Determination of ^{226}Ra in sediments by ICP-MS:
A comparative study of three sample preparation approaches

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Three protocols (Method I: ion chromatography (IC) and extraction chromatography (EC), Method II: precipitation followed by IC, and Method III: adsorption onto MnO$_2$ followed by IC-EC) were investigated to determine their applicability for the separation and pre-concentration of ^{226}Ra in sediments. ^{226}Ra recoveries, measured using the isotope dilution method with ^{228}Ra as yield tracer, and the removal of spectral and non-spectral interferences were evaluated. The formation of polyatomic interferences at $m/z = 226$ from elements found in the matrix of sediments was also investigated to assess the level of separation required. Methods I and III were found to be the most effective with respect to recoveries and interference removal. The efficiency of a rapid microwave based protocol for the complete digestion of 1 g of sediment is also described. The method was tested and ^{226}Ra concentrations in the millibecquerel range (fg) were determined in a standard reference material and sediment cores collected from Lake Baikal.

Introduction

Similar to many naturally-occurring radioisotopes that belong to the ^{238}U decay series, ^{226}Ra (half-life: $1.622 \cdot 10^3$ y) has been found to be a valuable tracer or chronometer in environmental disciplines such as geochemistry,[1–4] limnology,[5–7] and geology.[8–10] One important application is the determination of deposition rates of sediments based on ^{210}Pb:^{226}Ra ratio measurements.[6,11] While ^{226}Ra has been measured for decades using direct or indirect radiometric techniques such as α-[12–14] or γ-spectrometry,[5,7,15,16] the recent development of high sensitivity mass spectrometers has prompted the use of alternative instrumentation, such as thermal ionization mass spectrometry (TIMS) and inductively coupled plasma mass spectrometry (ICP-MS).[1,8–10,17–27] However, analyses using these techniques are still hampered by spectral and non-spectral interferences and the limited mass of the analyte present in the sample, especially in environmental matrices, such as sediment and soil. For this reason, separation and pre-concentration is imperative prior to the analysis.

Whereas many chromatographic protocols have been published for the separation/preconcentration of ^{226}Ra in solid environmental samples (e.g., mollusc shells, fish otoliths, silicate and volcanic rocks) with TIMS as determination method,[8,10,17–20] those published for ICP-MS have been mainly focused to the analysis of natural waters.[1,21,22,23,28,29] The fact that analyses of ^{226}Ra on solid matrices are not commonly performed by ICP-MS is perplexing, especially considering that an additional step of sample loading onto the filament is necessary for

TIMS. For this reason, ICP-MS analysis has the potential to provide simpler and faster ^{226}Ra measurements in solid matrices than TIMS, especially if a multi-collector ICP-MS, which has similar to TIMS instrumental precision for isotope ratio measurements, is used.

Based on this premise that ICP-MS can compete with TIMS for ^{226}Ra measurements with respect to use, accuracy, and detectability, three distinctive sample preparation methods were investigated to establish their applicability for the determination of ^{226}Ra in sediments by plasma ionization mass spectrometry: Method I: ion chromatography (IC) and extraction chromatography (EC),[30] Method II: precipitation followed by IC,[22] Method III: adsorption onto MnO$_2$ followed by IC-EC.[19] All three techniques were originally designed for either different mass spectrometric approaches (TIMS) and/or sample matrices (i.e., geologic rocks, soils, and calcified structures). First, the effect of some elements on the potential formation of molecular interferences at $m/z = 226$ was investigated to establish the level of sample purification required. Second, the applicability of three separation methods for ICP-MS was evaluated and reported based on analytical parameters such as yield recovery, reproducibility, and matrix removal efficiency. Finally, ^{226}Ra concentrations in a standard reference material (SRM) and Lake Baikal sediments (BIL-2) were measured by ICP-MS.

Experimental

Instrumentation

Determination of ^{226}Ra content in sediments was performed using a double focusing sector field (SF) ICP-MS (Finnigan Element2, Bremen, Germany). The ICP-SFMS was used at low-resolution mode to provide

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maximum instrumental sensitivity. This instrument was chosen because it provides the best instrumental sensitivity, and therefore, the lowest detection limits. An Apex Q high-sensitivity sample introduction system equipped with a 100 µl·min^{-1} nebulizer (Elemental Scientific Inc., Ohama, NE, USA) was used to further enhance sensitivity.[31] The instrument was optimized daily using a 60 pg·l^{-1} ^{226}Ra standard solution. Optimized conditions for the determination of ^{226}Ra using ICP-SFMS are presented in Table 1.

