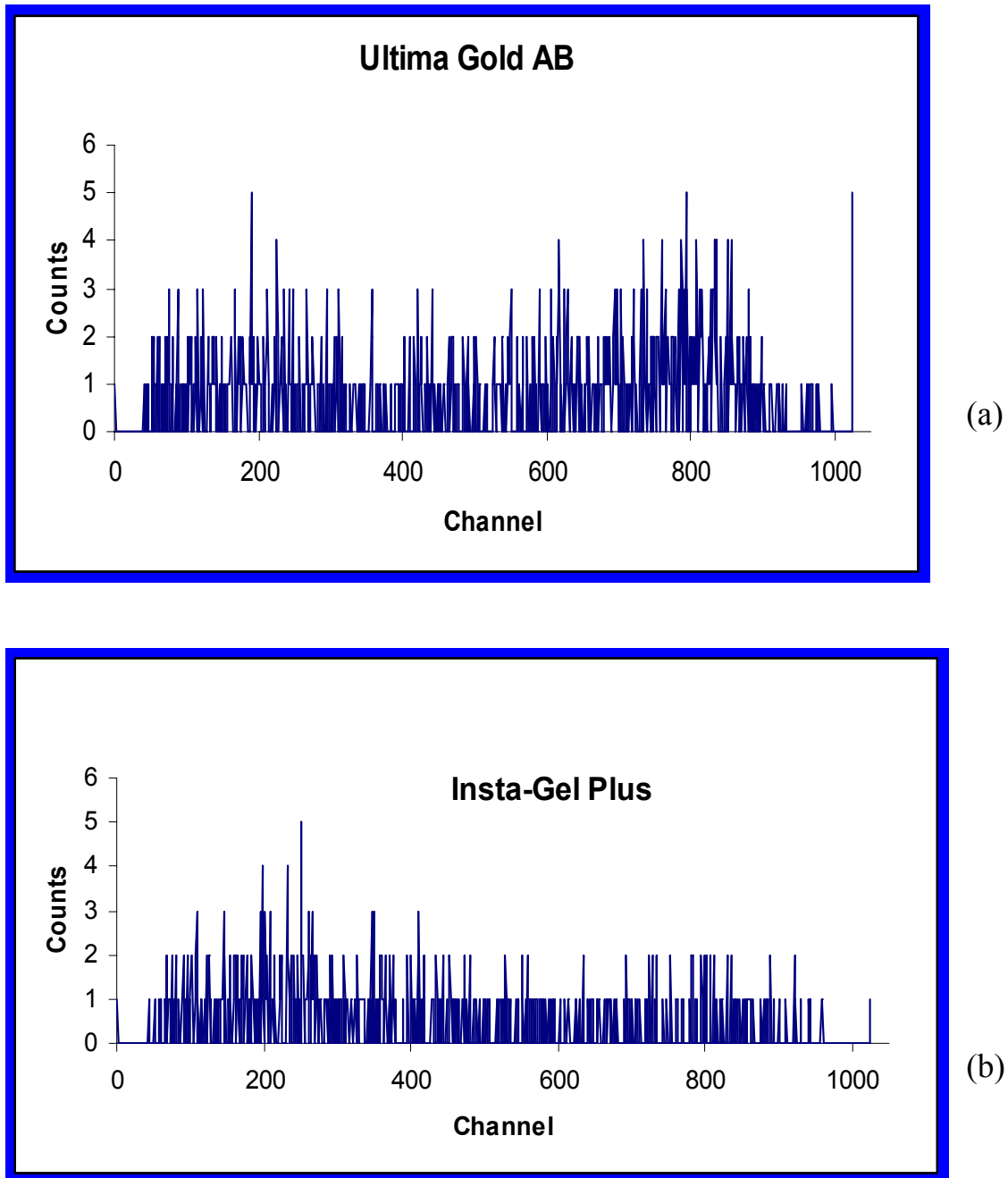
Figure 8. Background beta-particle spectra measured for 120 minutes with the Wallac Quantulus 1220™ of the liquid scintillation cocktails based on (a) Ultima Gold AB and (b) Insta-Gel Plus

For water-1 for the radium recovery we obtained a mean value of 96 % and the values are comparable with the results obtained by Nour et al. in natural waters (96.3 %). In case of water-2 we obtained lower recoveries; the mean value obtained was 77 %. We observed that

water-2 has a higher content of silica and this can be a reason for lower recovery. The results are mean values of 20 samples of each type of mineral water.

Separate experiments were performed for the determination of chemical recovery of [228]Ac from the second Diphonix column. A natural thorium solution in equilibrium was used and the [228]Ac was isolated. The latter was determined by measuring its 911 keV gamma-ray line using a HPGe detector and it was used to evaluate the chemical recovery. The mean value for the chemical recovery obtained from three replicate experiments was 82.7 %.

In Table 4 the activity concentration results for [228]Ra in the two mineral waters analysed in this work are presented and compared with the activity concentration of [228]Ra obtained via ingrowth of [228]Th and alpha-particle spectrometry. The counting time in the liquid scintillation counter was 120 minutes for each sample and the results were corrected for background, for decay during measurement and for decay to the reference date of 1 May 2006, 0:00 UTC. Figure 9 and 10, respectively, show the β - particle spectra of an [228]Ac standard sample and of the samples water - 1, water - 2 and the blank.

In case of water-1 the activity concentration of [228]Ra varied between 20.2 mBq·L^{-1} and 28.5 mBq·L^{-1} with a mean value and standard deviation of (23.5 ± 2.6) mBq·L^{-1}. For water-2, the activity concentration varied between 60.6 mBq·L^{-1} and 75.2 mBq·L^{-1} with a mean value of (66.8 ± 4.3) mBq·L^{-1}. The results are mean values of 20 samples of 1.5 and 3 L each, respectively. The values are confirmed by alpha-particle spectrometry of [228]Th, granddaughter of [228]Ra grown in during one year.

For the method described in this work, radiochemical separation of [228]Ac and LSC, we determined a minimum detectable activity concentration, using the Currie equation (1968), of 9 mBq·L^{-1} using a sample of 1.5 L, 120 minutes counting time and a chemical yield of 96 %.

