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Continuous online determination of ^{226}Ra in liquid effluents using
automated column chromatography-ICP-MS

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Abstract:

A measurement system capable of continuous on-line matrix removal, pre-concentration and analysis of ^{226}Ra using pre-packed columns coupled to a flow injection system and an ICP-MS was developed. Full instrumental control of both the ICP-MS and the flow injection system provided automatic integration of the transient signals. The flow injection system was programmed to control column conditioning, sample loading, column rinsing, analyte elution and column cleaning operations employing appropriate solutions. The application of this system to the ^{226}Ra analysis of an industrial liquid effluent was demonstrated. Using this particular instrument together with pre-concentration and matrix removal procedures, a limit of detection of 5.4 fg L^{-1} (2 mBq L^{-1}) and a method detection limit of 16.2 fg L^{-1} (6 mBq L^{-1}) were achieved for the measurement of ^{226}Ra using a 25 mL sample volume. Total time for sample handling and analysis is approximately ten minutes. The concentration of ^{226}Ra in a discharged effluent sample was 0.73 pg L^{-1} (27 mBq L^{-1}), which is in good agreement with the value of 0.81 pg L^{-1} (30 mBq L^{-1}) measured using conventional alpha counting techniques.

Keywords: ^{226}Ra , pre-concentration, online measurement, matrix removal, ICP-MS

Draft

Graphical Abstract:

1. Introduction

Liquid wastes are generated at many stages of the uranium (U) production cycle, which uses process water and chemicals, including crushing, grinding, leaching, precipitation and tailings disposal and management^[1]. Typically these aqueous solutions may contain both the major radioactive contaminants, uranium and radium (^{226}Ra is a product of the ^{238}U decay series and is the longest-lived isotope of radium with a half-life of 1602 years) and other radioactive and non-radioactive elements and compounds. If not properly treated and contained, they can contaminate drinking water resources^[2] or enter the food chain^[3], potentially harming the environment and endangering the health and wellbeing of human populations. Since radium is chemically similar to calcium, it has the potential to substitute in the mineral formation of bones. Inhalation, ingestion or body exposure to radium can cause cancer and other disorders^[4]. Therefore, the monitoring of ^{226}Ra in liquid effluents is a crucial and well-recognized aspect of environmental protection related to uranium mining and processing^[1, 5].

Concentrations of ^{226}Ra in liquid effluents discharged during U extraction and processing vary but generally are less than 2.7 pg L^{-1} (100 mBq L^{-1}) depending on the treatment procedure and initial radium concentration in the feed water. Radiometric techniques such as alpha spectrometry and gamma-ray spectrometry or liquid scintillation counting have been well established for ^{226}Ra concentration determination^[6-9]. For example, a detection limit of 0.27 pg L^{-1} (10 mBq L^{-1}) with a 10% uncertainty was reported using alpha spectrometry^[6]; an even lower detection limit of 0.16 pg L^{-1} (6 mBq L^{-1}) using only 6 mL of sample solution was reported using an alpha liquid scintillation technique^[9]. Unfortunately these methods involve both tedious sample preparation and long radiometric counting times. Thermal ionization mass spectrometry (TIMS) also has been employed for the determination of ^{226}Ra ^[10], however, it too involves time-

and labor-consuming sample preparation as well as more complicated and expensive instrumentation. Inductively coupled plasma mass spectrometry (ICP-MS), which is an extremely sensitive and established analytical tool for the determination of elemental concentrations and isotope ratios in the trace and ultra-trace range, also has been used for the determination of radionuclides^[11-13]. ICP-MS has been shown to provide high sensitivity and good accuracy and precision in the measurement of a number of radionuclides with relatively simple or no sample preparation. ICP-MS is thus well suited for the determination of radium in environmental samples^[14-16].

