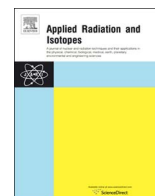




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## Development of a method for rapid analysis of Ra-226 in groundwater and discharge water samples by ICP-QQQ-MS

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## ABSTRACT

A novel and rapid method has been developed for pre-concentration and measurement of <sup>226</sup>Ra in groundwater and discharge water samples using the latest generation triple quadrupole inductively coupled plasma mass spectrometry (ICP-QQQ-MS). Cation exchange and extraction chromatography are capable of pre-concentration factors of ~200 based on 1 L samples. The sensitivity and interference removal capability of ICP-QQQ-MS was assessed from spiked groundwaters, with the introduction of He collision gas required to minimise instrument background in high-matrix samples. The technique developed is potentially capable of detecting <sup>226</sup>Ra activities as low as 5 mBq L<sup>-1</sup> when combined with pre-concentration prior to measurement.

## 1. Introduction

Industrial exploitation of mineral resources creates waste in which natural series isotopes, in particular <sup>226</sup>Ra, <sup>210</sup>Pb and <sup>210</sup>Po, are often concentrated to levels that are hazardous to human health. Radium-226 is present naturally in groundwaters, owing to interaction with uranium-bearing minerals, and its abundance varies depending on local geology (Smedley, 2010). Advances in extraction technologies and production strategies, such as horizontal drilling, has allowed for the efficient and economical extraction of natural gas through hydraulic fracturing. This process also produces large quantities of flowback waters, which can contain elevated activities of radium and also high levels of multiple elements that can make measurements challenging (U.S. Geological Survey (2011); Nelson et al. (2014)). When ingested, radium follows the same metabolic pathways as calcium and is readily incorporated into the bones, contributing significantly to radiological dose (UNSCEAR, 2013). Consequently, producers of such waters are required to comply with very stringent limits when discharging into water courses; for the United Kingdom, the limit for <sup>226</sup>Ra in discharged waters is 10 mBq L<sup>-1</sup> [EPR, 2011]. Such a low regulatory target presents a serious challenge to analysts when attempting to differentiate natural background from industrial contamination [Read et al. (2013)].

Radium-226 (half-life 1600 years) is predominantly analysed using radiometric techniques, most routinely low-background gamma spectrometry, low level liquid scintillation counting (LSC) and alpha spectrometry (Jia and Jia, 2012). Alpha spectrometry offers direct

measurement with no ingrowth time; very low detection limits; activity concentration measurement of all alpha-emitting radium isotopes, including <sup>228</sup>Ra via <sup>228</sup>Th if there is sufficient time for ingrowth, and good spectral resolution (FWHM ≥ 30 keV), which permits the determination of the different radium isotopes. Jia and Jia (2012) concluded that the minimum detectable activity (MDA, 0.1 mBq L<sup>-1</sup>) of alpha spectrometry is about two orders of magnitude lower than low-background gamma spectrometry and LSC techniques. Alpha spectrometry, has therefore dominated in environmental and geological studies where maximum sensitivity is required (Hancock and Martin, 1991; Crespo and Jiménez, 1997; Crespo, 2000; Purkl and Eisenhauer, 2003; Jia et al., 2007).

The disadvantage of alpha spectrometry for low-level <sup>226</sup>Ra measurement is that extensive chemical separation is required, followed by count times of several days, limiting sample throughput. Rapid measurement of <sup>226</sup>Ra may also be feasible by inductively coupled plasma mass spectrometry (ICP-MS) (Park et al. (1999); Joannon and Pin, 2001; Larivière et al., 2003; Ghaleb et al., 2004; Moldovan et al., 2004; Larivière et al., 2005; Varga, 2007; Leermakers et al., 2009; Hsieh and Gideon, 2011; Cobia et al., 2015). Detection limits as low as 3.7 Bq L<sup>-1</sup> for <sup>226</sup>Ra have been achieved and, when paired with highly efficient sample introduction systems, sensitivity can be improved by a further order of magnitude Larivière et al. (2005).

The aim of this study is to investigate the potential of the latest generation triple quadrupole ICP-MS (ICP-QQQ-MS) in the development of a rapid, robust and reproducible method for the analysis of <sup>226</sup>Ra in environmental level groundwater samples as an alternative to

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alpha spectrometry for routine groundwater monitoring. The procedure developed combines pre-concentration with ICP-QQQ-MS measurement, with the aim of using the instrument's collision cell capabilities to remove  $^{226}\text{Ra}$  interferences not removed during pre-concentration, significantly reducing the procedural time compared to additional offline chemical separation.