Reagents and chemicals

Trace metal grade nitric, hydrochloric, sulphuric, and hydrofluoric acids (Fisher, Ottawa, ON, Canada) were used for sample preparation. Distilled water was re-purified using a Milli-Q system (Millipore, MA, USA) at 18 MΩ cm. $Na_2C_{10}H_{14}O_8 \cdot 2H_2O$ (i.e., EDTA-2Na), CH_3COONH_4, $Pb(NO_3)_2$, and Na_2SO_4 salts (all from Fisher, Ottawa, ON, Canada) were used to prepare solutions for Method II. For Method III, 0.5M solutions of $KMnO_4$ (Fisher, Ottawa, ON, Canada) and $MnCl_2 \cdot 4H_2O$ (Anachemia Science, Mississauga, ON, Canada) were obtained by dissolving the appropriate amount of salt in Milli-Q water. A stock solution of 10 µg·l^{-1} (370·10^3 Bq·kg^{-1}) of ^{226}Ra (AECL, Chalk River, ON, Canada) in 5% HCl was used to prepare standard solutions using serial dilution in 2% (v/v) HNO_3, and to spike samples.

Table 1. Instrumental conditions used for the detection of ^{226,228}Ra by ICP-MS

Instrumental parameters	Element2 SF-ICP-MS
Torch position	Optimized daily
Sample flow rate, µl/min	130 (self-aspirating)
Gas flow, l/min	
Cooling	16.08
Auxiliary	0.90
Sample	1.031
RF power, W	1200
Guard electrode	On
Lenses, V	
Extraction	−2000
Focus	−826
X-deflection	−5.53
Shape	121.00
Y-deflection	−4.74
Detector voltage, V	2650
Sampling cone	1.1 mm nickel
Skimmer cone	0.8 mm nickel
m/z monitored	103, 226, 228
Number of passes	5
Number of replicates	10
Acquisition time, s	23
Apex-Q system parameters	
Nebulizer	100 µl/min PFA microflow
Spray chamber temperature, °C	100
Peltier-cooled multipass condenser temperature, °C	2

Two commercially available resins (AG50W-X8 and Sr*Spec) were used for the pre-concentration and the separation of ^{226}Ra in sediments. Resin volumes of 10 and 25 ml (AG50W-X8, 200–400 mesh particle size from Eichrom, Darien, IL) were packed into Econo-Pack® and glass econo-columns®, respectively (Bio-Rad, Mississauga, ON, Canada). Pre-packed 2-ml cartridges of Sr*Spec resin (Eichrom, Darien, IL) were used for Methods I and III.

Mono-elemental solutions (1000 µg·ml^{-1}) of Sr, Ba, La, Ce, Nd, Pb, Bi, Y, Mo, W, and Cd (PlasmaCAL, SCP Science, Baie D'Urfé, Qc, Canada) were used to prepare the various standards for the evaluation of molecular interferences. These standards (in 2% v/v HNO_3) were prepared for concentrations ranging from 10 to 500 mg·l^{-1}, based on the expected elemental concentration in sediments. A 1000 µg·ml^{-1} solution of rhodium (PlasmaCAL, SCP Science, Baie D'Urfé, QC, Canada) was used to spike standards and samples in order to determine the signal attenuation resulting from other elements present in the plasma.

^{228}Ra standard preparation

The ^{228}Ra tracer was prepared from an old $Th(NO_3)_4$ salt (to assure secular equilibrium between ^{232}Th and ^{228}Ra). 10 g of this salt, dissolved in 15 ml of 7M HNO_3, was purified using an anion-exchange resin (AG1-X8, 100–200 mesh). The Th solution was loaded onto the resin, which was subsequently rinsed with 50 ml of 7M HNO_3. The loading and rising solutions with ^{228}Ra were combined, evaporated to dryness and redissolved in 5 ml of 2% (v/v) HNO_3. The Th fraction was then eluted using 12M HCl. The fraction containing ^{228}Ra was further purified using stage 1 and 2 from Method III (Table 2). The residue obtained after evaporation to dryness was redissolved in 2.5 ml of 2% (v/v) HNO_3. The Ra composition of the ^{228}Ra stock solution was determined by mass spectrometry using ^{226}Ra-calibrated standards. All samples analyzed in this study were spiked with 172 fg of ^{228}Ra in order to evaluate ^{226}Ra recovery throughout the digestion and separation processes.

