International Journal of Mass Spectrometry 294 (2010) 112–115

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Short communication

High precision determination of ^{228}Ra and ^{228}Ra/^{226}Ra isotope ratio in natural waters by MC-ICPMS

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ARTICLE INFO

Article history:
Received 9 April 2010
Received in revised form 9 May 2010
Accepted 10 May 2010
Available online 15 May 2010

Keywords:
Radium isotopes
^{226}Ra
^{228}Ra
The Sea of Galilee
MC-ICPMS

ABSTRACT

A new methodology has been developed for precise and accurate determination of ^{228}Ra and the radium isotope ratio (^{228}Ra/^{226}Ra) by multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) in natural water. The method was tested on waters from Lake Kinneret (The Sea of Galilee) and saline springs that flow into it.

The radium is pre-concentrated from 60 L of Lake Kinneret water (or 2 L of the saline springs water) by co-precipitation with MnO_2. The separation of radium from the matrix elements was conducted by BioRad® AG50W-X8 and Sr Spec® resins. The instrumental limit of detection for ^{226}Ra and ^{228}Ra was 5 fg mL^{-1} (0.05 ppq) or 0.1 and 30 dpm L^{-1}, respectively, and the absolute limit of detection 0.005 fg. Internal precision of the radium isotope ratio (^{228}Ra/^{226}Ra) in Lake Kinneret for ^{228}Ra concentration as low as 0.10 fg L^{-1} (0.06 dpm L^{-1}) was 2.8% (2σ) and external precision was 10% (2σ, $n = 9$).

1. Introduction

All four Ra isotopes, ^{226}Ra ($t_{1/2} = 1620$ y), ^{228}Ra ($t_{1/2} = 5.75$ y), and ^{224}Ra ($t_{1/2} = 3.66$ d), ^{223}Ra ($t_{1/2} = 11.4$d) (the so-called Ra "quartet" [1,2]) as well as ^{222}Rn ($t_{1/2} = 3.83$ d) are supplied into Lake Kinneret (The Sea of Galilee in the north of Israel, one of the major freshwater reservoirs of the country) by numerous subaerial and submerged saline springs. The discharges of these springs determine the lake's salinity, which is a major concern of the Israeli water authorities. The relation between salts and Ra inputs into Lake Kinneret makes the Ra quartet a potential tool for estimating short-term variations in salt inputs in a similar way used for estimating submarine groundwater discharge [3–5]. The large dynamic range in the decay constants of these radionuclides enables estimating the salts input rate while correcting for nuclides loss by adsorption on particles within the lake.

Traditionally the short lived Ra isotopes (^{224}Ra and ^{223}Ra) are being measured by means of the delayed coincidence counter system, RaDeCC [6] (Scientific Computer Instruments, USA), whereas the longer lived ^{226}Ra and ^{228}Ra were determined by various variations of α and γ counting [1,2,7–9]. A precise and accurate determination of ^{228}Ra is particularly important for Lake Kinneret because its half-life is similar to the residence time of water in the lake [3]. Here we propose an alternative determination of ^{226}Ra and ^{228}Ra using an MC-ICPMS. The major advantages of the proposed method compared to the conventional α and γ counting are higher analytical precision.

Mass-spectrometric determination of ^{226}Ra and ^{228}Ra by thermal ionization mass spectrometry (TIMS) was used earlier [10–12], the analysis is time consuming and often subjected to organic interferences [12]. ICP-MS [13–15], double focusing sector filed ICP-MS (ICP-SFMS) [16] and MC-ICPMS [17] techniques were used successfully for the determination of ^{226}Ra but up do date were never applied for ^{228}Ra. This is due to the extremely low concentrations of ^{228}Ra in natural waters (sub fg L^{-1}) and molecular mass interferences. The structure of the collector system of the MC-ICPMS determines its high precision in measuring ion ratios. The collector system is equipped with Faraday collectors and ion counters, each independently adjustable allowing simultaneous isotopic detection. Using this configuration, the ^{226}Ra and ^{228}Ra concentrations and the ^{228}Ra/^{226}Ra isotopic ratios were measured simultaneously by multiple ion counters, obtaining high precision even with low signals.

