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A new rapid protocol for ^{226}Ra separation and preconcentration in natural water samples using molecular recognition technology for ICP-MS analysis

Abstract

A new rapid protocol for ^{226}Ra separation and preconcentration in natural water samples was developed before its determination by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). For this purpose, the commercially available Ra specific resin AnaLig[®] Ra-01 was used. This resin shows a high selectivity for radium in a large range of acid concentrations and no affinity or possible elution of ^{226}Ra interfering elements. The distribution coefficients of Ra and other elements over a wide range of acid (HCl and HNO₃) concentrations were obtained. Due to the high radium selectivity, the new developed protocol uses only 50 mg of dry resin and its performance was evaluated using 100 mL of three natural waters with different ionic strengths, doped with a known quantity of ^{226}Ra . Radium was successfully separated and preconcentrated yielding recoveries ranging between 72% and 86%. In parallel with the characterisation of the resin sorption properties, a detailed study of polyatomic interferences was carried out in our ICP-MS allowing to identify the prominent elements favouring interferences at $m/z = 226$. Furthermore, a ^{226}Ra sensitivity comparison between different ICP-MS instruments and configurations was done in order to determine high sensitivity conditions for radium analysis.

Keywords: Radium, separation, AnaLig[®] Ra-01, recognition technology, ICP-MS/MS, extraction chromatography

1. Introduction

Radium 226 is the most abundant radium isotope with a half-life of 1600 years present in ^{238}U decay chain. In the last few decades, uranium, coal or phosphate mining activities have released radium in the environment leading to radium activities significantly higher than the geochemical background level (Azouazi et al., 2001; Carvalho et al., 2007; Chalupnik and Wysocka, 2008; Cuvier et al., 2015; Pluta and Trembacowski, 2001; Vandenhove et al., 2006). Due to its high specific activity and to its chemical properties favoring its accumulation in human bones increasing the internal radiation dose, ^{226}Ra is considered to be one of the most radiotoxic naturally occurring isotopes (Jia and Jia, 2012; St-Amant et al., 2011). For this reason, it is important to understand its geochemical behavior and to identify the transfer pathways between the environment and humans. This requires being able to achieve high precision ^{226}Ra measurements in environmental samples.

Reported ^{226}Ra activities for natural water samples rarely exceed 30 mBq.L^{-1} . Activities in river water generally range between 0.5 and 20 mBq.L^{-1} and for other surface areas, such as lakes are also within a narrow range (0.5 – 15 mBq/L), similar to that observed for river water (Vandenhove et al., 2019). Seawater ^{226}Ra activities are particularly low ranging from 0.1 to 7 mBq.L^{-1} (Bourquin et al., 2011; IAEA, 2014) and groundwater activities are highly variable ranging from some tens of mBq.L^{-1} to several Bq.L^{-1} (IAEA, 2014).

Traditional methods for ^{226}Ra analysis are radiometric techniques such as alpha and gamma spectrometry, radon 222 emanation and liquid scintillation (Godoy et al., 2016; Jia and Jia, 2012; Perrier et al., 2016; Song et al., 2017; van Beek et al., 2010). However, these techniques require large volume samples ($\approx 100 \text{ mL}$ to several liters), the achievement of secular equilibrium with radon 222 (≈ 30 days) and generally two to three days of counting for low ^{226}Ra activities (Jia and Jia, 2012).

Initially, Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) technique focused on longer-lived radionuclides (i.e. ^{238}U , ^{232}Th) where their low specific activities favored atom-counting over radiometric techniques. In the past few decades improvements in instrument sensitivity achieved through advances in sample introduction, mass spectrometry configuration and vacuum pump technologies, has opened up the possibility of using ICP-MS for quantification of shorter-lived radionuclides, significantly reducing the analytical time for such analyses. During this period, ^{226}Ra analysis with ICP-MS has grown significantly (Bourquin et al.,

2011; Copia et al., 2015; Cozzella et al., 2011; Foster et al., 2004; Ghaleb et al., 2004; Hodge and Laing, 1994; Hsieh and Henderson, 2011; Joannon and Pin, 2001; Lagacé et al., 2017; Lariviere et al., 2007; Lariviere et al., 2003; Lariviere et al., 2005; Park et al., 1999; Pietruszka et al., 2002). However, one of the major drawbacks in analyzing ^{226}Ra with this method is the presence of polyatomic interferences deteriorating the measurement accuracy (Epov et al., 2003; Lagacé et al., 2017; Lariviere et al., 2007; Lariviere et al., 2003; Park et al., 1999; van Es et al., 2017a; van Es et al., 2017b). Some of the most prominent ones according to the literature correspond to $^{88}\text{Sr}^{138}\text{Ba}^+$, $^{208}\text{Pb}^{18}\text{O}^+$, $^{209}\text{Bi}^{16}\text{O}^{1}\text{H}^+$, $^{40}\text{Ar}^{40}\text{Ar}^{146}\text{Nd}^+$ and $^{40}\text{Ar}^{186}\text{W}^+$. ^{226}Ra polyatomic interferences mainly originate from reactions occurring with the elements of the sample matrix in the plasma. In order to overcome this problem, an ICP-MS/MS with N_2O as the reaction gas in the collision reaction cell has been successfully used in a recent work (Wærsted et al., 2018). However, chemical purification of samples before radium analysis remains the most commonly used procedure.

A wide variety of protocols and resins can be found in the literature capable of isolating and preconcentrating ^{226}Ra , such as MnO_2 resin (Moon et al., 2003) or Mn-fiber (Bourquin et al., 2008), MnO_2 -PAN (Dulanská et al., 2015), TK100 resin (van Es et al., 2017b), Radium Rad Disks (Fons-Castells et al., 2017; Joannon and Pin, 2001), AnaLig[®] Sr-01 (Dulanská et al., 2016), water-soluble crown ethers (Chiarizia et al., 1999) and crown ether functionalized magnetic nanoparticles (Mesnic et al., 2013). Most of the protocols for ICP-MS applications use cation exchange resin such as AG-50W-X8 or Ln crown ether resin in combination with strontium specific resin such as Sr-Spec (Benkhedda et al., 2005; Chabaux et al., 1994; Copia et al., 2015; Cozzella et al., 2011; Joannon and Pin, 2001; Lariviere et al., 2005). In our knowledge, none of the study considers the commercially available resin AnaLig[®] Ra-01 which was developed for Ra recognition. The aim of this work is therefore to test the resin with the objective to develop a potential new rapid protocol for the separation and preconcentration of ^{226}Ra in natural samples applicable to mass spectrometric measurements. Optimizations of ^{226}Ra separation on AnaLig[®] Ra-01 and measurements by ICP-MS/MS were investigated in detail.