Table 4. Activity concentration of [228]Ra in mineral waters for the reference date 1 May 2006, 0:00 UTC obtained by radiochemical separation of [228]Ac and LSC (column 2) and determined via ingrowth of [228]Th and alpha-particle spectrometry (column 3). The uncertainty is given as standard deviation *s*

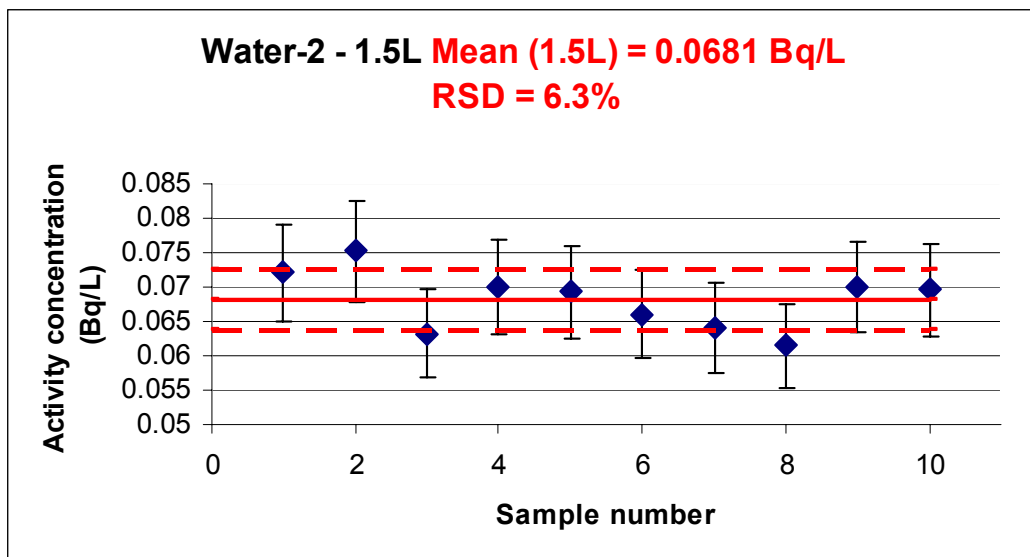| Sample	Activity concentration mBq·L^{-1}	
	Liquid scintillation counting	Alpha-spectrometry
Water-1	**23.5 ± 2.6**	**29.0 ± 1.4**
Water-2	**66.8 ± 4.3**	**69.5 ± 1.4**

A plot of the obtained activity concentration of [228]Ra in water-1 (1.5 L and 3 L, respectively) and water-2 (1.5 L and 3 L, respectively) are presented in graph 1 and graph 2 for water-1 and graph 3 and graph 4 for water-2, respectively. The solid and the dashed red lines indicated in graphs 1 to 4, respectively, represent the mean values and the standard deviations. The error bars indicate combined standard uncertainties of the individual measurement.
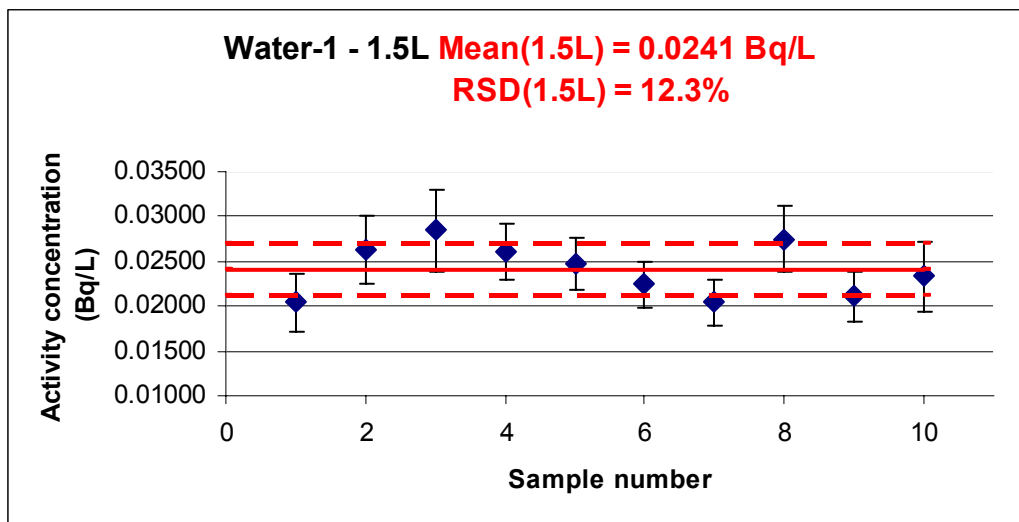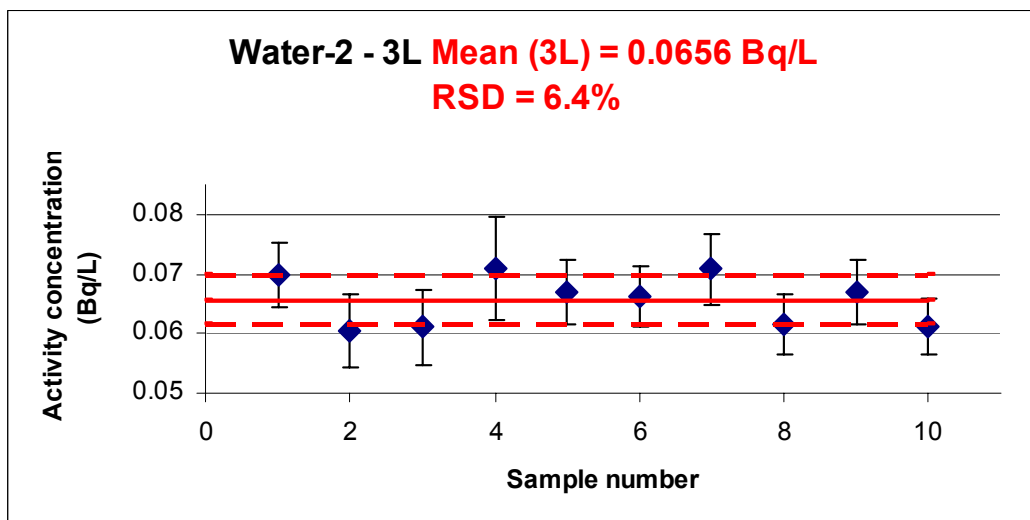

Graph 1. Activity concentration of [228]Ra in sample water-1 for 1.5 L
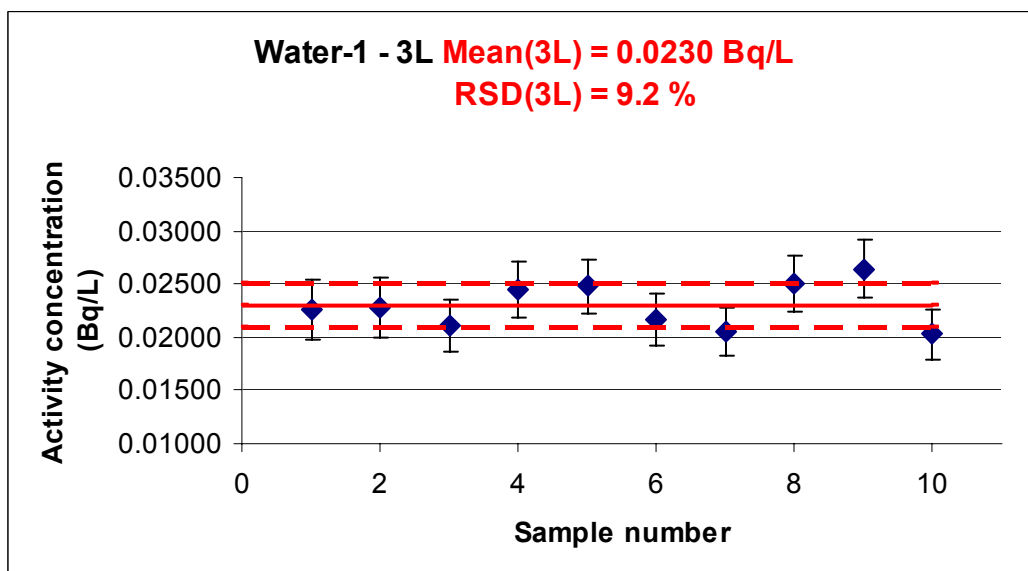
Graph 2. Activity concentration of [228]Ra in sample water-1 for 3 L