2. Experimental

2.1. MC-ICPMS experimental conditions

The MC-ICPMS used for the determination of ^{226}Ra and ^{228}Ra concentrations and the ^{228}Ra/^{226}Ra isotopic ratios was Nu plasma

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doi:10.1016/j.ijms.2010.05.011

Table 1
MC-ICPMS instrumental conditions.

Parameter	Condition
RF power	1200 W
Coolant flow	12 ml min^{-1}
Auxiliary flow	1.25 ml min^{-1}
Nebulizer gas flow	0.49 ml min^{-1}
Interface cones	Nickel
Lens setting	Optimized for maximum analyte signal intensity
Instrument resolution	~300
Nebulizer	PFA 50 μl min^{-1}
Spray chamber temperature	110 °C
Desolvator temperature	160 °C
Sweep gas (argon)	3.2 L min^{-1}
Sensitivity	10,000 cps ppt^{-1} for ^{226}Ra
Integration time	10 cycles of 10 s

(Nu Instrument UK) coupled to a desolvation nebulizer DSN 100 (Nu Instruments, UK). The optimized experimental conditions of the MC-ICPMS system are summarized in Table 1. The gain of the ion counters of the MC-ICPMS as well as the mass discrimination correction was daily performed using a 10 ppb uranium standard NBL112A [18]. The experimental parameters of the instrument were adjusted by maximizing the signal of ^{226}Ra using a 1 ng L^{-1} (1 ppt) standard solution (V.G. Khlopin Radium Institute & RITVERC GmbH, Russia).

2.2. Standards and reagents

The solutions were diluted with high purity deionized water (18 MΩ cm^{-1}), prepared by a Barnstead NANO pure system. All acids and chemicals used for the separation of Ra were supra-grade (Merck). Stock solutions of 0.5 M $KMnO_4$ and 0.5 M $MnCl_2{\cdot}2H_2O$ were prepared by dissolving the salts in deionized water. These solutions were used for pre-concentrating the dissolved Ra by co-precipitating it from relatively large water samples. The ion exchange resins used in the Ra purification procedure were BioRad® AG 50W-X8, 200–400 mesh, 10 mL and 8 mL (BioRad, USA) and Sr Spec® resin (Eichrom Technologies, Inc., USA).

The external calibration for quantitative analysis of ^{226}Ra and ^{228}Ra was conducted with the 1 ppt ^{226}Ra standard reference solution. The same reference solution was used for ^{228}Ra quantitative analysis assuming that the instrumental response of ^{226}Ra and ^{228}Ra in MC-ICPMS are the same. Signals were integrated over ten cycles of 10 s each.

2.3. Water sampling and co-precipitation of Ra with MnO_2 (Fig. 1)

The low concentration of radium in Lake Kinneret requires its pre-concentration and separation from matrix elements prior to the MC-ICPMS measurement. Therefore, 60 L of Lake Kinneret water were collected from several depths (depending on the hydrographic conditions) into three 20 L plastic containers using a submersible pump. The saline springs contain much higher Ra concentrations, so only 2–4 L of water were sampled. The samples were filtered on-line during pumping (Flotrex 0.45 micron G.E.) and each container was immediately acidified to pH 2 and shipped to the laboratory for further treatment within 48 h.

In the laboratory, the contents of each container were transferred to a large bucket equipped with a draining valve at a level of 5.5 cm above the bottom. The Ra pre-concentration was conducted as follows (Fig. 1):

