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Application of ICP-QMS for the determination of ultratrace-levels of ^{226}Ra in geothermal water and sediment samples

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Abstract A rapid, accurate and less labor intensive approach to determining ^{226}Ra in environmental samples was examined; this utilized quadrupole-based inductively coupled plasma mass spectrometry (ICP-QMS). The procedure used chemical separation by ion exchange chromatography to remove most of the matrices after coprecipitation with $BaSO_4$. The average chemical recovery of the NIST SRM preparation method ranged from 60.5 to 85.9% using ^{133}Ba as internal tracer by gamma counting. This technique was capable of completing a ^{226}Ra measurement within 3 min. It did not require an in-growth period to allow radon and its progeny to achieve secular equilibrium with the parent ^{226}Ra as is needed for liquid scintillation analyzer (LSA). The method detection limits for the determination of ^{226}Ra in geothermal water and sediment samples were 0.02 mBq L^{-1} (0.558 fg L^{-1}) and 0.10 Bq kg^{-1} (2.79 fg g^{-1}), respectively. The results obtained with various natural samples and the suitability of the method when applied to various environmental matrices such as geothermal water and sediment are discussed. When ICP-QMS was compared to double-focusing magnetic sector field inductively coupled plasma mass spectrometry (ICP-SFMS), good agreement was obtained with a correlation coefficient, $r^2 = 0.982$.

Keywords ^{226}Ra · Inductively coupled plasma mass spectrometry (ICP-MS) · Geothermal water · Sediment · Coprecipitation

Introduction

Radium is a naturally occurring element that is found mainly in rocks, soil and some mineral and underground waters. Its isotopes, all of which are radioactive, are generated from the natural series of ^{238}U, ^{235}U and ^{232}Th. Among them it is worthwhile mentioning that ^{226}Ra, well known for its long half-life ($t_{1/2} = 1600 \pm 7$ years), is widely spread in the environment and therefore is considered to be one of the major contributors to the human population's internal dose [1, 2]. Absorption of any radium retained in soil or dissolved in water by plants and animals makes possible its incorporation into the trophic chain. On the other hand, radium content in natural waters has been used as a geochemical tracer to evaluate environmental and geophysical processes that take place on/within the Earth's crust or in the oceans [3, 4]. In addition, natural waters originating in areas near uranium mines, thermal waters, etc., usually have radium concentrations that needed to be assessed in order to determine the water's suitability for consumption and whether the radium in these waters affects the population dose.

Several analytical techniques have been applied to determine the level of ^{226}Ra in liquid samples. The most frequently used method for the determination of ^{226}Ra in water is an indirect method measuring the ingrowth of ^{222}Rn [5–7]; another radiochemical method employs alpha spectrometry [8–11]. However, in the case of the radon emanation technique, a minimum waiting time of 30 days for the ingrowth is required in order to achieve secular equilibrium. ^{222}Rn, a gas, is also a major potential problem during sample

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handling. The sample preparation for the alpha spectrometry method uses electroplating or micro-deposition via barium sulfate co-precipitation and is tedious, labor-intensive and analyst-dependent since matrix effects may lead to self-absorption or peak broadening; furthermore, interfering radionuclides need to be removed. Another factor affecting this technique is the need to obtain a low detection limit, also called the minimum detectable activity (MDA) as defined by Currie [12]. This results in the counting time by alpha spectrometer being as long as 3 days after electrodeposition for environmental samples [13]. Although gamma spectrometry, without additional sample preparation for water samples, can also be used for directly measuring ^{226}Ra and ^{228}Ra, a gamma-ray of 186.21 keV emitted from ^{226}Ra is not resolvable from that of ^{235}U, which interferes at 185.72 keV. Therefore, the 186 keV peak method needs to be corrected relative to the uranium concentration and specific activity of natural uranium [14, 15]. In addition, there is a low gamma emission probability (3.28%) in terms of arrival at the detector [16] and the measurement of environmental samples often has a small counting yield and therefore needs longer counting times. Taking the above into account, it is clear that the determination of ^{226}Ra is time consuming.

Compared to the conventional acid leaching, microwave digestion has several significant advantages and these include important reductions in sample preparation time, a lower use of acid reagents and better chemical yields [17]. Hodge and Laing [18] used cation exchange for the separation and preconcentration of ^{226}Ra in drinking water. Compared with the radioactivity measurements described above, inductively coupled plasma mass spectrometry (ICP-MS) is a powerful and widespread multi-elemental method that is being increasingly applied to the determination of long-lived radionuclides [19]. This is because it involves simple analytical procedures, has a short measurement time, is capability of determining the isotope ratio and has excellent sensitivity in the ultratrace concentration range (pg ~ fg mL^{-1}). Quadrupole ICP-MS has been evaluated for use in these measurements and a method detection limit of 1 pg L^{-1} has been reported [18]. In this work, the separation of ^{226}Ra from the matrix in geothermal water and sediments was performed using Dowex chromatographic resin followed by ICP-QMS detection.

