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Radiochemical Separation and Measurement by Mass Spectrometry with Magnetic Sector with Inductively Coupled Plasma source (ICP-SFMS) of Plutonium Isotopes in Soil Samples

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Abstract The aim of this work is twofold: to optimize the radiochemical separation of Plutonium (Pu) from soil samples, and to measure the Pu concentration. Soil samples were prepared using acid digestion assisted by microwaves; then, Pu purification was carried out with Pu AG1X8 resin. Pu isotopes were measured using Mass Spectrometry with Magnetic Sector with Inductively Coupled Plasma source (ICP-SFMS). In order to reduce the interference due to the presence of $^{238}UH^+$ in the samples a desolvation system (Apex) was used. The limit of detection (LOD) of Pu was determined. The efficiency of Pu recovery from soil samples varies from 70 to 93%.

Keywords: Plutonium isotopes, Radiochemical separation, Soil, ICP-SFMS

1. INTRODUCTION

Plutonium (Pu) is an anthropogenic element with radioactive properties and is distributed considerably in the environment as a result of nuclear weapons tests mainly [3]. Other sources of Pu are related to controlled or accidental spills in reprocessing facilities of nuclear fuel, nuclear power plants and weapons factories. According to data published by Choppin, since 1945 more than 2×10^{20} Bq of radioactivity have been released into the atmosphere in the testing of nuclear weapons, while the contribution of radioactivity from

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involving nuclear reactor systems accumulated a total of 5 x 10^{18}Bq. Pu emits alpha particles and gamma radiation, said particles are helium nuclei, highly ionizing power. Therefore, the Pu is considered radiotoxic representing a high health risk. In humans, the incorporation of Pu can occur by several routes: intravenous, ingestion and inhalation, skin absorption or through wounds [2]. In general it is important to remember that the exposure dose decreases with the square of the distance from the source and increases linearly with exposure time and the activity of the source [9]. Therefore, keep the shortest time possible and away from the source. In the case of Pu is radiotoxic and management must be done using a glove box, in the absence there of using hood in optimal conditions, lenses and mask, carry a personal dosimeter for individual monitoring, always wear rubber gloves or latex gloves when working with these sources. Never throw radioactive material to drain. Deposit waste in special containers according to local regulations, labeling everything that deals with complete information (radionuclide, date, activity, user) and in all cases, at the end of their work carefully wash hands with water and soap [10].

Pu was discovered in 1940 as a result of production and chemical identification isotope ^{238}Pu resulting from the bombardment of uranium (U) with deuterons in the cyclotron of the University of California, Berkeley, and by the year 1942 for the first time could isolate a compound of this element. Contains 20 isotopes, due its nuclear features ^{239}Pu (24,110 years half-life) is by far the most interesting from the strategic point of view; it is used in the dosimetric assessments Professionally Exposed Personnel (PEP) and contributes to the radiological risk. It was discovered in early 1941 by bombarding natural U with an intense neutron flux obtained therefrom cyclotron. For this reason, it is of great importance determining their concentration, and is required exhaustive controls to ensure that standards legally established radiation safety are met, a fact which requires the development of precise, accurate and sensitive quantification methods [7, 11].

Traditionally, long half-life radionuclides have been determined by radiometric [4]. In this case, radiometric methods such as alpha spectrometry (AS) contains good characteristic, where this technique is low cost in routine analysis and it have been most frequently used for the determination of radionuclides in environmental samples. However, the^{240}Pu/^{239}Pu ratio, which is important to define the origin of Pu, cannot be determined by AS due to the energies of the emitted alpha particles are very close [12]. Nowadays, the techniques of mass spectrometry (MS) such as Mass Spectrometry source Inductively coupled Plasma (ICP-MS), the Mass Spectrometry Thermal Ionization (TIMS) and Mass Spectrometry Accelerators (AMS) are widely used to radionuclides determine and characterization of radioactive waste, this is because of its accuracy and sensitivity for measuring radionuclide long half-life [8]. The AMS and TIMS have disadvantages against ICP-MS, therefore the ICP-MS has become an accepted and popular alternative for the determination of long-lived radionuclides at concentration levels ultra-trace. Specifically the design of magnetic sector (ICP-SFMS) is often used in these studies due to its high sensitivity and low background, however it is important to acknowledge that the calibration or tuning is a decisive stage and relatively complicated [5].