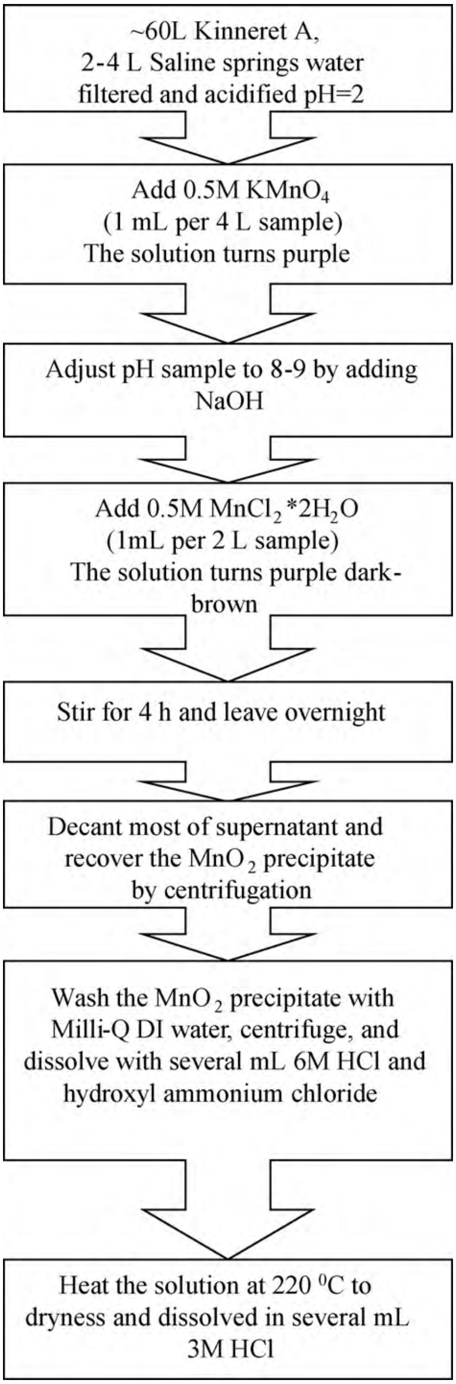

Fig. 1. Flow chart of the water sampling and Ra pre-concentration procedure.

1. 0.5 M $KMnO_4$ solution was added (1 mL per 4 L of sample), turning the solution purple and then the pH was adjusted to 8–9 with 2 N NaOH.
2. 0.5 M $MnCl_2{\cdot}2H_2O$ solution was added (1 mL per 2 L of sample). A dark-brown precipitate of manganese dioxide appeared ($2MnO_4^- + 3Mn^{2+} + 2H_2O \rightarrow 5MnO_2(s) + 4H^+$).
3. The solution was stirred for several hours and left overnight until the precipitate has settled on the bottom of the bucket.
4. The draining valve was opened and most of the supernatant was decanted. The MnO_2 precipitate was recovered by centrifugation, washed with a minimum volume of DDW and centrifuged again.

Table 2
Details of ion exchange columns order, composition and chemistry and volumes of different eluents used for separation and purification of Ra from the pre-concentrated samples.

	Column order		
	1	2	3 and 4
Resin	BioRad® AG50W-X8, 200–400 mesh, 10 mL	BioRad® AG50W-X8, 200–400 mesh, 8 mL	Sr Spec®
Resin volume	2.5 mL	1 mL	1.5 mL
Condition	10 mL 3N HCl	5 mL 3N HCl	4 mL 3N HNO_3
Load	5–10 mL 3N HCl	2 mL 3N HCl	1 mL 3N HNO_3
Wash	10 mL 3N HCl	7 mL 3N HCl	1 mL 3N HNO_3
Elute	8 mL 5N HNO_3	7 mL 6N HCl	2.5 mL 3N HNO_3
Eluted fraction	Ra and Ba	Ra and part of Ba	Ra

5. The solids were dissolved with 6 M HCl and hydroxyl ammonium chloride, and the solution was transferred to a beaker. The gradual disappearance (few seconds) of the brownish color indicated the complete reduction of Mn^{4+} to Mn^{2+}.
6. At the end of the reduction the solution was evaporated to dryness (at 220 °C) and re-dissolved with few mL of 3 M HCl. At the end of this stage, the Ra in the original water sample was concentrated by a factor of 20,000 and 1300 for the 60 L and 4 L samples, respectively.

2.4. *Separation and purification of Ra*

A sequence of four ion exchange columns was used for separating and purifying the Ra from the pre-concentrated samples (Table 1) [19]. Ra and Ba were first separated using two ion exchange columns (columns 1 and 2, Table 2). The Th is retained on the columns at this stage, thus eliminating interferences of ^{228}Th on the ^{228}Ra peak. The Ra was efficiently separated from Ba by passing the eluents of column 2 through two consecutive columns packed with Sr Spec® resin columns 3 and 4, Table 2). The columns were packed with fresh Sr Spec® resin in each separation to ensure efficient separation of Ra from Ba and eliminate columns "memory" effect. The eluent of each column was evaporated to dryness and re-dissolved before loading on the next column (acid concentrations and volumes specified in Table 2, fourth row). The final solution containing the Ra for the MC-ICPMS measurement was 3 mL 0.1N HNO_3.

