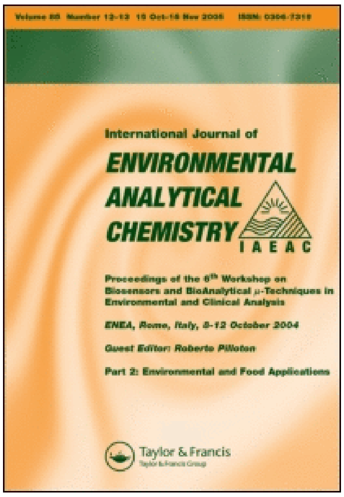

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Investigation of radioactive lead, uranium, and thorium in environmental waters by extraction chromatography resins

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A time-saving and sensitive method for monitoring low concentration (activities) of ^{210}Pb, ^{232}Th, and ^{230}Th and ^{238}U, ^{234}U, and ^{235}U in water samples has been developed. Through the combination of co-precipitation and extraction chromatography by 3M RAD disks and UTEVA (Eichrom) columns effective radiochemical separation of the analytes was carried out. Thorium and uranium activities were determined by alpha spectrometry and lead activity by LSC, respectively. The minimal detectable activities obtained were 0.6 Bq m^{-3} for uranium, 0.29 Bq m^{-3} for thorium, and 2.5 Bq m^{-3} for ^{210}Pb. More than 150 different waters were analysed for uranium content and only 30 for lead and thorium. The investigations are still in progress.

Keywords: Extraction chromatography; Natural radioactivity; Water

1. Introduction

^{210}Pb, ^{232}Th, ^{228}Th, and ^{230}Th and ^{238}U, ^{234}U, and ^{235}U, elements of the uranium or thorium decay families, are naturally occurring radionuclides in the environment. They can be found in variable concentrations in environmental water samples of groundwater, surface, and drinking water. Their concentrations depend on the interaction between water and the surrounding rock or soil [1, 2]. These naturally occurring radionuclides constitute an important component in humans' natural radiation background. Our interest in these radionuclides mainly follows environmental purposes, for example their chemical characteristics (toxicity) [3] and the possibility of using them as tracers in geo-hydrology. The variety of analysed samples made a fast, reproducible, and sensitive method mandatory to estimate low concentrations (activities) of these radionuclides.

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The aim of the present investigation is to apply and optimize the monitoring methodology for lead, uranium, and thorium, and measure their concentrations in various underground and surface waters in Luxembourg.

2. Experimental

Different chemical procedures exist for determination of lead, uranium, and thorium in water samples. The most commonly used methods are co-precipitation, solvent extraction, and ion exchange [4–8]. These methods are somewhat complicated and time-consuming, and produce organic waste.

The combination of iron hydroxide co-precipitation followed by extraction chromatography provides the opportunity for a fast and effective radiochemical separation of the analytes. Extraction chromatography resins consist of inert beads that are coated by an organic extracting agent, enabling selective extraction of a number of elements from an aqueous solution. There exist two geometric configurations: as extraction chromatography beads for standard gravimetric columns and as disks for more rapid extraction of the elements. For the aims of the present work, we used both forms. One is the filter-disk (3M RADDISK) for ^{210}Pb, and the other in the form of a column (UTEVA) for uranium and thorium. Both can be regenerated and reused three or four times following the same procedure as for the analysis. Several tests were performed previously to ensure that there would be no interference between the samples in this re-use. The chemical yield was unaffected too, and the only disadvantage was the increased time of analysis after each use.

A flow chart of the radiochemical separation of the compounds analysed in the water samples is presented in figure 1. All the reagents used, unless otherwise stated, were of pure analysis grade, and deionized water was always used.

In order to control the purity of the laboratory glass and of the supported materials, a blank sample was prepared, containing only the tracers, carriers, and HCl, and passed trough the whole chemical procedure. In a similar way, a standard sample with 1 mL of natural uranium solution (1.23 Bq/sample) added was prepared. Checks on the chemical yield for the Th via LSC and U/Th separation interferences were performed using a standard uranium solution in secular equilibrium with ^{234}Th.

