

A combined method of neutron activation analysis and radiometric measurements for ^{234}U and ^{238}U determination in soil samples of low uranium concentration

Eduardo Montoya^{1,*}, Pablo Mendoza¹, Patricia Bedregal¹, Oscar Baltuano¹, Isaac Cohen^{2,3}

¹ División de Técnicas Analíticas Nucleares, Instituto Peruano de Energía Nuclear, Av. Canadá 1470, Lima 41, Perú

² Universidad Tecnológica Nacional, Facultad Regional Avellaneda, Secretaría de Ciencia, Tecnología y Posgrado. Av. Mitre 750, 1870 Avellaneda, República Argentina

³ Universidad Tecnológica Nacional, Facultad Regional Buenos Aires, Departamento de Ingeniería Química, Av. Medrano 951, C1179AAQ Buenos Aires, República Argentina

Resumen

Se ha desarrollado un método que combina el análisis por activación neutrónica instrumental y la espectrometría alfa de alta resolución, para la determinación de las actividades de ^{234}U y ^{238}U en muestras geológicas de bajo contenido de uranio. El contenido de ^{238}U se determina mediante análisis por activación neutrónica según el método del k sub cero, mientras que la relación $^{234}\text{U} / ^{238}\text{U}$ se mide mediante espectrometría alfa, después del aislamiento y electrodeposición del uranio extraído mediante una lixiviación con HCl 6M. La principal ventaja del método es la simplicidad de las operaciones químicas, incluyendo el hecho de que las etapas destinadas a asegurar el mismo estado químico para el trazador y las especies de uranio presentes en la muestra, no es necesaria. El método se ha aplicado a muestras de suelo de sitios de la costa norte del Perú. La concentración encontrada de uranio varía entre 3 a 40 mg/kg y la composición isotópica corresponde a uranio natural, con una incertidumbre de aproximadamente 10%.

Abstract

A method that combines the use of non-destructive neutron activation analysis and high-resolution α spectrometry has been developed for determination of the activities of ^{234}U and ^{238}U in geological samples of low uranium content. The ^{238}U content is determined by k_0 -based neutron activation analysis, whereas the $^{234}\text{U} / ^{238}\text{U}$ relationship is measured by α spectrometry after isolation and electrodeposition of the uranium extracted from a lixiviation with 6 M HCl. The main advantage of the method is the simplicity of the chemical operations, including the fact that the steps destined to assure similar chemical state for the tracer and the uranium species present in the sample are not necessary. The method was applied to soil samples from sites of the north Peru coast. Uranium concentration range 3 to 40 mg/kg and the isotopic composition correspond to natural uranium, with about 10 % uncertainty.

1. Introduction

Quantitative analysis of the isotopic composition of uranium is important for environmental, geochemical and nuclear safeguard purposes [1-3].

The relationship between ^{234}U and ^{238}U in a closed system should be constant, since both are part of a secular equilibrium with the latter as the beginner of the chain. This situation can be different in natural systems, where the slightly different geochemical behavior of thorium and protactinium, in

comparison with uranium, may cause some fractioning. For instance, $^{234}\text{U}/^{238}\text{U}$ activity ratios ranging from 0.5 to 1.2 have been found in soils [2,4]. Some authors proposed, as an additional cause for disequilibrium, that ^{234}U is more easily lixiviated than ^{238}U , after the recoil of the nucleus when emitting an alpha particle [5,6].

The well established technique of alpha spectrometry is still the option for determination of $^{234}\text{U}/^{238}\text{U}$ ratios in soils and

* Corresponding author: emontoya@ipen.gob.pe

other geological samples with low uranium concentration. The validation of a method using high resolution ICP-OES has been recently published [1], as a convenient fast alternative to the *mass spectrometry based techniques such as TIMS, MC-ICP-MS and single collector UICP-MS*, but it requires uranium concentrations of about 100 mg.l^{-1} in the final solution and is not sensitive enough for the determination of the natural isotope ^{234}U .

The traditional method for alpha spectrometry is tiresome and time-consuming. Besides the fact that the final measurement very often requires times of the order of few hundred hours, the chemical procedures to isolate uranium from all interferences, leading to a final electrodeposited very thin film of pure uranium onto a clean steel dish, are somewhat complicated [7-10]. Moreover, they are not quantitative, so that ^{232}U [2,7,9,10] or even ^{233}U [8] are traditionally used as a tracers, to assess the chemical yield. As a basic requisite, uranium has to be in the same oxidation state and chemical form both tracer and in the sample, fact that complicates the wet chemistry used to bring the element into solution.