Graph 3. Activity concentration of ^{228}Ra in sample water-2 for 1.5 L

Graph 4. Activity concentration of ^{228}Ra in sample water-2 for 3 L

The half-life of ^{228}Ac, which we obtained experimentally, is 6.15 hours and is comparable with the value from literature of 6.14 hours (graph 5).
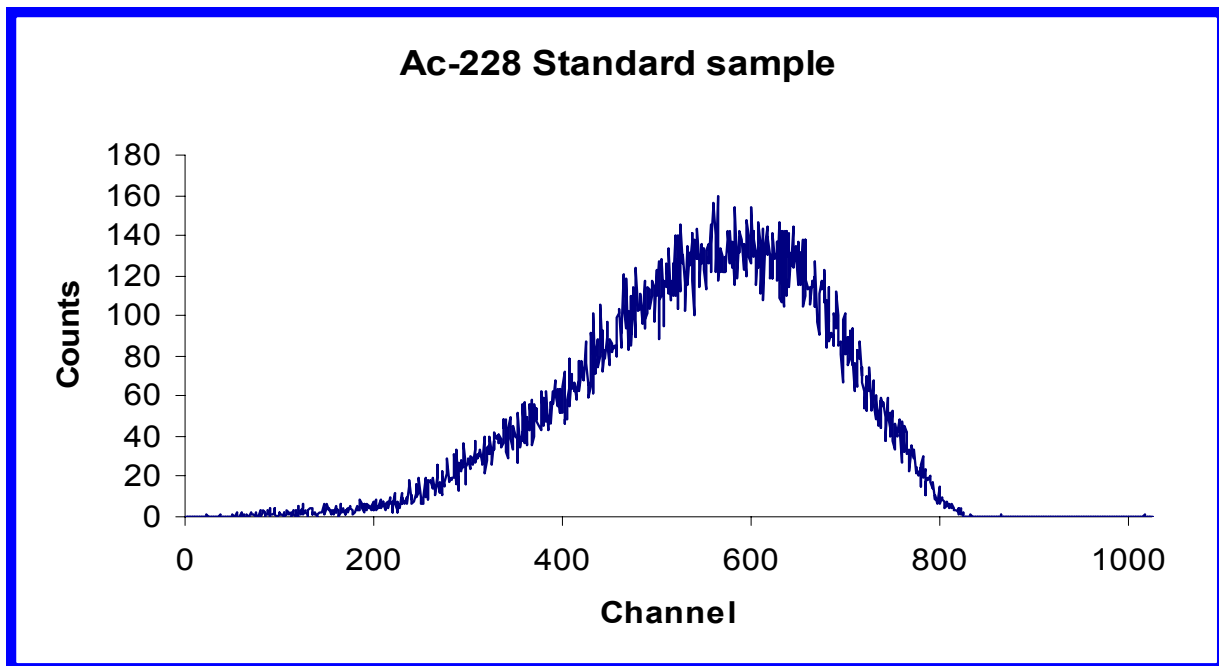
Figure 9. **²²⁸Ac standard sample measured with the Wallac Quantulus 1220™**
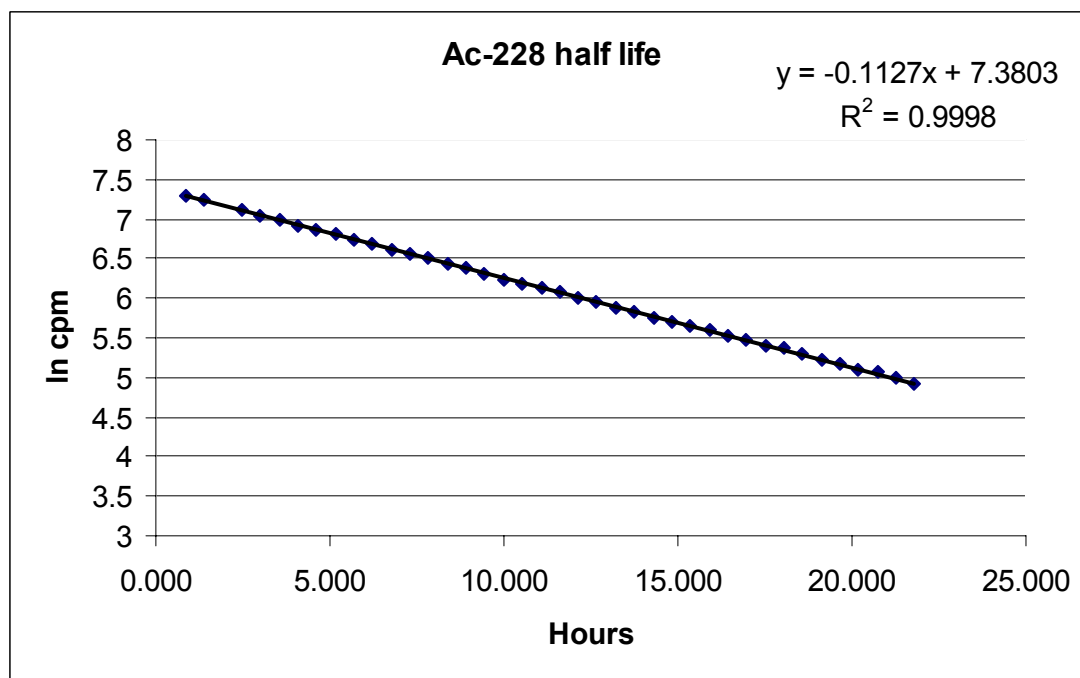
Graph 5. **Experimental determination of ²²⁸Ac half-life**
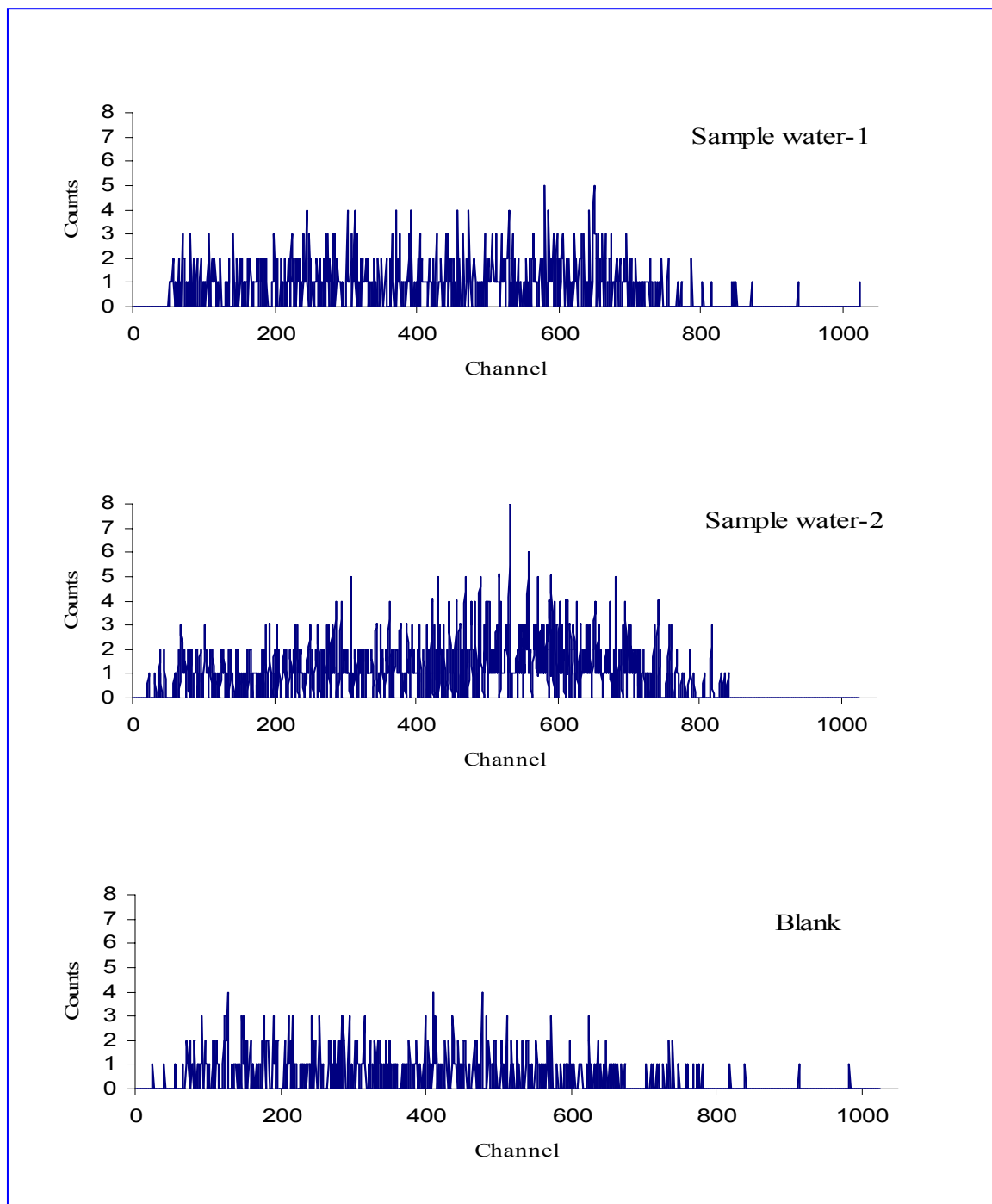
Figure 10. **Beta-particle spectra of ^{228}Ac measured with the Wallac Quantulus 1220^{TM} in two mineral water samples and blank. Measurement time was 120 minutes**