2. Experimental

2.1. Reagents and materials

High purity acids were obtained by distillation (Savillex[®] DST-1000 system) from hydrochloric acid (HCl, Merck, Emsure 37 %) and nitric acid (HNO_3 , VWR Chemicals, Normapur 68 %). For solution basification,

ammonia (NH₃, Suprapur 20 %, Merck) was used. Deionized water was produced by a Millipore system (18.2 MΩ.cm⁻¹ resistivity). All sample dilutions and solutions for elemental analysis were performed with 0.5 mol.L⁻¹ (M) HNO₃. The same acid was used as the blank and for instrument washing procedure between standard and samples. Savillex PFA vials (30 ml) were used for batch experiments after cleaning with analytical grade concentrated HNO₃ and distilled water.

To investigate the element distribution coefficients for the AnaLig® Ra-01, a synthetic 4 µg.g⁻¹ multi-element solution (Na, Mg, Ca, Fe, Sr, In, Cs, Ba, Nd, W, Tl, Pb, Bi, Th and U) was made with commercial standard mono-element solutions (Aristar, BDH Chemical), in 0.5 M HNO₃. ¹⁰³Rh was used as internal standard at 0.01 ng.g⁻¹ (Aristar, BDH Chemical). For batch and column experiments, HNO₃ and HCl solutions were used from 0.01 M to 10 M. The eluent solution for Ra was prepared by dissolving a nitrilotriacetic acid (NTA, Honeywell Chemicals, 99 %) in dilute ammonia solution to reach a concentration of 0.12 M and a pH of 10. All Ra solutions were prepared from an in house ²²⁶Ra standard solution in 1 M HNO₃, with a specific activity of 1.2×10⁷ mBq.L⁻¹. The Ra specific resin used in this work is the AnaLig® Ra-01 (lots: 110109DZ123E and 180207DZ124F-2) provided by IBC Avanced Technologies. This resin has a mesh size of 60 – 100 and a binding capacity of 0.1 - 0.2 mmol.g⁻¹.

In order to study the AnaLig® Ra-01 performances in natural sample matrices, 100 mL of three waters with different ionic strengths, acidified with HCl to a final pH ≈ 1, were doped with the same ²²⁶Ra quantity (final concentration 10⁴ mBq.L⁻¹): Volvic® of Danone, Hepar® of Nestlé and a natural sample of seawater. The seawater was collected at Wimereux (North Sea - France) in March 2017 and filtered at 0.45 µm before acidification. This high activity was chosen in order to ensure a sufficient ²²⁶Ra activity after its extraction from the doped natural samples allowing a precise determination of the chemistry yield. Moreover this high activity overwrites the naturally occurring ²²⁶Ra. Physicochemical compositions of waters are summarized in Table 1.

2.2. Instrumentation

All measurements were performed using an Agilent 8800 ICP-MS/MS (Agilent Technologies, Tokyo, Japan) installed at the LELI laboratory of the Institut de Radioprotection et de Sûreté Nucléaire (IRSN). In this study, ICP-MS/MS was run in single quadrupole mode and an APEX-HF (hydrofluoric acid resistant sample inlet system) with a PFA MicroFlow nebulizer (Elemental Scientific (ESI), USA) in self-aspiration mode (≈ 330 µL.min⁻¹) was used as the introduction system. We opted for not using the collision reaction cell with the gases

provided by the manufacturer (He, H, O₂) and the mode MS/MS due to a significant decrease of the instrumental sensitivity. In order to evaluate the APEX sensitivity-gain compared to the introduction system provided by the manufacturer (Scott spray chamber), the Scott spray chamber was used once with the PFA nebulizer. All analyses were performed using the x-lens with nickel sampler and skimmer cones.

In order to minimize the consumption of ²²⁶Ra solution, the instrument was optimized daily with a uranium solution (1 ng.g⁻¹) and then settings were refined for a ²²⁶Ra pure solution (0.27 pg.g⁻¹, 10⁴ mBq.L⁻¹) to finalize the optimization.

The performances of our ICP-MS/MS in terms of sensitivity, Limits Of Detection (LOD) and Limits Of Quantification (LOQ) were compared to an ICAP-Q (Thermo Fisher Scientific, Bremen, Germany) and an Element 2 (Thermo Fisher Scientific, Bremen, Germany) housed at LERCA and LMRE respectively, two IRSN laboratories. These two instruments were used with an APEX-Q connected to a desolvation unit. For the comparison, the same standard radium (10⁴ Bq.L⁻¹ of ²²⁶Ra) and blank (0.5 M HNO₃) solutions were used. The operating conditions for the three ICP-MS instruments are given in Table 2.

Determination of distribution coefficients

Batch experiments were carried out to evaluate the sorption capacity of AnaLig® Ra-01 resin for a wide range of acid concentrations varying from 0.01 M to 10 M for HCl and HNO₃ acids. To this aim, a series of vials (PFA, 30 mL) containing 2 mL HCl or HNO₃, 50 ng.g⁻¹ of multielement and 6×10⁴ mBq.L⁻¹ of ²²⁶Ra were used. 50 mg of dry resin preliminary washed (5 mL of ultrapure water) and preconditioned with the respective batch acid was added to each vial and left for one day (around 20 h) in a shaking table. The sample was then filtered through a polyethylene filter (VWR) at 0.45 μm in order to eliminate the Analig Ra-01 resin particles and evaporated to dryness before being redissolved in 2 ml of 0.5 M HNO₃ and analyzed by ICP-MS/MS. For each batch test, a blank sample was done (vials with resin and acid without multi-element and Ra solution) and the blank element contribution was subtracted to the signal of the corresponding element in batch test.

The sorption was quantified by the distribution coefficients (K_d) calculated using Equation 1:

$$K_d = \left(\frac{CPS_i - CPS_f}{CPS_f} \right) \times \left(\frac{V}{m} \right) \quad (\text{Equation 1})$$

where CPS_i and CPS_f are the initial and final counts per second (cps) of the multi-element solution before and after contact with the resin. V is the volume of the batch solution (mL) and m is the mass of the AnaLig® Ra-01 resin (g).

K_d values was an average of triplicate samples and uncertainties were calculated according to equation 2:

$$Uncertainty = k \times \frac{STD}{\sqrt{n}} \quad (\text{Equation 2})$$

where k is the coverage factor (for this study $k = 2$), STD is the standard deviation of the triplicate samples and n is the number of measurements (for this study $n = 3$).

