BASAL CONCENTRATION OF URANIUM AND THORIUM IN ZACATECAS, MEXICO
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1. Introduction

Radioactive substances defined as materials that contain unstable atoms that produce ionizing radiation, one of an electromagnetic nature (X-rays, gamma rays) and the other, made up of particles (alpha, beta, neutrons, etc.) through nuclear reorganization. Primordial radionuclides, defined as radionuclides present since the formation of the Earth about $4.6 \cdot 10^9$ years ago, play an essential role in understanding our planet's geological conditions throughout its existence. The radioactivity initiated by the decay in the chain of ^{232}Th, ^{235}U, and ^{238}U is responsible for the presence in the Earth of radioisotopes of lead, polonium, bismuth, astatine, radon, francium, radium, and protactinium [2].

Ionizing radiation is one of the most widely analyzed "toxic" agents. The importance of understanding the multiple effects they produce on living beings comes from their massive use in the medical diagnosis and treatment of cancer since the beginning of the 20th century [3].

Natural radioactivity can be subdivided into two groups: that existing in the terrestrial environment and that coming from space. Cosmogenic radionuclides originate from cosmic [4] radiation bombardment from the nuclei of elements in the atmosphere and rocks. This interaction transforms its configuration and elements into radioactive elements. Terrestrial radionuclides, also known as primordial radionuclides, have been in the Earth since its formation. The primordial radionuclides are grouped in decay series or appear individually. Primordial radionuclides have long half-lives, which can compare to the Earth's estimated age ($4.5 \cdot 10^9$ years). These isotopes are still present in their radioactive form on our planet, having half-lives longer than the solar system's formation.

Actinides are the 15 chemical elements included in the periodic table between atomic numbers 89 to 103. The two main actinides present in nature are uranium (U) and thorium (Th). Uranium has 3 important natural isotopes ^{234}U, ^{235}U, and ^{238}U, of which the latter two are progenitors of the natural radioactive series. Natural thorium (Th) considered monoisotopic as it had a natural abundance of 100% of ^{232}Th, but recently in the 2013 IUPAC technical report, its natural abundance has been updated to 99.98% ± 0.02 [5].

The health hazard represented by radionuclides' existence in the environment comes from the ability of elements to enter the body, either by ingestion or by inhalation (Fig. 1). Once inside and depending on its metabolism and chemical and radioactive properties, the affected tissues' cells are irradiated, which produces changes in pH within them to irreparable damage to their genetic material. Radioactive isotopes emitting low-energy alpha and beta particles, which are almost innocuous due to these particles' low penetration capacity through the skin, cause damage when either of these two exposure routes incorporate them into the body [3].

The objectives of the monitoring programs are: a) the protection of the population and the environment, b) provide information to the population on the variation of the amounts of radionuclides present in the environment where they live or carry out their work, c) maintain a temporary record to assess the impact of the nuclear industry or NORM industries, d) establish the existing radioactive background before any activity capable of modifying the content of radionuclides in the environment and e) verify the predictions of environmental models to adjust them if necessary to reduce uncertainties in dose assessment [1].

Their radiotoxicity and chemotoxicity characterize the chemical elements that are studied in this experimental work. Analytical and instrumental methods have advantages and disadvantages. Selecting the most appropriate technique both from the analytical and economic point of view requires a comparative study of the results obtained and evaluating its possible application in the samples used for this study.

This work aims to apply the main analytical, radiochemical, and instrumental techniques for determining uranium and thorium in samples from the State of Zacatecas (Mexico).
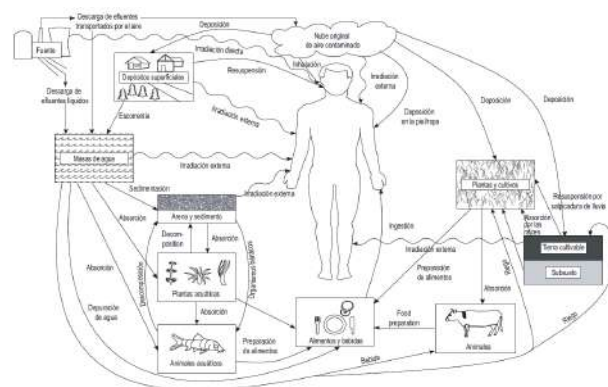

Fig. 1 *Possible routes of exposure of members of the population due to natural radionuclides and/or discharges of radioactive materials into the environment [5].*