Experimental

Instrumentation

ICP-QMS

The Quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-QMS) instrument used in this work was a Thermo Xseries II (Thermo, Bremen, Germany) with the Xs^{-} interface®, a new ion extraction system and a low background noise of less than 0.5 counts per second. The Xs^{-} interface is designed to offer enhanced sensitivity for ultra-trace analysis for masses above 80 amu without elevating the background levels when using negative extraction voltages [20]. The ICP torch was shielded with a grounded silver electrode. Plasma shielding was also introduced into ICP-QMS by Thermo. The PlasmaScreen® was inserted between the quartz ICP torch and RF load coil to prevent capacitive coupling from the load coil into the ICP, and secondary discharge between the ICP and sampling cone is thus eliminated [19]. A design using a shielded torch not only provides low ion energy spread but also enhances the sensitivity (high signal/background) without compromising the extremely low background. The new protective ion extraction (π Extraction) optics control the energies of ions from the plasma so the ions entering the reaction chamber of collision cell technology (CCT) are ideal for both reactive chemistry and kinetic energy discrimination. This leads to an extremely low background equivalent concentration (BEC) and improves the interference removal capabilities. The instrument was equipped with a conventional Meinhard type pneumatic concentric nebulizer and a quartz and single-pass conical impact bead spray chamber that was cooled to 3 °C by Peltier controller. In order to reduce as far as possible handling of the highly radioactive ^{226}Ra, the instrument was tuned using a 1.0 ng mL^{-1} single-element standard plasma solution, namely ^{238}U prepared from 1000 μg mL^{-1} ^{238}U (SPEX Industries, Edison, NJ, USA) prior to analysis. The optimization was carried out with respect to the ^{238}U maximum sensitivity. Mass calibration of the instrument was performed periodically. During the analysis, great care must be taken to avoid contamination problems and memory effects. The instrument was installed in a class 10 K (less than 10,000 particles per cubic feet) clean laboratory to prevent sample contamination during measurement and the introduction system of ICP-MS was housed in a class 100 (less than 100 particles per cubic feet) clean booth. As a rule, the glassware, the sampler and skimmer cones must be regularly and carefully cleaned to ensure the lowest background and the best sensitivity and stability. The optimized experimental conditions of the ICP-QMS that were used for the ^{226}Ra determinations are summarized in Table 1. Blank solutions were also always measured to check for the presence of possible isobaric overlaps on masses used for the measurement and background correction.

ICP-SFMS

The analytical results of ICP-QMS were compared with those of a double-focusing magnetic sector field inductively coupled plasma mass spectrometer equipped with a

Table 1 Instrument operating conditions and data acquisition parameters for the quadrupole ICP-MS

Instrument	Thermo Xseries II
ICP ion source	Hot plasma
Rf forward power (W)	1250
Rf reflective power (W)	2
Argon gas flow	
Cooling (L/min)	13
Nebulizer (L/min)	0.9
Auxiliary (L/min)	0.9
Nebulizer type	Quartz concentric nebulizer
Spray chamber	Glass single pass cyclonic spray chamber with fixed impact bead
Quadrupole working pressure	
Expansion	1.9×10^{0} mbar
Analysis	8.1×10^{-7} mbar
Sampling cone	Platinum with 1.1-mm orifice
Skimmer cone	Platinum with 0.75-mm orifice
Sample uptake and wash time	30 and 60 s
Solution uptake	1 mL/min (self-aspiration mode)
Data acquisition parameters	
Main run	Peak jumping
Scanning mass	226 *m/z*
Dwell time	300 ms
Sweeps	100
Acquisition time	30 s
Number of points per peak	1
Number of runs per sample	3
Survey run (*m/z* 224 to 228)	
Dwell time	0.6
Acquisition time	16 s
Optimization criterion maximum ion intensity for 1 ng/mL ^{238}U	>2E5 cps

secondary electron multiplier (ICP-SFMS; Element 2, Thermo Electron, Bremen, Germany). The optimized operating parameters for the above instrument are summarized in Table 2. The high resolution ICP-MS was usually applied in its low-resolution mode in order to improve the equipment's sensitivity. Calibration was performed from 6.89 fg mL^{-1} to 3.45 pg mL^{-1} with a fair correlation coefficient ($r^2 = 0.9998$). For the Xseries II and Element 2, the electron multiplier must be used only in pulse counting mode and not in the analogue mode, i.e., for count rates below 3×10^{6} counts per second (cps) for the analyte.