## 2. Method development

### 2.1. Radium Pre-concentration and Separation

The distribution coefficient ( $K_d$ ) was determined over a range of HCl and  $\text{HNO}_3$  concentrations for group 2 elements (Ca, Sr, Ba and Ra) and Cs on TK100 (Triskem International, 100–150 mesh) and cation exchange (AG $^{\circ}$ 50W-X8, Bio-Rad, 200–400 mesh, hydrogen form) resins. Standard element solutions at starting concentrations from 1000–10,000  $\text{mg L}^{-1}$  were purchased from Fluka Analytical and Fisher Scientific.

To determine resin performance for high volume samples, a 1 L mixed stable element standard solution was loaded and eluted from each resin under optimal HCl and  $\text{HNO}_3$  conditions, which were determined from the  $K_d$  results and the literature. The loading and elution profiles of multiple stable elements, (100  $\text{mg L}^{-1}$  Cs, Mg, Ca, Sr, Ba, Th and U in 1 L deionised water) were investigated. Prior to loading, the AG $^{\circ}$ 50W-X8 was washed with 10 M  $\text{HNO}_3$  (30 mL) to remove contaminants present on the resin. An aliquot (1 mL) of each load solution was retained to determine the initial content and each resin was pre-conditioned with 0.01 M  $\text{HNO}_3/\text{HCl}$ . The loading profile was obtained through the collection of 20  $\times$  50 mL fractions. Samples loaded with AG $^{\circ}$ 50W-X8 underwent a washing stage in 3 M  $\text{HNO}_3/\text{HCl}$  (20 mL); 5  $\times$  4 mL fractions were collected. AG $^{\circ}$ 50W-X8 samples were eluted in 8 M  $\text{HNO}_3/\text{HCl}$  (10 mL) and the TK100 in 1 M  $\text{HNO}_3/\text{HCl}$  (10 mL; 5  $\times$  2 mL fractions).

### 2.2. Measurement by ICP-MS

All measurements were carried out using an Agilent 8800 triple quadrupole ICP-QQQ-MS. The instrument is equipped with an octopole collision-reaction cell positioned between two quadrupole mass filters. The instrument was fitted with quartz double-pass spray chamber, a MicroMist nebuliser (Glass Expansion) and nickel sample and skimmer cones (Crawford Scientific). The instrument performance in both Single Quad (only one mass filter operating) and MS/MS (both mass filters operating) modes was investigated for  $^{226}\text{Ra}$  sensitivity and interference removal capabilities. The impact of potential polyatomic interferences at  $m/z = 226$  ( $^{88}\text{Sr}^{138}\text{Ba}^+$ ,  $^{87}\text{Sr}^{139}\text{La}^+$ ,  $^{86}\text{Sr}^{140}\text{Ce}^+$ ,  $^{208}\text{Pb}^{18}\text{O}^+$ ,  $^{186}\text{W}^{40}\text{Ar}^+$ , and  $^{97}\text{Mo}^{129}\text{Xe}^+$ ) was investigated by introducing  $^{87/88}\text{Sr} + ^{138}\text{Ba}$ ,  $^{87/88}\text{Sr} + ^{139}\text{La}$ ,  $^{87/88}\text{Sr} + ^{140}\text{Ce}$ ,  $^{186}\text{W}$  ( $^{40}\text{Ar}$  is the plasma gas) and Pb standards at concentrations ranging from 1  $\mu\text{g L}^{-1}$  to 100  $\text{mg L}^{-1}$ . Standards were prepared in  $\text{HNO}_3$  (Trace Analysis Grade, Fisher Scientific) and diluted to approximately 3% (v/v) with ultrapure water obtained using an ELGA purelabflex water purification system (18  $\text{M}\Omega\text{ cm}$ , < 5 ppb Total Organic Carbon, ELGA, Veolia Water). The sensitivity of ICP-QQQ-MS to Ra was determined using a range of standards (0.001–1  $\text{Bq mL}^{-1}$ ). Groundwater samples were then spiked over the same activity concentration range to assess matrix interferences.

