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Automated Preconcentration and Matrix Removal for Ultratrace Determination of Radium in Environmental Waters

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Introduction

Radium is a naturally occurring element that originates from the decay chains of U and Th. Consequently, environmental waters, especially those from areas with high U content, may contain trace amounts of Ra. Human activities such as the mining and processing of uranium or thorium may also lead to elevated radium concentrations in discharge waters.

Due to its radioactivity and no beneficial biological role, even a low concentration of radium in environmental waters is hazardous to human health. As a result, the World Health Organization (WHO) and many national and regional authorities have developed regulations for the monitoring of radium in water, both for human consumption and for industrial processes or wastewater discharge. These regulations for radium in drinking water are extremely stringent, often below the detection capability of even modern ICP-MS instruments when used in direct analysis mode without any sample purification or matrix removal.

Alpha spectrometry or other analytical techniques may be used to determine Ra, but they are slow and require extensive manual sample preparation. ICPMS is a preferred analytical technique due to its rapid analysis time and low detection limits, but accuracy may be reduced by certain polyatomic interferences and matrix effects. Fortunately, various preconcentration and matrix removal techniques have been demonstrated in the literature to reduce or eliminate ICPMS matrix effects and remove matrix-based polyatomic interferences for the accurate determination of Ra in natural waters.[1,2] However, many of these techniques require manual sample preparation and multiple offline column extraction steps or unreliable inline column separations using peristaltic pump tubing.

The present work demonstrates an automated system for the ultratrace determination of Ra in environmental waters by ICPMS using syringe-driven preconcentration and matrix removal. Untreated or slightly acidified, high-matrix environmental water may be directly analyzed by automatic standard additions or automatic external calibration. Detection limits of 0.25 mBq/L (7 ppqt) are achieved for [226]Ra from the preconcentration of a 9 mL sample.

Elemental Scientific

System Overview

This work was done with a ᴛʀᴜ*FAST* SP2, apex 2Q, and quadrupole ICPMS.

ᴛʀᴜ*FAST* SP2

- Autosampler in enclosed cabinet

- prep*FAST* syringe module for autocalibration, autodilution, and automatic standard additions

- Dedicated syringe module for preconcentration and matrix removal

- Line-valve assembly configured for 2-column preconcentration/matrix separation procedure

ᴛʀᴜ*FAST* SP2

apex 2Q

- Desolvating nebulizer system with high sample transport efficiency for maximum sensitivity

- Integrated mass flow controller for introduction of nitrogen gas for improved oxide ratio and precision

apex 2Q

ICPMS

- Thermo iCAP Q

- Optimized in KEDS for collisional focusing and reduction of any residual polyatomic interferences (e.g., $^{138}Ba\,^{88}Sr^+$)

The system was automatically optimized using the GetReady valve and a 100 ppt tuning solution. Sensitivity for $^{238}U^+$ was found to be approximately 10M cps/ppb in KEDS mode.