Microwave digestion system

The microwave device (Model MARS-5, CEM, Matthews, North Carolina, USA) comprises a power system with selectable output of 0–1200 W at a frequency of 2.45 GHz, a Teflon-coated cavity with fan and tubing to vent fumes, a digital computer that can hold 100 programs with up to five stages each, an alternating turntable-rotating system for homogeneous heating and a 14-position sample carousel. A pressure sensor (ESP-1500 Plus) was attached to the control vessel to monitor the pressure and the pressure maximum was set at 350 psi. An optical fiber was used to monitor and control the digestion temperature up to 210 °C via a feedback system (EST-300 Plus). The sample and digestive reagents were mixed and digested in a double-walled vessel (HP-500 Plus, volume ~ 100 mL), which consists of a chemically resistant inner shell and cover made of Teflon PFA and an Ultem polyetherimide outer shell. To protect the digestion vessel from excessive pressures, a special cap (Autovent Plus) was used to release any excessive pressure and then the vessel was immediately resealed to prevent loss of sample and volatile analytes.

Table 2 Instrument operating conditions and data acquisition parameters for the ICP-SFMS

Instrument	Thermo Element 2
ICP ion source	Hot plasma
Plasma power (W)	1200
Gas flow rate (L/min)	
Cooling	16.0
Sample	0.978
Auxiliary	0.98
Guard electrode	On
Spray chamber	HF-resistant PFA spray chamber
Nebulizer	100 μL/min (self-aspirating) with PFA microflow
Lenses (V)	
Extraction	−2000
Focus	−940
X-deflection	3.01
Y-deflection	4.13
Shape	120.00
Sampling cone	Platinum with 1.1-mm orifice
Skimmer cone	Platinum with 0.8-mm orifice
Detector voltage (V)	2040
Data acquisition parameters	
Resolution	Low; 300
Isotope monitored	^{226}Ra
Detection mode	Counting
Mass window (%)	150
Mass range (amu)	225.465–226.596
Magnet mass	226.031
Setting time	0.300 s
Sample time	0.1000 s
Samples per peak	10
Search window (%)	150
Integration window (%)	50
Scan type	E-Scan
Integration type	Average

^{133}Ba measurement of chemical recovery by gamma spectrometer

The major difficulty in the calculation of chemical recovery for radium is the lack of other suitable radium isotopes. The naturally occurring nuclide ^{224}Ra has a very short half life of 3.66 days and the other not naturally occurring alpha emitter, ^{225}Ra, also has a short half life of 14.8 days; thus these are not suitable yield tracers. However, another alkaline element, ^{133}Ba has a similar chemical behavior to ^{226}Ra and has an acceptable long half-life of 10.66 years. As a gamma emitter ($E\gamma = 356$ keV, 60.5%), it has the advantages of being readily detectable [21].

The LabSOCS (Laboratory Sourceless Object Counting System) package characterized by Canberra MCA for specific HPGe detector using NIST-traceable sources and a MCNP (Monte-Caro) model was employed in this work. The detailed information about source, density, geometry and the dimensions of glass ampoule, matrix etc., needed to be established as well as the efficiency curve that was generated. After this, the curve could be applied to the spectrum using normal gamma spectral analytical methodologies.

Apparatus

A 50 mL conical polysulfone filter fitted into a filtering funnel (Gelman science, Inc., Ann Arbor, MI, No.4204) and glass microfiber filters (Whatman International Ltd., England), specifically GF/C 47 mmφ circles cut into 25 mm diameter membranes, were used for filtering any insoluble matter remaining in solution; this was done by vacuum filtration. The inside of the chimney must be kept free of scratches and abrasions and polished if necessary so that it will drain smoothly and completely [2].

Standards and reagents

A stock solution of approximately 67.08 μg L^{-1} (2482 Bq kg^{-1}) of ^{226}Ra in 1 M HCl radioactivity standard (SRM 4967A) was purchased from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA). Working standard solutions in the pg ~ fg mL^{-1} range were made by gravimetric serial dilution of the standard reference material. To evaluate the reliability of the determinations of the ^{226}Ra concentration, certified material [SRM-4357] (a blend of ocean sediments collected off the coast of Sellafield, UK and from Chesapeake Bay, USA) was obtained from NIST, USA. The other certified material, SRM-4354 (freshwater lake sediment), with an uncertified value of ^{226}Ra, was also chosen as method validation of the measurements. A cation exchange resin of the sulfonic type used in this study, namely Bio-Rad AG 50W-X12 (200–400 mesh particle size); this was washed with ultra-pure water to remove the very fine particles [18] and preconditioned with 0.3 M HCl before use. All reagents used were analytical grade or better. 65% HNO_3, 37% HCl and 48% HF were purchased from Merck (Darmstadt, Germany) and these were Suprapur® grade and used for sample pretreatment, column cleaning, conditioning and cation exchange separations. Ultrapur® grade (Merck, Darmstadt, Germany) nitric acid was used for the serial dilution of standard solution. Ultra-pure water was also obtained from a Milli-Q Gradient (18 MΩ) water purifier (Millipore, Billerica, MA, USA) and used for dilution throughout this study. All sample preparation and measurement procedures were performed under clean room conditions (Class 10,000).