2- Study Area

For this work, samples of undisturbed soil have been used (it has not used for housing, agriculture, or mining, without apparent anthropogenic alteration) from the State of Zacatecas (Mexico) (Figure 2) and its surroundings. The 33 sampling points chosen were from areas without apparent anthropogenic alteration; four samples belong to the state of Aguascalientes, another to

the state of Nuevo León, and the rest, 28 samples, to the state of Zacatecas. Interest focused on Villa de Cos, in whose territory there are atypical values of concentration and activity of uranium and thorium. Soil samples were taken from the surface at a depth of 10 cm. The samples were transferred to the laboratory for drying and homogenization. Three aliquots of each sample were prepared to perform different analytical techniques.

3- Materials and Reagents

For this work, glassware in general, has been used, as well as a heating rack, Teflon glasses, ceramic capsules, a desiccator, and plastic syringes.

The reagents used were hydrochloric acid 37% (HCl), nitric acid 65% (HNO_3), hydrofluoric acid 48% (HF). Reagent grade acids have been used since none has a measurable presence of uranium and thorium on its label, its objectives.

TEVA and UTEVA ion exchange resins from Eichrom Technologies Inc. (USA) and ^{232}U and ^{229}Th tracers certified and supplied by CIEMAT (Madrid, Spain) have also been used.

Various laboratory instruments used: analytical balance, muffle, stove, Milestone Ethos Plus microwave digestion oven, microwave oven Teflon reactor equipment, centrifuge, "S" type electrodeposition cell supplied by Tracerlab GmbH (Koeln, Germany). The measuring instruments were S8 Tiger X-ray fluorescence and G8 Discover X-ray diffraction both from Bruker Corporation (USA), ICP-OES 725-ES, ICP-MS 7500c from Agilent Technologies (California, USA). The ICP-SF-MS instrument used at CIEMAT was Element® XR manufactured by Thermo Scientific (Bremen, Germany).

Two certified reference materials used: GBW07402 supplied by the Institute of Geophysical and Geochemical Exploration (Langfang, China) and CRM IAEA-312 by the International Atomic Energy Agency (Vienna, Austria). The certified values are shown in Table 1.
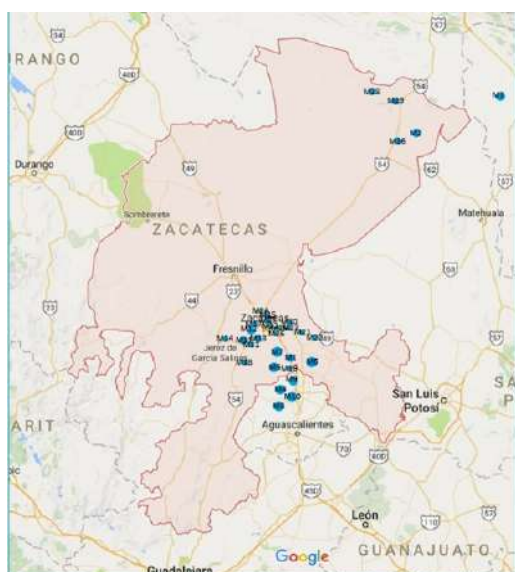

Fig. 2 Location of sampling sites.

4- Analytical Procedure

The flow chart in Figure 3 shows the common critical paths of the analytical techniques for uranium and thorium used in this work.

For ICP techniques (optical and mass), preparing samples for analysis is common to all.

For each analytical technique, specific procedures will be carried out for each analysis according to the instrumental technique requirements that will be discussed later.

X-ray fluorescence. Nine grams of soil weighed, and 4 ml of Elvacite 20% added as a binder. A tablet prepared that will be measured directly on the instrument.

ICP-OES, ICP-MS, ICP-SF-MS. For these techniques, 0.5 g of the sample weighed to which 3 ml of HF, 5 ml of HCl, and 8 ml of HNO_3 added and subjected to microwave digestion. The solution obtained is divided into three parts, from which the appropriate dilutions for each analytical technique are prepared. After each aliquot, it was transferred to a Teflon beaker and heated in a sand bath until dry, avoiding boiling. This removes all acids, including hydrofluoric acid, that can damage glassware. After drying, 5 ml of concentrated HNO_3 added to the Teflon beaker, and the residue dissolved. The Teflon beaker was then heated in a sand bath and allowed to dry for the second time. See Figure 3. Subsequently, 1 ml of concentrated HNO_3 added to dissolve the residue completely. The flask capped at 25 ml. It filtered through a 0.45 µm nylon filter. The calibration curves were made with certified standards with average values of $R^2 \sim 0.9995$.

a-spectrometry (AlphaSpec). For this technique, 2 grams of soil weighed, then 0.1 Bq of ^{232}U and ^{229}Th tracer was added, and it was subjected to digestion. For the digestion of the samples, 3 ml of HF, 5 ml of HCl, and 8 ml of HNO_3 were used. All acids concentrated and reagent grade.