Sample preparation

A sediment core collected from Lake Ruban (Parc des Laurentides, QC, Canada) was used as a reference matrix to compare the efficiency of each method for the determination of ^{226}Ra. Samples collected were mixed, homogenized, dried overnight at 106 °C, and were finally separated into sub-samples of approximately 1 g. Each sub-sample was transferred into a porcelain crucible, spiked with 3.5 pg of ^{226}Ra, ashed at 900 °C for 30 minutes using a muffle furnace, and then cooled for 2 hours in a desiccator. A microwave sample

digestion was performed with a microwave digestion labstation (Ethos Pro) and evaporation unit (MMR-12 rotor) from Milestone (ATS Scientific Inc., Burlington, ON, Canada) using repetitive digestion/evaporation cycles (Table 3). This procedure leads to a complete digestion of the sample. The residue from cycle 4 was redissolved to achieve a final volume of 45 ml at a HCl molarity of 6M for Method I, 20 ml (4M HCl) for Method II, and 2 ml (6M HCl) for Method III, respectively. The complete digestion and redissolution

of the samples took approximately 8 hours, including the ashing, digestion, and evaporation processes. Determination of [226]Ra concentration in sediment collected from Lake Baikal (for further details)[32] and a freshwater lake sediment standard reference material (SRM-4354, NIST, Gaithersburg, MD) was also performed. These samples were treated using the same digestion protocol as the reference matrix and analyzed using Methods I and III (see below).

Table 2. Description of the chromatographic protocols used in Methods I, II, and III for the separation of Ra in sediments

	Stage 1	Stage 2	Stage 3
Method I			
Resin type	AG50W-X8	AG50W-X8	Sr*Spec®
Resin volume, ml	25	10	2
Conditioning	50 ml 6M HCl	20 ml 6M HCl	20 ml 3M HNO$_3$
Sample loading	45 ml 6M HCl	5 ml 6M HCl	1 ml 3M HNO$_3$
Washing	3×33 ml 6M HCl	3 x 20 ml 6M HCl	–
Elution	200 ml 6M HCl	90 ml 6M HCl	10 ml 3M HNO$_3$
Redissolution	5 ml 6M HCl	1 ml 3M HNO$_3$	3.5 ml 2% (v/v) HNO$_3$
Method II			
Resin type	AG50W-X8		
Resin volume, ml	10		
Conditioning	50 ml 0.3M HCl		
Sample loading	20 ml 0.1M EDTA : 5M CH$_3$COONH$_4$ (20:1)		
Washing	50 ml 0.1M EDTA		
	50 ml 1.5M CH$_3$COONH$_4$ (in 0.1M HNO$_3$)		
	50 ml 0.3M HCl		
	20 ml 3M HCl		
Elution	50 ml 6M HCl		
	50 ml 4M HNO$_3$		
Redissolution	3.5 ml 2% (v/v) HNO$_3$		
Method III			
Resin type	AG50W-X8	AG50W-X8	Sr*Spec®
Resin volume, ml	10	10	2
Conditioning	20 ml 6M HCl	20 ml 6M HCl	20 ml 3M HNO$_3$
Sample loading	20 ml 6M HCl	5 ml 6M HCl	1 ml 3M HNO$_3$
Washing	3×15 ml 6M HCl	3×20 ml 6M HCl	–
Elution	90 ml 6M HCl	90 ml 6M HCl	10 ml 3M HNO$_3$
Redissolution	5 ml 6M HCl	1 ml 3M HNO$_3$	3.5 ml 2% (v/v) HNO$_3$

Table 3. Digestion/evaporation protocols used for the determination of [226]Ra in sediments

Cycle	Step	Reagents	Volume, ml	Microwave conditions
1	Digestion	HNO$_3$	10	Increase to 1000 W for 10 min
		HF	10	Hold at 1000 W for 10 min
	Evaporation	–	–	Hold at 800 W for 20 min
2	Digestion	HNO$_3$	10	Increase to 1000 W for 10 min
		HF	10	Hold at 1000 W for 10 min
	Evaporation	–	–	Hold at 800 W for 20 min
3	Digestion	HCl	15	Increase to 1000 W for 10 min
		HNO$_3$	5	Hold at 1000 W for 10 min
	Evaporation	–	–	Hold at 800 W for 20 min
4	Digestion	HCl	10	Increase to 1000 W for 10 min
				Hold at 1000 W for 10 min

