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Radionuclide Determination In Surface Water Samples By Inductively Coupled Plasma With Sector Field Mass Spectrometry (ICP-SFMS)

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Abstract The determination of naturally occurring radionuclides in the environment by inductively coupled plasma mass spectrometry of high resolution (ICP-SFMS) has gained recognition over the last fifteen years, relative to the radiometric techniques, as the result of improvement in instrumental performance, sample introduction equipment and sample preparation. With the increase in instrumental sensitivity, it is now possible to measure ultratrace levels of many radioisotopes.

The aim of this work was to determined the natural radionuclides (^{232}Th, ^{234}U, ^{235}U and ^{238}U) in surface water using Inductively Coupled Plasma-Sector Field Mass Spectrometry (ICP-SFMS). The samples were sampling from Lerma river, State of Mexico at february to april 2015. The process of treatment of sample consisted in perform an acid digestion according to the 3015A USEPA method followed of the direct measurement in ICP-SFMS. Results obtained were: a) identify the presence of ^{232}Th, ^{234}U, ^{235}U and ^{238}U isotopes in water, b) isotopic ratios were for ^{234}U/^{238}U=1.133 ± 0.016. ICP-SFMS has gained popularity in the field of radiochemistry, particularly as a method of detection for long lived-actinides.

Keywords: ICP-SFMS, surface water, water pollution, quantification limits, detection limits, trace elements

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Romero-Guzmán, E.T.
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1. INTRODUCTION

This study focuses on radiogenic isotopes of U ($^{234}U/^{238}U$) in water. Systems have been used as natural tracer of hydrologic processes in a variety of settings. In this work, we have investigated U isotopes as a possible means of assessing the transport of it through superficial water. The basis of this method is that ^{234}U and ^{238}U commonly exhibit disequilibrium in open-system aqueous systems. Under closed system conditions, ^{234}U and ^{238}U are in secular equilibrium with an activity ratio ($AR^{234}/^{238}$) of unity and an atom ratio of 0.00005472-0.00000011. In terms of radioactivity, the $^{234}U/^{238}U$ equilibrium is defined as unity activity ratio, as both these nuclides are members of the same series and emit alpha-particles, i.e. the quotient of the abundance and half-life is similar for both nuclides ($54.8 \times 10^{-6}/2.45 \times 10^5 = 1/4.47 \times 10^9$). However, when aquatic systems are in contact with minerals, selective leaching processes lead to preferential dissolution and transport of ^{234}U, resulting in enhancement of the $^{234}U/^{238}U$ ratio. In most water bodies, this ratio may be above the unit activity ratio, and a value as high as 20 was reported. Another motivation for specifically studying U is that there has been a growing interest in monitoring various radionuclides that can affect directly human health. To meet these objectives, we have conducted a preliminary feasibility study of surface water from monitoring locations along, river stations. U isotopes and concentrations have been determined herein by inductively coupled plasma mass spectrometry sector field (ICP-SFMS).

2. EXPERIMENTAL

2.1 Instrumentation

Measurements were performed with an ICP-SFMS (Element 2/XR from Thermo Fisher Scientific Germany). Aqueous samples were introduced with an SC-2 DX autosampler from Element Scientific Inc. (ESI) and a microconcentric nebulizer coupled to a Twister with a Helix 50 mL cyclonic borosilicate glass spray chamber (Elemental Scientific Inc., USA). The torch of the ICP-SFMS instrument (Elemental Scientific Inc., USA) was shielded with a grounded platinum electrode (GuardElectrodeTM, Thermo Scientific). (GuardElectrodeTM, Thermo Scientific, Germany).

2.2 Materials and reagents

The mass calibration of ICP-SFMS was performed using a certified multi-element solution XXIII (Ba, B, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Y, Th, and U) from Merck (Germany). For optimization of method used mass offset in ICP-SFMS was performed by using a certified multi-elements solution of 10 µg L-1 for Be, B, Na, Sr, Ag, Cd, Ba, Hg, Tl, Pb, Bi, Th, U, Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, K and As) from National Institute of Standards & Technology, NIST USA, and aliquot of 1 µg L-1of a In external standard solution (Merck, Germany) was used during the measurements for monitoring the instrumental stability. The solutions were prepared using analytical grade reagents from Merck (Germany). High purity water (> 18 MΩ/cm) was obtained from a Milli-Q® Reference (Millipore México). Nitric acid was purified by distillation in a Milestone Duopur (Milestone s.r.l., Italy) sub-boiling system. Certified Ar gas (99.999%) was supplied by INFRA, S.A. de C.V. México. filtered using cellulose nitrate membrane filters Whatman from GE Healthcare Life Sciences (Proveedor Científico S.A. México).