Sample description

The water samples were taken from DìRèGŭ thermal spring in the Beitou geothermal area of Taipei, which is famous and has been studied previously to detect the rare mineral Hokutolite [22]. The hydrogeological context of these springs has been described in detail elsewhere [23, 24]. The water contains relatively high levels of sodium (400–690 ppm), magnesium (55–80 ppm), calcium (180–259 ppm), strontium (685–981 ppb) and barium (0.18–0.28 ppm) with a total dry solids (TDS) of 774–1227 ppm. The samples were filtered through a 0.45 μm membrane to remove insoluble materials in water by suction filtration.

Separation of ^{226}Ra

Taking into account the extreme salinity of the studied waters (TDS ~ 1 g L^{-1}), their direct ICP-MS analysis for Ra was not possible. Therefore, an analytical procedure was adapted from Kim et al. [25]. The separation method was based on cation exchange chromatography to remove most of the anionic and cationic elements from the bulk material (Fe, Mg, Mn, etc.); these had less affinity for the resin than radium and barium and were not strongly retained with dilute mineral acids [26].

Geothermal water samples

A schematic flow chart showing the procedure for the separation of ^{226}Ra from the geothermal water samples is shown in Fig. 1. In order to achieve a lower instrumental detection limit (IDL), it is necessary to use a large sample volume. Five liter of the geothermal water was added to a beaker and because the high acidity (pH 1–2) of the sample prevented ion adsorption on the container walls and the propagation of microorganisms, no additional acid was added. After adding 1 g of ^{133}Ba (47.8 Bg g^{-1}) as a radiochemical yield tracer, the sample was placed on a stirrer plate continuously using a Teflon-covered magnetic

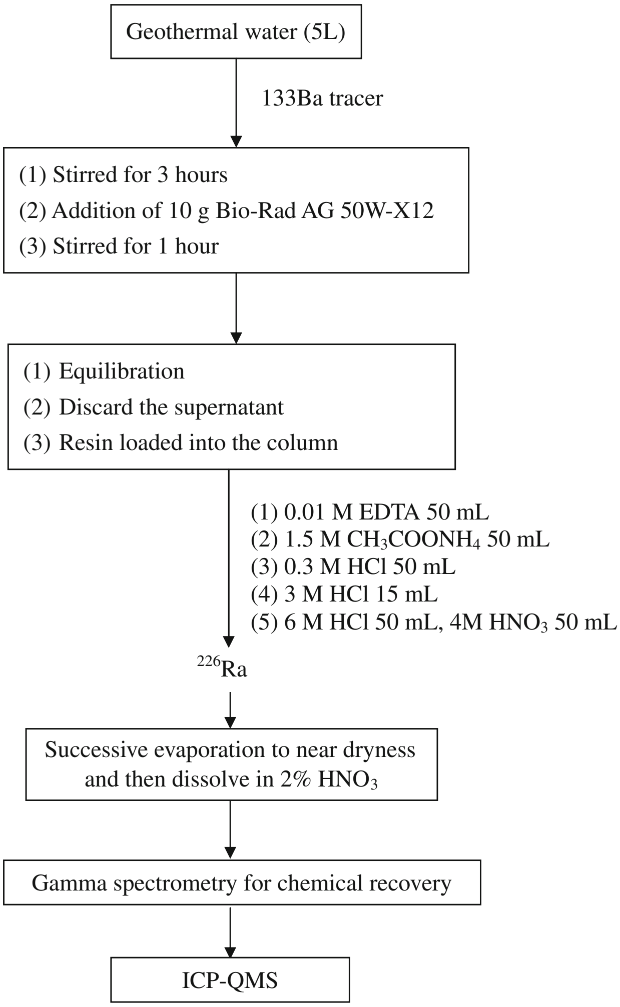

Fig. 1 Schematic diagram of the separation procedures for ^{226}Ra in geothermal water