After eliminating the acids by evaporation, the separation stage begins using ion exchange resins UTEVA® for uranium and TEVA® for thorium. A column with UTEVA® chromatographic extraction resin preconditioned with 5 ml of 3M HNO_3. The centrifuge tubes' solution is transferred to the column, allowing it to flow through it by gravity. At this stage, the uranium is retained in the resin. Once the eluent has been collected, 15 ml of 8M HNO_3 added to each column. This last solution removes polonium isotopes, including ^{210}Po that interferes in the measurement of ^{232}U by alpha spectrometry. The alpha particles emitted by the ^{232}U tracer and by ^{210}Po emitted at 5.320 and 5.307 MeV respectively, very close energies, being ^{210}Po a spectrographic interferer.

Th and Np were partially removed from the resin by adding 5 ml of 9M HCl to the column and allowing it to drain. This wash achieves a chlorinated medium in the resin. Traces of plutonium, neptunium, and thorium that had not been removed in previous steps disappear when 20 ml of 5M oxalic acid/0.05M HCl is added to the column. The uranium was eluted from the resin with 15 ml of 1M HCl. The solution containing the uranium is brought to

dryness once 5 ml of HNO_3 have been added. The residue obtained is treated with 2 ml of 0.34 M $NaHSO_4$/1M H_2SO_4 and 5 ml of concentrated HNO_3 and slowly evaporated to dryness, avoiding boiling. The final stage consists of adding 10 ml of the electrolyte solution, which is in a 1M $(NH4)_2SO_4$ solution adjusted to pH 3.5.

Once the sample has transferred to the electrodeposition cell, four drops of thymol blue and ammonia are added until reaching a turn of the indicator to salmon color or an approximate pH between 2 and 3. The distance between the steel disk containing the sample and the platinum electrode has optimized, the sample and the electrode separated at the height of 8 mm. The applied current was 600 mA for 90 minutes.

At the end of this time, 1 ml of ammonia is added, continuing the current flow for one more minute. Once this time has elapsed, the flow of current stops (Figure 3). The cell solution discarded, and the disk (containing uranium) is washed three times with 0.15M NH_3. The cell disassembled, and the steel disk was washed with ethyl alcohol. The disk is dried in an oven at a controlled temperature of 80ºC for 15 minutes to fix it.

The α-spectrometry system calibrated for efficiency and energy with a certified triple source of ^{233}U + ^{239}Pu +

^{241}Am with a total alpha activity of 78.3 ± 1.6 Bq. The disks with the sample and the blank counted in a α-spectrometry system for 300000 s at 15 mm.

In the case of thorium, the following separation procedure has followed. The TEVA® resin (10 g) in the separation cartridge was conditioned with 5 ml of 3M HNO_3. As it contains a large amount of resin, a vacuum must be used to achieve a reasonable flow rate (1-2 ml/min). Once the resin has been conditioned in this nitric medium, the solution (containing the digested soil sample) is transferred to the TEVA® cartridge reservoir. The Th this medium is retained in the resin. The resin is washed with 5 ml of 3M HNO_3, removing the uranium, americium, and neptunium (V). The vacuum cut off, and the effluents discarded. 30 ml of 3M HNO_3 added to the TEVA® cartridge. Then activate the vacuum. Allow the solution to pass entirely through the TEVA® cartridge at 1-2 mL/min. Turn off the vacuum and discard the eluate. Subsequently, 15 ml of 9M HCl is added to the TEVA® cartridge to elute the thorium by activating the vacuum.