2.1 *Pre-treatment*

An 800 mL water sample was acidified by adding 6 mL of concentrated HCl before spiking it with chemical recovery tracers: 0.2 mL of ^{232}U (solution 0.2474 Bq mL^{-1}) and 8 mg Pb(II) carrier.

The water sample was heated to 60°C, and 0.5 mL of a 0.18 mg mL^{-1} Fe(II) carrier solution was added and stirred for half an hour. During the stirring process, the pH was adjusted to 9.0–10.0 with concentrated ammonia. The solution was cooled, and the precipitation left to settle. The supernatant was discarded and the precipitate washed with water. Finally, the precipitate was dissolved in 3 M HNO_3, awaiting further chemical treatment.

2.2.1 Lead-210 determination. The prepared sample/precipitate solution was filtered slowly by passing the solution at a rate of 6 mL min^{-1} through a 3M

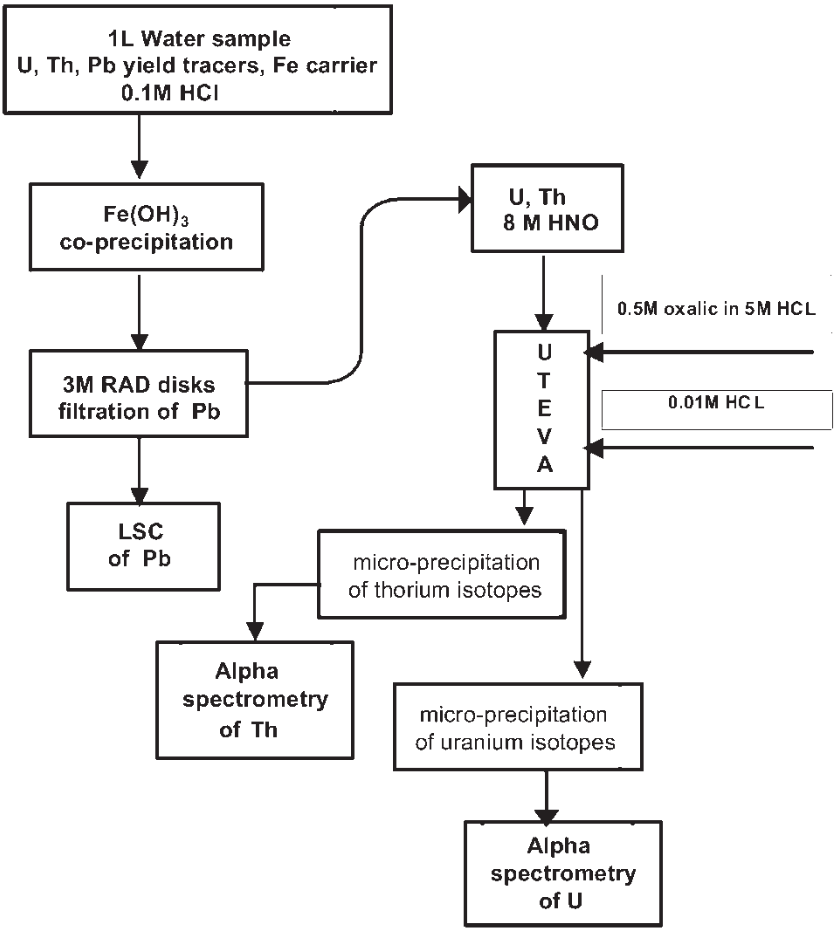

Figure 1. Flow chart of the radiochemical separation of uranium, thorium, and lead in water.

RAD filter-disk. The remaining solution was collected for further uranium/thorium separation.

The 3 M RAD filter consists of a resin AnLag implanted in PTFE filters. Previously, we investigated several properties of these filters [9] and obtained they behave as a crown-ether Sr spec resin (Eichrom Inc.). After the filter was dried, lead was eluted with 0.02 M Na EDTA. The elute was mixed with an OptiSafe HiPhase 3 (Perkin Elmer Inc.) scintillation cocktail in low-potassium glass scintillation vials. The ^{210}Pb activity was measured by liquid scintillation spectrometry (LSC) using a Gardian Wallac Oy device for 1 or 10 h.