stirrer bar for 3 h. Then 10 g amount of cation exchange resin was added and the mixture continuously stirred for 1 h. After the resin had settled out, the supernatant was discarded and the resin was placed in a glass column (24 cm length × 2 cm i.d.) with a quartz wool plug at the bottom. The resin was then washed with 50 mL of 0.01 M EDTA solution and the resin bed was never allowed to dry. Following this, 50 mL of 1.5 M ammonium acetate was passed through the column to remove most of the interfering metals (e.g., Mg, Ca, Fe, etc.) that have less affinity for the resin than radium and barium [21]. The resin was next gradually washed with 50 mL of 0.3 M HCl and 15 mL of 3 M HCl to remove the EDTA and ammonium acetate, respectively, from the resin. Finally, the radium and barium fraction was stripped with 50 mL of 6 M HCl followed by 50 mL of 4 M HNO_3. The eluate was evaporated to almost complete dryness on a hot plate and this was followed by the successive addition of several drops of concentrated HNO_3 and H_2O_2 in order to destroy any residual organic substances. The sample was again evaporated to near dryness, dissolved in approximately 5 mL of 2% (v/v) HNO_3 with slight heating and then transferred to a glass ampoule, which was subsequently sealed. After determination of the chemical recovery by measuring the presence of ^{133}Ba using high purity germanium gamma spectrometer (HPGe detector, Canberra USA) and a 5 min count, the solution was injected into the ICP-QMS.

Sediment samples

As is shown in Fig. 2, the chemical separation procedure for ^{226}Ra is more complicated in solid samples or reference materials than in geothermal water because of the bulky matrix. The fresh sediment samples were dried at 110 °C overnight, sieved through a 100 mesh and then homogenized. Around one gram of dry sediment was used for each analysis. After adding ^{133}Ba as the internal tracer to monitor chemical yield, the samples were digested and leached with a mixture consisting of 9 mL HNO_3, 3 mL HCl and 6 mL HF in the microwave oven at 210 °C for 20 min. The operating parameters of the microwave system were set as follows: microwave power, 600 W, 100%; ramp up time, 15 min.; holding time, 20 min; cooling time, 30 min. On completion of the heating cycle, each vessel was allowed to cool before transferring the contents to PFA beakers. The digested solution was then evaporated to near dryness and the residues were dissolved in a mixture of 2 mL concentrated HNO_3 and 4 mL H_2O_2 to remove any traces of HF and organic compounds. The samples were evaporated again to near dryness and dissolved in 20 mL of 4 M HCl and the insoluble substances retained in the solution were allowed to stand for some time, then the solution was filtered under vacuum through a 25 mm polysulfone filter. After the addition of 5 mg of Pb^{2+} carrier to the filtrate and the mixture was stirred for several minutes then 1 mL of H_2SO_4 (98%) was added. This resulted in the Ra being co-precipitated with the Pb as the sulfate, $Pb(Ra)SO_4$. The co-precipitate was then dissolved in the mixture of 15 mL of 0.1 M EDTA and 1 mL of 5 M CH_3COONH_4. After adjusting the pH to 4.5–5.0 with HNO_3, the solution was passed through a cation exchange column. The subsequent separation stages were the same as for the geothermal water described above.