Elution profiles

Elution profiles were performed using a homemade column (150 μ L) in which 50 mg dried AnaLig® Ra-01 resin were packed (Figure 1). The column was made using a PFA frit, PFA tube and connectors in PEEK. The outlet of the column was directly connected to a peristaltic pump to ensure a constant flow-rate (around 100 μ L.min⁻¹) of the solutions. The low flow-rate allowed avoiding column back pressures maximizing interactions between the mobile and stationary phase. Elution strategy was based on K_d values and preliminary tests were done with a synthetic solution before the application of the protocol in natural water samples. Before the sample loading step, the column was washed with ultrapure water (5 mL) and conditioned with 0.1 M HCl (5 mL). Then, 0.1 M HCl solution (2 mL) containing 6×10^4 mBq.L⁻¹ of ²²⁶Ra and 50 ng.g⁻¹ (each element) of multi-element solution was loaded onto the column, followed by a selective elution. A fraction collection was performed in order to generate elution profiles of the elements. Each fraction was evaporated to dryness before being made up in 2 ml of 0.5 M HNO₃, and analyzed by ICP-MS/MS. The recovery rate of each element was calculated using equation 3:

$$\text{Recovery rate} = \left(\frac{CPS_f}{CPS_i} \right) \times \left(\frac{V_f}{V_i} \right) \times 100 \quad (\text{Equation 3})$$

where CPS_i is the initial counts per second for the multielement solution with Ra before column load and, CPS_f is the final counts per second in the collected fractions after passing through the resin, V_i is the volume of the loaded solution and V_f is the volume of the analyzed solution (after fraction dilution).

3. Results and discussion

3.1. ICP-MS sensitivity performances

As can be seen in Figure 2, the APEX-HF improved signal sensitivity for the Agilent 8800 compared to Scott spray chamber by a factor of 10. The LOD and LOQ were found to be 68 mBq.L^{-1} and 204 mBq.L^{-1} for the Scott spray chamber and 8 mBq.L^{-1} and 23 mBq.L^{-1} for the APEX, respectively. With the Scott spray chamber, sensitivity of radium was found to be similar to that obtained by van Es et al. (van Es et al., 2017b), around 9 CPS/Bq.L^{-1} . Results of LOD and LOQ obtained with ICAP-Q were close to Agilent 8800 with APEX configuration: 6 mBq.L^{-1} and 12 mBq.L^{-1} respectively. However, sample uptake for the ICAP-Q was 58 % higher than that used for the Agilent 8800. Even with a 25 % smaller sample uptake compared to the Agilent 8800, performances achieved with the Element 2 were by far the best with a LOD of 1 mBq.L^{-1} and a LOQ of 2 mBq.L^{-1} . The higher extraction potential applied to the interface and an improved ion transmission can explain this important sensitivity increase compared to the quadrupole ICP-MS systems. The total ICP-MS analysis time per sample, including sample uptake, Ra analysis and washout is $\approx 7 \text{ min}$.

Interferences

The major drawback of ICP-MS analysis is the presence of spectral interferences due to sample matrix. The aim of the study is to identify the main polyatomic interferences at $m/z = 226$ using mono-element Nd, Pb, Bi, W and a mixture of Sr and Ba (weight ratio 1:1) solutions at different concentrations between 20 and $290 \mu\text{g L}^{-1}$. For this study the APEX-HF was used as the introduction system in our ICP-MS/MS.

The objective was to obtain a high-count rate favoring the generation of polyatomic interferences at $m/z = 226$ and to establish a correlation between the count rate of the element and the signal at $m/z = 226$. Our results (Figure 3) showed that the main spectral interferences at $m/z = 226$ were due to $^{186}\text{W}^+$ in combination with $^{40}\text{Ar}^+$ and to $^{209}\text{Bi}^+$ due to $^{209}\text{Bi}^{16}\text{OH}^+$ and/or $^{209}\text{Bi}^{17}\text{O}^+$. In order to figure out which of two Bi polyatomic interferences contribute to the signal at $m/z = 226$, a supplementary test was made. This test consists of correcting the measured signal at $m/z = 225$ ($^{209}\text{Bi}^{16}\text{O}^+$) for the oxygen natural isotope abundance to calculate the $^{209}\text{Bi}^{17}\text{O}^+$ contribution at $m/z = 226$ (Equation 4).

$$S_{Bi^{17}O} = S_{Bi^{16}O} \times \left(\frac{A_{17O}}{A_{16O}} \right) \quad (\text{Equation 4})$$

where $S_{Bi^{17}O}$ and $S_{Bi^{16}O}$ are the calculated and measured at $m/z = 226$ and $m/z = 225$ signals respectively, A_{17O} and A_{16O} , are the oxygen natural isotope abundances for ^{17}O and ^{16}O respectively. Our results showed that 99 % of the Bi interference at $m/z = 226$ is due to $^{209}Bi^{16}OH^+$. $^{209}Bi^{16}O^1H^+$ is one of the predominant interferences thus ^{209}Bi cannot be used as a potential internal standard for ^{226}Ra analysis.

Furthermore, Pb interference due to $^{208}Pb^{18}O^+$ was found to be in the instrumental background for $^{208}Pb^+$ count rates less than 6×10^7 CPS. On the contrary, no significant interference was observed for $^{88}Sr^{138}Ba^+$ (slope $\approx 10^{-11}$) and $^{40}Ar^{40}Ar^{146}Nd^+$ (slope 10^{-10}) for Sr, Ba and Nd count rates at concentrations (≈ 300 ppb) tested in this work.

Polyatomic interferences are strongly dependent to the introduction system used for radium analyses: no polyatomic interferences were observed by van Es and co-workers (van Es et al., 2017a) for matrix concentrations up to $100 \mu g.g^{-1}$ with Scott spray chamber.

Distribution coefficients

Na, Mg, Ca, Fe, Mo, In, Cs, Nd, W, Bi, Th, and U were not retained by the AnaLig® Ra-01 resin for both HCl and HNO₃ conditions from 0.01 M to 10 M (data not shown). Only Sr, Ba, Tl, Pb, and Ra were retained by AnaLig® Ra-01: K_d values of these elements are presented as a function of HCl and HNO₃ concentration in Figure 4. Ra is well retained by the resin in the whole range of HNO₃ and HCl concentration 0.01 M to 10 M with a minimum K_d value of $254 mL.g^{-1}$. Consequently, results suggest that the Ra elution from the resin using HCl or HNO₃ would be challenging. For Pb and Tl, a weak retention is observed for high HCl concentrations (> 6 M). Ba and Sr are retained by the resin in the whole range of acids concentrations. However, a minimum retention for Ba and Sr is showed for 6 M and 0.1 M of HCl, respectively. Therefore, according to the batch results, sample loading was done in 0.1 M HCl allowing strong Ra and low Sr retention and washing was performed with 6 M HCl for Pb, Tl and 10 % of Ba elution.