## 3. Results and discussion

### 3.1. Radium pre-concentration and separation

Both AG $^{\circ}$ 50 and TK100 show a strong affinity for Sr, Ba and Ra at 0.01–0.1 M HCl and  $\text{HNO}_3$  concentrations, which allows for direct loading of acidified samples immediately post-collection. The  $K_d$  values for Ra on TK100 resin were 2–3 orders of magnitude lower than on A

G $^{\circ}$ 50 at acid concentrations of 0.01–0.1 M, with peak values of  $7 \times 10^2$  and  $6 \times 10^4$ , respectively. However, TK100 was more selective than A G $^{\circ}$ 50, showing no affinity at pH2 for Ca, a major element in most groundwaters and flowback. Elution of Ra from TK100 resin and AG $^{\circ}$ 50 resin is achieved using > 1 M  $\text{HNO}_3$  and > 6 M  $\text{HNO}_3$ , respectively. Full characterisation of TK100 resin for measurement of  $^{226}\text{Ra}$  in water samples has been undertaken (van Es et al., 2017), whilst AG $^{\circ}$ 50-based separation of  $^{226}\text{Ra}$  has been applied to previous ICP-MS studies (Sharabi et al., 2010; Copia et al., 2015; Zhang et al., 2015).

One-litre water samples containing multiple stable elements (Cs, Mg, Ca, Sr, Ba, Th and U) were acidified to pH2 with  $\text{HNO}_3$  or HCl and loaded onto the resin in 50 mL aliquots. No breakthrough of any of the elements was observed during the loading stage on AG $^{\circ}$ 50W-X8. However, on TK100 resin, under both conditions studied, Cs and Mg were eluted in the load fraction. Retention on TK100 resin increased in the order Ba > Sr > Ca > Mg, suggesting Ra would be well retained, as supported by the  $K_d$  results. The low retention of Cs suggests Group 1 elements are not well retained on TK100, although additional data are required to confirm the trend for the other Group 1 elements. Both U and Th were strongly retained on each of the resins in all fractions tested, which, in the case of TK100, is in agreement with previous studies (Surman et al., 2014). Recoveries of elements in the elution fraction are presented in Table 1.

TK100 may be less robust than AG $^{\circ}$ 50 for high matrix samples; however, its improved selectivity must also be considered. Taking into account the retention of Ba on all resins, it is unlikely that breakthrough of Ra would be observed in samples under the loading conditions studied, given the similarity in  $K_d$  values obtained for Ba and Ra. The low recoveries for some elements on AG $^{\circ}$ 50 could be overcome by increasing the elution volume or using complexing agents, such as EDTA or oxalic acid, although further investigation is required. Following elution, samples are evaporated to dryness and re-dissolved in approximately 5 mL of 2% (v/v)  $\text{HNO}_3$  for ICP-QQQ-MS measurement, representing a pre-concentration factor of 200 from a 1 L starting sample.

### 3.2. Measurement by ICP-MS

There is no stable isobaric interference at  $m/z$  226, although there are multiple potential polyatomic interferences, including  $^{88}\text{Sr}^{138}\text{Ba}^+$ ,  $^{87}\text{Sr}^{139}\text{La}^+$ ,  $^{86}\text{Sr}^{140}\text{Ce}^+$ ,  $^{208}\text{Pb}^{18}\text{O}^+$ ,  $^{186}\text{W}^{40}\text{Ar}^+$ , and  $^{97}\text{Mo}^{129}\text{Xe}^+$ . Previous studies have suggested that separation of Ra from Ba is particularly important (Zhang et al., 2015). However, at concentrations up to 100  $\text{mg L}^{-1}$ , none of the potential interferences increased the background at  $m/z = 226$  in both Single Quad and MS/MS mode, suggesting that it is not necessary for samples to undergo extensive chemical separation prior to measurement.

As well as Single Quad and MS/MS modes,  $^{226}\text{Ra}$  standards were run with He introduced into the collision-reaction cell (0.5 and 1.0  $\text{mL min}^{-1}$ ; Table 2). The sensitivity in Single Quad mode was double that of MS/MS mode and because the interferences described are formed during sample introduction, there is no benefit to operating with an additional mass filter.

**Table 1**  
Recoveries of Cs, Mg, Sr and Ba on AG $^{\circ}$ 50 and TK100 resins from 1 L water samples.

Element	Recoveries/%			
	AG50 $^{\circ}$ -X8		TK100	
	$\text{HNO}_3$	HCl	$\text{HNO}_3$	HCl
Mg	32	35	50	65
Sr	28	36	40	68
Ba	29	4	44	83
Cs	28	27	44	43

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