Two reference materials have used to verify the results of this study, Table 1

***Table 1** Soil values used as reference material*

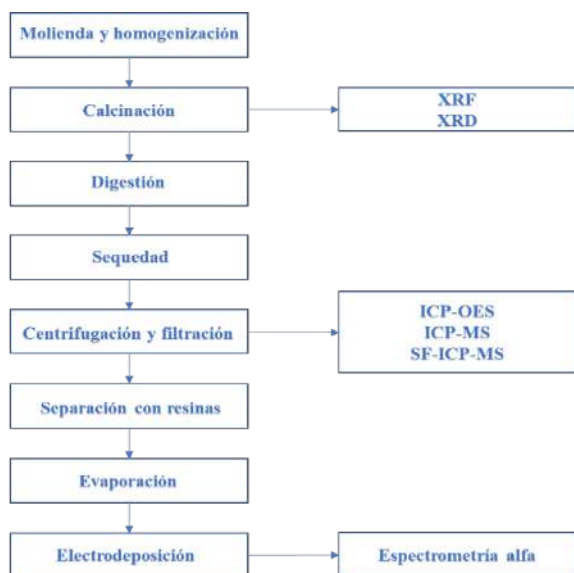|	Valores certificados CRM GSS-2		Valores certificados CRM IAEA-312	
	$C_{muestra}$ (mg·Kg^{-1})	Intervalo de confianza (mg·Kg^{-1})	$C_{muestra}$ (mg·Kg^{-1})	Intervalo de confianza del 95% (mg·Kg^{-1})
Uranio	1.4	1.1-1.7	16.5	15.7-17.4
Torio	16.6	15.8 – 17.4	91.4	81.4 – 101.4

***Fig. 3** Block diagram that summarizes the steps to be carried out in the various analytical techniques. Steps common to all techniques and unique treatments observed for each technique.*

5- Results and Discussion

Table 2 shows a summary of the results of the uranium concentration in the soil by all the techniques used. The

uncertainty of XRF is not included since it is considered a semi-quantitative technique in this work.

It can be seen that the sample L1-M21 presents a concentration higher than the average in all the techniques used in this work. In the rest of the samples, the concentration is more homogeneous.

Table 3 shows the hypothesis tests for paired samples of all the techniques used. It observed that there are no significant differences between ICP-MS and α-spectrometry. There are also no significant differences between ICP-SF-MS and α-spectrometry. In the rest of the techniques, there are significant differences.

In the determination of thorium in soil, it was found that the concentration is more heterogeneous than in uranium. Nevertheless, a higher concentration was observed in Table 4 in the L2-M17 sample obtained by α-spectrometry. However, α-spectrometry has been considered the most reliable technique.

Table 5 shows that the only techniques that do not present significant differences between them are α-spectrometry and ICP-MS. Among all the other techniques, there are significant differences.

The L1-M21 sample taken from Villa de Cos, 70 km north of Zacatecas (23.301015N - 102.354814W) and one kilometer from the town, presents a uranium concentration significantly higher than the general

average. Nevertheless, in thorium, it shows a slight decrease concerning the average concentration. These anomalies are because the sample was collected on a lagoon slope that was formerly saline. The accumulation of uranium in this area is due to the displacement of water towards the lagoon, dragging the sales and water-soluble compounds.

The analytical techniques used in this work to determine uranium and thorium in soil have advantages and disadvantages.

The X-ray techniques used helped characterize the soil. These data allowed us to obtain the soil's particularities and consider the possible interferences during the analysis in the other techniques. Determining the concentration in a semi-quantitative way provides an approximate concentration reference point and preparing the appropriate dilutions for each instrument's sensitivity. This information facilitates the reading of the samples in other analytical techniques, especially in mass spectrometry. The main disadvantage of XRF is the semi-quantitative nature of the data provided

Soil sample preparation for reading in ICP-OES, ICP-MS, and ICP-SF-MS techniques has been simplified, omitting the addition of tracers and the separation or purification of uranium and thorium. When unable to run this step, the sample will contain interfering compounds in the readings, especially when measured in ICP-OES. Mass spectrometry, ICP-MS, and ICP-SF-MS do not present significant problems in the determination of uranium. However, in ICP-SF-MS, thorium values are low compared to the other techniques. Abnormal readings occur due to the presence of thorium mineral complexes that have survived digestion and passage through plasma. If the same solution obtained after digestion is used for the three spectrometric techniques, it is impossible to add isotopic tracer, since ICP-OES does not distinguish masses, only elements.

In the techniques of mass spectrometry and optical emission, the steps in the preparation of the sample have been shortened to the maximum to reduce the risk of analyte loss. The simplification of sample preparation is, in itself, one of the objectives of this work.