1.3 Preparation of samples

Surface water samples used in this study were collected from various monitoring events from Lerma river by staff from the Earth Sciences from UAM-Lerma during the period between January to May 2015, Figure 1. The samples were acidified with 2% HNO_3, followed by filtration using cellulose nitrate membrane filters for avoided the particles in suspension. From these solutions were taken 1 mL and then led to volume of 50 mL with a 2% HNO_3 that contain internal standard for measurement by ICP-SFMS. Additional, samples blanks were prepared same treatment that samples water from the river.

Table 1 shows the instrumental parameters of ICP-SFMS. All steps of the optimization of method by ICP-SFMS to obtain the conditions better on measurements of radionuclides and element trace have been previously described.

3. RESULTS AND DISCUSSION

3.1 Limits of detection (LODs) and Limits of quantification (LOQs)

Several parameters have been taken into account and evaluated for the optimization of the analytical method for quantitative determination of trace elements in waters, such as; linearity of calibration curves, LODs, LOQs and the precision in terms of relative standard deviation (RDS). LODs were estimated for each analyte with the standard error of y-intercepts of regression

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Table 1: Instrumental conditions optimized for the measurement of radionuclides and trace metals in surface water by ICP-SFMS.

Parameter	**Value**
Solution uptake rate, mL min^{-1}	0.1
RF power, W	1325
Cool gas flow rate, L min^{-1}	16.0
Auxiliary gas flow rate, L min^{-1}	0.75
Nebulizer gas flow rate, L min^{-1}	1.036
Ion extraction lens potential, V	-2000
Mass Resolution (m/m)	LRM = 300
	MRM = 4000
	HRM = 10000
Isotopes	LRM: ^{107}Ag, ^{111}Cd, ^{137}Ba, ^{202}Hg, ^{205}Tl, ^{208}Pb, ^{209}Bi, ^{232}Th, ^{234}U, ^{235}U, ^{238}U
	MRM:^{24}Mg, ^{27}Al, ^{44}Ca, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{63}Cu, ^{66}Zn,
	HRM: ^{75}As
Samples per peak	100
Setting time, ms	10
Sample time, ms	10
Points per width	10
Peak shift	1.0
Mass window, %	80
Integration window, %	10
Scan type	E-scan
Detection mode	Triple (ion counting, analogue and Faraday)
Total analysis time per sample, min	4
Sample / skimmer cone	Nickel
Spray chamber	Twister helix, 50 mL cyclonic, borosilicate glass
Nebulizer	MicroMist U-series nebulizer 0.1 mL min^{-1}
Parameter	Value
Solution uptake rate, mL min^{-1}	0.1
RF power, W	1325

analysis (σ) and the slope (S) of the standard curves, using the following equation LOD=3σ/S and LOQs were estimated in the same manner from the equation LOQ=10σ/S [11]. RSD was calculated through the total analysis and them was less that 5% for each element. The results that were obtained of LODs and LODs were consistent with other research where trace elements were quantification by ICP-SFMS. The results of lineal regression (R2), LODs and LOQs are shown in Table 2.

The calibration curves are show in Figure 1.

The activity ratio results indicate that most of the values are very close to the expected ratios for surface water (1.133 ± 0.016). Uranium concentrations increase faster for the monitoring sites. The transport of the water by the effluent increases the uranium concentration maybe due of the increase of phosphate for the phosphate fertilizers.

Table 2: Calibration curves, LOD and LOQ of each isotope by ICP-SFMS.