The effective, direct determination of ^{226}Ra by ICP-MS is very difficult, due to ultra-low concentrations of ^{226}Ra (usually lower than the limit of detection (LOD) of most ICP-MS instruments) present in almost all samples together with significantly high matrix element concentrations. There are a number of molecular ions including $^{88}\text{Sr}^{138}\text{Ba}^+$, $^{87}\text{Sr}^{139}\text{La}^+$, $^{86}\text{Sr}^{140}\text{Ce}^+$, $^{208}\text{Pb}^{18}\text{O}^+$, $^{186}\text{W}^{40}\text{Ar}^+$, $^{209}\text{Bi}^{16}\text{O}^1\text{H}^+$, $^{88}\text{Sr}^{138}\text{Ba}^+$, $^{97}\text{Mo}^{129}\text{Xe}^+$ that can potentially interfere at $m/z^+ 226$ ^[15, 17]. In addition, the high sample matrix may also impact the analyte signal to noise ratio. Different instrumental approaches, such as a mass spectrometer equipped with a collision cell (ICP-CC-MS)^[17] and a double focusing sector field instrument (ICP-SFMS) in high resolution mode^[18] have thus been proposed for the direct determination of ^{226}Ra in environmental samples. While these approaches can reduce some interfering ions, they also reduce ion transfer efficiency resulting in poorer instrumental detection limits. Therefore, in order to determine ^{226}Ra by ICP-MS at trace and ultra-trace levels in environmental samples and/or in liquid effluents, matrix separation and pre-concentration methods appear to offer a better strategy. Different pre-concentration methods have been successfully demonstrated for ^{226}Ra determination, including cation exchange resins^{[14][19][20]}, radium-specific solid phase

extraction disks^{[21][22]}, co-precipitation^[23], and adsorption using commercially available MnO₂ resin^[24]. For example, Zoriy et al.^[15] used a tandem of a laboratory prepared filter, based on MnO₂, and Eichrom 'Sr-specific' resin for pre-concentration and separation of radium from matrix elements in water samples. A detection limit of 0.02 fg mL⁻¹ (0.72 mBq L⁻¹) was reported for this technique employing 200 mL of sample solution.

The inclusion of multiple pre-concentration and separation stages can make the analytical procedure complex and tedious to execute. Automated on-line matrix separation and analyte pre-concentration methods are promising tools for the rapid and effective determination of elements at low levels in different matrices. While liquid chromatography can be used for the automation of some methods, flow injection – column chromatography is better suited for others, particularly where strong acids are being used as eluants or carrier solutions. For instance, Benkhedda et.al^[25] developed a method for the pre-concentration/separation of ²²⁶Ra in natural waters using a flow injection analysis system (FIAS). Their sequential on-line ion exchange pre-concentration process was then coupled with an ICP-MS. The reported detection limit using a 20 mL sample was 0.46 pg L⁻¹ (17 mBq L⁻¹). On-line separation and pre-concentration methods have been reported not only for the determination of ²²⁶Ra but also for other analytes. Larivière et al.^[26] developed an automated system for on-line pre-concentration, separation and detection of plutonium in a urine sample by coupling a multi-solvent delivery system with remotely-controlled switching modules and an ICP-MS. However, as mentioned above, automated methods for the analysis of ultra-low concentrations of analytes, usually require a combination of matrix removal, pre-concentration of the analyte and measurement by mass spectrometry, usually through the offline evaluation of a transient signal. Most mass spectrometer software/flow injection system combinations are poorly suited to this set of conditions. The major problems are

poor handling of transient signals within the control software of the ICP-MS, lack of true chromatographic peak identification quantification capabilities and problems associated with the interfacing of flow injection systems with ICP-MS systems.

The purpose this study was to develop a ^{226}Ra analysis system suitable for integration into an effluent treatment system in an industrial setting such as at a uranium mining operation. Moreover, to be used in a remote mining situation, the method – instrumentation combination should be rugged and able to be operated and maintained by technical staff. To satisfy the demands of such an application the system should be rapid, selective and sensitive and should be able to perform the analysis and data evaluation online on a continuous basis.

2. Experimental

2.1. ICP-MS and SC-Fast Instrumentation

A high sensitivity quadrupole-based inductively coupled plasma (ICP) mass spectrometer (Varian 810-MS, Varian Inc. Scientific Instruments, Victoria, Australia now marketed as Bruker 810) consisting of an ICP source and 90 degree ion mirror and low noise double off-axis quadrupole mass analyser was used for the measurements of ^{226}Ra . The solution introduction system to the ICP-MS consisted of a Micromist low flow glass nebulizer with a Peltier cooled double pass glass spray chamber system. The instrument conditions were optimized daily to achieve maximum sensitivity in the analyte mass range (ca. 1,000,000 cps for 1 ppb of ^{115}In).

On-line pre-concentration of the sample was performed employing an SC-Fast (Elemental Scientific Inc., Omaha, NE, USA) flow injection system. The SC Autosampler Dual Valve Fast is a completely automated sample introduction system with two 6 port switching valves. The SC Fast Autosampler program together with the Varian ICP-MS and Galaxie chromatographic

software allowed total instrumental control (both ICP-MS and SC-Fast), automatic data collection and integration of the transient signals.