GetReady Valve

2-column Preconcentration and Matrix Separation

- Ultrapure, fluoropolymer flow path
- Eliminate contamination from manual sample handling
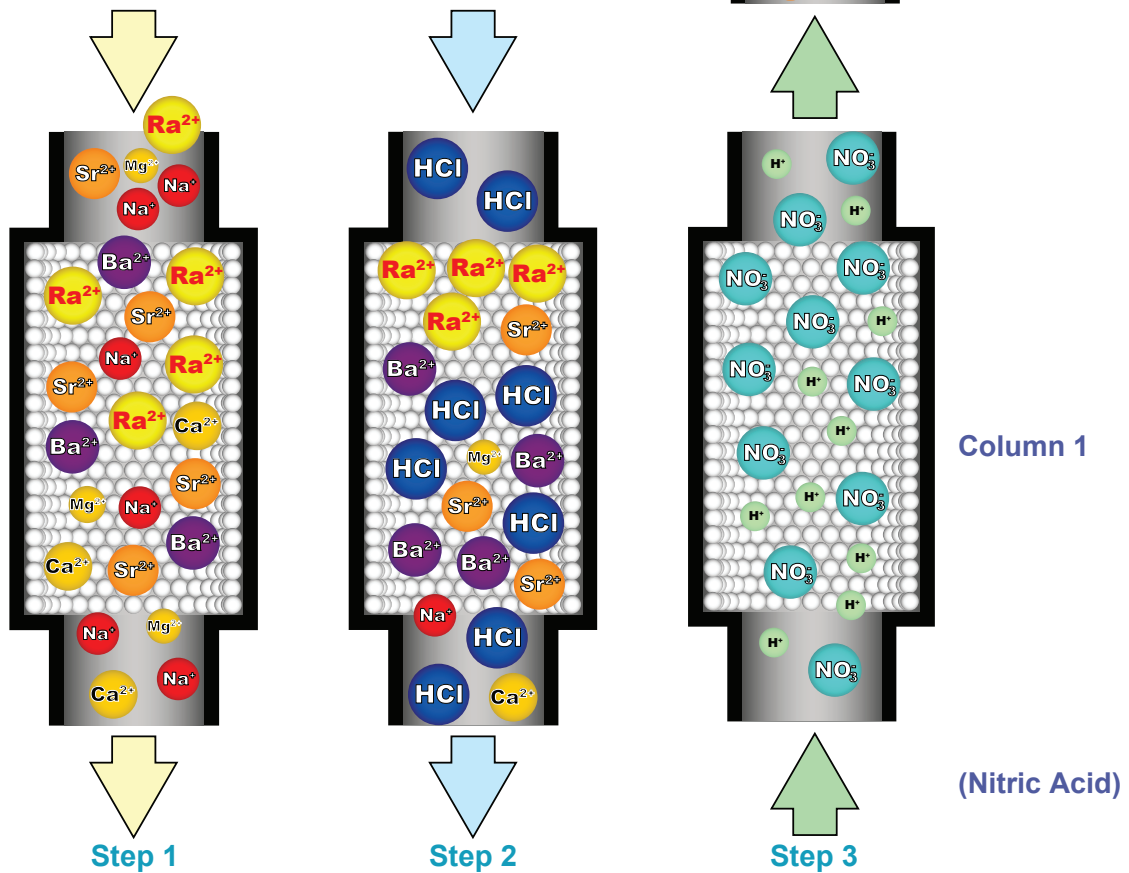- Reusable resins may be used for many samples

Step 1
- Load sample onto the column with DI water.

Step 2
- Wash most matrix from the column using **HCl**.

Step 3
- Separate **Ra** from residual **Ba** and **Sr** using **HNO₃**.

Column 2

Column 1

(Nitric Acid)

Step 1

Step 2

Step 3

3

Automatic Sample Preparation

- 9 mL undiluted sample is syringe-loaded onto an injection loop.

- Sample is automatically transferred to a secondary loop with an optional automatic dilution.

- During the transfer, a standard addition spike may be added to automatically build a standard addition calibration.

- The resulting sample (diluted/undiluted, unspiked/spiked) is automatically loaded onto a preconcentration column.
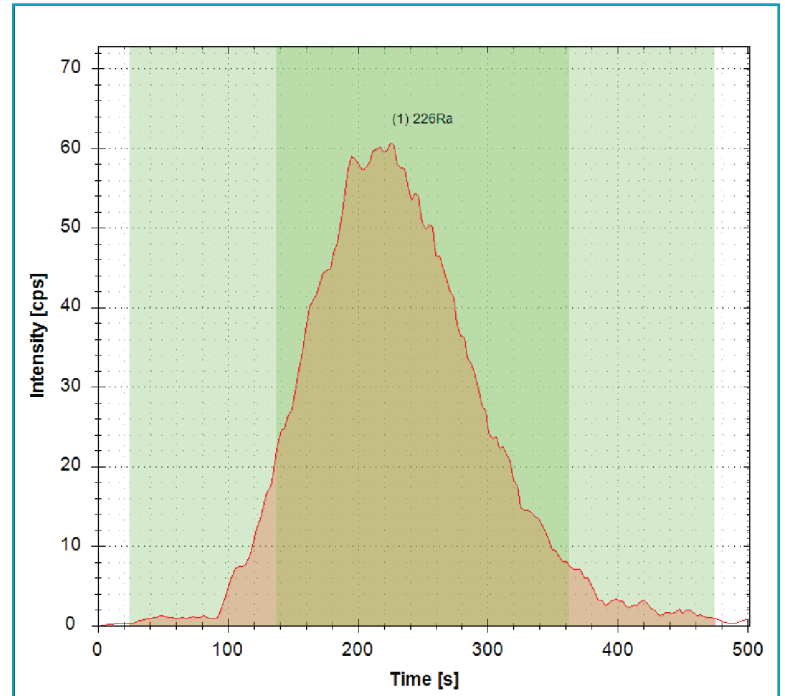