Elution profiles

A fraction collection was performed in order to establish the element elution profile. To this aim, 2 mL of 0.1 M HCl synthetic solution (multi-element and Ra solution) was loaded onto prewashed and conditioned column. After sample loading, the column was washed with 5 mL of 0.1 M HCl (5 x 1 mL) and 5 mL of 6 M HCl (5 x 1 mL) to remove the sample matrix.

For Ra elution, preliminary tests were performed using NTA solution in columns loaded with a known quantity of ^{226}Ra . The optimal conditions for Ra solution were found to be 0.12M of NTA at pH =10. Radium was eluted in 7 fractions of 200 μL and one of 500 μL . Figure 5 presents the elution profiles of the element as a function of loaded volume. As it can be seen, during sample loading and 0.1 M HCl, 80 % of Sr and 70 % of Tl elute. The rest of Tl and Pb were eluted in 6 M HCl whereas Ba elution was not successful in 6 M HCl. Ba coeluates with Ra with the NTA solution. Recovery rates for the elements range around 100 % except Ba showing a recovery of 180 %. This can be attributed to Ba contribution coming from the resin beads degradation in NTA basic solution. In fact, laboratory characterization of the resin showed that the resin beads contain high Ba and Sr contents (data not shown). The different protocol steps were summarized in table 4.

Ra fractions were mixed with concentrated HClO_4 and heated to 180°C to oxidize and eliminate organic matter. Then all solutions were evaporated to dryness before being made up in 0.5 M HNO_3 for ICP-MS/MS analysis. However, despite the NTA evaporation, a decrease of ^{226}Ra sensitivity was observed in the Ra fractions. We believe that this signal decrease is related to the NTA matrix effects and to counter this problem ^{103}Rh was used as internal standard to correct for the signal deviation. The performances of the internal standard correction are shown in Figure 6. As can be seen, after signal correction, ^{226}Ra recovery in NTA 0.12 M was found $\approx 100\%$.

Protocol testing on water samples

Experiments were performed to evaluate the protocol performances with three natural water samples (100 mL) characterized by different ionic strengths. Two drinking waters (Volvic® and Hepar®) and a seawater sample were doped with ^{226}Ra to a final activity of 10^4 mBq.L^{-1} . All samples were acidified at pH 1 using a 6 M HCl solution. This important quantity of ^{226}Ra was chosen in order to overwrite naturally-occurring ^{226}Ra present in the samples and to ensure a sufficient ^{226}Ra activity after extraction allowing a precise determination of the chemistry yield. Three columns (Figure 1) were used and 100 mL of each sample was loaded using a peristaltic pump with a flow rate of 0.1 mL.min^{-1} . After the sample loading the sample matrices

and the interfering elements were eluted with 5 mL of 0.1 M HCl and then 5 mL of 6 M HCl (Table 4). Radium was isolated in 3 fractions of 1 mL of NTA. The NTA digestion procedure with HClO₄ was applied in all Ra fractions. Then all fractions were evaporated to dryness before being made up in 5 mL of 0.5 M HNO₃. After the sample loading the whole extraction protocol it has taken ≈ 3h and the three samples were handled simultaneously.

Sample matrices and interfering elements were efficiently removed and radium recoveries were found to be around 86 %, 88 % and 73 %, for Volvic[®], Hepar[®] and seawater respectively (Table 3). The analytical precision for the three natural waters ranges between 10% and 15% (for a coverage factor k =2). The major part of the radium was eluted during the first 1 mL of NTA. These observations confirm that: (i) the extraction chromatography procedure was efficient with waters having different chemical compositions and (ii) radium can be eluted in small volumes allowing an important preconcentration factor (≈20).

4. Conclusion

This work presents a new fast ²²⁶Ra separation protocol using the Analig[®] Ra-01 resin. Batch and column results showed high specificity for ²²⁶Ra in a wide range of acid concentrations to 0.01 M from 10 M. Radium competitor elements were found to be only Sr, Ba, Tl and Pb. The determination of distribution coefficients allowed identifying conditions for their elution before radium fraction. Radium elution was performed with 0.12 M NTA. Ba coelutes with Ra, however Ba itself cannot interfere with ²²⁶Ra in ICP-MS analysis. The protocol was tested using a synthetic multielement solution doped with ²²⁶Ra and our result showed that the sample matrix and the interfering elements were efficiently separated from Ra. Furthermore, radium recovery for the synthetic multi-element solution was total.

The developed protocol was tested using three natural waters, two drinking waters and a seawater sample, doped with a known quantity of ²²⁶Ra. Radium was separated from the sample matrix and recoveries were found to be better than 85 % and 70 % for the drinking waters and seawater, respectively. This new protocol uses a single small volume resin minimizing the consumption of reagents and the produced waste volume (< 25 mL per sample) and reduces the handling time for Ra extraction compared to classical protocols. Taking into account the preconcentration factor achieved for the three natural waters (≈ 20), a LOD and LOQ of ≈ 0.4

mBq.L⁻¹ and ≈ 1.25 mBq.L⁻¹ respectively, can be obtained. Despite these encouraging results we believe that the use of ²²⁸Ra as an internal tracer to correct for chemistry yield could improve the performances of this new protocol opening up a wide field of applications especially in environmental sciences.