2.2.2 Uranium and thorium isotope determination. The solution obtained after the lead separation was adjusted to 8 M HNO_3, several drops of ascorbic acid were added, and then the solution was introduced into a UTEVA (Eichrom Inc.) chromatographic column where thorium and uranium were retained [10]. To ensure complete removal of any iron that might have adhered on the column, the column was washed with 10 mL of 3 M HNO_3. After converting the column in chloride form with 9 M HCl–0.1 M NaI, thorium was stripped by passing 20 mL of 5 M HCl–0.05 M oxalic acid through the column. Note that we did not use the 9 M HCL fraction for thorium determination, as this often contains Np, Pu, and other disruptive elements. Uranium was collected after passing 15 mL of 0.01 M HCl on the column. Both fractions (i.e., 'U' and 'Th') were evaporated to dryness and re-dissolved in 15 mL of 1 M HCl and 5 M HCl, respectively. To each fraction, titanium or cerium chlorides were added, and micro-precipitation with 100 µL of Nd(II) was carried out. The precipitate was deposited on 0.2 µm plastic filters (Gelman Inc.) via filtration, which were finally glued on iron disks as supports. The alpha spectra of the uranium and thorium radionuclides were collected using Canberra PIPS detectors with an active surface area of 900 mm^2.

2.3 *Chemical yield*

The chemical yield of uranium isotopes was estimated, taking into account the counts of the tracer ^{232}U in the alpha spectra. In the case of thorium, the yield was determined via ^{234}Th, produced by ^{238}U similar to the approach proposed by Walpes *et al.* [11]. After thorium separation, a fraction of the sample was measured by LSC to determine the chemical yield.

The yield of the chemical procedure for lead was based on a gravimetric measurement of the stable lead carrier added. Before the filtration, the mass of the 3M RAD disk was measured with a high degree of accuracy. After retaining the ^{210}Pb, it was measured again and a third time after lead elution with alkaline EDTA. Before each mass measurement, the filter was dried.

3. Results and discussion

The method described here was used to determine the uranium content in more than 150 samples. Most of the measurements were performed in the context of a national screening project [12]. Seventeen surface waters and five infiltration and seven drilled well samples were analysed for ^{210}Pb measurement. Thorium determinations were performed for 16 samples. The investigations are still in progress. The aim of this campaign is to continue with new parameters that allow us to describe different interactions between groundwater/surface water and several spatial and surface distributions.

The surface waters were collected at catchments areas of the rivers Hovelingerbach and Weierbach, situated on Jurassic sandstone formations for the first river, and on lower Devonian formations for the second. The underground water samples were collected either in sources or in wells.

3.1 *Analytical conditions*

A typical spectrum of uranium isotopes and the tracer ^{232}U for yield purposes is presented in figure 2; another spectrum for thorium isotopes is shown in figure 3.