α-spectrometry is the most reliable technique to determine uranium and thorium, with the disadvantage of requiring extensive preparation and reading processes and high cost per sample. However, the long process increases the risk of analyte loss, but tracers' use allows us to know this loss and take it into account during the calculation stage. In an emergency, it is not possible to use this technique; first, it will be advisable, due to the urgency, to use a rapid technique, such as ICP-MS, and later, to corroborate the values obtained in both techniques.

The results obtained for uranium by ICP-SF-MS were similar to ICP-MS and alpha spectrometry. However, lower Th values were obtained in thorium concentrations, with a systematic deviation at lower

concentrations by the mass spectrometry technique. This leads to consider the existence of bias due to:

- The use of reagents without sufficient purity for the preparation of samples and dilutions and, above all, different from those used to formulate the calibration line solutions.

Also, having prepared the samples in one laboratory and measured in another.

- Effects originated by subtracting the signal from the reaction target, related to the matrix.

- Not complete digestion of the sample. It is very common in geological samples, especially in sediments and even more if they come from an igneous environment, that we find particles of refractory minerals (spinels, zircons ...) that are not going to dissolve easily by the procedure described in this work and that usually trap in its appreciable interior amounts of U, Th. Filtration can cause small losses of refractories.

6- Conclusions

This work has tested the main analytical techniques for determining uranium and thorium in soil, XRF, ICP-OES, ICP-MS, ICP-SF-MS, and alpha spectrometry, making a study of the optimal instrumental measurement conditions and statistically comparing the results of all of them.

The analytical procedure for spectroscopic measurements by ICP-OES, ICP-MS, and ICP-SF-MS has been simplified to 5 stages, omitting the separation/purification. The determination of uranium by mass spectrometry carried out with these steps has turned out to be fast, reliable, with a reduction in the time used in the analysis and reducing costs for some techniques.

However, the ICP-OES technique presented high uranium and thorium concentration levels in all samples due to ionization interferences due to the presence of high amounts of easily ionizable elements, such as sodium, potassium, and calcium, which generally exist in the soil matrix. In this technique, a satisfactory separation/purification of the analyte is recommended before its instrumental quantification using more steps.

The uranium results obtained by ICP-MS were fast and reliable despite performing a minimum chemical treatment of the sample and not using an isotopic tracer. There were no interferences in the determination of uranium when 0.5 g of soil sample was used. The thorium measurement was unstable due to the high tendency of thorium oxide formation, causing inconsistent readings due to polyatomic interferences.

The ICP-SF-MS technique showed no interference problems in the uranium measurement, although additional dilutions were required to avoid saturating the instrument readings. This technique's main advantages are the high sensitivity, and excellent spectral resolution of the masses, and the simultaneous

detection of different *m/z*. The main drawback is the high analytical cost per sample.

α-spectrometry is the best reliability technique, having the disadvantage of requiring long times for sample preparation, instrumental measurement, and high analytical costs. However, this technique has the advantage of providing isotopic ratios and having low detection limits. The mineralization of the soil sample analyzed by α-spectrometry uses a smaller amount of sample (2 g) with the procedure used in this work, which turns out to be one-fifth of that recommended by the ASTM C1000-11 technique, with excellent results. Good radiochemical separation of uranium was obtained since no presence of other radionuclides was detected in the spectrum.

The ICP-OES technique does not show reliable results; the values obtained were very high compared to other mass spectrometry techniques. Concentration values of 14.3 and 25.4 mg·Kg^{-1} of uranium and thorium respectively were obtained, taking into account in the analysis, the sample with anomalous contents from Villa de Cos. This technique does not admit the reductions of the separation/purification steps proposed in this work.

The ICP-MS technique showed average results of 2.3 and 12.8 mg·Kg^{-1} of uranium and thorium. This instrumental technique is one of the fastest and most reliable. Statistical tests of the null hypothesis in paired samples analyzed by other methods indicate no significant differences between the results of the uranium concentration quantified by ICP-MS and by alpha spectrometry.

The results obtained on uranium and thorium by ICP-SF-MS were 2.6 and 3.2 mg·Kg^{-1}, respectively, with uranium values very close to those obtained by ICP-MS and alpha spectrometry. Lower concentrations of Th were obtained with a systematic deviation at lower concentrations by this technique. However, the sensitivity and linearity of the analytes' signal in the calibration lines are those expected for this technique. This leads to considering the existence of bias due either to the sample's preparation or the introduction of the sample.

