



## Determination of $^{234}\text{U}$ and $^{238}\text{U}$ Activities in Soil by Liquid Scintillation and High-Resolution Alpha Spectrometry

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### ARTICLE INFORMATION

Received: September 24, 2020  
Accepted: January 07, 2021  
Published Online: February 10, 2021

#### Keywords:

Uranium, Alpha spectrometry, IAEA-375



DOI: [10.15415/jnp.2021.82014](https://doi.org/10.15415/jnp.2021.82014)

### ABSTRACT

Uranium is a radioactive element with a special presence in the rocks, waters, sediments, soils, and plants at the state of Chihuahua. The activity ratio of  $^{238}\text{U}/^{234}\text{U}$  is used to explain the uranium transport by surface water and its deposition in arid environments. In this work, the activity concentration of natural U isotopes is determined by PERALS liquid scintillation and high-resolution alpha spectrometry (AS, Canberra camera 7401VR) in the Environmental Radiological Surveillance Laboratory (LVRA) at CIMAV, Chihuahua. Uranium is extracted from soils through the scintillating liquid extractor URAEX for PERALS, with chemical recovery (CR) of 80 – 85 %, and through the ion exchange resin UTEVA + electrode position by the Hallstadius method, with CR of 85 – 90 %, for AS. The procedures of  $^{234}\text{U}$  and  $^{238}\text{U}$  activity concentration (AC) determination in soils were validated by their application to the certified reference material IAEA-375. The resulting values were in the reference range of the certified or informative values. Both procedures were applied to 6 representative soil samples, with AC of the same order of magnitude or greater, and similar CR and compatible results. Both procedures are satisfactory for the purposes of LVRA research and in general.

### 1. Introduction

In the State of Chihuahua, 56 uranium deposits locations have been recognized. Recently two important deposits of uranium minerals, Victorino and San Marcos I, were characterized [1-2]. Bazán Barrón in 1978 [3] described the uranium deposits in the state of Chihuahua and the Mexican Republic, mainly indicating the genesis and deposition of molybdenum and uranium minerals, particularly in the Sierra de Peña Blanca in the municipality of Aldama, Chihuahua.

Metallic uranium oxidizes immediately, and it does not exist in nature. Uranium presents five oxidation states, but only two are stable. The tetravalent species U(IV) forms  $\text{UO}_2$ , hydroxides, hydrated fluorides, and phosphates of exceptionally low solubility. The hexavalent species U(VI) forms the uranyl or uranyl ( $\text{UO}_2$ )<sup>+2</sup> ion, the  $\text{UO}_3$  and the  $\text{U}_3\text{O}_8$  form. The uranyl ion is soluble in water [4].

The health damage associated with uranium depends on its chemical and physical form and the route of exposure. The uranium chemical toxicity is the main cause of concern because soluble uranium causes damage to kidney tissue [5].

Uranium, under reduction conditions, acquires a +4 valence and is insoluble; under oxidation conditions, it takes valence +6 and forms the uranyl ion ( $\text{UO}_2$ )<sup>+2</sup>, soluble. Igneous rocks and minerals commonly present a uranium +4 oxidation state [4]. The  $^{234}\text{U}/^{238}\text{U}$  activity ratio (AR) is often far from the equilibrium value in water and can also occur in rocks [6]. This disequilibrium is related to the phenomenon of change in oxidation status due to alpha decay or the effects of “recoil” [4]. The uranium activity in soils is approximately 15 Bq / kg of  $^{238}\text{U}$  (about 1.2 mg / kg) with a typical activity of 10–50 Bq / kg (0.4 to 2 mg / kg) [7- 8].

The purpose of this work is to contrast the characteristics and results of the extraction and determination methods for the activity concentrations of natural uranium isotopes by liquid scintillation and high resolution alpha spectrometries, applied to typical soils of Chihuahua, which are also applied to sediments. For this, the techniques were applied for the determination of activity concentrations of  $^{234}\text{U}$  and  $^{238}\text{U}$  in a certified soil reference material and to 6 laboratory samples. The discussion of results allowed to suggest the relative uncertainties of the activity concentration determinations, appropriate for the applied methods.