III.4.2. ^{210}Po, ^{234}U and ^{238}U results

Polonium and uranium isotopes were co-precipitated with manganese dioxide or iron hydroxide from mineral waters. For the determination of these isotopes two procedures were applied: procedure-1, in which uranium isotopes were separated first using UTEVA resin and then polonium isotopes by self deposition on copper disks; and procedure-2, in which polonium isotopes were separated first and then uranium isotopes.

Comparing the two co-precipitation methods for determination of polonium isotopes, we obtained a higher chemical recovery using manganese dioxide than iron hydroxide: 88 % and 75 %, respectively. The results are the mean values of nine samples using different water volumes (1.5 L, 3 L and 4.5 L). For different volumes of water samples, the chemical recovery did not show a significant variation: 77 %, 88 % and 83 %, respectively, were found as presented in figure 11. Looking at the two procedures which were applied for the determination of polonium isotopes, using procedure-2, when polonium isotopes are separated first, we have a higher chemical recovery than if procedure-1 is used: 86 % and 78 %, respectively. As can be observed from the results, the manganese dioxide co-precipitation method gives higher values of chemical recovery when procedure-2 is applied than when procedure-1 is used, 100 % and 74 %, respectively. The same higher recovery was observed in case of iron hydroxide co-precipitation methods when procedure-2 is applied than procedure-1, 78 % and 72 %, respectively.

In case of uranium isotopes, when different volumes of water samples were used (1.5 L, 3 L and 4.5 L, respectively) a decrease in the chemical recovery with the increase of sample volume was observed. For 1.5 L, 3 L and 4.5 L the chemical recovery was 92 %, 81 % and 64 %, respectively, presented in figure 12. If we look at the pre-concentration procedures, a higher chemical recovery can be observed using procedure-1 than procedure-2, 83 % and 68 %, respectively. Also when iron hydroxide is used as co-precipitation method, procedure-1 renders higher values than procedure-2, 82 % and 67 %, respectively. Higher values of the chemical recovery of uranium isotopes were also obtained with procedure-1 than procedure-2 when using manganese dioxide as co-precipitation method, 76 % and 66 %, respectively.