Figures captions

Figure 1: Home-made microcolumn with 50 mg of dry resin

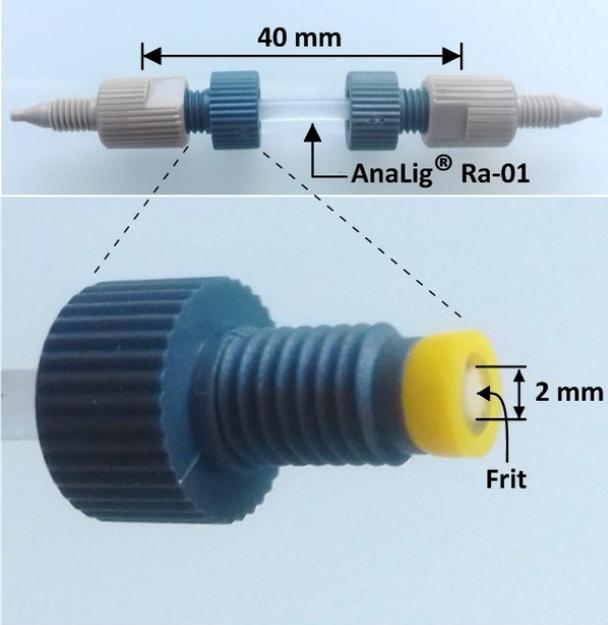


Figure 2: Sensitivity, LOD and LOQ for ²²⁶Ra with different ICP-MS instruments and configurations

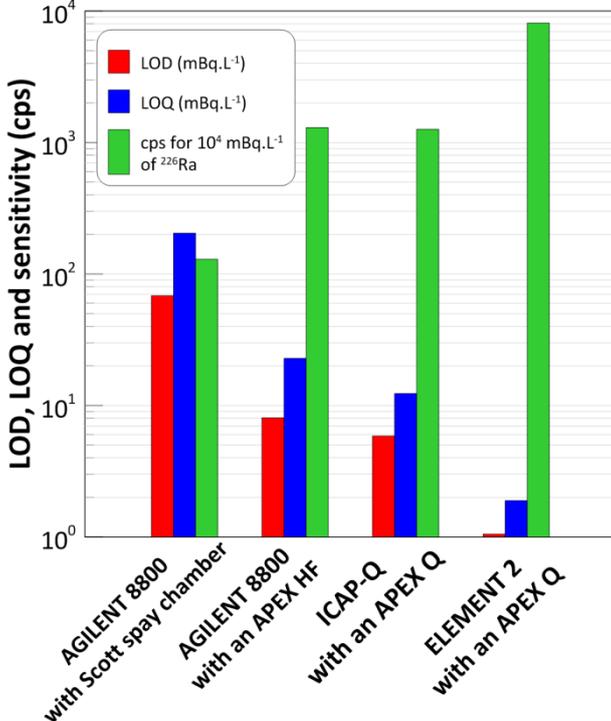


Figure 3: Polyatomic interferences of Bi (20 to 100 ppb), Pb (20 to 140 ppb) and W (20 to 170 ppb) at m/z = 226. For this study the APEX-HF was used as the introduction system.

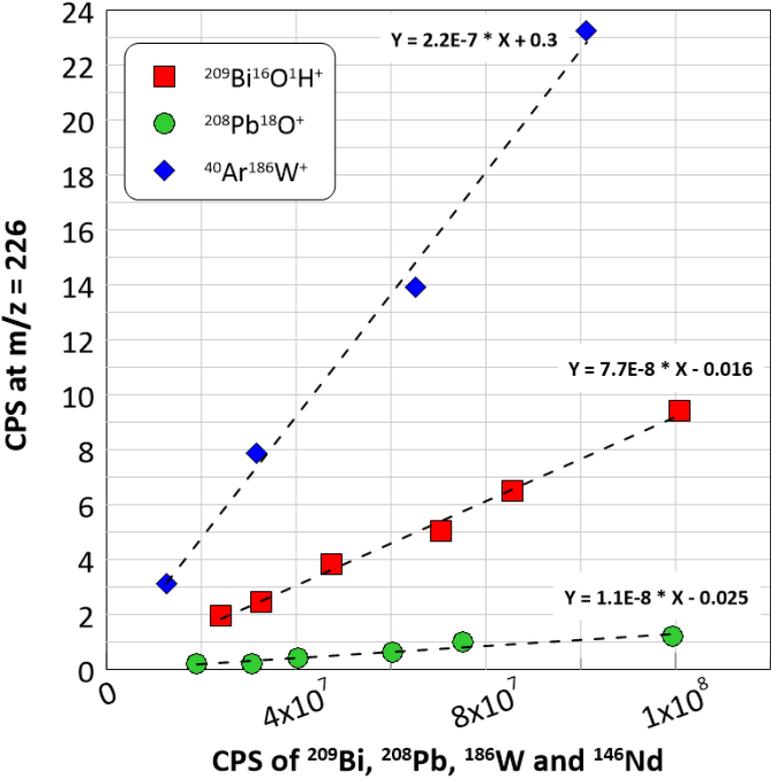


Figure 4: Distribution coefficients K_d (mg.L^{-1}) of different elements in Analig® Ra-01 resin for HNO_3 and HCl medium (no retention for alkali metals, transition metals, lanthanides and actinides).

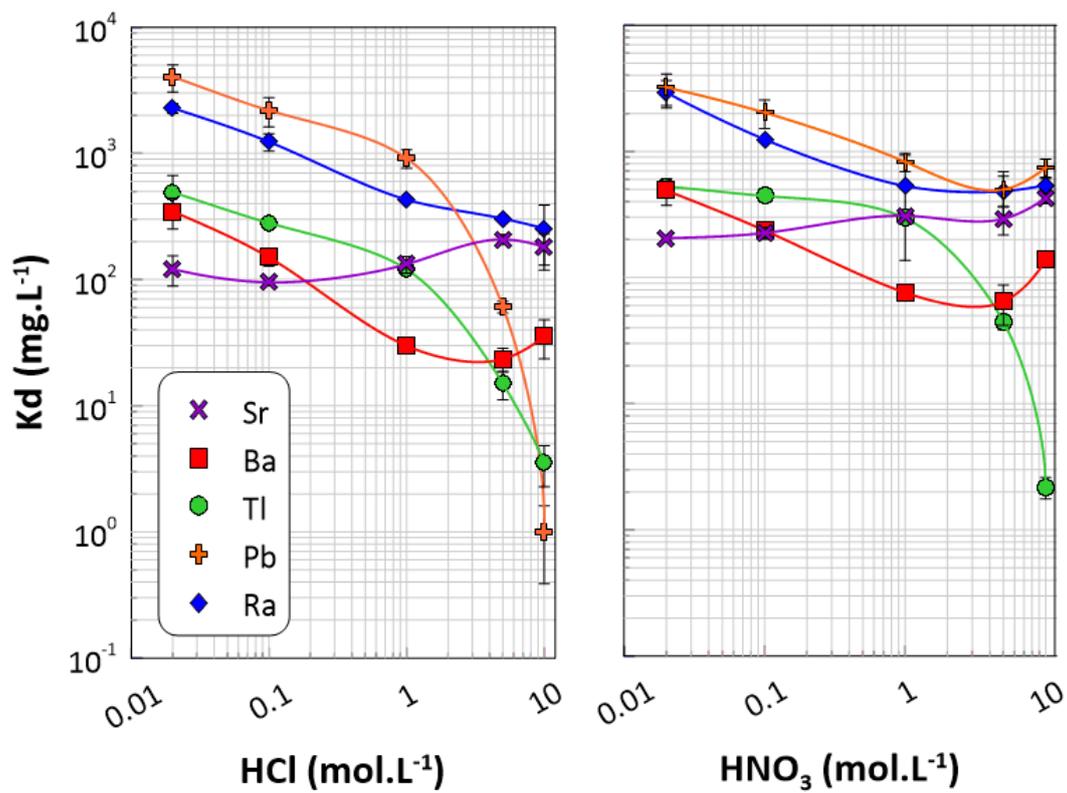


Figure 5: Elution curves for the elements (no retention for alkali metals, transition metals, lanthanides and actinides).