Dilute nitric acid with automatic standard addition spike of 100 mBq/L (2.7 ppq) ^{226}Ra
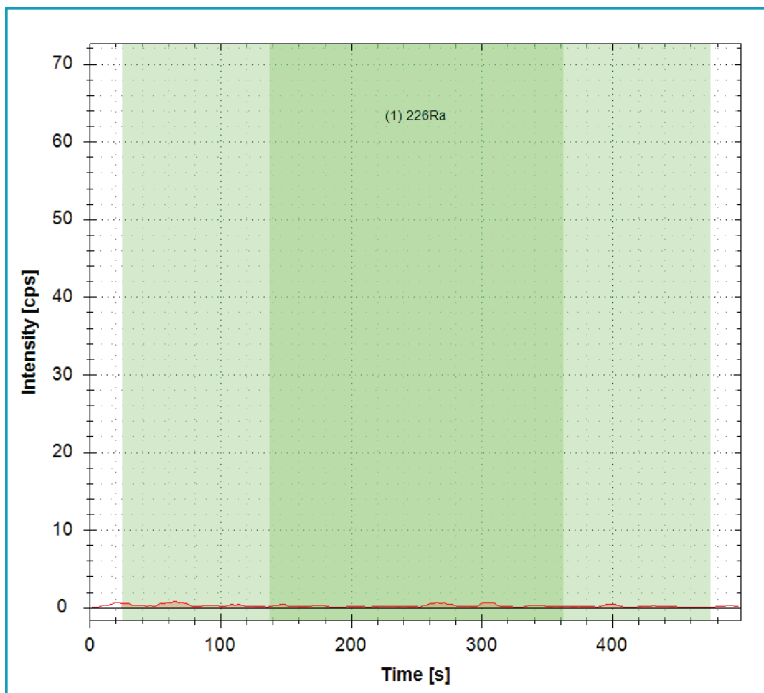
Dilute nitric acid blank after the highest standard addition calibration spike of 100 mBq/L ^{226}Ra, demonstrating excellent washout

Results and Discussion

Groundwater from parts of the Upper Midwest is known to contain naturally occurring Ra that is sometimes above the EPA recommended Maximum Contaminant Level (MCL) of 5 pCi/L (5 ppq, 185 mBq/L). To test the performance of the TRU*FAST*, a groundwater sample (J1) was retrieved from a well located in the Loess Hills near the town of Honey Creek, Iowa, USA.
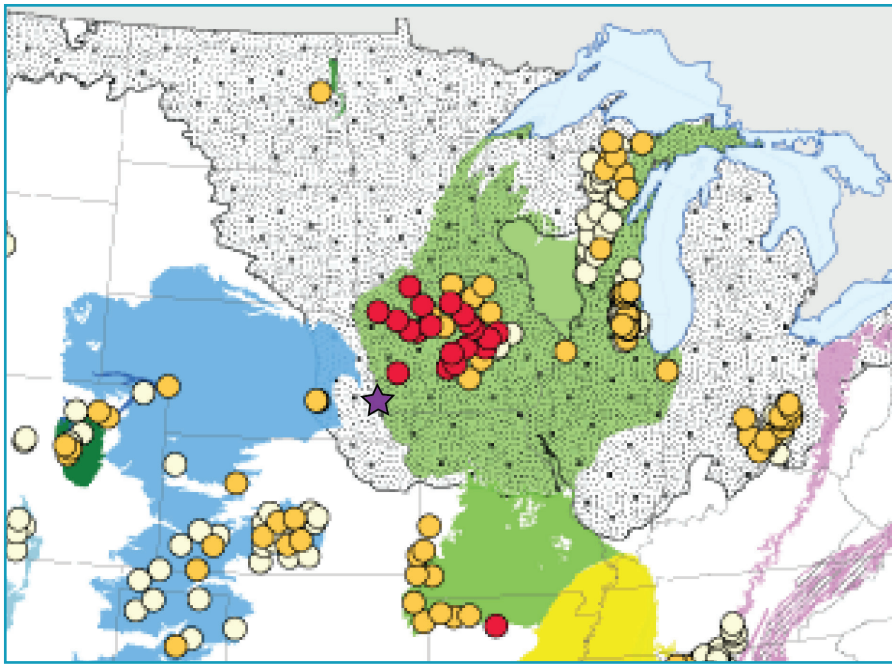
Map from USGS[3] showing elevated Ra concentrations in well water in aquifers in the Upper Midwest region of the United States. The Honey Creek, Iowa, sample location is shown as a purple star on the map.