## 2. Materials and Methods

### 2.1. Samples

The certified reference material IAEA-375 is a soil collected from Brjansk region, Russia, in July 1990 by the International Atomic Energy Agency Seibersdorf Laboratory. The abundant material was processed in the laboratory's facilities and distributed in about 50 laboratories around the world for an intercomparing exercise. The complete description, sample processing, instructions and reference information and informative values of the soil, among other details, are described in the Reference Sheet IAEA / AL / 375[9].

Six soil samples were obtained in an area of the town of Jimenez, Chihuahua. They were used to verify the repeatability of procedures for determining the activity of the isotopes  $^{238}\text{U}$  and  $^{234}\text{U}$ . The samples were air-dried before undergoing the procedures described below.

### 2.2. Radiochemical Procedure to Determine the Concentration of $^{238}\text{U}$ and $^{234}\text{U}$ in Soil Samples and Reference Material IAEA-375

Samples were traced with a certified activity solution of  $^{232}\text{U}$  from the NPL of the United Kingdom to quantify the activities of natural uranium isotopes. Then, they were digested with  $\text{HNO}_{3(c)}$  (J.T. Baker),  $\text{HClO}_{4(c)}$  (J.T. Baker), and  $\text{HF}_{(c)}$  (Meyer), in Parr acid digestion vessels model 4745, at  $145^\circ\text{C}$  for 9 hours. The uranium activities of the natural uranium isotopes were calculated in both procedures using the ratio of intensities of the alpha transitions of the respective isotopes (equation 1).

Two ways of separation and purification of U were used; both procedures are detailed in Figure 1.

The first procedure was measured by liquid scintillation (LS) in a PERALS (ORDELA, Inc.) spectrometer. The procedure described by McDowell [10] was applied, the extracting scintillation liquid URAEX<sup>®</sup> (ETRAC) was used.

The second one was measured by the Alpha Spectroscopy (AS) Canberra camera 7401VR. To guarantee the extraction of uranium only, the solution resulting from digestion was filtered through a UTEVA<sup>®</sup> ion exchange resin (Eichrom) [11]. The extracted uranium solution was electrodeposited on a stainless steel planchette by the Hallstadius method [12]. The planchette was placed in an alpha chamber 7401VR under vacuum and measured for 48 hours.

To verify quality, the analysis of the isotope  $^{238}\text{U}$  content in the reference material was performed by inductively coupled plasma mass spectrometry (ICP-MS). A fraction of the IAEA-375 sample was homogenized and guaranteed a particle size of less than  $2\ \mu\text{m}$ . Then 0.2 g were taken from this sample. Microwave digestion was performed, adding 10 ml of  $\text{HNO}_3$  (c) and 5 ml of  $\text{HCl}$  (c), and the sediment treatment and digestion method established by EPA 3051 was applied.

### 2.3. Activity Calculation

Activity is determined separately for uranium isotopes ( $^{238}\text{U}$  and  $^{234}\text{U}$ ) present in the samples, applying equation:

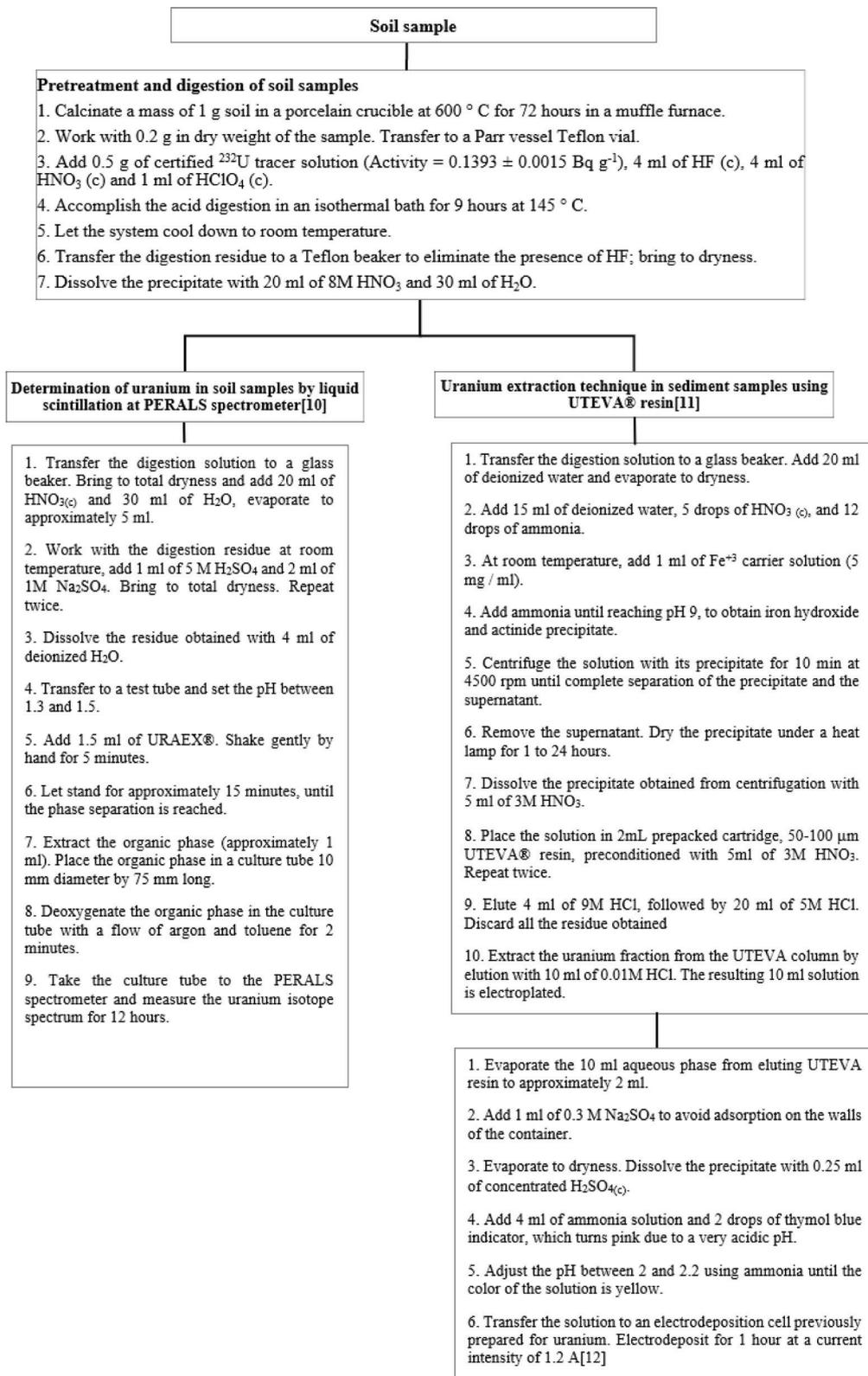
$$A = \text{cps}_{\alpha \text{ isotope}} A_{\text{tracer}} / \text{cps}_{\alpha \text{ tracer}} \text{ (Bq)} \quad (1)$$

Where  $\text{cps}_{\alpha \text{ isotope}}$  is the counting rate of the isotope of interest registered in the sample measurement,  $A_{\text{tracer}}$  is the tracer activity ( $^{232}\text{U}$ ) added to the sample and  $\text{cps}_{\alpha \text{ tracer}}$  is the counting rate of tracer added registered in the sample measurement.

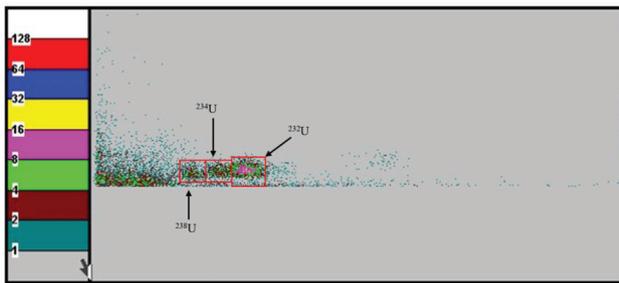
## 3. Results and Discussion

Uranium isotopes spectra are presented in Figures 2 and 3. In Figure 2 the energies are presented on the abscissa and the pulse time on the ordinate. The horizontal cut is made so as not to show the background of beta particles, whose pulses are shorter than those, corresponding to alpha particles. The peaks of  $^{232}\text{U}$ ,  $^{234}\text{U}$  and  $^{238}\text{U}$  isotopes are found at energies 5322 keV, 4772 keV and 4198 keV, respectively, in both Figure 2 and 3.