3. Results and discussion

3.1. *Recovery of Ra during the pre-concentration and separation procedures*

The recovery of the pre-concentration and separation procedure was evaluated by adding a spike of 0.01 μg ^{226}Ra solution to 1 L artificial Lake water (chemical composition—Na: 100 mg L^{-1}; Ca: 50 mg L^{-1}; Sr: 0.2 mg L^{-1} and Ba: 0.02 mg L^{-1}) following by MC-ICPMS analysis. Alternatively, the procedure recovery can be determined by independent analysis of ^{226}Ra on ca. 4 L of lake water (and/or 200 mL of saline springs water) collected from the same pump batch. The ^{226}Ra analysis was performed using the Rn emanation method followed by α-counting [7]. Using this procedure, it was possible to determine the recovery for each sample. The radium recovery of the separation–purification procedure was found to be always better than 90%.

3.2. *Interferences in the Ra spectrum*

3.2.1. *Isobaric interferences*

As mentioned above (see Section 2.4), possible isobaric interferences of ^{228}Th on ^{228}Ra were eliminated by columns 1 and 2 (Table 2) that efficiently retain all the Th in the pre-concentrated solutions.

3.2.2. *Molecular interferences*

Molecular interferences of Ba components on the ^{228}Ra peak were described in earlier studies [17,19] using separation procedures that included only the first three ion exchange columns (Table 2). The interfering phenomenon was a slight shift toward lower mass in the ^{228}Ra peak shape. We also found the typical shift in the in the ^{228}Ra peak shape (Fig. 2a) and relatively high Ba concentration (up to 20 ppm) in the eluents of column 3. In order to overcome this problem we modified the separation procedure by adding a fourth Sr Spec® ion exchange column (column 4 in Table 2) and replaced the resin in columns 3 and 4 after each separation. The new procedure yielded "end" solutions (after column 4) containing sub ppb levels of Ba and excellent MC-ICPMS peak shapes of ^{228}Ra (Fig. 2b).

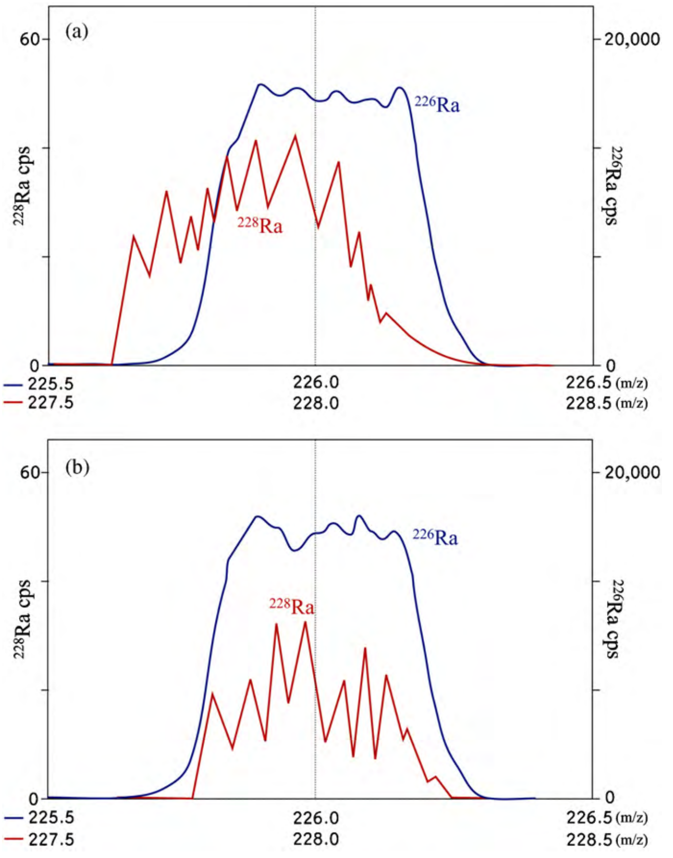

Fig. 2. Peak shapes of ^{226}Ra (blue) and ^{228}Ra (red) in Lake Kinneret water. (a) After three columns procedure [17,19]; (b) after the modified procedure used in this study. Note that the shift in ^{228}Ra peak (a) was completely eliminated by the modified procedure (b).