Well and radium concentration
- ○ Less than 1 pCi/L (<37 mBq/L)
- ● 1 to 4.99 pCi/L (37 – 185 mBq/L)
- ● Greater than or equal to 5 pCi/L (≥185 mBq/L)

|	^{226}Ra
Canada MAC[1]	0.5 Bq/L
WHO Guidance Level in water[2]	1 Bq/L
US EPA MCL[3]	0.19 Bq/L (5 pCi/L)
TRU*FAST* SP2 detection limit	<0.010 Bq/L
*1 Bq/L = 27 pCi/L = 27 pg/L	

Guidelines for maximum allowable concentration of radium in water from Canada[1], World Health Organization[2] and USA Environmental Protection Agency[3].

Results and Discussion

The Ra concentration was determined from two separate calibrations to compare the Ra extraction efficiency in varying matrices. First, the concentration of Ra was measured in triplicate in sample J1, unspiked and auto-spiked at 50 mBq/L, using an automatic external calibration prepared by auto-spiking a dilute nitric acid blank with varying concentrations of Ra. The determined concentration was compared to that found by performing an automatic standard addition calibration using sample J1 as the calibration matrix.
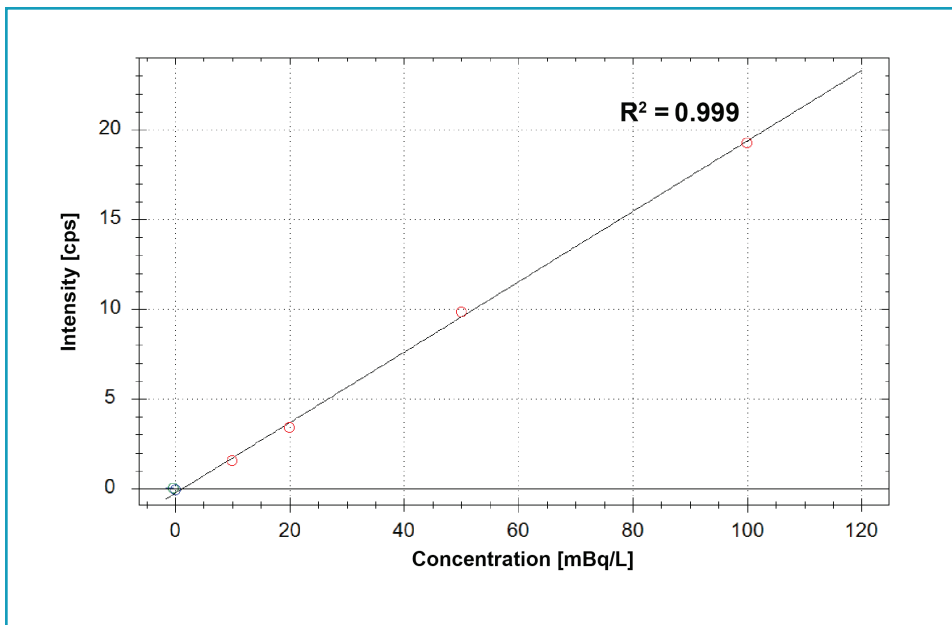
Automatic external calibration prepared by auto-spiking a dilute nitric acid blank
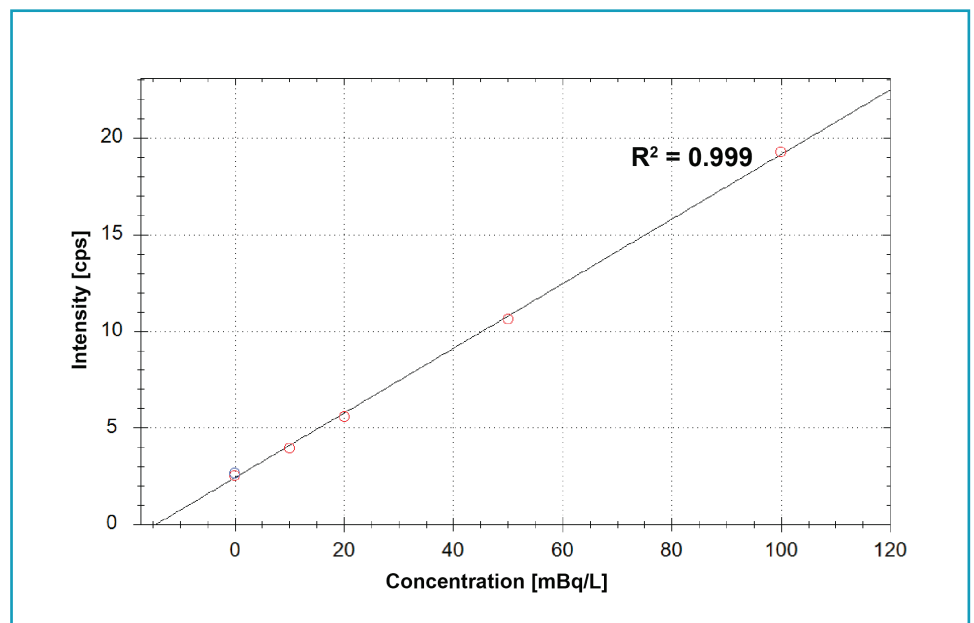
Standard addition calibration using sample J1 as the calibration matrix