The high resolution of the AS spectrum is contrasting compared to the spectrum obtained by liquid scintillation. The extraction and measurement procedure using the liquid scintillation method is less complicated and shorter than those of AS, and for this reason its use is usually recommended for routine work or when the number of samples to be processed is large. Table 1 shows the results for the IAEA-375 CRM, for comparison of the three procedures applied.

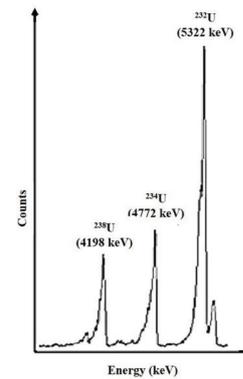


**Figure 1:** Flow chart of the sample pretreatment and digestion, common for LS and AS determinations of  $^{238}\text{U}$  and  $^{234}\text{U}$  activities, and details of the respective chemical procedures for each type of measurement.



**Figure 2:** Spectrum of the reference material IAEA-375 with  $^{232}\text{U}$  tracer in the PERALS spectrometer. The colors of the pixels correspond to the recorded pulses, according to the scale of the left band. The rectangles correspond to the regions of interest (ROI).

The activity and mass concentration values reflected in Table 1 are within the limits reported in the Reference Sheet of the IAEA-375 certified material, thereby validating the results of the soil samples analyzed by the two procedures. The  $^{238}\text{U}$  concentrations were calculated by the average of the activities of the two repetitions of each method. The relative uncertainty is 2%. The certified value of the uranium mass of IAEA-375 has a confidence interval that implies a relative standard deviation of 5.2%, with results obtained by 30 laboratories. The recommended



**Figure 3:** Spectrum of the reference material IAEA-375 with the  $^{232}\text{U}$  tracer in the alpha spectrometer.

value of the activity of  $^{238}\text{U}$  for the IAEA-375 material has a confidence interval that implies a relative standard deviation of the order of 10% with results obtained by 7 laboratories.

Table 2 shows the activity concentration results for six soil samples, obtained by both procedures, the extraction using the UTEVA<sup>®</sup> resin and high-resolution alpha spectrometry, as well as using the URAEX<sup>®</sup> extracting scintillator + PERALS spectrometer.

**Table 1:** Concentration and concentration activity results from the IAEA-375 reference material by the different procedures and equipment PERALS liquid scintillation, high resolution alpha spectrometry and ICP-MS.

Isotope	Activity	Activity concentration	AR	IAEA-375	% CR
<b>URAEX extraction technique</b>					
$^{238}\text{U}$	4.96	22.80(2)	0.94	19.0 - 29.8	91.9
$^{234}\text{U}$	3.13	21.53(2)		17-32.5	
$^{238}\text{U}$	4.33	21.76(1)	0.90	19.0-29.8	95.52
$^{234}\text{U}$	3.58	19.64(1)		17-32.5	
$^{238}\text{U}$ mass mean value (mg/kg)		1.80(4)		1.66-2.05 <sup>a</sup>	-
<b>Uranium extraction technique using UTEVA</b>					
$^{238}\text{U}$	4.61	22.11(2)	0.77	19.0-29.8	96.73
$^{234}\text{U}$	3.55	17.04(2)		17-32.5	
$^{238}\text{U}$	4.26	20.46(1)	0.86	19.0-29.8	95.02
$^{234}\text{U}$	3.67	17.61(1)		17-32.5	
$^{238}\text{U}$ mass mean value (mg/kg)		1.72(7)		1.66-2.05 <sup>b</sup>	
<b>Determination of total uranium by ICP-MS</b>					
ppm (mg/kg)		1.8		1.66-2.05 <sup>b</sup>	

(a), (b) range values from the reference sheet of the reference material IAEA-375. CR-chemical recovery values. AR – activity ratio of  $^{234}\text{U}/^{238}\text{U}$ . The uncertainty value of the last figures is presented in parentheses.

**Table 2:** Comparison of U activity concentrations obtained by liquid scintillation and alpha spectrometry methods in soil samples.

