



Quantification of ^{226}Ra at environmental relevant levels in natural waters by ICP-MS: Optimization, validation and limitations of an extraction and preconcentration approach



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ABSTRACT

Radium (Ra) at environmental relevant levels in natural waters was determined by ICP-MS after an off-line pre-concentration procedure. The latter consisted of Ra selective elution from potential interfering elements (i.e. other alkaline earth cations: Ba^{2+} , Sr^{2+} , Ca^{2+} , Mg^{2+}) on a series of two different ion exchange resins (AG50W-X8 and Sr-resin). The overall analytical method was optimized according to the instrumental performance, the volume of water sample loaded on resins, and the sample salinity. Longer acquisition time (up to 150 s) was required to ensure stable measurement of Ra by ICP-MS at ultra trace level (1.0 pg L^{-1}). For a synthetic groundwater spiked with Ra at 10.0 pg L^{-1} , the analytical procedure demonstrated efficient separation of the analyte from its potential interfering elements and a complete recovery, independent of the sample volume tested from 10 up to 100 mL. For synthetic seawater spiked at a level of 10.0 pg L^{-1} of Ra, the total load of salts on the two resins should not exceed 0.35 g in order to ensure a complete separation and recovery of Ra. The method was validated on natural waters (i.e. groundwater, freshwater and seawater samples) spiked with Ra at different levels (0.0, 0.5, 1.0 and 5.0 pg L^{-1}). Absolute Ra detection limits were determined at 0.020 pg L^{-1} (0.73 mBq L^{-1}) and 0.12 pg L^{-1} (4.4 mBq L^{-1}) respectively for 60.0 mL of freshwater sample and for 10.0 mL of seawater.

1. Introduction

As a member of the uranium and thorium decay chains, radium (Ra) is a naturally occurring radioactive element whose principal isotope, ^{226}Ra , is an alpha emitter of relatively long half-life ($t_{1/2}=1602$ years). Recently, Ra has been proposed as an indicator of contamination of aquatic subsurface ecosystems caused by the shale gas industry [1,2]. Under high salinity and reducing conditions, such as in the water used in the fracking process, mobilization of natural Ra from uranium rich source rock is favored [3]. The disposal of the hypersaline wastewater from unconventional and conventional gas extraction is problematic as it could potentially lead to an important leakage of radium in the environment and impact aquatic ecosystems [4]. Considering the rapid expansion of natural gas extraction, accurate and precise measurements of Ra are of prime importance. However, in addition to the low concentration of Ra in many environmental matrices, the diversity of water sample types, i.e. either natural waters or wastewaters with low, high or very high salinity, certainly represents an additional challenge for analytical measurements and monitoring programs.

To date, Ra in environmental samples has been measured successfully by several techniques using either radiometric instrumentation such as radon emanation [5], alpha-ray spectrometry [6], gamma-ray spectrometry [7], and liquid scintillation spectrometry [8]; or more recently with mass spectrometry instrumentation including thermal ionization mass spectrometry (TIMS) [9] and inductively coupled plasma mass spectrometry (ICP-MS) [10]. Radiometric methods such as alpha spectrometry and liquid scintillation are still widely used within the scientific community and remain the instrumentation of choice for EPA's (US Environmental Protection Agency) Ra isotopes in drinking water methods such as Methods 903.0, 903.1, 903.2 and 901.1 [11]. These radiometric approaches however present several inconveniences when it comes to analyzing large number of samples or samples with very low concentrations of Ra and of limited volume. Although being robust in assessing Ra concentration in drinking water, radiometric methods are subject to long analytical time due to both lengthy ingrowth periods and prolonged counting times [6,8] as well as matrix complication [12], making co-precipitation or other laborious steps mandatory [10,13,14]. Furthermore, they require sample volumes of up to several litres for water with low Ra levels [6,8]. Liquid

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scintillation techniques, for instance, based on ^{222}Rn ingrowth to assess radium concentration, may require up to 30 days for a secular equilibrium to be reached [10], while potential leaking of ^{222}Rn as a gas could occur during that critical time period, considerably complicating sample handling [13,15].

In the last decade, mass spectrometry approaches and particularly inductively coupled plasma mass spectrometry (ICP-MS) have been on the rise for measurement applications of long-lived radionuclides in environmental matrices [16]. Besides reaching detection limits as low as those of radiometric methods for ^{226}Ra , ICP-MS techniques present the advantages of much shorter sample preparation and analysis time, and of a detection specific to the analyte [13,17]. The principal challenge of this instrumentation for the direct measurements of Ra, especially at such low levels (pg L^{-1}), resides in both spectral and non-spectral interferences inherent to the sample's matrix [18]. Polyatomic interferences such as $^{88}\text{Sr}^{138}\text{Ba}$ due to the presence of Ba and Sr in the analyzed solution could induce positive bias on the ^{226}Ra measurements and lead to significantly overestimated concentrations of Ra [19]. Conversely, it has also been shown that high concentrations of Ca, Mg and associates in the sample's matrix, by affecting the ionization efficiency of the plasma, could reduce the sensitivity of the ICP-MS and therefore generate underestimated results [16,19].