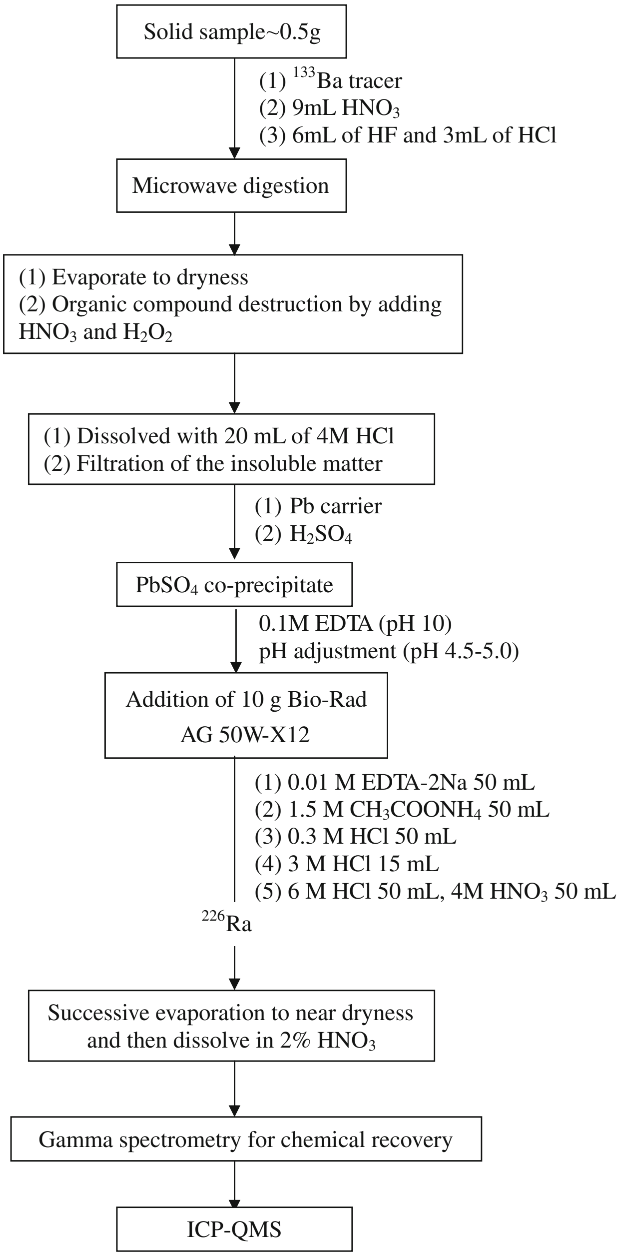

Fig. 2 Schematic diagram of the separation procedures for ^{226}Ra in sediment

Results and discussion

Microwave digestion

Compared to conventional leaching, which has been used until recently in our laboratory, the digestion time using microwave uniform heating was reduced markedly from 10 h to less than 3 h. The advantages of microwave digestion over conventional sample preparation techniques include a short sample preparation time, the use of less acid for the digestion, better pressure/temperature control, increased automation, and more flexibility.

Instrumental sensitivity, background level and limit of detection

Figure 3 shows the calibration curve for ^{226}Ra; a straight line was obtained for concentrations in the range from 1.28 mBq mL^{-1} (0.0345 ppt) to 255 mBq mL^{-1} (6.89 ppt) with a good correlation coefficient ($r^2 = 0.999987$). Calibration curves constructed this way cannot be used for quantification if they show a coefficient of correlation less than 0.99 as this reflects a deviation from linearity large enough to give inaccurate results. Table 3 displays the counts for each ^{226}Ra standard solution measured by ICP-QMS. The signals obtained while scanning from mass 224 to mass 228 for 2% HNO_3 and for 1.28 mBq mL^{-1} (0.0345 ppt) ^{226}Ra are illustrated in Fig. 4; these results suggest that even at the such low concentrations, ICP-QMS shows good sensitivity (approximately 6.28 cps); this means that the count rate for determining ^{226}Ra in geothermal water and sediment samples is adequate. A good signal/background ratio is also required for optimum detection limit of analyte. Instrument detection limits (IDL) were calculated based on the calibration curves. Reagent blanks were analyzed in order to observe any influence of the reagents and the methodology of chemical separation on intensity in the 226 *m/z* region. Since there was no ^{226}Ra contamination during the sample preparation process, the counts of a blank final solution that went through the same sample preparation process as the water samples came out to be the same as those of pure 2% HNO_3 solution without the chemical separation procedure. In this study, the matrix was 2% HNO_3 containing the dissolved residues from the cation exchange procedure. Based on this result, the standard deviation of the blank counts was less than 0.1 cps and hence the IDL for ^{226}Ra by ICP-MS, determined as the concentration corresponding to three times the standard deviation, was approximately 20.6 mBq L^{-1} (0.558 ppq); this was calculated using seven replicate measurements of the calibration blank (2% nitric acid) that had been pumped into plasma. Since 1000-fold of enrichment of the geothermal water was used in the sample preparation, the method detection limit (MDL) was calculated to be 0.02 mBq L^{-1} (0.558 fg L^{-1}), which is better

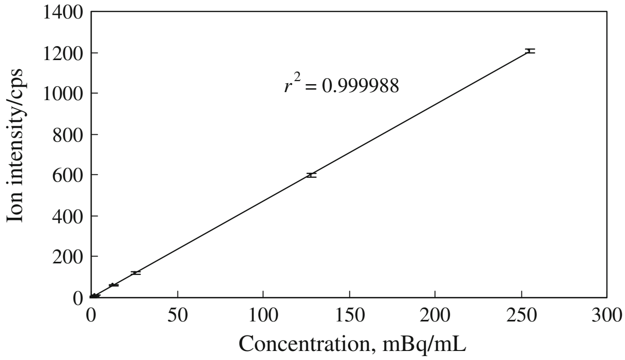

Fig. 3 A calibration curve of ^{226}Ra standard solution

Table 3 Counts of ^{226}Ra standard solution measured by ICP-QMS

^{226}Ra standard (mBq mL^{-1})	Measured counts	Standard deviation (2σ)	RSD (%)
0	0.0524	0.065	62.0
1.28	6.278	0.767	6.11
2.55	12.30	1.49	6.05
12.78	63.09	3.08	2.44
25.49	120.35	5.61	2.33
127.65	599.15	10.27	0.86
254.93	1207.24	10.72	0.44