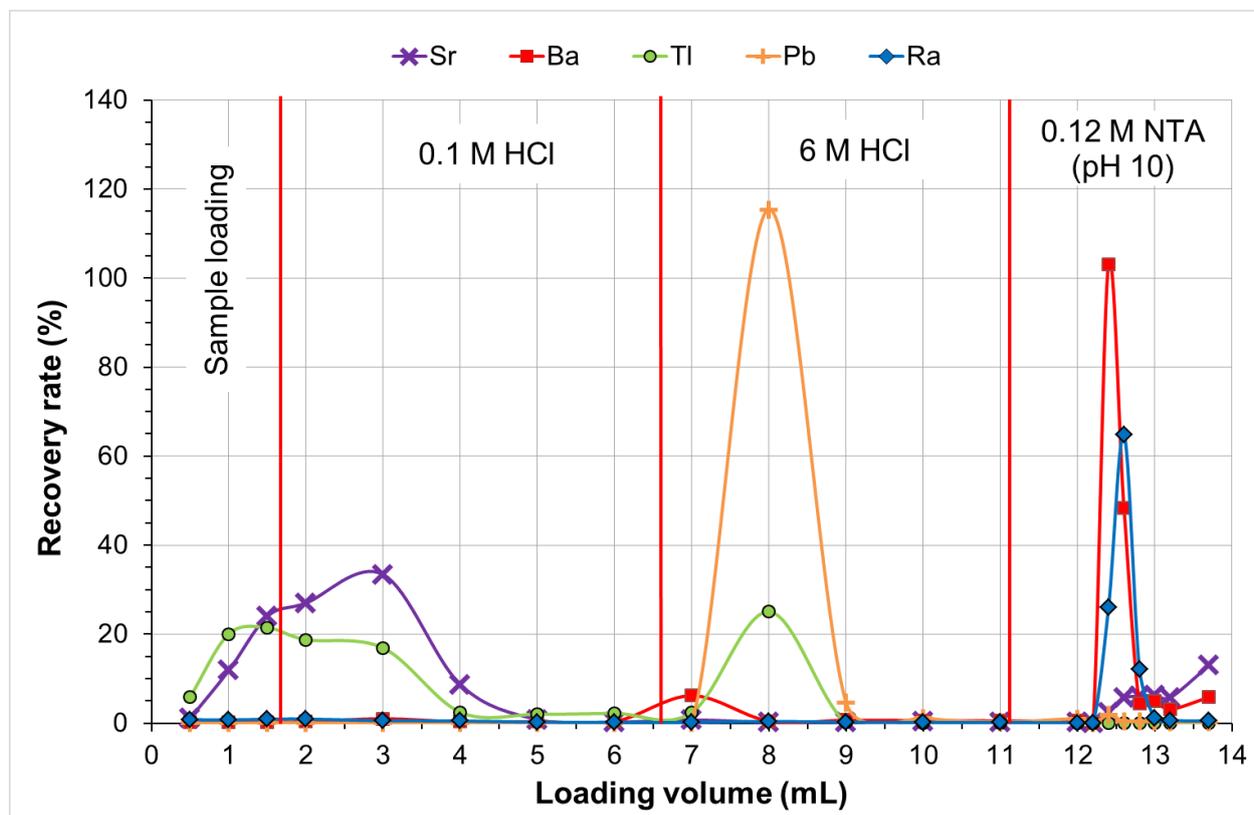


Figure 6: Correction of the matrix effect with ^{103}Rh (100 ppt) as the internal standard. Where $V_{\text{NTA}}/V_{\text{HNO}_3}$ is the ratio in volume of NTA (after digestion) in HNO_3 0.5M final solution ready for ^{226}Ra analysis. The dashed line represents the $^{226}\text{Ra}/^{103}\text{Rh}$ ratio without NTA addition. It is clear that ^{103}Rh efficiently corrects within uncertainties the NTA matrix effect.

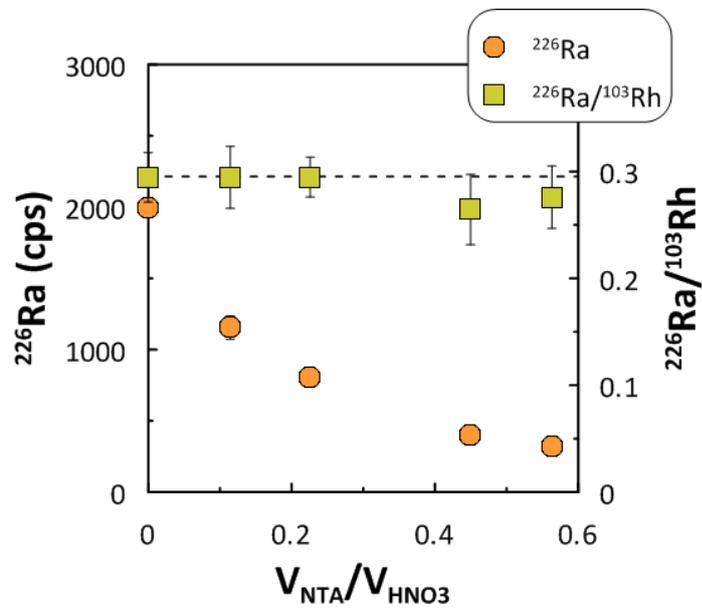


Table captions

Table 1: Element concentrations in Volvic® (Danone), Hepar® (Nestlé Waters) and seawater sample.

| Water Element (mg.L ⁻¹) | Volvic® | Hepar® | Seawater |
|---|---------|----------|-------------|
| Ca | 13 ± 1 | 563 ± 56 | 419 ± 42 |
| Mg | 9 ± 1 | 120 ± 12 | 1 237 ± 124 |
| Na | 11 ± 1 | 14 ± 1 | 9 295 ± 930 |
| K | 6 ± 1 | 14 ± 1 | 574 ± 58 |