Radium separation and pre-concentration

Method I: This protocol is based on the use of ion-exchange and extraction chromatography for the separation and pre-concentration of radium. It is a variation of the protocol proposed by CHABAUX et al.[30] for the determination of ^{226}Ra in volcanic rocks by TIMS (Table 2). The changes done in this study are associated with the use of Sr*spec cartridges in the final stage. Since these cartridges contain more resin than the home-packed columns, which were used by CHABAUX et al.,[30] the elution conditions for Ra were re-optimized. A 25 ml of resin (AG50W-X8) was cleaned successively with volumes (20 ml) of 6M HCl, 2M HCl, and 6M HCl and preconditioned with 50 ml of 6M HCl. The sample (45 ml) in 6M HCl was then loaded onto the column at a flow rate of about 1 ml·min^{-1}. The resin was rinsed with 3×33 ml (6M HCl) to remove most of the bulk matrix, followed by elution of the Ra and part of the Ba with 200 ml of 6M HCl. The last fraction was then evaporated to dryness using a hotplate and redissolved in 5 ml of 6M HCl. This solution was loaded onto 10 ml of resin (AG50W-X8), followed by 3×20 ml 6M HCl to reduce any residual matrix constituents and 90 ml 6M HCl to elute Ra. The eluate was evaporated to dryness and redissolved in 1 ml of 3M HNO$_3$ (solution A). In order to thoroughly remove traces of Sr and Ba, the solution A was loaded through a 2 ml cartridge with Sr*Spec resin, which was previously cleaned with volumes (20 ml) of 3M HNO$_3$, H$_2$O, and 3M HNO$_3$, and preconditioned with 20 ml of 3M HNO$_3$. Fractions of solution A were collected together with the following 10 ml of 3M HNO$_3$ rinse solution loaded through the Sr*Spec resin and evaporated to dryness. The residue was redissolved in 3.5 ml of 2% HNO$_3$ (v/v) containing 10 μg·l^{-1} of Rh as an internal standard.

Method II: This approach is based on a co-precipitation step followed by an ion-exchange separation that has been used by KIM et al.[22] for the determination of ^{226}Ra in soil. After the redissolution of the digested sample in 20 ml of 4M HCl, the sample was diluted to 300 ml using Milli-Q water. 50 mg of Pb^{2+} were added to the solution, followed by 10 ml of 10% (w/v) Na$_2$SO$_4$ and then 1 ml of concentrated H$_2$SO$_4$. Addition of these reagents creates a visible white precipitate that contains Ra. The precipitate was separated from the solution through centrifugation, washing, and redissolution in 20 ml of a mixture of EDTA-2Na and 5M CH$_3$COONH$_4$ (20:1). The pH of this solution was adjusted to 5 using concentrated HNO$_3$. The final solution was loaded onto a 10 ml resin volume (AG50W-X8). The resin was then rinsed

sequentially with 0.1M EDTA-2Na, 1.5M CH$_3$COONH$_4$ in 0.1M HNO$_3$, 0.3M HCl, and 3M HCl (Table 2). Ra and Ba were eluted from the resin using successively 50 ml of 6M HCl and 50 ml of 4M HNO$_3$. The collected fraction was evaporated to dryness and the residue was redissolved in 3.5 ml of 2% (v/v) HNO$_3$ containing Rh (10 μg·l^{-1}) as an internal standard.

Method III: This approach is based on the specific co-precipitation of Ba and Ra onto manganese oxide (MnO$_2$) followed by ion-exchange and extraction chromatography. It was applied by GHALEB et al.[19] for the determination of ^{226}Ra in coral structures. After redissolution of the sample in 2 ml of 6M HCl, the sample was diluted by 200 ml of Milli-Q water. 100 μl of a 0.5M KMnO$_4$ solution were added to the sample. The sample was then heated for 1 hour at 80 °C, cooled, and then the pH was adjusted to 8.5 using 1M NaOH. After that, 200 μl of 0.5M MnCl$_2$·4H$_2$O was added to initiate MnO$_2$ precipitation. After stirring and allowing the solution to settle, the supernatant was discarded and the precipitate redissolved in 20 ml of HNO$_3$: HCl (1 : 1), which was evaporated to dryness. The residue was redissolved in 20 ml of 6M HCl and then directed for the separation step using ion-exchange chromatography (Table 3). The following separation procedure is the one proposed by CHABAUX et al.[30] with the exception of stage III that was slightly modified due to the use of different resin volume. So, in this work the sample solution was loaded onto a 10 ml of resin (AG50W-X8), which was then rinsed with 3×15 ml of 6M HCl. Ra and part of the Ba were eluted using 90 ml of 6M HCl, which was evaporated to dryness and separated using purification stage 2 and 3 of Method I.

Results and discussion

Polyatomic interferences

The presence of molecular interferences is problematic for ultra-trace measurements, including radionuclides such as ^{226}Ra. EPOV et al.[24] have reviewed the possible elemental combinations that could lead to a signal at $m/z = 226$, and investigated the formation of these interferences concentrations inferior to 1 mg·l^{-1} by collision cell (CC) ICP-MS. However, since different types of sample digestion (complete digestion vs. leaching), instruments (SF-ICPMS vs. ICP-CC-MS), and introduction systems (Apex-Q vs. Aridus) were used in this study and by EPOV,[24] respectively, reinvestigation of the presence of polyatomic interferences at $m/z = 226$ was performed (Table 4).