Isotopes	R^2	LOD (ng L^{-1})	LOQ (ng L^{-1})
^{107}Ag	1.000	0.5677 ± 0.0302	5.6766 ± 0.3016
^{111}Cd	0.999	0.2680 ± 0.0341	2.6803 ± 0.3411
^{137}Ba	1.000	0.9706 ± 0.0015	9.7063 ± 0.0152
^{208}Pb	1.000	0.8842 ± 0.0104	8.8418 ± 0.1038
^{209}Bi	0.996	3.8682 ± 0.0182	38.6818 ± 0.1818
^{27}Al	0.999	2.5218 ± 0.1657	25.2184 ± 1.6571
^{52}Cr	1.000	0.5655 ± 0.0208	5.6555 ± 0.2082
^{55}Mn	1.000	0.1933 ± 0.0033	1.9335 ± 0.0326
^{56}Fe	0.999	0.3377 ± 0.0138	3.3766 ± 0.1379
^{59}Co	1.000	0.1952 ± 0.0028	1.9518 ± 0.0282
^{60}Ni	1.000	0.1640 ± 0.0019	1.6404 ± 0.0186
^{66}Zn	0.999	0.3347 ± 0.0131	3.3471 ± 0.1307
^{232}Th	0.995	0.0632 ± 0.0172	0.6320 ± 0.3511
^{234}U	0.999	0.0572 ± 0.0108	0.5720 ± 0.2322
^{235}U	1.000	0.0953 ± 0.0123	0.9539 ± 0.0326
^{238}U	0.999	0.1267 ± 0.0138	1.2674 ± 0.1379

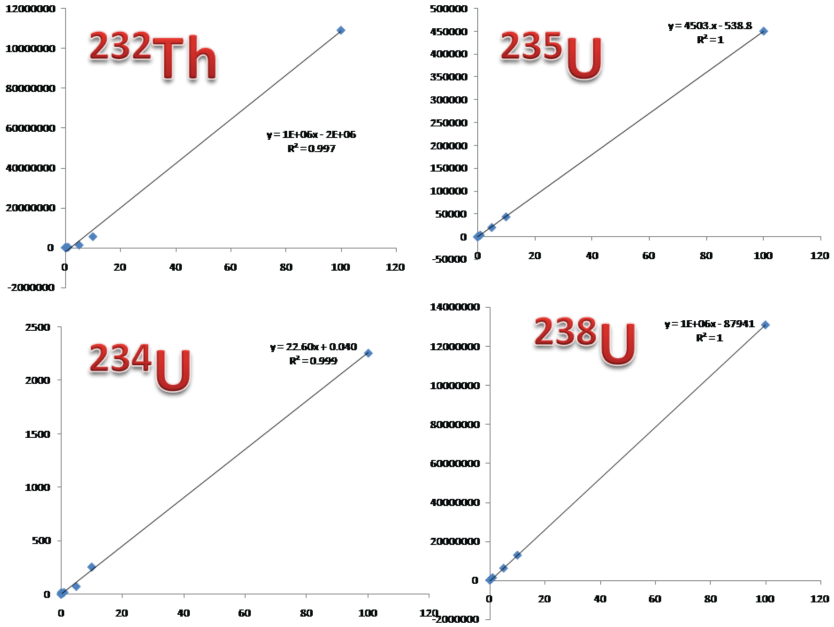

Figure 1: Calibration curves.

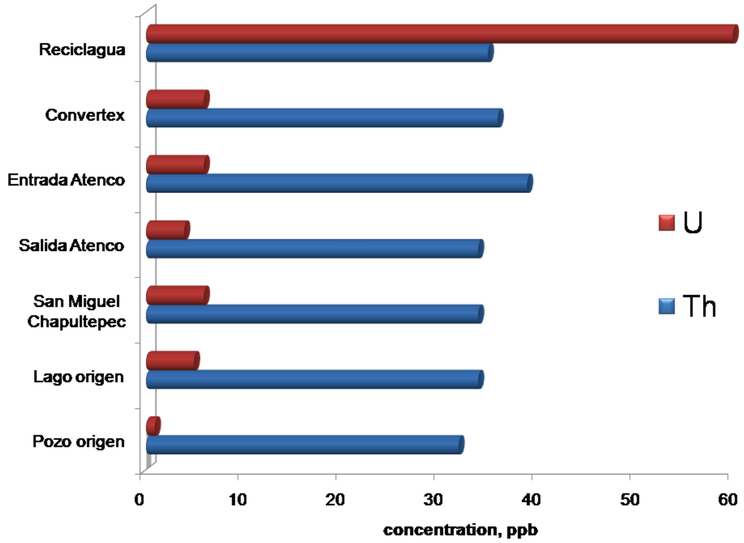

Figure 2: Radionuclides concentration in Lerma river.

4. CONCLUSIONS

The presence of ^{232}Th, ^{234}U, ^{235}U and ^{238}U isotopes in surface water was identified. ^{234}U/^{238}U ratios also vary due to anthropogenic discharge. Isotopic ratios were for ^{234}U/^{238}U=1.133 ± 0.016. ICP-SFMS has gained popularity in the field of radiochemistry, particularly as a method of detection for long lived-actinides.

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