Soil contamination by radionuclides of long half-life has been pronounced assevere environmental problem. They contain minerals, organic matter, small living organisms, so it requires a soil samples processing [6]. So the determination of the Pu isotope by ICP-SFMS in complex matrices (soil) is recently a topic of great interest. The global fallout plutonium in soil, introduced by nuclear detonations in the past century, has been extensively studied not only for the purpose of radiological assessments, but also in various studies in which Pu is used as a geochemical tracer, such as soil erosion, sediment dating, desertification studies and estimation of aerosol residence time in the stratosphere [13].

The aim of this study was to determine the concentration of Pu isotopes in synthetic soil samples in order to evaluate the performance of the separation process and the quantification technique.

2. EXPERIMENTAL

2.1 Sample preparation

Sample 1 (M1) and sample 2 (M2) were synthetic samples of uncontaminated soil and Pu isotope tracing with known concentrations. It was noteworthy that became a blind exercise. Sample was weighed three times being 0.1 g and it was digested according to USEPA method 3052. Subsequently evaporated to get rid of the HF, then preconcentrated and purified those samples to obtained a Pu fraction, this was done by using the separation method using ion exchange chromatography AG1X8 resin with a particle size 100-200 micronsof (BioRad Laboratories, Inc.). The process of radiochemical separation was as follows: obtained in the first instance the fraction of U, using 80 mL of 8M HNO_3, then the fraction containing strontium (Sr) and americium (Am) was obtained using 4 fractions of 15 mL of the same concentration and the same acid, then the fraction of thorium (Th) eluting was obtained with 55 mL of 12M HCl, finally the Pu fraction was obtained using three fractions of 15 mL of 0.5M HCl and

NH_3OHCl that lets you change the oxidation state of Pu (Pu^{+3} to Pu^{+4}). Pu fraction obtained was evaporated to dryness at 60°C, and then all samples were recovered with high pure HNO_3 at 2% v/v, and the final volume of samples to measurement to ICP-SFMS was 10 mL.

The standard of ^{242}Pu was obtained from the National Physical Laboratory (NPL, UK). The pattern was diluted with nitric acid (HNO_3) 5% v/v, to obtain a stock solution of $1.33x10^3$ $pgmL^{-1}$ concentration (6.391 $mBqmL^{-1}$). For mass calibration of ICP-SFMS a multi-elemental certified XXIII (Ba, B, Co, Fe, Ga, In, K, Li, Lu, Na, Rh, Sc, Y, Tl and U) solution was used Merck (Germany). The solutions were prepared with water of high purity (>18Ω cm^{-1}) obtained from Milli-Q Element A10 Century (Millipore Iberica, Spain) and ultrapure HNO_3 which was obtained by distillation at sub-boiling (Duopur, Milestone Srl , Italy). Concentrated HCl (35%), HNO_3 (70%) and HF(23%), and hydroxylamine hydrochloride (NH_3OHCl) was used.

2.2 Quantification of Pu

It was performed using ICP-SFMS ELEMENT 2/ELEMENT XR (Thermo Fisher Scientific, Bremen, Germany). The system of introducing the sample used is an Apex desolvater nebulizer (CETAC Technologies, Inc., USA) with a microflow nebulizer PFA-100 (Elemental Scientific Inc., USA). The aqueous samples were introduced into the desolvater in continuous flow mode using an autosampler CETAC ASX-520 (CETAC Technologies, Inc., USA), in Figure 1