Table 4. Apparent ^{226}Ra concentration observed in the presence of some interfering elements

Element	Polyatomic interferences	Concentration, μg·l^{-1}	Apparent ^{226}Ra concentration, pg·l^{-1}	Resolution*
W	^{186}W^{40}Ar	100	5	2080
		1 000	53	
		10 000	1 059	
Bi	^{209}Bi^{16}O^{1}H	100	5	5347
		1 000	92	
Pb	^{208}Pb^{18}O	1 000	9	4557
		10 000	68	
		100 000	666	
Sr/Ce	^{86}Sr^{140}Ce	100 000	49	1073
Sr/La	^{87}Sr^{139}La	10 000	4	1076
		100 000	35	
Sr/Ba	^{88}Sr^{138}Ba	100 000	38	1054
		500 000	68	

* Resolution required to separate the polyatomic interference and ^{226}Ra peaks.

The first type of polyatomic interferences investigated was the single-charged di-elemental ion (^{113}Cd$_2^+$). At concentrations ranging from 10 to 1000 μg·l^{-1}, no detectable signal at $m/z = 226$ was observed. Also, the possible formation of polyatomic interferences between inert gases (other than Ar) present as impurities in the plasma (Xe, Kr) and some transition (Mo) and lanthanide elements (Ce, Nd) was studied. Again, at concentrations as high as 100 mg·l^{-1}, no change in the background signal at $m/z = 226$ was detected. Therefore, the formation of ^{92}Mo^{134}Xe, ^{94}Mo^{132}Xe, ^{95}Mo^{131}Xe, ^{96}Mo^{130}Xe, ^{97}Mo^{129}Xe, ^{98}Mo^{128}Xe, ^{100}Mo^{126}Xe, ^{140}Ce^{86}Kr, ^{143}Nd^{83}Kr, ^{144}Nd^{82}Kr, ^{146}Nd^{80}Kr, and ^{148}Nd^{78}Kr are unlikely, at least in the current instrumental setup. In addition, two argide molecular ions were suggested by EPOV et al.[24] as possible interferences: ^{146}Nd^{40}Ar^{40}Ar and ^{186}W^{40}Ar. Only ^{186}W^{40}Ar interference was shown to produce a signal at $m/z = 226$. This interference was observable with concentration as low as 100 μg·l^{-1} (Table 4), which is in concordance with data previously published[23,24] for other instrumental configuration.

Many Pb and Bi oxides and hydroxides (i.e., ^{208}Pb^{18}O, ^{208}Pb^{17}O^{1}H, ^{208}Pb^{16}O^{1}H$_2$, ^{209}Bi^{16}O^{1}H, and ^{209}Bi^{17}O) can possibly generate an interfering signal with ^{226}Ra, especially if the aerosol is not completely dried. Detectable signal at $m/z = 226$ was observed when the elemental concentration in solution for Pb and Bi was equal to 1 and 0.1 mg·l^{-1}, respectively (Table 4). Previous experiments[24] had not shown any interference at $m/z = 226$ with Bi, since the range of concentrations was lower than the one tested in this study and that study used a membrane desolvation introduction system

(Aridus, CETAC, Ohama, USA), which more effectively reduced water vapor,[33] and hence, lowered the creation of oxides, hydrides and hydroxides.

Finally, the formation of polyatomic interferences generated by two major components of the sample was investigated. At elemental concentrations higher than 100, 10, and 100 mg·l^{-1}, the signal intensity generated by [^{86}Sr^{140}Ce/^{88}Sr^{138}Ce], ^{87}Sr^{139}La, and ^{88}Sr^{138}Ba, respectively, was sufficient to hamper the determination of radium at $m/z = 226$ (Table 4). Oppositely, no increase in the signal background was measured when Ba and Y were present together even at concentrations as high as 100 mg·l^{-1}. In conclusion, when developing a sample preparation method for ^{226}Ra, it is imperative to minimize the presence of W, Pb, and Bi and to a lesser extent Sr, Ba, Ce, and La in the ^{226}Ra fraction.

Radium separation and pre-concentration methods

In order to assess the applicability of the three proposed protocols, method evaluation was done using three performance indicators: the yield recoveries, the selectivity factor (SelF), and the internal standard response (ISR) (Table 5).