The results for the activity concentrations of ^{210}Po, ^{234}U and ^{238}U are presented in Table 5. The reference values given in Table 5 for the activity concentrations of ^{234}U and ^{238}U were determined using the data from two independent laboratories: Bundesamt für Strahlenschutz (BfS, Germany) and our own laboratory at IRMM using co-precipitation with iron (III)

hydroxide, radiochemical separation on UTEVA columns and preparing the source for alpha-particle spectrometry by micro-precipitation with CeF_3. A detailed description of the established reference values is given by Spasova et al. (2008). Figures 13 and 14, respectively, show uranium and polonium isotope spectra of the water samples separated using procedure-2 and procedure-1, respectively.
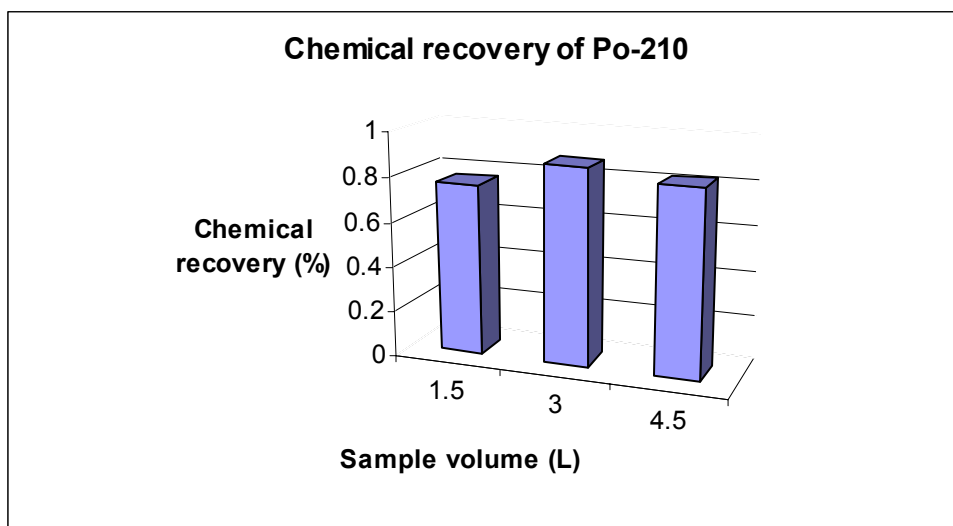

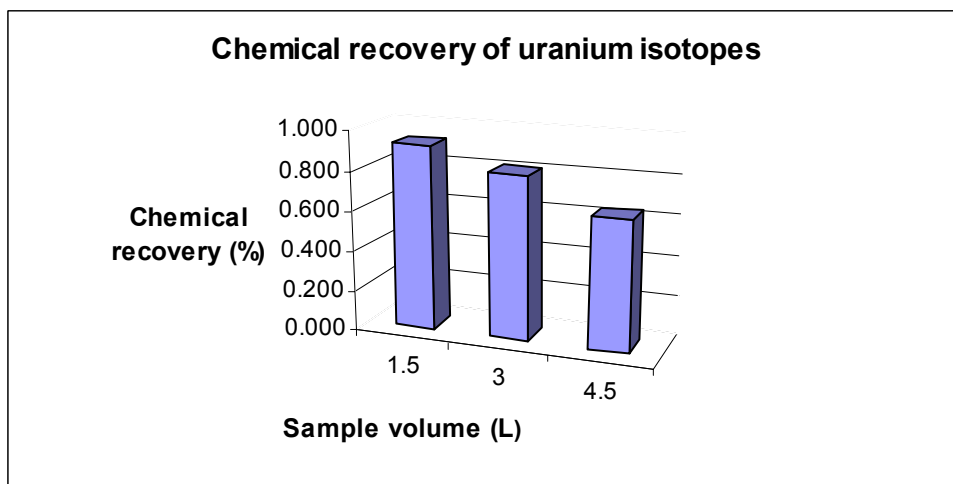**Figure 11.**   **The influence of the sample volume on chemical recovery of ^{210}Po**

Figure 12.   **The influence of the sample volume on chemical recovery of uranium isotopes**

Table 5. Comparison of the results obtained using Procedure-1 and Procedure-2 for determination of ^{210}Po, ^{234}U and ^{238}U in water samples in mBq/L (reference date 1 May 2006, 0:00 UTC)

Sample	Isotope	Procedure-1[a]		Procedure-2[a]		Reference value[b]
		Fe(OH)$_3$ precipitation	MnO$_2$ precipitation	Fe(OH)$_3$ precipitation	MnO$_2$ precipitation	
W-1	^{234}U	14.5 ± 1.6	14.5 ± 1.6	14.6 ± 1.4	14.5 ± 1.4	15.1 ± 1.2
	^{238}U	10.5 ± 1.4	10.9 ± 1.4	10.8 ± 1.2	10.9 ± 1.2	11.3 ± 0.8
	^{210}Po	4.2 ± 0.2	4.2 ± 0.2	4.2 ± 0.2	4.1 ± 0.3	
W-3 batch A	^{234}U	46.7 ± 2.1	43.8 ± 2.6	45.1 ± 2.3	44.4 ± 2.2	43.9 ± 1.6
	^{238}U	24.6 ± 1.2	22.3 ± 1.4	24.7 ± 1.4	23.6 ± 1.2	21.7 ± 1.0
	^{210}Po	1.01 ± 0.21	0.91 ± 0.19	0.95 ± 0.21	0.84 ± 0.17	
W-3 batch B	^{234}U	41.4 ± 2.0	39.0 ± 2.0	38.7 ± 2.8	40.4 ± 2.0	40.9 ± 1.5
	^{238}U	21.2 ± 1.2	19.6 ± 1.4	19.5 ± 1.6	21.6 ± 1.2	20.5 ± 1.0
	^{210}Po	0.46 ± 0.10	0.49 ± 0.11	0.57 ± 0.14	0.48 ± 0.11	

[a] uncertainty values reported as combined uncertainty expanded by a coverage factor k=2

