

Micro-extraction procedures for the determination of Ra-226 in well waters by SF-ICP-MS

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Received 29 July 2004; received in revised form 27 September 2004; accepted 27 September 2004

Available online 18 December 2004

Abstract

The radium-226 ($t_{1/2} = 1622$ years) content of highly alkaline well water collected from the United Arab Emirates (UAE) was measured by double focusing sector-field inductively coupled plasma-mass spectrometry (SF-ICP-MS) after separation of the radium from other alkaline earth elements using a newly developed procedure. The results were comparable with those obtained by α -spectrometry for samples with concentrations ranging from 6.75 to 459 pg/L (0.25 to 17 Bq/L). Instrumental sensitivity on matrix-free samples was compared for two sample introduction systems, i.e. an Apex-Q high sensitivity system and a concentric nebulizer. A 12-fold improvement in sensitivity (instrumental detection limit = 1.5 pg/L or 55 mBq/L) was found when the Apex-Q system was used. Two chromatographic methods were tested for the sequential separation of the alkaline earth elements contained in the well water samples in order to reduce matrix and polyatomic interference effects. Optimal elution parameters were determined and used for the separation and pre-concentration of Ra-226 in those samples. A method detection limit of 0.189 pg/L (7 mBq/L), which corresponds to a mass of 0.38 fg of Ra-226 in the sample, was achieved. Only 2 mL of sample is necessary when a combination of 50 W-X8 and Sr*Spec resin, which are reusable, are utilized for the separation. This new analytical protocol significantly reduces sample preparation time resulting in a throughput rate of approximately 20 samples in only 8 h; faster than the other published extraction procedures.

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Keywords: Radium-226; Radionuclides; ICP-MS; Chromatography; Water; Alkaline earth elements

1. Introduction

Ra-226 ($t_{1/2} = 1622$ years) is one of the most radiotoxic of the naturally occurring radioisotopes. Its partial solubility in natural waters and its metabolic behaviour, which is similar to that of alkaline earth metals, can lead to high concentrations and long residence times in bones, cells, and/or tissues. For these reasons, Ra-226 measurements in water must be performed in order to evaluate the potential contribution of water to the internal dose [1,2].

Several radiometric approaches have been developed to assess the concentration of Ra-226 in drinking and natural waters. The applicable methods include Rn-222 emanation [3,4], γ -spectrometry [5,6] and α -spectrometry [1,7,8] or liquid scintillation counting [9,10] of Ra-226. However, in order to achieve precise and accurate measurements, these techniques often require large volumes of sample (e.g. 1 L), thorough chemical separation of the analyte from the matrix constituent using techniques such as co-precipitation or solvent extraction [3], or in the case of Rn-222 emanation, an in-growth period as long as 1 month [4].

Mass spectrometric determination of Ra-226 using both thermal ionization mass spectrometry (TIMS) [11,12] and inductively coupled plasma-mass spectrometry (ICP-MS) [13–18] has been reported, mostly for drinking water. Both

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TIMS and ICP-MS are effective in determining Ra-226 at low concentrations (<1 pg/L) using a limited sample size (10–1000 mL) but because TIMS requires lengthy sample preparation procedures, the sample throughput is significantly lower. Hence ICP-MS is better suited for the determination of Ra-226 in aqueous matrices and for rapid determination of multiple samples.

With the recent development of high-sensitivity mass spectrometers and high-efficiency introduction systems, instrumental detection limits are now below the acceptable concentrations of Ra-226 in drinking waters set by many national and international regulations [19–21]. As a result, the pre-concentration of Ra-226 can be perceived as obsolete. However, it has been demonstrated that spectral and non-spectral interferences (matrix effects) generate variation in the precision of direct Ra-226 measurements [14,15]. Consequently, in the process of developing a rapid analytical protocol for the measurement of Ra-226 in drinking water, separation efficiency should prevail on pre-concentration efficiency.

Extraction procedures applicable to ICP-MS have been developed using a combination of extraction and ion chromatography [16], ion exchange chromatography using high capacity resin [13,22], and commercially available Ra-specific disks [3]. Although simpler, the method using Ra-specific disks leads to the co-extraction of other elements (i.e. Sr, Ba, and Pb), which have been shown to lead to the formation of polyatomic interferences [14]. This problem was solved by Hodge and Laing [13] and Larivière et al. [16] who used longer elution times and extraction chromatography, respectively. The elution of Ra-226 from the extraction disks and ion exchange resin also requires the digestion of the filter [17] or significant amounts of eluent [22], respectively, in order to achieve quantitative recoveries.