The SelF represents the efficiency of a method for eliminating some interfering elements (i.e., Sr, Ba, La, Ce, W, Pb, and Bi) with respect to the analyte ^{226}Ra. It is calculated by dividing the mass of the element (in μg) resulting from the digestion of 1 g of sediment by the mass (μg) this element into the final ^{226}Ra fraction [Eq. (1)]. The higher the value of SelF for an element is, the lower the interfering elemental concentration in the ^{226}Ra fraction is, meaning a better selectivity of the separation.

Table 5. Figures of merit for the three analytical methods investigated

	Method I	Method II	Method III
[226]Ra chemical yield, %	83 ± 13	21 ± 26	55 ± 1
Internal standard response, ISR, %	95 ± 2	26 ± 15	98 ± 3
Selectivity factor (SelF)*			
Strontium	>150 000	3 468	>2 000 000
Barium	240	22	520
Lanthanum	10	1 500	33
Cerium	4	840	13
Tungsten	550	90	1 000
Lead	8 000	<0**	>35 000
Bismuth	480	660	190
Detection limit, DL, pg·g^{-1}	0.006	0.025	0.010
Quantification limit, QL, pg·g^{-1}	0.020	0.083	0.033

$$* \ \text{SelF} = \frac{\text{concentration of X } (\mu g/g) \times \text{mass of sample used (g)}}{\text{Concentration of X in } ^{226}\text{Ra fraction volume } (\mu g) \times ^{226}\text{Ra fraction volume}} \qquad (1)$$

** Due to the addition of Pb as a carrier.
Number of replicates for each method = 3.

The ISR approach is based on the change of signal of an internal standard (in this case, [103]Rh) due to different concentrations of concomitant ions from sample matrix after separation that are present in the plasma.[21] A higher ISR generally indicates that this effect is lower when the sample is introduced in the plasma. [103]Rh was used as an internal standard instead of [209]Bi, as proposed by JOANNON and PIN,[21] to reduce the risk of formation of polyatomic interferences as discussed in the previous section.

Method I (Table 2): From the many cationic exchange resins available, poly(styrenesulfonic acid) cross-linked with divinylbenzene resin (50W-X8) has been extensively used for Ra separation, mainly due to its capacity to effectively separate Ra from some of alkaline earth metals (i.e., Be, Mg, Ca, and Sr) in hydrochloric acid.[23,31,34–37] To further purify the Ra fraction, Sr*Spec was used mainly to remove any residual Sr and Ba that would still be present in this fraction. Using 3M HNO_3, the difference in the distribution ratio between Ba and Ra is the greatest, resulting in retention of Ba onto the resin and the elution of Ra. The combination of IEC and EXC was used by CHABAUX et al.[30] for the determination of [226]Ra in volcanic rocks and has since been used extensively, mainly in α-spectrometry and TIMS.[8,9,17,19] Method I was found to have the highest [226]Ra yield recovery, with an average of 83±13% for three spiked replicates (Table 5). This recovery is comparable to those obtained by CHABAUX et al.[30] for volcanic rocks. The SelF and ISR obtained for this approach also indicate that it is effective for the separation of most of the interferences and the bulk matrix constituents.

Method II (Table 2): Co-precipitation of Ra using Pb[38] or Ba[13,39,40] is a technique frequently used in radiometric counting, since it is a rapid method to reduce the sample size. As a result of high concentrations of ions resulting from the addition of a carrier, it is imperative to use chromatographic approach to reduce the carrier concentration, which otherwise will most likely lead to significant matrix effects in ICP-MS measurements. Method II gave the lowest yield recovery and the poorest ISR (Table 5). Although it has been tested by KIM et al.,[22] authors did not mentioned their yield recovery or the separation efficiency of the method. In addition, it is important to note that presence of the carrier (Pb) and some interfering ions such as Ba was not completely eliminated. Therefore, even if the carrier was changed from Pb to Ba, this approach would still be least effective at providing samples adequate for ICP-MS determination, unless significant modifications to the separation protocol are done. For these reasons, Method II was not further tested for the determination of [226]Ra in sediment by ICP-MS.

Method III (Table 2): Ra and Ba can be adsorbed specifically onto MnO_2 crystal surfaces at neutral to alkaline pHs.[29,41,42] After separation from the liquid phase and a redissolution of the precipitate, a similar separation protocol to Method I was used. Method III, proposed by GHALEB et al.[19] and modified in this study for our matrix type, yielded a lower recovery than Method I (55% vs. 83%); however, highly reproducibility were obtained for Method III (Table 5). A yield recovery was found to be 66% for the adsorption process, which is consistent with the results obtained by MOON et al.[41] It is believed, based on MOON et al.[41] results, that lowering the pH between 4 and 8 helps increasing the absorption yield.