Samples	ALPHA SPECTROMETRY				PERALS		
	Isotope	Activity concentration (Bq/g)	U total (Bq/g)	AR	Activity concentration (Bq/g)	U total (Bq/g)	AR
Soil-1	<sup>234</sup> U	0.419(4)			0.404(5)		
	<sup>235</sup> U	0.003(4)	<b>0.704(7)</b>	1.48	ND	<b>0.676(7)</b>	1.48
	<sup>238</sup> U	0.282(4)			0.272(5)		
Soil-2	<sup>234</sup> U	0.089(8)			0.081(9)		
	<sup>235</sup> U	0.004(8)	<b>0.164(14)</b>	1.25	ND	<b>0.143(13)</b>	1.32
	<sup>238</sup> U	0.071(8)			0.061(2)		
Soil-3	<sup>234</sup> U	0.035(2)			0.030(2)		
	<sup>235</sup> U	0.002(2)	<b>0.064(3)</b>	1.29	ND	<b>0.057(3)</b>	1.11
	<sup>238</sup> U	0.027(2)			0.027(2)		
Soil-4	<sup>234</sup> U	0.048(6)			0.059(8)		
	<sup>235</sup> U	0.000(6)	<b>0.093(8)</b>	1.09	ND	<b>0.101(11)</b>	1.43
	<sup>238</sup> U	0.044(6)			0.041(8)		
Soil-5	<sup>234</sup> U	0.036(1)			0.026(2)		
	<sup>235</sup> U	0.002(1)	<b>0.060(2)</b>	1.63	ND	<b>0.051(3)</b>	1.04
	<sup>238</sup> U	0.022(1)			0.025(2)		
Soil-6	<sup>234</sup> U	0.035(1)			0.028(5)		
	<sup>235</sup> U	0.015(1)	<b>0.078(2)</b>	1.25	ND	<b>0.052(7)</b>	1.16
	<sup>238</sup> U	0.028(1)			0.024(5)		

\* ND - Activity not detected by the device. AR – activity ratio of <sup>234</sup>U/ <sup>238</sup>U. The uncertainty of the last figure is presented in parentheses.

The two methods applied to the soil samples in Table 2 produce values for the U isotopes activities that show uncertainties resulting from the counting rate statistics. The PERALS and alpha spectrometry values differ from the average of the two methods by a relative deviation between 2 and 8%, not considering those uncertainties. The application of the *Student's t test of paired samples* to the results of the total uranium activity concentrations of the 6 soils studied causes a statistical result of the values of the two procedures as different with value of  $P < 0.001$ , since the variance within the groups is small.

The difference in values between the two methods is due to the chemical differences in the uranium extraction procedures and the physical differences in the detection of alpha particles. These cause more significant uncertainties than the counting statistics. These latter uncertainties can be neglected in comparison with those of physical or chemical origin. The activity results for <sup>234</sup>U and <sup>238</sup>U of our methods should be reported with 10 % relative uncertainties, and not with the ones resulting from the uncertainty of the counting rate.

Table 2 also shows the isotopic activity ratio values AR (<sup>234</sup>U / <sup>238</sup>U) for the studied samples, with all values

AR>1. This isotopic relationship results can be explained by the fact that <sup>234</sup>U atoms have been subjected to the called “recoil” effect of the alpha decay resulting in oxidation conditions where they are more soluble than <sup>238</sup>U [13].

## Conclusions

The radiochemical methods for uranium extraction from soils through the scintillating liquid extractor URAEX for the PERALS and through the ion exchange resin UTEVA, for the determination of <sup>238</sup>U and <sup>234</sup>U implemented for soil were successfully validated, through its satisfactory application to the IAEA-375 CRM.

As the activity values of <sup>234</sup>U and <sup>238</sup>U of the CRM IAEA-375 have a confidence interval that implies a 10% relative uncertainty, it is suggested that the results of our methods for those activities should be reported with the same 10% relative uncertainties, and not with the ones, resulting from the counting rate uncertainties.

All these considerations allow us to conclude that the application of the methods described for the determination of uranium in soils in the LVRA produce reliable values.

## Competing Interests

The authors declare that there is no conflict of interests.

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## Journal of Nuclear Physics, Material Sciences, Radiation and Applications

Chitkara University, Saraswati Kendra, SCO 160-161, Sector 9-C, Chandigarh, 160009, India

Volume 8, Issue 2

February 2021

ISSN 2321-8649

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