The statistical tests of paired samples provide significant differences in uranium determination by ICP-MS and ICP-SF-MS, but these same statistical tests say that there are no significant differences between ICP-SF-MS and alpha spectrometry.

The average concentration of uranium (^{238}U) in surface soil obtained by α-spectrometry was 2.9 and thorium 10.75 mg·Kg^{-1}, this being the most reliable technique, but having the inconvenience of protracted and expensive processes.

Natural uranium has been found in high concentrations in the saline soil of the Villa de Cos area. The Mexican Geological Service (SGM) reported in 2008 a uranium concentration of 10 ppm of uranium in the Villa de Cos area, a value five times higher than the average existing in the earth's crust reported by UNSCEAR. The value obtained in this work (29.7 mg·Kg^{-1} of uranium) is three times greater than the SGM's average value.

The existing uranium concentration in the Villa de Cos's soil is insufficient for its commercial exploitation but promises interest from a radiological perspective. The SGM reports dating from the 1970s speak of an "anomaly" in the concentration of uranium in that area, thus confirming that it is a natural accumulation of uranium and does not come from discharges from other areas. The average concentration deduced from this work for the rest of the sampled areas is 2 mg·Kg^{-1} of uranium, which is very similar to the world average.

The instrumental techniques used in this work have drawbacks in the determination of thorium. The three ICP spectrometric techniques show heterogeneous concentrations. α-spectrometry, despite the drawback of the use of the ^{229}Th tracer due to the low energy "tail down", is the most reliable technique, although not very fast compared to mass spectrometry. There is no problem with isotopic ratios in the thorium measurement since natural thorium is practically monoisotopic (^{232}Th). The background or reference level of thorium for the soil samples from this area is 10.7 mg·Kg^{-1}.

The concentrations of uranium and thorium in Zacatecas soil are in the range of average values published by International Organizations, except Villa de Cos and Jerez for uranium and thorium, respectively.

Acknowledgment

7- References

[1]D. A. Atwood, Ed., *Radionuclides in the Environment*. Wiley, 2010.

[2]E. Bingham, B. Cohrssen, and C. H. Powell, "Ionizing Radiation," in *Patty's Toxicology ,Volumes 1-9*, John Wiley & Sons, Inc., 2012.

[3]UNSCEAR, "Sources and effects of ionizing radiation," United Nations Scientific Committee on the Effects of Atomic Radiation, New York, 2000.

[4]J. Meija *et al.*, "Isotopic compositions of the elements 2013 (IUPAC Technical Report)," *Pure and Applied Chemistry*, vol. 88, no. 3, pp. 293–306, 2016, doi: 10.1515/pac-2015-0503.

[5]IAEA, *Monitorización del medio ambiente y de las fuentes de radiación con fines de protección radiológica*. Viena, 2010.

Table 2 *A general summary of the uranium concentration in surface soil in mg · Kg⁻¹,*
C_{sample}=Concentration of the sample, u=uncertainty.