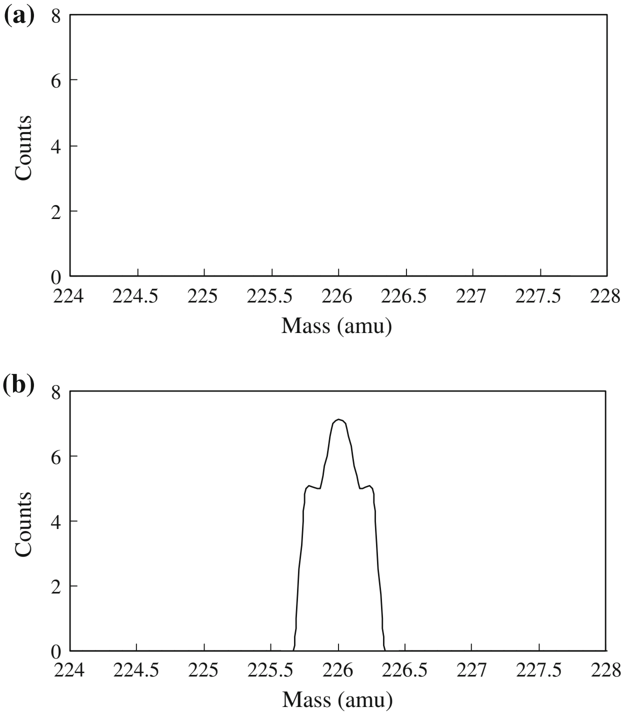

Fig. 4 Mass spectra of **a** blank (2% HNO_3) and **b** ^{226}Ra standard solution (1.28 mBq mL^{-1}) in 2% HNO_3

than that of radon emanation measurement at 2 mBq L^{-1} [27]. Similarly, the MDL for sediment samples was calculated to be 0.10 Bq kg^{-1} (2.79 fg g^{-1}). It was also noted that the background counts showed a relationship with the preceding sample, which indicates that precautions are very necessary in terms of washing by 2% nitric acid and deionized water between sample runs.

Quality control

In order to evaluate the precision and accuracy of the analytical method, two reference materials (SRM 4357 and SRM 4354) with different concentrations of ^{226}Ra were analyzed using the separation procedure. The average chemical recoveries estimated for SRM 4357 and 4354 were 74.2% and 69.2%, respectively. The precision was evaluated by the relative standard deviations. The accuracy was assessed in term of relative errors, which reflect the difference between the experimental means and advised values for the radium concentrations. From the data in Table 4, it can be seen that the mean ^{226}Ra concentrations obtained from the two reference materials are in good agreement with the recommended values.

Practical applications

Table 5 displayed the activity concentrations (ACs) of ^{226}Ra, ranging from 6.17 to 55.05 mBq L^{-1}, which were found in geothermal water and sediment collected at the DìRèGŭ spring of the Beitou Hot Spring Area, Taipei, Taiwan. The sample codes GW1/S1 to GW4/S4 specify geothermal water/sediment collected from DìRèGŭ itself; this was done in an area that is forbidden to tourists due to the very high temperature (~98 °C) and low pH value (~1.3–1.4) of this pond. The other sample codes, GW5 to GW11 indicated water samples obtained from upstream of the Beitou Creek, which runs down towards Beitou and various hot spring resorts. The sample codes GW5–GW8 and GW9–GW11 are, respectively, samples of the geothermal water mixed with Beitou Creek water and samples of the mixed geothermal/Beitou Creek water mixed further with wastewater discharged from nearby hot spring resorts. The ACs of ^{226}Ra in the GW1–GW4 DìRèGŭ samples are much higher, and also have high solid content, compared to normal drinking water or groundwater sampled in various areas of other countries [28, 29]; this implies that radiation

Table 5 ^{226}Ra concentrations in geothermal water and sediment samples determined by ICP-QMS

Sample code	^{226}Ra content (mBq L^{-1}/mBq g^{-1}, dry weight) ± 2σ
GW1	41.28 ± 2.11
GW2	45.80 ± 1.26
GW3	44.02 ± 2.12
GW4	55.05 ± 2.17
GW5	16.16 ± 1.25
GW6	13.81 ± 0.89
GW7	10.98 ± 0.73
GW8	6.37 ± 0.79
GW9	6.17 ± 0.52
GW10	6.30 ± 0.36
GW11	7.25 ± 0.50
S1	382.2 ± 18.8
S2	226.1 ± 14.5
S3	389.3 ± 18.0
S4	313.40 ± 16.3

Table 4 Quantitative results for ^{226}Ra in certified reference materials analyzed by ICP-QMS