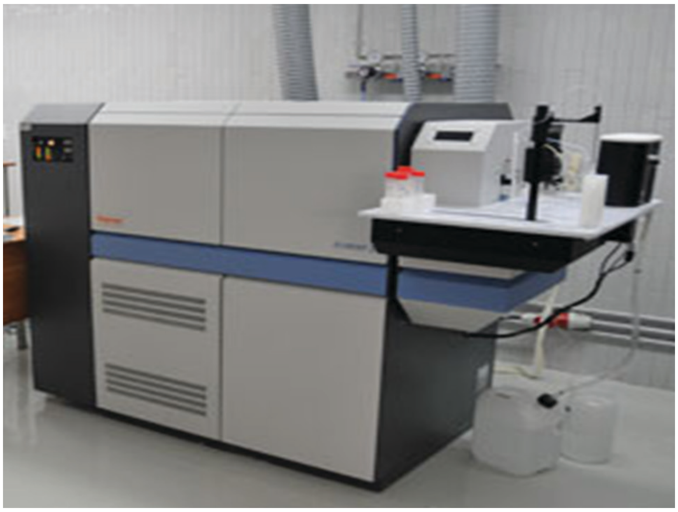

Figure 1: ICP-SFMSEquipment.

the apparatus is shown. The types of cones for ICP-SFMS to work in normal mode are sample cone and skimmer cone.

3. RESULTS AND DISCUSSION

Within the parameters used before optimizing measurement conditions by ICP-SFMS, Apex-ICP-SFMS and Apex-Inter JET-ICP-SFMS were the stability test. During this test the accuracy were measured in terms of Relative Standard Deviation (RSD) for ^{7}Li, ^{115}In and ^{238}U. The results were less than 2%, is a desired value. In the optimization of the region of interest, *mass offset*, Pu isotope was considered 80% of integration of the region, this has qualified appropriate since the Limits of Detection (LOD) and therefore the limits of quantitation (LOQ) if they are desirable as they are of the order of few fgmL^{-1}. In the tuning parameters, Table 1, for the three modes of measurement by ICP-SFMS, there are changes in the conditions for each mode, this in order to detect and quantify the plutonium found in ultra-trace. The change is mostly reflected in the positions of the torch and the flow of the sample gas. An important parameter is the voltage electron multiplier detector (SEM), which must be constant and less than 2800 volts (V) to prevent wear and maintain the same detector efficiency.

Table 2, shows the intensities are displayed in counts per second (cps) with their respective standard deviations in Low Resolution (LR= 300), corresponding to the internal standard used (^{242}Pu) measured in the calibration curve in which a correlation coefficient was obtained 0.9978. Increasing orders of magnitude which is translated in obtaining higher sensitivity and consequently better determination of Pu isotopes observed.

Table 3, shows the concentrations obtained of the ^{239}Pu, ^{240}Pu, ^{241}Pu isotopes in soil samples M1 and M2 are reported. Only measured by one way, Apex-Inter JET-ICP-SFMS, since Pu is found in small quantities and precise determination of the isotope Pu by ICP-SFMS normal mode is hampered by ^{238}UH^{+} and ^{238}UH$_{2}$, which interfere with ^{239}Pu and ^{240}Pu isotopes, respectively, due to the presence of U. It is also of great importance that the Pu purification using a separation method, as it was in this case by column chromatography with ion exchange resins AG1X8 BioRad, the radiochemical yields (RY) obtained (Table 3) show to be good, that is, there was little loss of Pu during anion exchange separation. The aim of using coupling equipment and the full chemical treatment of samples was to eliminate the afore mentioned interference and obtain the desired results, in relation to the above the Apex system is a desolvater for aqueous systems, the system allows remove water and pre-concentrate the samples in a split second by a carrier gas (high purity

Table 1: Tuning parameters.