Samples	XRF	ICP-OES 409.013		ICP-MS ^{238}U		ICP-SF-MS ^{238}U		α-spec ^{238}U	
	C_{sample}	C_{sample}	u	C_{sample}	u	C_{sample}	u	C_{sample}	u
L1-M5	4	6.9	1.1	1.46	0.03	1.9	0.1	1.8	0.4
L1-M9	3	8.5	1.1	1.61	0.03	2	0.1	2.2	0.6
L1-M21	**23**	**39.7**	**1.2**	**12.9**	**0.07**	**15.3**	**0.1**	**29.7**	**6.6**
L2-M1	4	10.5	1.1	2.13	0.03	2.5	0.1	1.1	0.3
L2-M2	6	24.4	1.1	2.04	0.03	2.3	0.1	1.1	0.3
L2-M3	3	13.1	1.1	1.05	0.03	1.3	0.1	1.3	0.6
L2-M4	3	8.4	1.1	2.41	0.03	2.7	0.1	2.9	0.7
L2-M5	3	8	1.1	2.2	0.03	2.5	0.1	2.6	0.6
L2-M6	2	5.6	1.1	1.02	0.03	1.2	0.1	2	0.4
L2-M7	3	11	1.1	1.9	0.03	2.2	0.1	2	0.4
L2-M8	6	8.7	1.1	1.92	0.03	2.2	0.1	2.3	0.5
L2-M9	4	8.8	1.1	2.53	0.03	2.8	0.1	2.7	0.6
L2-M10	4	11.2	1.1	2.59	0.03	2.8	0.1	2.7	0.6
L2-M11	5	10.5	1.1	2.57	0.03	3	0.1	2.5	0.6
L2-M12	4	14.4	1.1	2.93	0.03	2.9	0.1	3.2	0.7
L2-M13	3	11.3	1.1	2.04	0.03	2.3	0.1	2.3	0.5
L2-M14	4	18.8	1.1	2.08	0.03	2.4	0.1	2.1	0.5
L2-M15	3	12.2	1.1	1.39	0.03	1.7	0.1	1.4	0.3
L2-M16	6	29.2	1.1	2.37	0.03	2.7	0.1	3.5	0.8
L2-M17	3	10.6	1.1	1.32	0.03	1.7	0.1	1.5	0.3
L2-M18	4	6.7	1.1	2.67	0.03	2.9	0.1	2.7	0.6
L2-M19	3	13.8	1.1	1.02	0.03	1.3	0.1	1	0.2
L2-M20	3	6.8	1.1	1.6	0.03	1.8	0.1	1.4	0.4
L2-M21	3	14.1	1.1	3.14	0.03	3.5	0.1	2.4	0.5
L2-M22	2	8.9	1.1	1.65	0.03	1.2	0.1	1.7	0.4
L2-M23	4	14.2	1.1	2.45	0.03	2.6	0.1	2.2	0.5
L2-M24	3	21.4	1.1	0.54	0.03	0.8	0.1	0.4	0.1
L2-M25	4	23.2	1.1	1.99	0.03	1.9	0.1	1.9	0.4
L2-M26	3	19	1	1.55	0.03	1.8	0.1	1.5	0.3
L2-M27	4	14.3	1.1	2.48	0.03	2.8	0.1	2.9	0.6
L2-M28	7	20.5	1.1	3.46	0.04	3.8	0.1	3.7	0.8
L2-M29	6	29.2	1.1	2.19	0.03	2.5	0.1	2.4	0.5
L2-M30	4	10.5	1.1	1.86	0.03	2	0.1	1.7	0.4
Average	**4.42**	**14.38**	**1.1**	**2.33**	**0.03**	**2.64**	**0.1**	**2.93**	**0.67**
Without the abnormal sample	**3.84**	**13.58**	**1.1**	**2.01**	**0.03**	**2.25**	**0.1**	**2.1**	**0.48**

Table 3 *Summary of hypothesis tests for paired samples of all the techniques used for uranium.*

Rigged Samples For Uranium	Signs test		Signed Ranges Test	
	P value	Conclusion	P value	Conclusion
XRF – ICP-OES	5.45038E-9	H0 rejection	1.75051E-7	H0 rejection
XRF – ICP-MS	3.80727E-8	H0 rejection	1.91114E-7	H0 rejection
XRF – ICP-SF-MS	6.35271E-8	H0 rejection	3.17867E-7	H0 rejection
XRF – AlphaSpec	6.35271E-8	H0 rejection	6.35271E-8	H0 rejection
ICP-OES – ICP-MS	5.45038E-9	H0 rejection	1.75662E-7	H0 rejection
ICP-OES – ICP-SF-MS	9.10858E-9	H0 rejection	2.58883E-7	H0 rejection
ICP-OES – AphaSpec	5.45038E-9	H0 rejection	1.75509E-7	H0 rejection
ICP-MS – ICP-SF-MS	0.0000022164	H0 rejection	0.00000546952	H0 rejection
ICP-MS – AlphaSpec	0.0667527	Accepted H0	0.0513906	Accepted H0
ICP-SF-MS– AlphaSpec	0.111611	Accepted H0	0.133438	Accepted H0