The aim of the present paper is to compare: (1) two introduction systems (Apex-Q and concentric nebulizer) coupled to a double focusing sector-field (SF) ICP-MS for the direct determination of Ra-226 in well waters and (2) two analytical protocols for the separation of Ra from alkaline earth elements, which interfere with the direct measurement of Ra-226. As a test of the efficiency of the method, the Ra-226 content of highly mineralized well waters was analyzed using SF-ICP-MS after chromatographic separation, and compared with α -spectrometry measurements.

2. Experimental

2.1. Reagents and chemicals

Trace metal grade nitric and hydrochloric acids (Fisher Scientific, Ottawa, Ont., Canada) were used for sample and eluent preparation. A stock solution of 10 $\mu\text{g/L}$ ($370 \times 10^3 \text{ Bq kg}^{-1}$) of ^{226}Ra (AECL, Chalk River, Ont., Canada) in 5% HCl was used to prepare standard solutions and spikes. Matrix-matched standards were prepared using

mono-elemental solutions of Ca, Mg, Sr, and Ba (SCP Science, Baie D'Urfé, Que., Canada).

Three commercially available ionic resins (ion exchange, Sr*Spec, and Ln) were used for the pre-concentration and the separation of Ra-226. Extraction resins were purchased from Eichrom Technologies (Darien, IL, USA). Sr*Spec is a crown ether, bis-4,4'(5')-[*tert*-butylcyclohexano]-18-crown-6, impregnated on an AmberchromTM resin [23]. Cartridges of di(2-ethylhexyl) orthophosphoric acid (HDEHP, hereafter called Ln resin) were used in this experiment to separate alkaline earth elements from some interfering elements (e.g. Pb, La, Ce, and Nd) [15,24]. Ln and Sr*Spec resins were supplied as 2 mL cartridges containing 50–100 μm particles. Cartridges of cationic ion exchange resin (50 W-X8) were made by placing one gram of the resin between two frits in a 2 mL cartridge supplied by Eichrom Technologies. All the resins were reused after they have been appropriately rinsed and conditioned. The samples were loaded onto the cartridges by pouring the solution into a disposable 5 mL syringe (Becton-Dickinson and Company, Rutherford, NJ, USA), which was used as a reservoir.

2.2. Instrumentation

To determine the Ra-226 content of the various well water samples, a SF-ICP-MS (Finnigan Element2, Bremen, Germany) was used in low-resolution mode, which provides the maximal instrument sensitivity. An Apex Q high-sensitivity system (Elemental Scientific Inc., Omaha, NE, USA) and a conventional Meinhard glass concentric nebulizer (hereafter called Meinhard concentric nebulizer, MCN) were used as sample introduction systems in order to determine their impact on instrument sensitivity for the determination of Ra-226. The SF-ICP-MS was optimized daily using a 60 pg/L Ra-226 standard solution. Concentrations and elution profiles of Mg, Ca, Sr, and Ba, however, were determined using an Elan-5000 ICP-MS (Perkin-Elmer Sciex, Concord, Ont., Canada) during the optimization of the matrix removal protocol. This instrument was used to avoid deterioration of the Element2 detector caused by the high concentrations of these elements in the water samples and also because the sensitivity of the Elan-5000 was sufficient for the concentrations measured. Optimized conditions for the determination of Ra-226 using the Apex-Q and MCN as well as the instrument conditions used for the SF-ICP-MS and the Elan-5000 are presented in Table 1.

In order to validate the analytical protocol, the results obtained by ICP-MS for the well water samples were compared with those obtained using radiometric measurements. The EPA 903.0 method was used [25]. Ra-226 was separated from the sample matrix by co-precipitation with lead sulphate. The Ra was then precipitated with barium sulphate. This precipitate was dissolved in EDTA and a toluene based scintillant was added. Rn-222, the daughter isotope of Ra-226, partitions into the toluene phase. The chemical yield was determined by adding known amounts of Ba-133 tracer to the water samples.

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