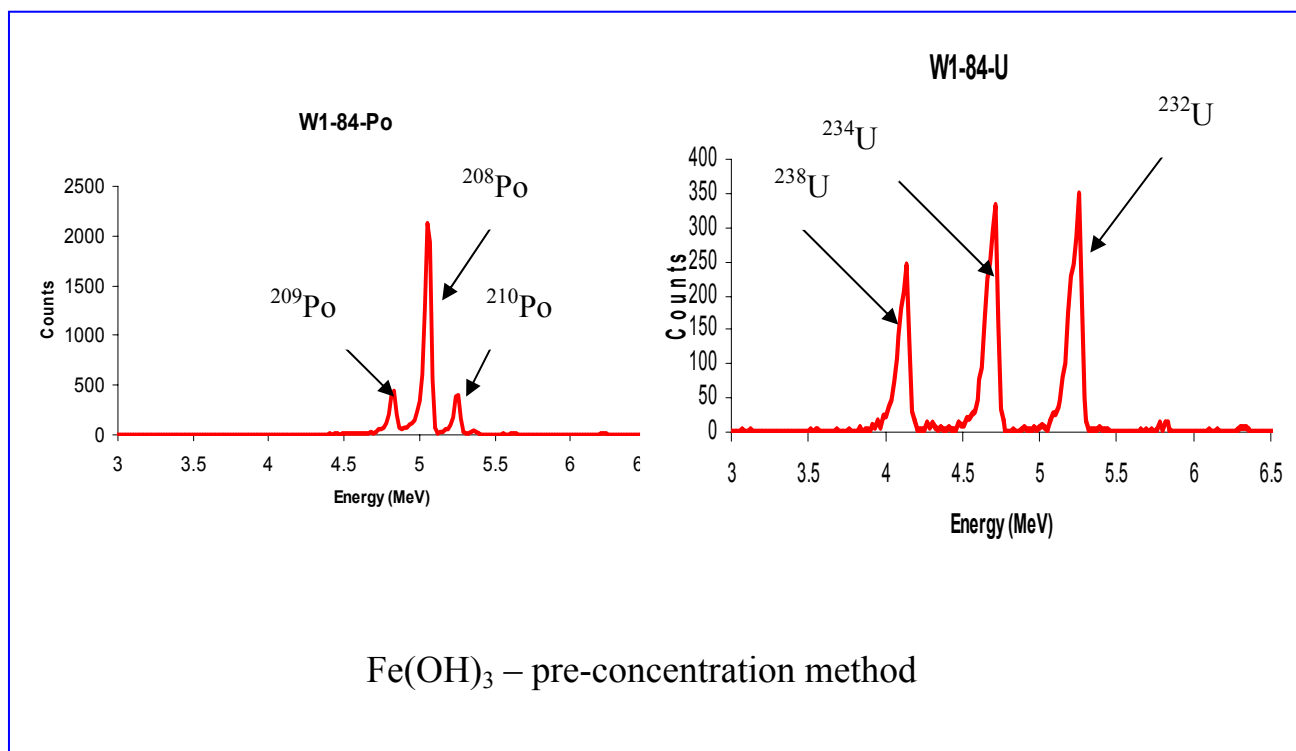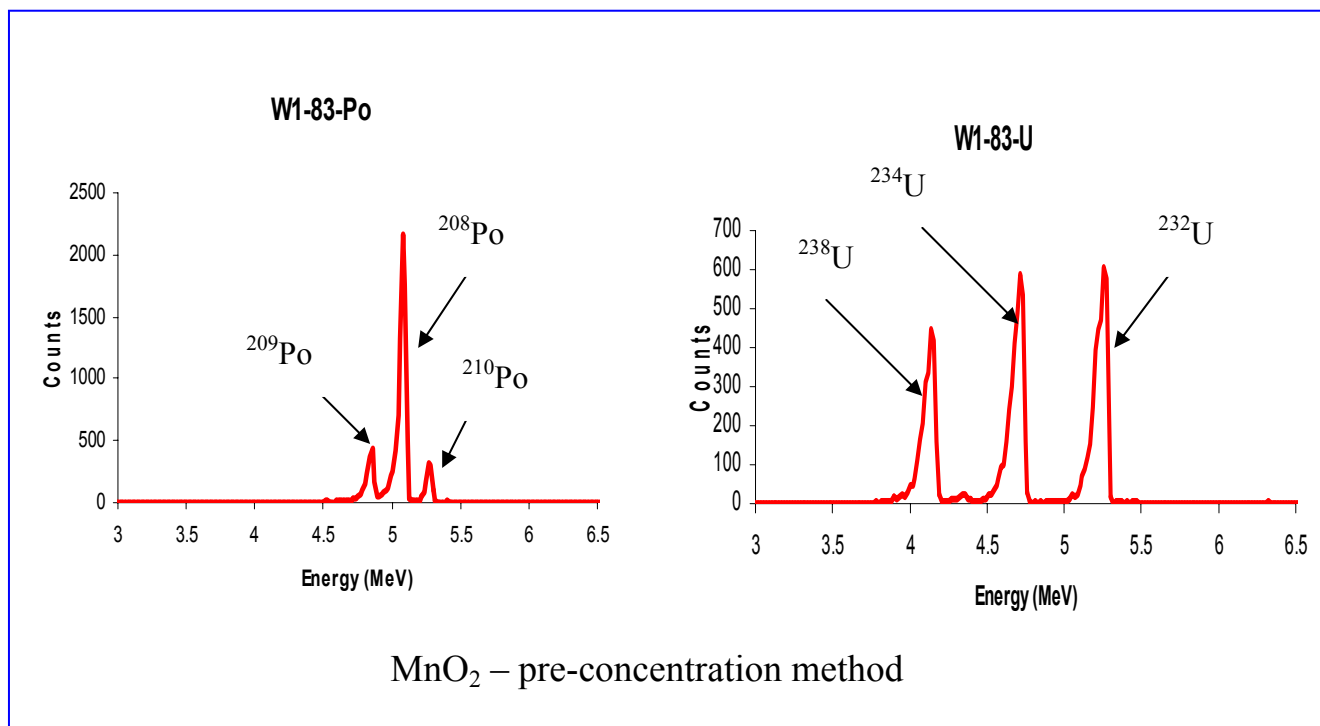[b] uncertainty values reported as combined standard uncertainty

PROCEDURE-2

MnO$_2$ – pre-concentration method

Fe(OH)$_3$ – pre-concentration method

Figure 13. **Alpha-particle spectra of isolated polonium and uranium isotopes using procedure-2**