The separation and pre-concentration procedures consist of several steps including column conditioning, sample loading, column rinsing, analyte elution and column cleaning employing several different reagent streams. Each step was optimized to minimize time required while maintaining complete recovery of the radium.

2.2. Standards and samples

For pre-concentration and separation of radium from the sample matrix, AG 50W-X8 resin (Bio-Rad Laboratories, Hercules, CA, USA) and Sr*spec resin (Eichrom Technologies Inc, Darien, IL, USA) were used. Pre-packaged 2-mL cartridges with AG 50W-X8 resin were purchased, while the second column was prepared in the laboratory by dry packing 50 mg of Sr*spec resin in a cartridge that was custom fabricated by Elemental Scientific (Omaha, NE, USA) followed by hydration of the resin. Dimensions of the column are shown in Figure 1. Nitric and hydrochloric acids used were trace metal grade (Fisher Scientific, ON, Canada). High purity water (HPW) meeting resistivity over $18 \text{ M}\Omega\text{cm}^{-1}$ was prepared with a Millipore Milli-Q-Plus water purification system. The following reagents were employed in the procedure: (1) HPW for AG 50W-X8 column preconditioning; (2) 5 M HNO_3 solution for Sr*spec column preconditioning and for Ra elution and (3) 1.75 M HCl solution for removing (washing out) matrix components, including Ba and Sr from the AG 50W-X8 column. After collection, water samples were acidified with HNO_3 to 2% (v/v). A standard stock solution ($10 \mu\text{g L}^{-1}$) of ^{226}Ra (AECL, Chalk River, ON, Canada) was diluted with a solution of 2% HNO_3 to prepare Ra calibration standards of 0.001, 0.01 and 0.1 ng L^{-1} .

2.3. On-line flow injection, pre-concentration and matrix removal

The Ra pre-concentration/separation procedure consists of four steps including sample loading, column rinsing (matrix removal), analyte elution and column conditioning all of which are optimized for on-line pre-concentration of Ra and matrix removal (Figure 2). During the sample loading step (Figure 2-1), both valves (V1 and V2) are in load position allowing 25 mL of the sample to flow through the AG 50W-X8 column (C1). The Sr column (C2) is rinsed with HPW.

In the second step of the analysis, simultaneously the Sr*spec column (C2) is preconditioned with 5M HNO₃ and C1 is rinsed with 1.75M HCl to remove constituents retained during the sample loading cycle. Figure 2-2 shows the column rinsing step with V1 in load position and V2 in inject position. This allows 25 mL of the rinse solution (1.75M HCl) to flow through C1 flushing off the majority of the sample matrix constituents from C1 while a 5M HNO₃ solution is passed through C2 for preconditioning. During the elution step (Figure 2-3), V1 moves to inject position and V2 remains in inject position directing 12.5 mL of eluant (5 M HNO₃) through C1 and C2 at a flow rate of 2.5 mL min⁻¹ to the ICP-MS instrument. During this step, Ra along with any remaining Sr and Ba are eluted from C1 and directed to C2, where they are separated because of their different retention characteristics. In the last step of the procedure (Figure 2-4) both V1 and V2 are in load position and the system is flushed with HPW to prepare for the next sample. During this step, HPW is passed through C1 and C2 at a flow rate of 5 mL min⁻¹ for 60 seconds. The transient signal of ²²⁶Ra measured by the system is shown in Figure 3.