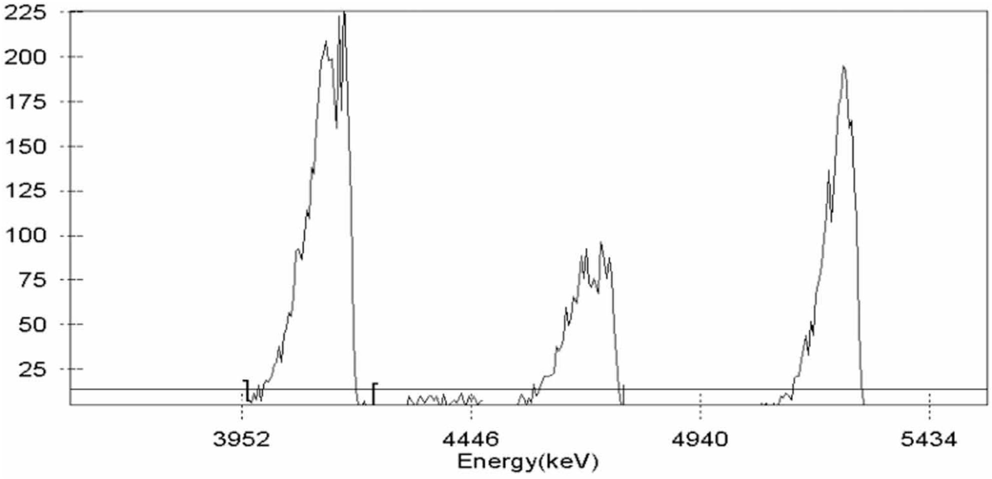

Figure 2. Alpha spectrum of U-238, U-235, and U-234 (4.197, 4.775, 4.4 MeV), the yield tracer U-232 (5.324 MeV), and the superposed background spectrum (green).

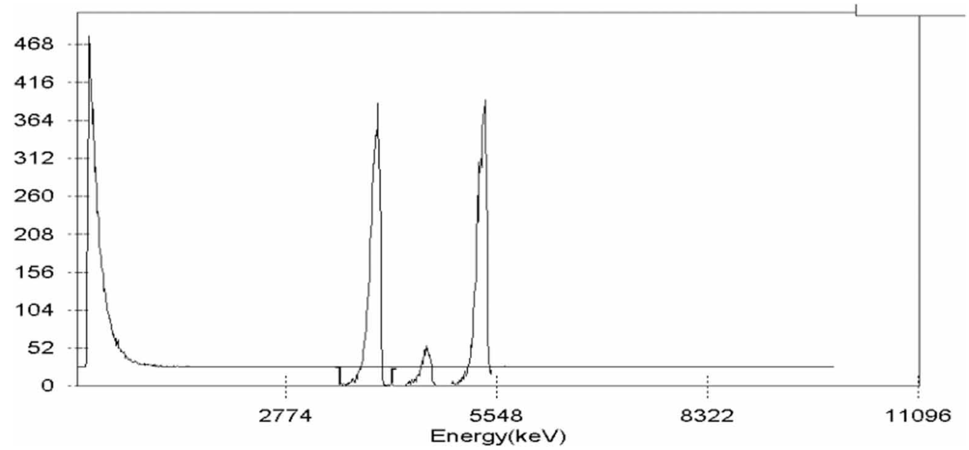

Figure 3. Alpha spectrum of Th-232, Th-230, and Th-228 (4.013, 4.688, 54.423 MeV), and the superposed background spectrum (green).

The energy resolution is better than 150 keV [6]. This indicates the high quality of the methods used for the sample preparation.

The ^{210}Pb activity was determined by liquid scintillation spectrometry with a measuring time of 1 h. The Guardian LSC counter uses the pulse shape analyses technology to distinguish between alpha and beta spectra. The prepared sample containing ^{210}Pb is directly mixed with the scintillation cocktail OptiPhase HiSafe 3. The ^{210}Pb spectrum of one sample and the background are shown in the figure 4. The low background for the lead energy interval and a good counting efficiency enable us to determine the ^{210}Pb content down to 0.3 mBq L^{-1}. In the last case, the measuring time has to be increased to 10 h, compared with 1 h for routine measurements.

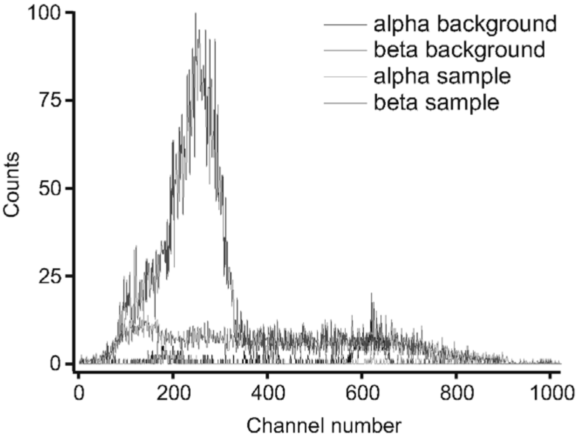

Figure 4. Liquid scintillation spectra of Pb-210.

Table 1. Main parameters for detection of uranium, thorium isotopes and lead.