To overcome these limitations, an off-line sample preparation using the combination of an extraction resin and an ion-exchange resin has been developed [1,20,21] to allow the separation of Ra respectively from spectral interfering elements and from matrix constituents. The sample is first eluted on a AG50W-X8 resin, a strong cation exchange resin in hydrogen form; and then on a Sr-Spec resin, an extraction resin made of 1.0 M of 4,4'(5')-di-*t*-butylcyclohexano 18-crown-6 (crown ether) in 1-octanol that retain specifically Ba and Sr under acidic condition [22]. Developed by Larivière et al. in 2005, the method was firstly optimized and validated for highly alkaline well waters with ^{226}Ra concentrations ranging from 6.75 to 459 pg L^{-1} [20]. Adding a pre-concentration step to the technique, Copia et al. succeeded in measuring spiked natural groundwater at Ra levels of 22 pg L^{-1} [21]. More recently, Zhang et al. were able, by increasing the quantity of resin used, to evaluate elevated concentration of Ra (up to 5000 pg L^{-1}) in high salinity wastewater samples generated from shale gas extraction [1]. While these authors successfully determined Ra in a wide variety of either synthetic or natural water samples, the range of concentrations investigated in these studies remains fairly high compared to naturally occurring levels of Ra expected in waters of unimpacted ecosystems. The method has yet to be assessed and optimized for very low contents of Ra in different water matrices. Reported Ra concentrations for natural water samples rarely exceed 1 pg L^{-1} in river and lake watersheds, and 0.1 pg L^{-1} in surface seawater [23]. In groundwater, past monitoring of private wells in New Brunswick, Canada revealed Ra concentrations ranging from 0.0027 to a maximum of 0.33 pg L^{-1} with a mean value of 0.0875 pg L^{-1} [24].

One objective of our research is to define a precise background level of Ra in private wells and watersheds of New Brunswick, Canada in areas targeted by the industry to develop shale gas extraction. In this work, the pre-concentration method proposed by Copia et al. [21] has been adapted and optimized in regards of sample volume loaded to ensure high recoveries and accurate determinations of low levels of Ra in various natural water types (groundwater, river water, and seawater). Not only focusing on the separation protocol, the aim of this study was to provide analytical details including data acquisition optimization, instrumental and overall method long-term reproducibility, figure of merits as well as a comprehensive discussion of potential shortcomings.

2. Material and methods

2.1. Reagents, standards and material

Trace metal grade concentrated nitric and hydrochloric acid (HNO_3 and HCl) used in this work were purchased from Fisher Scientific (Hampton, NH, USA). The 18.2- ΩM -grade water was provided by a Milli-Q water purification system from EMD-Millipore (Darmstadt, Germany). The gaseous argon and helium necessary for ICP-MS needs, were purchased from Praxair Canada and were of ultra-high purity (UHT 5.0: > 99.998% and > 99%, respectively).

All external calibration and internal standards used during quantitative analyses of Ca, Mg, Ba and Sr were made from serial dilutions of commercial single or multi-elemental stock solutions at 10 or 1000 mg L^{-1} obtained from either *PlasmaCAL* (SCP Science, Canada) or Inorganic Ventures (Delta Scientific, Canada). Ra calibration standards and spikes were made from the standard reference material SRM 4966A provided by the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and certified with a ^{226}Ra mass activity value of $(287.6 \pm 3.7) \times 10^3 \text{ Bq kg}^{-1}$. External and internal standard solutions as well as calibration blanks were prepared daily at appropriate mass fractions as the samples to be analyzed and were systematically sample acid-matrix matched.

For the separation of ^{226}Ra , chemical and material for both resins were purchased from Eichrom Technologies (Lisle, IL, USA). Sr-specific resin columns were supplied as pre-packaged 2 mL cartridges, each containing 1 g of 50–100 μm particles. Cation exchange columns were assembled using AG50W-X8 resin, 100–200 mesh, purchased in bulk. 1 g of the resin was enclosed between two frits into 2 mL cartridges. The column was complemented with a 20 mL cartridge reservoir and a 25 mL extension funnel to help sample loading. Prior to first use and reuses of columns, both resins were pre-washed and conditioned. Sr resin columns were rinsed using 10 mL of Milli-Q water. Cation exchange columns required a 3-step rinsing protocol using consecutively 10 mL of 4 M HNO_3 , 5 mL of Milli-Q water and finally, 10 mL of 1.7 M HCl .

2.2. Instrumentation and ICP-MS measurement procedure

Measurements were performed using Thermo Scientific iCAP-Q inductively coupled plasma mass spectrometer (ICP-MS; Bremen, Germany) interfaced with ASX-520 autosampler from CETAC Technologies (Omaha, NE, USA). For Ra analysis, the instrument was operated in the standard configuration (STD) and low-resolution mode. To further enhance instrumental detection sensitivity, the samples were introduced using an Apex-Q high efficiency introduction system (Elemental Scientific, Omaha, NE, USA) set in a free flow-mode using sample nebulizer gas of the ICP-MS. Internal standard solution, composed of a mixture of Tb, Ho and Bi ($5 \mu\text{g L}^{-1}$ in 2% v/v HNO_3), was mixed online with the sample prior to introduction into the Apex-Q during the whole sequence for instrumental drift correction purposes. Instrument parameters (e.g. nebulizer gas flow, torch settings and extraction lens voltage) were tuned daily for maximum ion intensity and signal stability. Operating conditions and instrumentation used are summarized in Supporting Information Table SI-1.

Data were acquired through 3 runs of 25 repeated measurements of 2 s each (dwell time), resulting in a total acquisition time of 150 s (see results and discussion). A typical measurement sequence included a full external calibration with Ra standards ranging up to 50.0 pg L^{-1} , and set of 8 samples bracketed by runs of instrumental blank and house-made Ra standard solutions (5.0 and 20.0 pg L^{-1} in 3% v/v HNO_3) for quality control. Instrumental Ra detection limit defined as $3 \text{ SD}_{\text{blank}}$ divided by the slope of the calibration curve was always better than 0.20 pg L^{-1} (7.3 mBq L^{-1}).

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