3. Results and discussion

3.1. Polyatomic interferences

As mentioned above there are two main challenges that must be overcome during the determination of ^{226}Ra by ICP-MS. The first one is the low concentration of ^{226}Ra in the sample. This challenge can be solved by pre-concentration. The second is the sample matrix which may contribute to the blank signal due to polyatomic interferences that can occur at $m/z = 226$ (e.g., $^{88}\text{Sr}^{138}\text{Ba}^+$, $^{87}\text{Sr}^{139}\text{La}^+$, $^{86}\text{Sr}^{140}\text{Ce}^+$, $^{208}\text{Pb}^{18}\text{O}^+$, $^{186}\text{W}^{40}\text{Ar}^+$, $^{209}\text{Bi}^{16}\text{O}^+\text{H}^+$, $^{88}\text{Sr}^{138}\text{Ba}^+$, $^{97}\text{Mo}^{129}\text{Xe}^+$) and affect the accurate quantification of ^{226}Ra . In the case of ^{186}W and ^{209}Bi interferences, $100\text{ }\mu\text{g L}^{-1}$ W and $100\text{ }\mu\text{g L}^{-1}$ Bi in solution can result in an apparent ^{226}Ra concentration of ca. 27 pg L^{-1} (1000 mBq L^{-1}) and 47 pg L^{-1} (1800 mBq L^{-1}), respectively. The same $100\text{ }\mu\text{g L}^{-1}$ concentration of ^{208}Pb in solution produces an apparent ^{226}Ra signal of ca. 0.027 pg L^{-1} (1 mBq L^{-1}). However, analysis of the effluent sample showed negligible quantities of ^{186}W , ^{209}Bi and ^{208}Pb . A concentration of $250\text{ }\mu\text{g L}^{-1}$ Mo in the sample didn't produce a significant apparent ^{226}Ra signal. The only elements that were found to be problematic were Ba and Sr. The presence of $450\text{ }\mu\text{g L}^{-1}$ Sr and $180\text{ }\mu\text{g L}^{-1}$ Ba, generated a signal at $m/z = 226$ corresponding to 9.7 pg L^{-1} (360 mBq L^{-1}) of ^{226}Ra , in the quadrupole-based ICP-MS. This interference is significant since the concentration of ^{226}Ra in actual effluent samples could be lower than 3 pg L^{-1} (111 mBq L^{-1}). The interference was resolved by adding the second column containing Sr*spec resin. As shown in Figure 4, the chromatographic separation is such that the Sr is eluted prior to the ^{226}Ra and the Ba after the ^{226}Ra is aspirated into the ICP-MS. Under the conditions used, Sr is not retained on the Sr*spec column allowing for it to be cleaned during the final flushing step with HPW.

3.2 *On-line quantification of ^{226}Ra in a discharged effluent water sample*

The ^{226}Ra concentration was determined in a discharged liquid effluent sample using the developed system and automated method with complete on-line data evaluation employing routines available in the Galaxie chromatography software. The quantification used a set of calibration standards that were processed automatically within the Galaxie chromatography software to generate a calibration curve, which was used for quantification of subsequent samples. The average spike recovery for replicates spiked with different levels of ^{226}Ra was 97% and the concentration of ^{226}Ra in the effluent sample was 0.73 pg L^{-1} (27 mBq L^{-1}) which is in good agreement with the value of 30 mBq L^{-1} reported from a radiometric measurement based on alpha counting.

3.3 *Analytical performance*

The effectiveness of the current system in pre-concentrating ^{226}Ra and separating it from Ba and Sr is illustrated in the ICP-MS signal for a 49 mL effluent sample spiked with 1 mL of $10 \text{ ng L}^{-1} \text{ }^{226}\text{Ra}$ (Figure 4). The profile for ^{226}Ra demonstrates that ^{138}Ba and ^{88}Sr are well separated in the sample stream entering the ICP-MS, preventing any detectable interference.

While the ICP-MS output is being captured by both ICP-MS Expert software and Galaxie chromatography software, final data processing, including integration, calibration and reprocessing of the sample data was performed via the Galaxie chromatography software. Figure 5 shows the elution profile of ^{226}Ra and its quantification in the Galaxie chromatography software for three ^{226}Ra solutions in 2% HNO_3 that were used as calibration standards and for an effluent sample spiked with ^{226}Ra . In the absence of any available certified reference materials that contain both Ra and a matrix similar to that found in typical U waste streams, we used the spiked effluent. The effluent sample contained a matrix that is high in elements with the potential to

cause interferences (e.g. Ba and Sr) but no Ra. Thus the exact concentration of Ra was known from the spike addition. The peak start and end time was set in the chromatography software to determine the peak of Ra. The chromatography software was configured to use peak area calculation and background subtraction. The peak areas of different concentration of Ra were used to build a standard curve for quantification analysis. The concentration of ^{226}Ra in the spiked effluent sample was 0.191 ng L^{-1} which is in good agreement with the spiked value of 0.2 ng L^{-1} . Precision of the ^{226}Ra determination using this procedure was $\pm 4.7\%$. Long term stability of the method was estimated by performing nine replicate determinations per day of a sample spiked to contain 0.1 ng L^{-1} of ^{226}Ra in a 50 mL solution for one week, employing the same columns. Results from these measurements show the relative precision varying between 2.7% and 5.8% . Total analysis time per sample was approximately ten minutes. This long term stability test also indicates the potential of the system for continuous measurement. Psuedo-continuous measurement, i.e., approximately once per 10 minutes, is possible and the chromatography associated with the method is robust and reproducible over a relatively long period, i.e., at least one week.