Radionuclide	U-238	U-235	U-234	Pb-210	Th-232	Th-230	Th-228
Background (counts)	4	2	5	558	7	3	16
Measuring time (s)	432,000	432,000	432,000	36,000	600,000	600,000	600,000
Volume (L)	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Yield (%)	87	87	87	86	78	78	83
Efficiency (%)	21	21	21	93	21	21	21
MDA (mBq L^{-1})[a]	0.16	0.12	0.18	4.8	0.13	0.07	0.34

[a] Detection limit calculated by Currie [13].

The main parameters for the analysed isotopes are represented in table 1. The minimal detectable activity (MDA) was defined by the following Currie [13] equation:

$$\mathrm{MDA} = \frac{2.71 + 4.66\sqrt{B \cdot t}}{\varepsilon \cdot Y \cdot V \cdot t}\ \mathrm{mBq\,L^{-1}},$$

where B denotes the background counts, ε the detector efficiency, Y the chemical yield, V the sample volume (L), and t the counting time (s).

For five samples, ^{210}P results of extraction chromatography resin method were compared with those obtained in the Laboratory of Environmental Radioactivity at the University of Extremadura [14]. They show a good agreement in the results, with a deviation of less than 8%. For uranium, the differences of the results are less than 5%.

For comparison purposes, the thorium content of six soil samples was measured by gamma spectrometry. After those samples were chemically destroyed, the solutions obtained were analysed following the procedure described. The deviation was around 15%, due mainly to the lower precision of gamma spectrometry.

To ensure quality control of the determined nuclides, usually 10% of all samples are analysed twice for uranium and thorium isotopes. In the case of samples with the ID 'P number', all were analysed twice with two different methods applied for ^{210}Pb.

3.2 *Sample results*

The results of all the analysed samples, for ^{210}Pb and uranium and thorium isotopic content, are presented in table 2. These allow us to conclude that no contamination is present. It is interesting to note that surface waters and water sampled in the subsurface have quite different concentrations compared with groundwater. The infiltration processes of surface water differ from those in sources and groundwater catchments.

For every analysed water sample, the activity ratios ^{238}U/^{232}Th and ^{230}Th/^{232}Th were calculated. From the results in table 2, one can see that these ratios may have very high values; in most cases, they can be attributed to the very low ^{232}Th concentrations and not to high ^{238}U and ^{230}Th concentrations. The mean ratio value of ^{238}U/^{232}Th for surface and soil infiltrated water is 2.4, whereas it exceeds 12 for underground water. It should be mentioned that in the investigated underground water with high ^{238}U/^{232}Th ratios, we remarked that the ^{210}Pb content is very low, and the ^{230}Th concentrations are twice as high as those of ^{232}Th [5]. This is associated with the higher solubility of uranium isotopes compared with thorium isotopes.

The data in table 2 also help to study the radioactive equilibrium disturbance within the uranium series. For each sample, the ratios ^{210}Pb/^{238}U, ^{234}U/^{238}U are calculated. As expected for surface waters, the ^{238}U/^{234}U ratio is close to 1 and reveals a secular equilibrium (normal background). In the same samples, the lead content exceeds by more than 30 times the uranium content related to the normal hydrological cycle and atmospheric precipitations.

The ^{234}U/^{238}U ratios in all drilled wells range from the very low value of 1.3 to a value of 5, with a mean value of 1.8. A correlation with increasing depth or fault zones is presumed, which causes the irregularities.

A more detailed interpretation of the results will be published after the end of the investigation campaign when sufficient data will be collected.

4. Conclusions

An extraction chromatography resin method has been used successfully to measure the radionuclides for the uranium and thorium natural series in environmental water samples.

The advantage of the proposed chemical procedure is the volume of the water sample, a sample of less than 1 L for the complete analyses. The step-by-step separation of the different radionuclides is less time-consuming than classical methods and poses less health risk to the operator and less risk to the environment. The whole procedure takes only a few hours and does not produce any radioactive or organic wastes.

The concentrations measured yield important information in connection with the chemical data and geological and hydrological specifications of the investigated areas.