Table 6. [226]Ra activity (in pg·g^{−1}) in sediments measured by ICP-MS after sample preparation using Methods I and III

Sample identification	Method I	Method III	Uncertified values
SRM-4354 (2)*	0.75 ± 0.05	0.66 ± 0.05	0.83
Lake Baikal (BIL-2) (3)	0.61 ± 0.11	0.50 ± 0.08	–

* Number of replicates.

Based on their analytical performances, both Methods I and III are effective for the separation and pre-concentration of [226]Ra in sediments. Method I is the most effective method for the pre-concentration of Ra; however, the efficiency of this process is variable, and so a yield tracer would need to be added. Since none of the stable elements measured was found to behave similarly to Ra, the only yield tracer applicable with this method is [228]Ra. On the contrary, Method III leads to lower yield recovery, but extremely reproducible results, which indicates that this approach can most likely be used without any tracer. With respect to [226]Ra detection and quantification, Methods I and III are applicable for environmental monitoring of sediments, since the quantification limits are only a few fg per g of sample.

Measurements of [226]Ra in sediments

In order to evaluate the analytical performance of the tested methods, a freshwater lake sediment (SRM-4354) was digested and treated using Methods I and III. This exercise was designed to evaluate the accuracy of both methods, but was also a tool to assess the efficiency of the microwave digestion. The recovery from digestion (more than 90%) was estimated by comparing the recovery measured for the SRM (Method I: 74±6%; Method III: 47±2%) using the isotope dilution method with [228]Ra spikes, and subtracting it from the recovery associated with the separation of [226]Ra (Table 5). These results were consistent throughout the samples measured, demonstrating the reproducibility of the digestion method (Table 6).

Sediments collected from Lake Baikal (BIL-2), which had never been analyzed for [226]Ra by mass spectrometry, were used to determine the versatility of the method for sediment with low organic carbon content (SRM-4354: 55.6% vs Lake Baikal: 1.7%) and higher silicate content. [226]Ra concentrations of 0.61±0.11 and 0.50±0.08 pg·g^{−1} were obtained for Methods I and III, respectively (Table 6). These results are in the same order of magnitude (<1 pg·g^{−1}) than other [226]Ra results obtained by radiometric means on different sediment cores collected from the same lake.[43] The relative standard deviations observed for both methods were higher than those observed for the SRM, possibly because of the lower content of Ra and the heterogeneity in the Lake Baikal sediment samples.

Conclusions

Two of the three analytical protocols tested for the separation of [226]Ra were applicable for ICP-MS determination. They led to reproducible results and were effective for the significant elimination of many elements that were found to be potential creators of molecular interferences at $m/z = 226$. The methods tested were rapid (approximately 2–3 days for the entire procedures, including the digestion) and provide detection limits in the fg range, below environmental levels. These methods also considerably reduce non-spectral interferences, which are problematic for the determination of ultra-trace levels of [226]Ra in complex matrices. Finally, a rapid (8 hours) digestion protocol, and suited for the digestion of sediment was developed and shown to lead to good recovery (>90%).

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References

1. D. A. Foster, M. Staubwasser, G. M. Henderson, Mar. Chem., 87 (2004) 59.
2. S. Purkl, A. Eisenhauer, Mar. Chem., 87 (2004) 137.
3. M. K. Scott, S. B. Moran, J. Environ. Radioact., 54 (2001) 163.
4. N. Xing, M. Chen, Y. P. Huang, P. H. Cai, Y. S. Qiu, Sci. China Ser. D-Earth Sci., 46 (2003) 516.
5. G. A. Aycik, D. Cetaku, H. N. Erten, I. Salihoglu, J. Radioanal. Nucl. Chem., 259 (2004) 177.
6. S. Miguel, J. P. Bolivar, R. Garcia-Tenorio, J. Paleolimnol., 29 (2003) 1.
7. J. N. Smith, S. B. Moran, R. W. Macdonald, Deep-Sea Res. Part I-Oceanogr. Res. Pap., 50 (2003) 397.
8. V. Liebetrau, A. Eisenhauer, N. Gussone, G. Worner, B. T. Hansen, T. Leipe, Geochim. Cosmochim. Acta, 66 (2002) 73.
9. A. J. Pietruszka, R. W. Carlson, E. H. Hauri, Chem. Geol., 188 (2002) 171.
10. T. Yokoyama, E. Nakamura, J. Anal. At. Spectrom., 19 (2004) 717.