A limit of detection (LOD) of 0.045 pg L^{-1} (1.67 mBq L^{-1}) for a 25 mL sample volume was calculated by dividing 3 standard deviations of the blank ($2\% \text{ HNO}_3$ measured 10 times) by the slope of the calibration curve. The method detection limit (MDL; Equation (i)), as defined by the US EPA, was estimated following the EPA recommended procedures^[28], by analyzing seven replicates of a ^{226}Ra sample with a nominal concentration of 0.225 pg L^{-1} (8.3 mBq L^{-1} , i.e. a level five times higher than the determined LOD). Results averaged 0.235 pg L^{-1} (8.7 mBq L^{-1}) with a standard deviation of $\pm 0.022 \text{ pg L}^{-1}$ (0.81 mBq L^{-1}).

$$\text{MDL} = T_{(n-1, 1-\alpha=0.99)} \times (s) = 3.14 \times 0.022 \text{ pg L}^{-1} = 0.07 \text{ pg L}^{-1} (2.59 \text{ mBq L}^{-1}) \quad (\text{i})$$

where $T_{(n-1, 1-\alpha=0.99)}$ is the student statistic at 99% confidence level with $n-1$ (6 in our case) degrees of freedom.

Recent improvements to the flow system with a size-reduced Sr resin column (50 mg) have shown that the system is capable of achieving similar sensitivities using 15 mL of sample and correspondingly reduced analysis times. Primarily the improvement results from improved peak resolution due to the column dimensions. Using a more recent version of the ICP-MS (the Bruker 820) and a 15 mL sample volume, a LOD of 0.05 pg L^{-1} (2 mBq L^{-1}) and MDL of 0.16 pg L^{-1} (6 mBq L^{-1}) were achieved.

As a part of the validation process of the method for use at mine site laboratories, a systematic comparison of ICP-MS measurements with alpha spectrometric measurements has been carried out. Data from the measurement of treated effluent from a mine are provided in Table 1. While ICP-MS based measurements were carried out at the mine site laboratory using the 50 mg column and the Bruker 820 ICP-MS, portions of the same samples were sent to an accredited environmental laboratory which used alpha spectrometry for the determination of radium.

Results for all samples (Table 1) are below 0.1 Bq/L , with an average value of 0.0575 Bq/L for alpha spectrometric data and 0.060 Bq/L for ICP-MS data. The differences observed are within 0.03 for any pair of assays, demonstrating the validity of the method when used in a mine laboratory setting. A comprehensive account of this study will be included in a future publication

4. Conclusions

A hardware system for continuous matrix removal/pre-concentration using pre-packed ion exchange columns coupled to an SC-Fast flow injection system and a Varian ICP-MS was

developed and tested successfully. The system was capable of performing automated pseudo-continuous determinations of ^{226}Ra at trace and ultra-trace levels in water and industrial effluent samples. The main advantage of the method is that it does not require further off-line data analysis since evaluation of the transient signals is handled entirely within the Galaxie chromatography software suite. Moreover, the method requires little operator intervention during the analytical cycle and takes only ten minutes per cycle. The method presented in this work can be easily adapted for routine analysis of ^{226}Ra in water samples such as the monitoring of radium in liquid effluents. The system has been installed and used routinely at a uranium mine site for over two years.

5. Acknowledgements

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End caps receive standard 1/4" threaded fittings.

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Figure 4. Separation of ^{226}Ra from Ba and Sr on Sr*spec resin using the SC-Fast flow injection system and a Varian ICP-MS: 49 mL of effluent sample spiked with 1 mL of 10 ng L^{-1} ^{226}Ra

Figure 5. Elution profile of the ^{226}Ra in the Galaxie chromatography software and on-line quantification of the ^{226}Ra

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400 Table 1. Comparison of ICP-MS and alpha spectrometric ^{226}Ra measurements in treated mine effluent samples.
401 Both alpha spectrometry and ICP-MS data are reported in units of Bq/L.
402

Alpha Spectrometry	ICP-MS	Difference
0.03	0.05	-0.02
0.03	0.06	-0.03
0.08	0.08	0
0.07	0.04	0.03
0.06	0.04	0.02
0.04	0.05	-0.01
0.04	0.05	-0.01
0.08	0.06	0.02
0.09	0.1	-0.01
0.04	0.05	-0.01
0.08	0.07	0.01
0.06	0.06	0
0.05	0.08	-0.03
0.08	0.07	0.01
0.04	0.05	-0.01
0.05	0.05	0

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