Table 2: ICP-MS operating conditions

| Sample introduction | Agilent 8800 | ICAP-Q | Element 2 |
|--|---|---|--|
| Sample gas (L. min ⁻¹) | 1.07 | 0.83 | 1.02 |
| Make up gas (L. min ⁻¹) | 0.16 | / | / |
| Auxiliary gas (L. min ⁻¹) | 0.92 | 0.86 | 0.25 |
| Sample uptake (µL. min ⁻¹) | 330 | 630 | 300 |
| Introduction system | APEX HF / Scott | APEX Q with a membrane desolvation module | APEX Q with a membrane desolvation module |
| ICP-MS conditions | | | |
| RF power (W) | 1 550 | 1 550 | 950 |
| ²²⁶ Ra sensitivity (CPS.ppm ⁻¹ , CPS/(Bq.mL ⁻¹)) | 4.8 x 10 ⁹ , 1.3 x 10 ⁵ | 4.7 x 10 ⁹ , 1.3 x 10 ⁵ | 3.0 x 10 ¹⁰ , 8.1 x 10 ⁵ |
| Acquisition parameters | | | |
| Peak shape (points) | 1 | 60 | 30 |
| Integration time (s) for ²²⁶ Ra | 5 | 0.5 | 0.3 |
| Number of sweeps per replicate | 20 | 100 | 170 |
| Number of replicates per sample | 5 | 5 | 3 |

Table 3: Radium recoveries for Volvic®, Hepar® and seawater sample

| Water | Fraction 1 (%) | Fraction 2 (%) | Fraction 3 (%) | Total recoveries (%) |
|-----------------|-----------------------|-----------------------|-----------------------|-----------------------------|
| Volvic® | 81.6 | 3.8 | 0.5 | 85.9 |
| Hepar® | 79.7 | 7.7 | 0.5 | 87.8 |
| Seawater | 67.5 | 4.7 | 0.3 | 72.5 |

Table 4: Final protocol for separation and pre-concentration of radium in environmental samples

| Step | Procedure | Volume (mL) | Eluent |
|-------------|-----------------------------|---|--------------------|
| 1 | Column rinsing | 5.0 | Ultrapure water |
| 2 | Column conditioning | 5.0 | 0.1 M HCl |
| 3 | Sample loading in 0.1 M HCl | 2 mL of synthetic solution 100 mL of water samples | |
| 4 | Sr, Cs, Ba, Tl elution | 5.0 | 0.1 M HCl |
| 5 | Ba, Tl, Pb elution | 5.0 | 6 M HCl |
| 7 | Ra elution | 1.0 | 0.12 M NTA (pH 10) |

References

- Azouazi, M., Ouahidi, Y., Fakhi, S., Andres, Y., Abbe, J.C., Benmansour, M., 2001. Natural radioactivity in phosphates, phosphogypsum and natural waters in Morocco. *Journal of environmental radioactivity* 54, 231-242.
- Benkhedda, K., Lariviere, D., Scott, S., Evans, D., 2005. Hyphenation of flow injection on-line preconcentration and ICP-MS for the rapid determination of ²²⁶Ra in natural waters. *Journal of Analytical Atomic Spectrometry* 20, 523-528.
- Bourquin, M., van Beek, P., Reyss, J.L., Riotte, J., Freydier, R., 2011. Determination of ²²⁶Ra concentrations in seawater and suspended particles (NW Pacific) using MC-ICP-MS. *Marine Chemistry* 126, 132-138.
- Bourquin, M., van Beek, P., Reyss, J.L., Souhaut, M., Charette, M.A., Jeandel, C., 2008. Comparison of techniques for pre-concentrating radium from seawater. *Marine Chemistry* 109, 226-237.
- Carvalho, F.P., Madruga, M.J., Reis, M.C., Alves, J.G., Oliveira, J.M., Gouveia, J., Silva, L., 2007. Radioactivity in the environment around past radium and uranium mining sites of Portugal. *Journal of environmental radioactivity* 96, 39-46.
- Chabaux, F., Othman, D.B., Birck, J.L., 1994. A new Ra-Ba chromatographic separation and its application to Ra mass-spectrometric measurement in volcanic rocks. *Chemical Geology* 114, 191-197.
- Chalupnik, S., Wysocka, M., 2008. Radium removal from mine waters in underground treatment installations. *Journal of environmental radioactivity* 99, 1548-1552.
- Chiarizia, R., Dietz, M.L., Horwitz, E.P., Burnett, W.C., Cable, P.H., 1999. Radium separation through complexation by aqueous crown ethers and ion exchange or solvent extraction *Separation Science and Technology* 34, 931-950.
- Copia, L., Nisi, S., Plastino, W., Ciarletti, M., Povinec, P.P., 2015. Low-level ²²⁶Ra determination in groundwater by SF-ICP-MS: optimization of separation and pre-concentration methods. *Journal of Analytical Science and Technology* 6, 22.
- Cozzella, M.L., Leila, A., Hernandez, R.S., 2011. Determination of ²²⁶Ra in urine samples by Q-ICP-MS: A method for routine analyses. *Radiation Measurements* 46, 109-111.
- Cuvier, A., Panza, F., Pourcelot, L., Foissard, B., Cagnat, X., Prunier, J., van Beek, P., Souhaut, M., Le Roux, G., 2015. Uranium decay daughters from isolated mines: Accumulation and sources. *Journal of environmental radioactivity* 149, 110-120.
- Dulanská, S., Gardoňová, V., Remenec, B., Mátel, Ľ., Cabáneková, H., 2016. Determination of ²²⁶Ra using molecular recognition technology product AnaLig® Sr-01. *Journal of Radioanalytical and Nuclear Chemistry* 309, 853-857.
- Dulanská, S., Gardoňová, V., Šebesta, F., Mátel, Ľ., 2015. A rapid determination of ²²⁶Ra in water using composite ion exchanger MnO₂-PAN. *Journal of Radioanalytical and Nuclear Chemistry* 303, 47-51.

Epov, V., Lariviere, D., Evans, R., Li, C., Cornett, R., 2003. Direct determination of ^{226}Ra in environmental matrices using collision cell inductively coupled plasma mass-spectrometry. *Journal of Radioanalytical and Nuclear Chemistry* 256, 53-60.

Fons-Castells, J., Oliva, J., Tent-Petrus, J., Llauradó, M., 2017. Simultaneous determination of ^{226}Ra , ^{228}Ra and ^{210}Pb in drinking water using 3M Empore™ RAD disk by LSC-PLS. *Applied Radiation and Isotopes* 124, 83-89.