PROCEDURE-1

MnO$_2$ – pre-concentration method
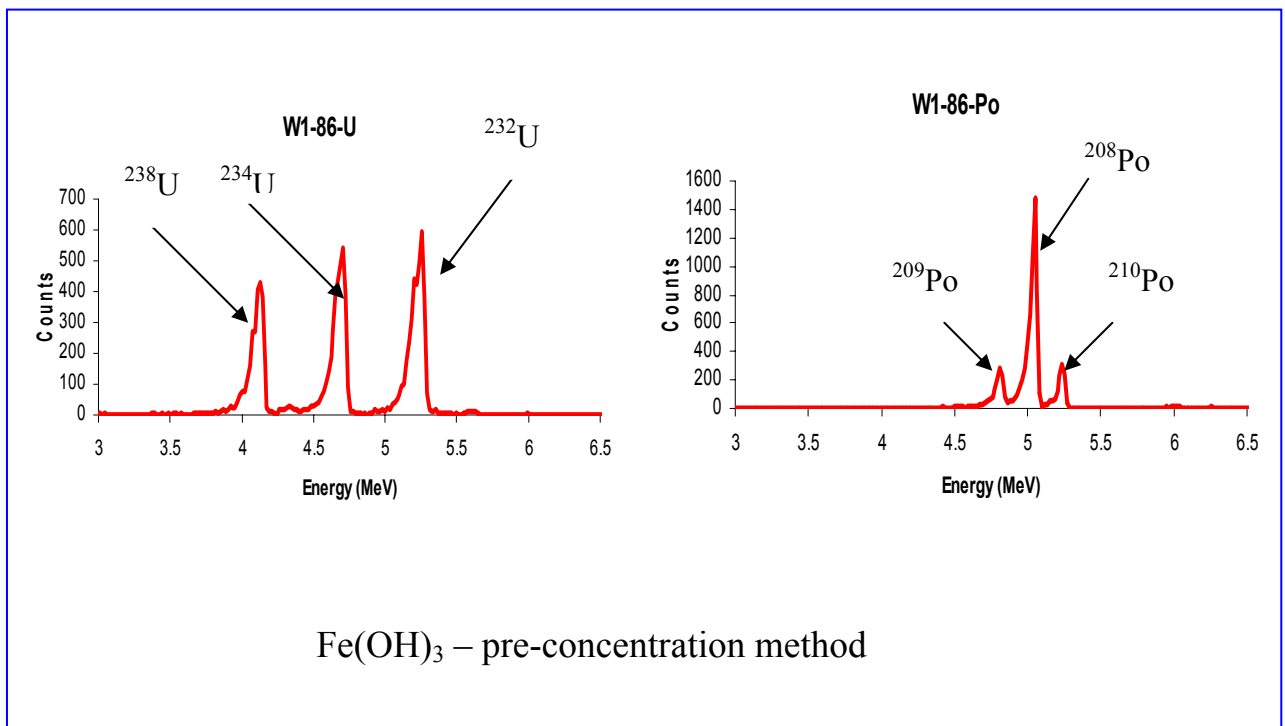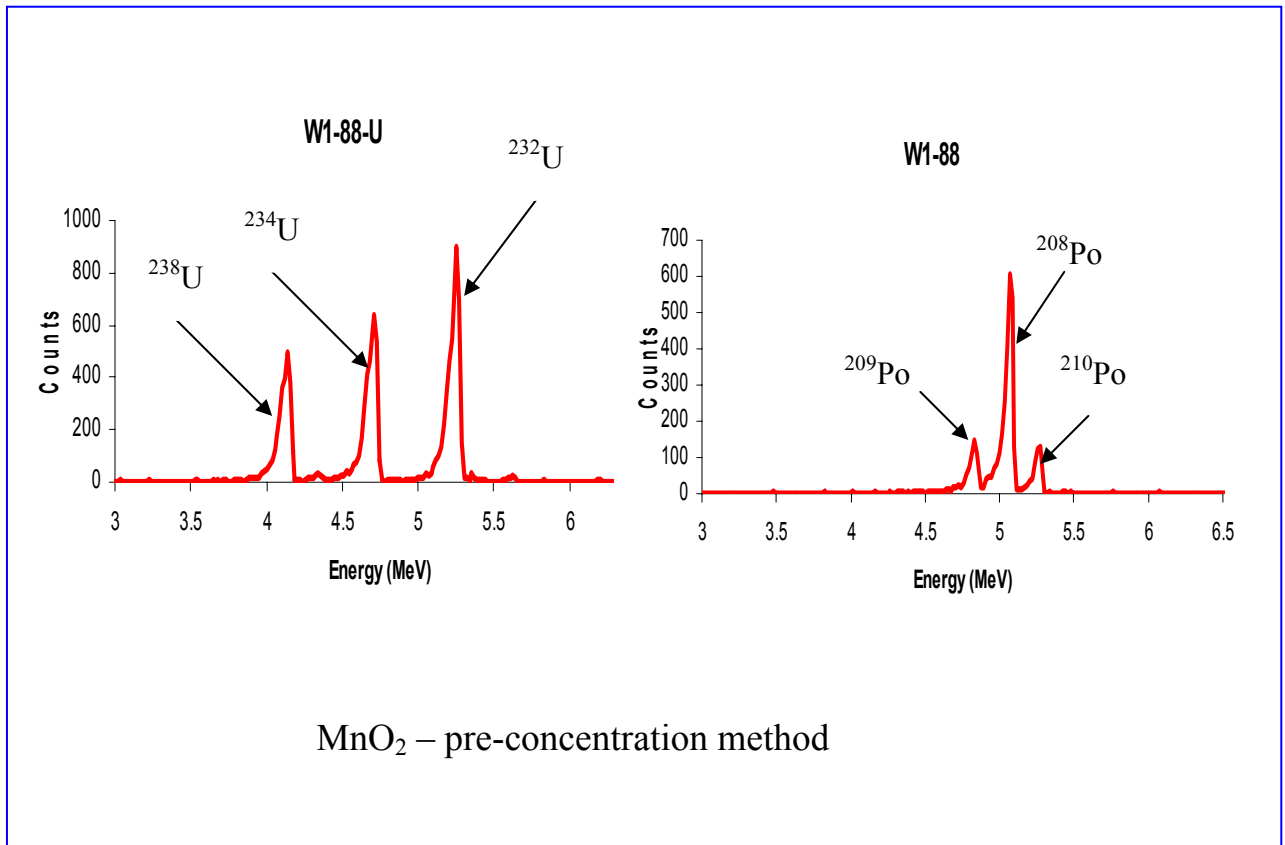

Fe(OH)$_3$ – pre-concentration method

Figure 14.   **Alpha-particle spectra of isolated polonium and uranium isotopes using procedure 1**

IV. EVALUATION OF THE MEASUREMENT UNCERTAINTY

Sources of uncertainty may be divided into two types:

- Type A: uncertainty components are evaluated from the experimental results.
- Type B: uncertainty components are evaluated from other information such as calibration certificates.

IV.1. Uncertainty budget for ^{228}Ra

The activity concentration of ^{228}Ra is calculated from equation (2):

$$A = \frac{N}{Eff \times R_{chem} \times V \times e^{-\lambda t_1}} \times \frac{\lambda \times t_2}{1 - e^{-\lambda t_2}} \tag{2}$$

where, N = net count rate (cps)

Eff = counting efficiency (%)

R_{chem} = chemical recovery (%)

V = volume of the sample (L)

t_1 = time from the first rinse of the column till start of measurement of ^{228}Ac (min)

t_2 = measurement time (min)

λ = decay constant of ^{228}Ac

The uncertainty associated with the *volume of the sample* is estimated using data from the manufacturer: for a flask of 1000 mL the uncertainty is ± 5 mL measured at a temperature of 20°C. The value of the uncertainty is given without confidence level or distribution information, so it is necessary to make an assumption and the standard uncertainty is calculated assuming a triangular distribution [EURACHEM guide, 2000].

The uncertainty associated with *weighing* of the tracer was estimated using the data from the repeatability of the balance on standard deviation as 0.02 mg.

$$\frac{0.02mg}{\sqrt{3}} = 0.012mg$$

The uncertainty associated with the *count rate* taking into account the standard deviation of the count rate for the sample and standard deviation for the count rate of the background.