11. J. A. Robbins, Geochemical and Geophysical Application of Radioactive Lead in The Biogeochemistry of Lead in the Environment, J. O. Nriagu, (Ed.) Elsevier/North-Holland, New York, 1978, p. 285.
12. J. L. Aguado, J. P. Bolivar, R. Garcia-Tenorio, J. Environ. Radioact., 74 (2004) 117.
13. J. G. Decaillon, M. Bickel, C. Hill, T. Altzitzoglou, Appl. Radiation Isotopes, 61 (2004) 409.
14. M. Yamamoto, H. Kawamura, Y. Igarashi, K. Shiraishi, K. Ueno, Radiochim. Acta, 55 (1991) 163.
15. Z. Papp, Z. Dezso, S. Daroczy, J. Radioanal. Nucl. Chem., 222 (1997) 171.
16. A. Paytan, W. S. Moore, M. Kastner, Geochim. Cosmochim. Acta, 60 (1996) 4313.
17. A. H. Andrews, K. H. Coale, J. L. Nowicki, C. Lundstrom, Z. Palacz, E. J. Burton, G. M. Cailliet, Can. J. Fish. Aquat. Sci., 56 (1999) 1329.
18. A. S. Cohen, R. K. Onions, Anal. Chem., 63 (1991) 2705.
19. B. Ghaleb, E. Pons-Branchu, P. Deschamps, J. Anal. At. Spectrom., 19 (2004) 906.
20. A. M. Volpe, J. A. Olivares, M. T. Murrell, Anal. Chem., 63 (1991) 913.
21. S. Joannon, C. Pin, J. Anal. At. Spectrom., 16 (2001) 32.
22. Y. J. Kim, C. K. Kim, C. S. Kim, J. Y. Yun, B. H. Rho, J. Radioanal. Nucl. Chem., 240 (1999) 613.
23. C. J. Park, P. J. Oh, H. Y. Kim, D. S. Lee, J. Anal. At. Spectrom., 14 (1999) 223.
24. V. N. Epov, D. Larivière, R. D. Evans, C. Li, R. J. Cornett, J. Radioanal. Nucl. Chem., 256 (2003) 53.
25. D. Larivière, V. N. Epov, R. D. Evans, R. J. Cornett, J. Anal. At. Spectrom., 18 (2003) 338.
26. R. S. McIntyre, D. C. Gregoire, C. L. Chakrabarti, J. Anal. At. Spectrom., 12 (1997) 547.
27. J. S. Alvarado, M. D. Erickson, J. Anal. At. Spectrom., 11 (1996) 923.
28. K. Benkhedda, D. Lariviere, S. Scott, D. Evans, J. Anal. At. Spectrom., 20 (2005) 523.
29. M. V. Zoriy, Z. Varga, C. Pickhardt, P. Ostapczuk, R. Hille, L. Halicz, I. Segal, J. S. Becker, J. Environ. Monit., 7 (2005) 514.
30. F. Chabaux, D. B. Othman, J. L. Birck, Chem. Geol., 114 (1994) 191.
31. D. Lariviere, V. N. Epov, K. M. Reiber, R. J. Cornett, R. D. Evans, Anal. Chim. Acta, 528 (2005) 175.
32. L. L. Petrov, Y. N. Kornakov, L. A. Persikova, E. A. Anchutina, Intern. J. Environ. Anal. Chem., 74 (1999) 275.
33. D. Wiederin, Initial Investigation of the New Apex Sample Inlet System for Finnigan MC-ICP-MS, Elemental Scientific, http://www.icpms.com/powerpoint/Apex-Neptune-short.ppt, last accessed 10/05/2006.
34. V. F. Hodge, G. A. Laing, Radiochim. Acta, 64 (1994) 211.
35. H. Higuchi, M. Uesugi, K. Sato, N. Ohashi, M. Noguchi, Anal. Chem., 56 (1984) 761.
36. Y. Miyake, Y. Sigimura, Stud. Oceanogr., 1 (1964) 274.
37. Y. Sugimura, H. Tsubota, J. Mar. Res., 21 (1963) 74.
38. B. Parsa, R. N. Obed, W. K. Nemeth, G. Suozzo, Health Phys., 86 (2004) 145.
39. L. Zikovsky, J. Radioanal. Nucl. Chem., 251 (2002) 329.
40. Q. J. Chen, X. L. Hou, Y. X. Yu, H. Dahlgaard, S. P. Nielsen, Anal. Chim. Acta, 466 (2002) 109.
41. D. S. Moon, W. C. Burnett, S. Nour, P. Horwitz, A. Bond, Appl. Radiation Isotopes, 59 (2003) 255.
42. L. Maggi, V. C. Crespi, M. T. Valentini Ganzerli, Analyst, 126 (2001) 399.
43. J. Boyle, A. Mackay, N. Rose, P. Appleby, J. Paleolimnol., 20 (1998) 135