Table 3
The measured values of ^{226}Ra and ^{228}Ra and the ^{228}Ra/^{226}Ra ratios obtained by MC-ICPMS (this study, lines marked by MS) and by α and γ counters ([4,5] lines marked by C). Note that γ counting measured directly only ^{228}Ra/^{226}Ra ratio, while MC-ICPMS analyzed directly ^{228}Ra concentration.

Water type		^{226}Ra		^{228}Ra		^{228}Ra/^{226}Ra (activity ratio)
		(dpm L^{-1})	(fg L^{-1})	(dpm L^{-1})	(fg L^{-1})	
Lake Kinneret	MS	0.35 ± 0.03 ($n = 9$)	160 ± 20 ($n = 9$)	0.06 ± 0.01 ($n = 9$)	0.10 ± 0.01 ($n = 9$)	0.18 ± 0.02 ($n = 9$)
	C	0.55 ± 0.24 ($n = 12$)	250 ± 100 ($n = 12$)	N.A.	N.A.	0.17 ± 0.16 ($n = 7$)
Saline springs (Fuliya)	MS	7.03 ± 0.39 ($n = 4$)	3200 ± 200 ($n = 4$)	1.06 ± 0.05 ($n = 4$)	1.8 ± 0.1 ($n = 4$)	0.150 ± 0.002 ($n = 4$)
	C	7.4 ($n = 1$)	3360 ($n = 1$)	N.A.	N.A.	0.13 ± 0.04 ($n = 6$)

3.3. ^{228}Ra concentration and ^{228}Ra/^{226}Ra isotopic ratio in Lake Kinneret and Saline springs

The results obtained for Lake Kinneret open water and saline springs (Fuliya) are summarized in Table 3. The internal precision for ^{228}Ra, at the very low concentration of Lake Kinneret was 3.8% (2σ) and external precision of 12% (2σ). The internal precision for ^{228}Ra and ^{228}Ra/^{226}Ra ratio in the saline springs (Fuliya) was 1.3% (2σ) and 1.5% (2σ), respectively, and the external precision was 5% (2σ) and 1.5% (2σ), respectively. Better precision for water samples can be achieved by increasing the sample volume (higher counting statistic). The ^{228}Ra/^{226}Ra activity ratios in both water types are in very good agreement with the previous results obtained by α and γ counting techniques [4,5], while the error was much smaller in the MC-ICPMS (Table 3).

Repeated analyses of standards and natural water showed that the instrumental limit of detection for the ^{226}Ra and ^{228}Ra was 0.05 fg mL^{-1} (0.05 ppq or 0.1 and 30 dpm L^{-1} for ^{226}Ra and ^{228}Ra respectively) and absolute limit of detection 0.005 fg (equivalent to 10^{-5} dpm for ^{226}Ra and 3×10^{-3} dpm for ^{228}Ra). Considering the 20,000 concentration factor of Ra applied in the least concentrated waters of Lake Kinneret, the final concentration of ^{226}Ra used for running the MC-ICPMS was 64,000 fold larger than its instrumental limit of detection, and 40-fold larger for ^{228}Ra (Table 3).

4. Conclusions

A precise, sensitive and accurate analytical method has been developed for the determination of ^{228}Ra and the ^{228}Ra/^{226}Ra isotopic ratio by MC-ICPMS. The new technique was based on preconcentration of Ra by co-precipitation with MnO_2. It was used for analyzing ^{228}Ra concentration and ^{228}Ra/^{226}Ra in Lake Kinneret and the surrounding saline springs and can be used for any water sample containing very low Ra concentration. The precision and absolute limit of detection is similar to those obtained by TIMS but less time consuming. The results measured by MC-ICPMS for natural samples were in good agreement with previous results obtained by α and γ counting techniques and the errors were considerably smaller. The high sensitivity and small errors in the determination of ^{228}Ra by MC-ICPMS enable the estimation of salts input into Lake Kinneret with rather high confidence. The relatively simple procedure for MC-ICPMS determination of ^{228}Ra provides an opportunity for a fast analysis of all four Ra isotopes without relying on a γ counting system.

Acknowledgments

We are grateful to Shlomo Ashkenazi and Ariel Gay of the Geological Survey of Israel for fieldwork and sampling. The research was partly supported by a grant from the Israeli Water and Sewage Authority and some of the field sampling travel funds (BL) were provided by the Moshe Shilo Minerva Center for Marine Biogeochemistry.

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