Net count = counts (sample) – counts (background)

The uncertainty associated to the *net* count rate is sum of the squares of the two uncertainties.

$$u(N) = \sqrt{\left(\frac{counts(sample)}{time(sample)} + \frac{counts(bkg)}{time(bkg)} \right)} \qquad (3)$$

The combined standard uncertainty is calculated from equation (4):

$$u(A_{228_{Ra}}) = A_{228_{Ra}} \times \sqrt{\left(\frac{u(N)}{N} \right)^2 + \left(\frac{u(R_{chem})}{R_{chem}} \right)^2 + \left(\frac{u(V)}{V} \right)^2 + \left(\frac{u(Eff)}{Eff} \right)^2} \qquad (4)$$

The uncertainty of the *radiochemical recovery* of the method is determined according to equation (5):

$$u(R_{chem}) = \sqrt{\left(u(R_{228_{Ra}}) \right)^2 + \left(u(R_{228_{Ac}}) \right)^2} \qquad (5)$$

The chemical recovery of ^{228}Ra ($R_{Ra\text{-}228}$) was calculated according to equation (1):

$$R_{Ra\text{-}228} = \left(\frac{A_{sample}}{t_{sample} \cdot m_{sample}} \right) \cdot \left(\frac{t_{Std} \cdot m_{Std}}{A_{Std}} \right), \qquad (1)$$

where:

A_{sample}, A_{Std} are the net areas of ^{133}Ba peak from the sample and the standard sample, respectively;

t_{sample}, t_{Std} are the counting times of sample and standard sample, respectively;

m_{sample}, m_{Std} are the masses of added ^{133}Ba in the sample and of ^{133}Ba in the standard sample respectively.

The relative standard uncertainty of the chemical yield is calculated with equation (6):

$$u(R_{Ra-228}) = R_{Ra-228} \sqrt{\left(\frac{u(A_{^{133}Ba-sample})}{A_{^{133}Ba-sample}}\right)^2 + \left(\frac{u(m_{^{133}Ba-sample})}{m_{^{133}Ba-sample}}\right)^2 + \left(\frac{u(A_{^{133}Ba-std})}{A_{^{133}Ba-std}}\right)^2 + \left(\frac{u(m_{^{133}Ba-std})}{m_{^{133}Ba-std}}\right)^2}$$

Uncertainty of the chemical recovery of ^{228}Ac is taken as standard deviation of three replicate experiments.

The uncertainty on the time of measurement is negligible.

Efficiency of the Wallac Quantulus 1220^{TM} is calculated using equation (7):

$$\varepsilon = \frac{N_{Ac-228Std}}{m_{Th} \times A_{Th} \times R_{Ac-228}} \tag{7,}$$

where: ε efficiency of beta-particle detector

       R_{Ac-228} recovery of the ^{228}Ac standard

       N_{Ac-228} net count rate of ^{228}Ac standard

       m_{Th} mass of added Th natural standard solution (g)

       A_{Th} activity of Th natural standard solution (Bq/g)

$$u(\varepsilon) = \varepsilon \sqrt{\left(\frac{u(A_{Th})}{A_{Th}}\right)^2 + \left(\frac{u(m_{Th})}{m_{Th}}\right)^2 + \left(\frac{uN_{Ac-228Std}}{N_{Ac-228Std}}\right)^2 + \left(\frac{u(R_{Ac-228Std})}{R_{Ac-228Std}}\right)^2} \tag{8}$$

IV.2. Uncertainty budget for polonium and uranium isotopes

The activity concentration of ^{210}Po and $^{234,\,238}$U is calculated from equation (9):

$$A_{^{210}\text{Po},\ ^{234,238}\text{U}} = \frac{P_{sample} \times m_{tracer} \times A_{tracer}}{P_{tracer} \times V_{sample}} \tag{9}$$

where:

$A_{radioisotope}$ = activity concentration of ^{210}Po, ^{234}U, and ^{238}U [Bq·L^{-1}],

P_{sample} = peak area of ^{210}Po, ^{234}U, ^{238}U

m_{tracer} = mass of added ^{208}Po+^{209}Po or ^{232}U tracer [g],

A_{tracer} = activity concentration of added ^{208}Po+^{209}Po or ^{232}U tracer [Bq·g^{-1}],

P_{tracer} = peak area of ^{208}Po+^{209}Po or ^{232}U tracer,

V_{sample} = volume of the water sample[L]

The combined standard uncertainty is calculated from equation (10):

$$u(A_{radioisotop}) = A_{radioisotop} * \sqrt{\left(\frac{u(P_{tracer})}{P_{tracer}}\right)^2 + \left(\frac{u(m_{tracer})}{m_{tracer}}\right)^2 + \left(\frac{u(A_{tracer})}{A_{tracer}}\right)^2 + \left(\frac{u(P_{sample})}{P_{sample}}\right)^2 + \left(\frac{u(m_{sample})}{m_{sample}}\right)^2}$$

The uncertainty associated with the *volume* of the sample, *weighing* of the tracer and the *net count rate* of the sample and the tracer, is described in section *IV.1*.

V. CONCLUSIONS

The radiochemical separation of ^{228}Ac, in view of the determination of ^{228}Ra, was done using two Diphonix resin columns and measured by liquid scintillation counting. The recovery of ^{228}Ra was determined using ^{133}Ba as a tracer. The purity of the fraction of ^{228}Ac resulting from the chemical separation was demonstrated by the determination of its half-life using a thorium standard solution. Liquid scintillation spectrometry is a suitable technique for the determination of ^{228}Ra, via its daughter ^{228}Ac, at low level activity concentrations in water. The results using this method are in good agreement with the values obtained via the ingrowth of ^{228}Th and alpha-particle spectrometry.

The sequential determination of ^{210}Po and uranium radioisotopes in drinking water was described. Two different methods were used for pre-concentration of radionuclides from the water samples: co-precipitation with $Fe(OH)_3$ and MnO_2, respectively. The polonium source was prepared by spontaneous deposition on a copper disc before and after uranium separation. The uranium isotopes were micro co-precipitated using CeF_3 before and after polonium separation. Higher recoveries for polonium isotopes were obtained when the MnO_2 co-precipitation method and procedure-2 (radiochemical separation of ^{210}Po was done before radiochemical separation of uranium isotopes) were applied. No significant difference in the chemical recovery of ^{210}Po from mineral waters was observed when different volumes of sample were used. For uranium isotopes a decrease in chemical recovery of the separation was observed with the increase of sample volume.

VI. ACKNOWLEDGEMENTS

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European Commission

Abstract
The importance of the determination of uranium, radium and polonium isotopes in drinking water is outlined, taking into account European legislation. An overview of a literature study of radiochemical and measurement techniques suitable for the determination of these radionuclides in water is briefly summarised. The method developed for the determination of ^{228}Ra consisting of radium preconcentration, radiochemical separation of radium and subsequent determination of the daughter ^{228}Ac with liquid scintillation counting is described. Two novel methods for the sequential radiochemical separation of polonium and uranium from water samples were developed and are described in detail. The ^{228}Ra activity concentration was determined in two mineral waters and obtained results are compared with the results of an alternative method, based on the ingrowth of ^{228}Th and alpha-particle spectrometry. The novel methods for polonium and uranium were applied to three different mineral waters, and the activity concentrations of ^{210}Po, ^{234}U and ^{238}U determined with alpha-particle spectrometry are compared among each other and with reference values determined for these waters with standard methods.

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