Table 2. Results for uranium, thorium, and lead concentrations (2σ) in several water samples from Luxembourg.

Sample ID	U-238 ($\mathrm{mBq\,L^{-1}}$)	U-235 ($\mathrm{mBq\,L^{-1}}$)	U-234 ($\mathrm{mBq\,L^{-1}}$)	Pb-210 ($\mathrm{mBq\,L^{-1}}$)	Th-232 ($\mathrm{mBq\,L^{-1}}$)	Th-230 ($\mathrm{mBq\,L^{-1}}$)	Th-228 ($\mathrm{mBq\,L^{-1}}$)
Hersberg-40	12.31 ± 0.07	2.45 ± 0.02	13.71 ± 0.11	29.5 ± 0.08	5.18 ± 0.03	3.37 ± 0.06	7.59 ± 0.09
Hersberg-37	6.01 ± 0.11	0.82 ± 0.03	5.33 ± 0.13	22.2 ± 0.07	14.46 ± 1.3	3.42 ± 0.06	15.9 ± 1.38
Vianden	1.62 ± 0.03	0.14 ± 0.02	0.38 ± 0.02	4.7 ± 0.03	7.72 ± 0.09	3.51 ± 0.05	6.78 ± 0.08
Haute-Sure	<0.285	<0.165	<0.215	22.5 ± 0.07	5.91 ± 0.08	3.86 ± 0.07	8.08 ± 0.10
Op der Hall	1.10 ± 0.04	1.27 ± 0.04	7.74 ± 0.31	<5	3.04 ± 0.03	4.94 ± 0.03	2.88 ± 0.11
Treilent	84.46 ± 0.59	6.35 ± 0.06	140.30 ± 0.98	<5	6.53 ± 0.04	10.26 ± 0.06	7.94 ± 0.27
FR-195–332	15.09 ± 0.57	1.59 ± 0.06	10.11 ± 0.55	<5	7.28 ± 0.04	4.37 ± 0.04	6.63 ± 0.20
FR-201–334	38.23 ± 0.88	1.79 ± 0.06	39.06 ± 0.9	<6	2.950.02	6.50 ± 0.09	4.06 ± 0.12
FR-281–332	29.00 ± 1.39	1.77 ± 0.10	76.93 ± 3.64	<5	1.080.02	2.04 ± 0.02	<5.30
FR-201–333	54.28 ± 0.90	2.75 ± 0.06	70.74 ± 1.17	13.5 ± 0.09	1.09 ± 0.02	4.08 ± 0.10	<7.11
P21	11.06 ± 0.36	0.11 ± 0.03	13.10 ± 0.42	35 ± 3.2	3.44 ± 0.09	0.79 ± 0.01	<5.08
P22	19.36 ± 0.11	1.43 ± 0.01	7.58 ± 0.02	<5	2.76 ± 0.01	0.80 ± 0.01	<4.68
P23	2.08 ± 0.09	0.42 ± 0.02	2.89 ± 0.13	34.99 ± 0.81	0.82 ± 0.11	1.14 ± 0.02	<5.23
P24	3.17 ± 0.21	0.38 ± 0.03	4.71 ± 0.29	56.7 ± 3.9	1.47 ± 0.01	1.35 ± 0.02	4.20 ± 0.89
RAM	22.39 ± 0.90	0.80 ± 0.04	25.58 ± 1.04	32.8 ± 3.3	0.75 ± 0.01	0.81 ± 0.01	<5.03
Creek	0.59 ± 0.05	0.04 ± 0.02	1.74 ± 0.12	4.1 ± 0.69	<2.16	0.66 ± 0.10	<4.48
Hoverlingerbach-1	2.30 ± 0.12	1.05 ± 0.06	4.41 ± 0.21	39.2 ± 0.06			
Hoverlingerbach-8	0.90 ± 0.05	0.19 ± 0.02	1.36 ± 0.06	20.7 ± 0.08			
Hoverlingerbach-22	29.46 ± 0.12	6.92 ± 0.09	25.96 ± 0.12	46.8 ± 0.05			

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