Measurement mode	**Normal mode**	**Apex**	**Apex-Inter JET**
Torch. X-Pos. [mm]	2.100	2.100	2.400
Torch. Y-Pos. [mm]	-1.500	-1.500	-1.300
Torch. Z-Pos. [mm]	-6.800	-6.900	-6.900
Plasma power [W]	1300	1300	1300
Peristaltic pump [rpm]	11.00	11.00	12.00
Cold Gas [L/min]	16.02	16.02	16.02
Faraday Detection [V]	-205.00	-205.00	-205.00
Auxiliary Gas [L/min]	0.80	0.80	1.40
Lens filter [V]	0	0	0
Sample gas [L/min]	0.993	0.921	0.705
Aditional gas 1 [L/min]	0	0	0
Extration [V]	-2000.00	-2000.00	-2000.00
Focus [V]	-915.30	-915.30	-850.00
Defletion-x [V]	2.00	2.00	1.85
Defletion-y [V]	-0.10	-0.10	1.49
Shape [V]	120.50	120.50	131.00
Rotation quadrupol 1 [V]	-3.64	-3.64	-1.52
Rotation quadrupol 2 [V]	-2.90	-2.90	-1.13
Focus quadrupol 1 [V]	-3.05	-3.05	-0.67
Focusquadrupol 2 [V]	0.15	0.15	0.15
VaVb [%]	0.070	0.070	0.070
Focus offset [%]	2.80	2.80	2.80
Matsuda- plate [V]	60.66	60.66	60.66
Deflection-SEM [V]	648	648	637
SEM [V]	2500	2500	2310

N_2). And the jet interface (inter JET) is an additional pump that can be attached to the computer to obtain greater sensitivity and avoid polyatomic interference in the plasma ionization.

No concentrations were determined by Apex-ICP-SFMS because in the measured samples were dissolved solids which could not introduce the desolvation system because it could clog the nebulizer and damage the equipment and therefore do not get adequate results.

The contamination factor was measured ($^{238}UH^+$contribution in ^{239}Pu) and this can be applied as a correction factor in routine tests ^{239}Pu in complex

Table 2: Intensity in cps of ^{242}Pu of the calibration curve.

Sequence / Isotope	**Normal mode**	**Apex**	**Apex-Inter JET**
	^{242}Pu (LR)	**^{242}Pu (LR)**	**^{242}Pu (LR)**
Blank 1	46.67 ± 4.80	571.48 ± 52.20	51306.45 ± 2652.30
Blank 2	3.33 ± 0.90	29.53 ± 9.30	53725.3 ± 34031.70
Standard 1	5.56 ± 0.00	67.07 ± 13.70	142.35 ± 19.70
Standard 2	15.19 ± 3.20	133.33 ± 11.50	65.79 ± 26.70
Standard 3	30.00 ± 5.10	310.29 ± 20.50	635.92 ± 36.80
Standard 4	38.89 ± 4.90	416.99 ± 75.20	991.86 ± 8.40
Standard 5	75.93 ± 14.2	513.14 ± 73.80	1285.69 ± 54.60
Standard 6	163.33 ± 2.90	914.63 ± 95.00	3622.10 ± 159.40
Standard 7	318.54 ± 21.10	2055.25 ± 191.00	5914.66 ± 326.30
Standard 8	513.03 ± 39.90	2979.97 ± 166.80	8894.84 ± 569.00
Standard 9	671.09 ± 30.08	6314.51 ± 358.40	12679.86 ± 625.20

Table 3: Concentrations of ^{239}Pu, ^{240}Pu, ^{241}Pu isotopes in soil samples: M1 and M2 and radiochemical yields obtained by radiochemical separation by column chromatography resins AG1X8.

	Sample (n=3)	**^{239}Pu (pgg^{-1})**	**^{240}Pu (pgg^{-1})**	**^{241}Pu (pgg^{-1})**	**RY (%)**
Apex-Inter JET-ICP-SFMS	M1	91.59 ± 7.33	11.58 ± 2.13	4.63 ± 1.07	82.18 ± 16.85
	M2	18.78 ± 4.78	3.43 ± 0.77	1.44 ± 0.51	76.16 ± 2.44

Table 4: Produced by contamination factor in ^{238}UH^{+} ^{239}Pu.