Foster, D.A., Staubwasser, M., Henderson, G.M., 2004. ^{226}Ra and Ba concentrations in the Ross Sea measured with multicollector ICP mass spectrometry. *Marine Chemistry* 87, 59-71.

Ghaleb, B., Pons-Branchu, E., Deschamps, P., 2004. Improved method for radium extraction from environmental samples and its analysis by thermal ionization mass spectrometry. *Journal of Analytical Atomic Spectrometry* 19, 906-910.

Godoy, J.M., Vianna, L.M., Godoy, M.L.D.P., Almeida, A.C., 2016. Determination of ^{226}Ra in produced water by liquid scintillation counting. *Journal of environmental radioactivity* 160, 25-27.

Hodge, V.F., Laing, G.A., 1994. An evaluation of the inductively coupled plasma mass spectrometer for the determination of radium-226 in drinking water. *Radiochimica Acta* 64, 211-216.

Hsieh, Y.-T., Henderson, G.M., 2011. Precise measurement of $^{228}\text{Ra}/^{226}\text{Ra}$ ratios and Ra concentrations in seawater samples by multi-collector ICP mass spectrometry. *Journal of Analytical Atomic Spectrometry* 26, 1338-1346.

IAEA, 2014. The Environmental Behaviour of Radium: Revised Edition. INTERNATIONAL ATOMIC ENERGY AGENCY, Vienna.

Jia, G., Jia, J., 2012. Determination of radium isotopes in environmental samples by gamma spectrometry, liquid scintillation counting and alpha spectrometry: a review of analytical methodology. *Journal of Environmental Radioactivity* 106, 98-119.

Joannon, S., Pin, C., 2001. Ultra-trace determination of ^{226}Ra in thermal waters by high sensitivity quadrupole ICP-mass spectrometry following selective extraction and concentration using radium-specific membrane disks. *Journal of Analytical Atomic Spectrometry* 16, 32-36.

Lagacé, F., Foucher, D., Surette, C., Clarisse, O., 2017. Quantification of ^{226}Ra at environmental relevant levels in natural waters by ICP-MS: Optimization, validation and limitations of an extraction and preconcentration approach. *Talanta* 167, 658-665.

Lariviere, D., Brownell, D., Epov, V., Cornett, R., Evans, R., 2007. Determination of ^{226}Ra in sediments by ICP-MS: A comparative study of three sample preparation approaches. *Journal of Radioanalytical and Nuclear Chemistry* 273, 337-344.

Lariviere, D., Epov, V., Evans, R., Cornett, R., 2003. Determination of radium-226 in environmental samples by inductively coupled plasma mass spectrometry after sequential selective extraction. *Journal of Analytical Atomic Spectrometry* 18, 338-343.

Lariviere, D., Epov, V., Reiber, K., Cornett, R., Evans, R., 2005. Micro-extraction procedures for the determination of Ra-226 in well waters by SF-ICP-MS. *Analytica chimica acta* 528, 175-182.

Mesnic, N., Sadi, B., Li, C., Lai, E., 2013. Application of magnetic nanoparticles for the extraction of radium-226 from water samples. *Journal of Radioanalytical and Nuclear Chemistry* 298, 1501-1509.

Moon, D.S., Burnett, W.C., Nour, S., Horwitz, P., Bond, A., 2003. Preconcentration of radium isotopes from natural waters using MnO₂ Resin. *Applied Radiation and Isotopes* 59, 255-262.

Park, C., Oh, P., Kim, H., Lee, D., 1999. Determination of ²²⁶Ra in mineral waters by high-resolution inductively coupled plasma mass spectrometry after sample preparation by cation exchange. *Journal of Analytical Atomic Spectrometry* 14, 223-227.

Perrier, F., Aupiais, J., Girault, F., Przylibski, T.A., Bouquerel, H., 2016. Optimized measurement of radium-226 concentration in liquid samples with radon-222 emanation. *Journal of environmental radioactivity* 157, 52-59.

Pietruszka, A.J., Carlson, R.W., Hauri, E.H., 2002. Precise and accurate measurement of ²²⁶Ra–²³⁰Th–²³⁸U disequilibria in volcanic rocks using plasma ionization multicollector mass spectrometry. *Chemical Geology* 188, 171-191.

Pluta, I., Trembacowski, A., 2001. Changes of the chemical composition of discharged coal mine water in the Rontok Pond, Upper Silesia, Poland. *Environmental Geology* 40, 454-457.

Song, L., Yang, Y., Luo, M., Ma, Y., Dai, X., 2017. Rapid determination of radium-224/226 in seawater sample by alpha spectrometry. *Journal of environmental radioactivity* 171, 169-175.

St-Amant, N., Whyte, J.C., Rousseau, M.-E., Lariviere, D., Kurt Ungar, R., Johnson, S., 2011. Radiostrontium and radium analysis in low-level environmental samples following a multi-stage semi-automated chromatographic sequential separation. *Applied Radiation and Isotopes* 69, 8-17.

van Beek, P., Souhaut, M., Reyss, J.L., 2010. Measuring the radium quartet (²²⁸Ra, ²²⁶Ra, ²²⁴Ra, ²²³Ra) in seawater samples using gamma spectrometry. *Journal of environmental radioactivity* 101, 521-529.

van Es, E., Russell, B., Ivanov, P., Read, D., 2017a. Development of a method for rapid analysis of Ra-226 in groundwater and discharge water samples by ICP-QQQ-MS. *Applied Radiation and Isotopes*.

van Es, E.M., Russell, B.C., Ivanov, P., Garcia Miranda, M., Read, D., Dirks, C., Happel, S., 2017b. The behaviour of (²²⁶Ra) in high-volume environmental water samples on TK100 resin. *J Radioanal Nucl Chem* 312, 105-110.

Vandenhove, H., Sweeck, L., Mallants, D., Vanmarcke, H., Aitkulov, A., Sadyrov, O., Savosin, M., Tolongutov, B., Mirzachev, M., Clerc, J.J., Quarch, H., Aitaliev, A., 2006. Assessment of radiation exposure in the uranium mining and milling area of Mailuu Suu, Kyrgyzstan. *Journal of Environmental Radioactivity* 88, 118-139.

Vandenhove, H., Verrezen, F., Landa, E.R., 2019. *Radionuclides in the Environment : Radium*.

Wærsted, F.M., Jensen, K.A., Reinoso-Maset, E., Skipperud, L., 2018. High Throughput, Direct Determination of ²²⁶Ra in Water and Digested Geological Samples. *Analytical Chemistry* 90, 12246-12252.