Results and Discussion

The results for sample J1 and detection limits are summarized in the tables below. There was some suppression of the internal standard (recovery 70% – 80%) for sample J1 compared to a dilute nitric acid blank and calibration due to residual matrix after preconcentration and matrix separation, but the determined concentrations were in reasonable agreement after internal standard correction.

Calibration Type	Sample	Determined Concentration (mBq/L)			Spike Recovery
Dilute Nitric Acid Calibration	J1 (n=3)	15.4	±	1.2	
	J1 + 50 mBq/L spike (n=3)	60.3	±	1.3	90%
Standard Addition Calibration	J1	13.4			
	J1 + 10 mBq/L spike (n=7)	22.6	±	0.8	92%

Detection limits		
	mBq/L	ppq
IDL (n=10, 3σ, dilute nitric acid blanks)	0.25	0.007
MDL (n=7, 3.14σ, J1 +10 mBq/L spike)	2.6	0.07

Conclusions

The TRU*FAST* system with ICPMS can quickly and accurately determine ^{226}Ra at concentrations suitable for compliance with environmental regulations throughout the world. The combination of excellent detection limits, low required sample volume, and high throughput make the system an attractive method for Ra determination.

References

1. Continuous online determination of ^{226}Ra in liquid effluents using automated column chromatography-ICPMS, R.D. Evans et. al., Canadian Journal of Chemistry, 2015, 93(11): 1226-1231, 10.1139/cjc-2015-0247

2. Analysis of Radium-226 in High Salinity Wastewater from Unconventional Gas Extraction by Inductively Coupled Plasma-Mass Spectrometry, Tieyuan Zhang et. al., Environ. Sci. Technol. 2015, 49 (5), pp 2969–2976, 10.1021/es504656q

3. Szabo, Zoltan, Fischer, J.M., and Hancock, T.C., 2012, Principal aquifers can contribute radium to sources of drinking water under certain geochemical conditions: U.S. Geological Survey Fact Sheet 2010-3113, 6 p.