Table 4 *General summary of thorium concentration in surface soil in mg Kg^{-1}*

Samples	XRF	ICP-OES 409.013		ICP-MS		ICP-SF-MS		α-spec ^{232}Th	
	C_{sample}	C_{sample}	u	C_{sample}	u	C_{sample}	u	C_{sample}	u
L1-M5	12	13.4	0.5	8.7	0.02	1.8	0.1	10.6	0.8
L1-M9	14	17.3	0.5	8	0.02	1.7	0.1	10.3	0.8
L1-M21	11	8	0.5	7.8	0.02	2	0.1	2.7	0.2
L2-M1	19	19	0.5	9.4	0.02	2.2	0.1	17.1	1.4
L2-M2	9	22.6	0.5	26.4	0.03	6.1	0.1	6.1	0.3
L2-M3	7	**57.8**	0.5	3.4	0.02	1	0.1	6.9	0.6
L2-M4	25	32.1	0.5	25.5	0.03	5.5	0.1	20.9	1.2
L2-M5	18	25.9	0.5	15.6	0.02	3.5	0.1	14.3	0.9
L2-M6	15	17.7	0.5	6.7	0.02	1.7	0.1	10.7	0.6
L2-M7	14	27.6	0.5	9.4	0.02	2.2	0.1	12.6	0.9
L2-M8	26	51	0.5	9.5	0.02	2.9	0.1	19.8	1.3
L2-M9	18	32.4	0.5	7	0.02	2.2	0.1	19.3	1.4
L2-M10	17	21.2	0.5	9.7	0.02	3	0.1	19.7	2.1
L2-M11	16	21.3	0.5	10.8	0.02	2.3	0.1	13.1	0.8
L2-M12	16	27.5	0.5	14.5	0.02	3.3	0.1	10.2	0.5
L2-M13	17	28	0.5	8.6	0.02	2	0.1	13.1	0.9
L2-M14	16	27.7	0.5	61	0.06	**13.6**	0.1	11.5	0.5
L2-M15	8	27.6	0.5	13.4	0.02	3.7	0.1	4.6	0.3
L2-M16	7	9.5	0.5	0.4	0.02	0.5	0.1	3.5	0.2
L2-M17	13	25.7	0.5	5.6	0.02	1.6	0.1	**28.5**	2.1
L2-M18	20	15	0.5	16.8	0.02	3.8	0.1	7.9	0.6
L2-M19	6	38	0.5	7.9	0.02	2.1	0.1	2.9	0.2
L2-M20	10	11.7	0.5	8.1	0.02	2	0.1	8.1	0.6
L2-M21	16	23.5	0.5	**28.2**	0.03	6.8	0.1	11.7	0.6
L2-M22	5	39.5	0.5	4.5	0.02	2.1	0.1	5.1	0.4
L2-M23	15	22.7	0.5	21.9	0.03	5.2	0.1	10.1	0.5
L2-M24	3	39.6	0.5	2.4	0.02	1.2	0.1	0.5	0.1
L2-M25	7	17.9	0.5	23.3	0.03	5.3	0.1	4.9	0.3
L2-M26	7	16.4	0.4	21.6	0.03	5.2	0.1	4.5	0.4
L2-M27	15	19.5	0.5	8.6	0.02	2.2	0.1	13.8	1.2
L2-M28	19	35.6	0.5	8.5	0.02	4.3	0.1	14.6	0.8
L2-M29	**35**	24.9	0.5	0.6	0.02	2.3	0.1	3.5	0.4
L2-M30	14	22.3	0.5	8.6	0.02	2.2	0.1	11.8	0.9
Average	**14.24**	**25.45**	**0.50**	**12.80**	**0.02**	**3.26**	**0.10**	**10.75**	**0.75**

Table 5 *Summary of hypothesis tests for paired samples of all the techniques used for thorium.*

Rigged Samples For Thorium	Signs test		Signed Ranges Test	
	P value	Conclusion	Valor -p	P value
XRF – ICP-OES	0.0000022164	Rechazo H0	0.00000507991	Rechazo H0
XRF – ICP-MS	5.45038E-9	Rechazo H0	1.75356E-7	Rechazo H0
XRF – ICP-SF-MS	5.45038E-9	Rechazo H0	1.75356E-7	Rechazo H0
XRF – AlphaSpec	0.000030927	Rechazo H0	0.0000166933	Rechazo H0
ICP-OES – ICP-MS	0.000465346	Rechazo H0	0.0000472191	Rechazo H0
ICP-OES – ICP-SF-MS	5.45038E-9	Rechazo H0	1.75585E-7	Rechazo H0
ICP-OES – AphaSpec	3.80727E-8	Rechazo H0	2.35864E-7	Rechazo H0
ICP-MS – ICP-SF-MS	2.38747E-7	Rechazo H0	2.45663E-7	Rechazo H0
ICP-MS – AlphaSpec	0.49896	Accepted H0	0.83137	Accepted H0
ICP-SF-MS– AlphaSpec	0.0000497876	Rechazo H0	0.00000140678	Rechazo H0