ICP-SFMS	**Apex-ICP-SFMS**	**Apex-Inter JET-ICP-SFMS**
9.08 X 10^{-9} ± 0.37x10^{-9}	2.70 X 10^{-9} ± 0.03 X 10^{-9}	6.73 X 10^{-10} ± 0.04 X 10^{-10}

samples such as soil, sediment and biological samples [1]. Table 4 shows the contamination factors, these were calculated with several calibration curves, the concentration of ^{238}U that employ 0.1 to 50 ng mL^{-1}. It also notes that the contamination factor decreases when making measurements with ICP-SFMS-Apex and Apex-InterJET-ICP-SFMS because avoid H^{+}.

In Table 5 are reported the LOD and LOQ obtained in measurements of ^{242}Pu by ICP-SFMS, Apex-ICP-SFMS and Apex-Inter JET-ICP-SFMS, prove

Table 5: Detection Limits (LOD) and Quantitation Limit (LOQ) obtained by ICP-SFMS, Apex-ICP-SFMS and Apex-Inter JET-ICP-SFMS for ^{242}Pu.

Measurement mode	LOD (fgmL^{-1})	LOQ (fgmL^{-1})
ICP-SFMS	8.36 ± 0.04	27.02 ± 0.14
Apex-ICP-SFMS	2.01 ± 0.01	5.56 ± 0.05
Apex-Inter JET-ICP-SFMS	1.70 ± 0.03	5.68 ± 0.08

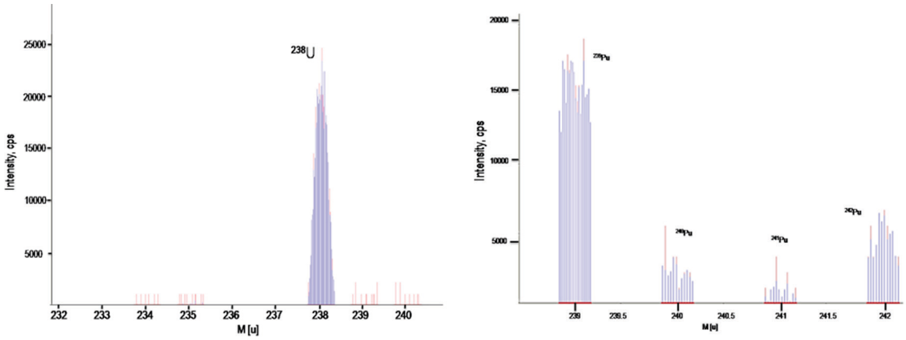

Figure 2: Spectra obtained by two measurement modes. (a) U isotopes by ICP-SFMS, (b) Pu isotopes measured by Apex-Inter JET-ICP-SFMS.

to be good results, comparing them with those already reported in the literature for different measurement techniques.

In Figure 2 the spectra obtained from the measurement of the Pu isotopes in (a) are exhibited only U isotopes for the normal mode, Pu isotopes cannot display in those samples because it was not performed radiochemical separated. In (b) Pu isotopes measured by Apex-Inter JET-ICP-SFMS and prior separation of Pu shown.

The method in this work was appropriate to measurement Pu isotopes in soil using Apex / Inter JET-ICP-SFMS, due the results obtained in the optimization of method, good linearity, LOD, LOQ and contamination factor have been low and similar to the reported results of another works (10^{-9}). In relation to the above, the results of the radiochemical yields are good, being in a range of 70-93%.

3. CONCLUSIONS

In this work the concentrations of Pu isotopes in synthetic soil samples were determined. The main finding was that increasing by 30% of the reagent amount to elute each fraction, relative to the protocol established in the laboratory, increasing the radiochemical yield, improving the efficiency in the separation of Pu.

Using ICP-SFMS with Apex and JET interface has an innovative approach in the area of basic research, particularly with a focus on determining concentrations of sub ultratrace levels. The results of LOD and LOQ obtained for the measurement of Pu isotope by the three measurement modes (ICP-SFMS, Apex-ICP-SFMS and Apex-inter JET-ICP-SFMS) proved to be successful, they are in the femtogram order per sample. Finally, the concentrations of Pu isotopes were obtained by Apex-Inter JET-ICP-SFMS system that offers better sensitivity.

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