Sample run	This study	Recovery (%)
NIST SRM 4357/1	13.79 ± 2.12	76.2
NIST SRM 4357/2	14.29 ± 1.73	74.2
NIST SRM 4357/3	10.29 ± 1.06	85.9
NIST SRM 4357/4	10.56 ± 0.53	60.5
Mean	12.23 ± 1.36	74.2
Certified values (mBq g^{-1} dry weight)	12.7 ± 0.4 (2σ)	
	10.3–15 (Mean result +95% confidence interval)	
NIST SRM 4354/1	26.57 ± 4.25	68.7
NIST SRM 4354/2	32.95 ± 3.19	66.8
NIST SRM 4354/3	28.02 ± 1.04	67.8
NIST SRM 4354/4	28.74 ± 2.21	73.6
Mean	29.07 ± 2.67	69.2
Non-certified values (mBq g^{-1} dry weight)	30	

dosage significantly exceeds background [30] around the source of geothermal water in DìRèGŭ. The decrease in ACs from the other samples as the sample sites move downstream can probably be attributed to dilution by rain water and domestic water, the latter being associated with the hot spring resorts and human activity in the downstream area.

Except for the cold spring at Aïn Oktor, the presence of very high AC values for ^{226}Ra, which range, between 110 and 3900 mBq L^{-1} for the thermal-mineral springs in Tunisia [31], are generally characterized by low uranium activity and high ^{226}Ra activity; this is due to the elevated temperatures and the concentration of chlorine. The distribution of ^{226}Ra is affected by temperature, salinity, and redox conditions [32]. This corroborates the fact that there is a strong correlation relationship ($r^2 \sim 0.7$–0.9) between the ^{226}Ra concentration in thermal water and the ionic concentrations of Ca^{2+}, Sr^{2+}, Pb^{2+}, SO_4^{2-} and Cl^- as well as other aquatic parameters such as pH, temperature, conductivity, redox potential.

The ACs of ^{226}Ra in the sediment samples also listed in Table 5 and range from 226.1 to 389.3 mBq g^{-1}. The ^{226}Ra mean AC values in the sediments of the Maderos river in a uranium mineralized region of Spain were found to be 189–1694 Bq kg^{-1} [33]. Much lower concentrations of ^{226}Ra have been found in other sediment samples, namely ranging from 5.53–96.22 Bq kg^{-1} for the Egyptian coast of the Red Sea [34] and an overall mean value of 23.48 Bq kg^{-1} for the Sindh coast of Arabian Sea [35]. These coastal regions are arid with very low rainfall and the sediment is mainly composed of sand. Therefore, the concentration and distribution pattern of ^{226}Ra in sediment can be used as an indicator of the radiological impact.

Intercomparison with ICP-SFMS

Figure 5 illustrated the relationship between the ^{226}Ra activity measured using ICP-QMS and similar measurements using ICP-SFMS for the same water samples. The 1:1 line plotted in the figure represented the situation where the results show satisfactory correlation between two measurement methods. The slope (m) of the linear regression calculation obtained by plotting the results from both methods was 0.986, with a linear regression coefficient (r^2) of 0.982.

Conclusions

The quadrupole-based ICP-MS (Xseries II) equipped with a high sensitivity Xs^- ion extraction interface is less expensive and is easy [36] to operate with conventional solution delivery using concentric nebulizer. An IDL of 0.558 fg g^{-1} could be achieved here for the determination of ^{226}Ra in environmental samples using the quadrupole ICP-MS system, provided there was enrichment and separation. The method detection limits for the analysis of thermal waters and sediment samples were 0.02 mBq L^{-1} and 0.10 Bq kg^{-1}, respectively. The analytical results for ICP-QMS also agree well with ICP-SFMS, which confirms that the ICP-QMS system has the potential to rival sophisticated double-focusing instruments when high mass resolution is not really required for the sector field. In addition, the parameter settings for the quadrupole detector are appropriately optimized for ultra-trace determination. These factors allow extremely low detection limits to be obtained without resorting to more expensive pieces of equipment such as magnetic sector mass spectrometers.

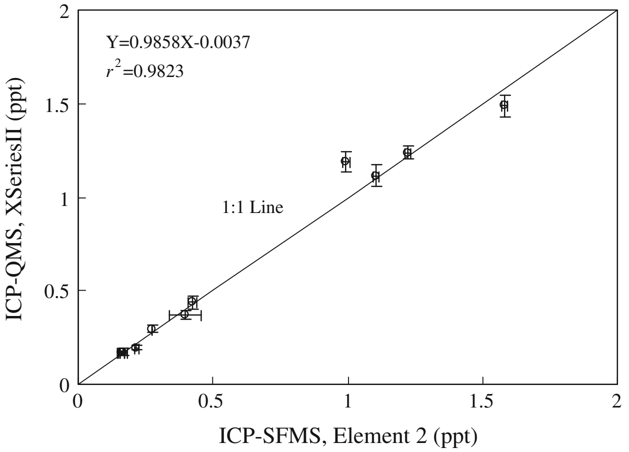

Fig. 5 Correlation results between ICP-QMS and ICP-SFMS for real samples

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