The present work deals with a new approach for simple, accurate and reliable determination of ^{234}U and ^{238}U activities in soils having low uranium concentration, which consists of a combined method with two steps: 1) Determination of the ^{238}U content by k_0 -based neutron activation analysis [11,12]; 2) Measurement of the $^{234}\text{U}/^{238}\text{U}$ relationship by α spectrometry after isolation and electrodeposition of the uranium extracted from a lixiviation with 6 M HCl. The possibility of using the second procedure is a direct derivation of the utilization of the first one: since the ^{238}U content is determined independently of the measurement by alpha spectrometry, there is no need of quantitative separations or alternative measurement of the chemical yield, this implying that the accomplishment of all chemical steps destined to assure similar chemical state for the tracer and the uranium species present in the sample are not necessary.

2. Experimental

The determination of ^{238}U was carried out by k_0 -INAA, in the conditions described by the authors in previous works [11,12].

Analytical grade chemicals were used for the isolation of uranium, as the initial step for the measurements by α spectrometry. Samples of 2 g - 20 g were leached, depending on the mass of the samples, with 20 ml to 200 ml of HCl 6M, by about ten days, with one cycle of warming (just below the boiling point) and shaking every morning. After decantation, the clear liquid fractions were heated and their volumes were reduced to 20 ml; in order to precipitate the lixiviated actinides together with the hydrated iron oxides, the medium was made alkaline with concentrated NH_4OH . After centrifugation, the liquid fractions were discarded and the precipitates dissolved in 20 ml of HCl 6M. Then, Fe(III) was extracted once with 20 ml of ethyl acetate. The aqueous fractions were evaporated to almost dryness and the residues dissolved in 10 ml of HCl 8M. These solutions were percolated through small chromatographic columns, packed with 4.2 ml of 200 – 300 mesh Dowex 1 – X8 resin. After washing the columns with 20 ml of HCl 8M [13], uranium, together with the remaining Fe(III) were eluted with 40 ml of HCl 0.8 M. The obtained liquid fractions were evaporated to almost dryness and the residues were dissolved with 10 ml of HCl 6M. The remaining Fe(III) was extracted again with 10 ml of ethyl acetate and the aqueous fractions were mixed with 10 ml of H_2SO_4 2M and evaporated to dryness. The dry residues were dissolved with 10 ml of the electroplating solution and electroplated onto clean steel disks, following the method described by LEE *et al* [10]. The steel disks were cleaned by electro polishing before electroplating, as described by Galán-López *et al.* [14]. Finally, the electrodeposited uranium was counted by 10000 to 300000 seconds, using a homemade high resolution alpha spectrometer, the characteristics of which will be published elsewhere [15].

3. Results and Discussion

The results obtained for a set of samples of soil, from a desert area of the northern coast of Peru, are summarized in Table 1. It can be seen that the isotopic composition

corresponds to natural uranium, result expected in a dry environment. The INAA methods used at the authors' laboratory have been already validated [11,12] for the determination of the overall element composition. In connection with the specific determination of ^{238}U , a certified standard reference material (NIST SRM 1633b Coal Fly Ash) was analyzed together with the samples. The concentration found, in $\text{mg}\cdot\text{kg}^{-1}$, was 9.2 ± 1.2 ($k=2$), which is in reasonable agreement with the reference value, 8.79 ± 0.36 ($k=2$).

The main source of uncertainty, in the uncertainty budget of the combined measurements of INAA and α spectrometry, corresponds to the k_0 -INAA determination of ^{238}U .

Figure 1 shows that high-resolution α spectra can be obtained with very good quality for natural samples with low uranium content by the homemade instrumentation. An alpha spectrum of uranium from a commercial atomic standard solution can be seen in Figure 2. The very low ratio of $^{234}\text{U} / ^{238}\text{U}$ activities indicates that the solution was prepared using depleted uranium, fact not reported by the manufacturer. A similar result for a commercial ICP – OES standard solution has been reported recently [1]. Taking into account the increasing importance of the quantitative determination of the isotopic composition of uranium in samples from diverse origins, a reasonable suggestion to the manufacturers of commercial uranium standard solutions is to provide the isotopic composition of their reagents.

4. Conclusions

Whenever available, INAA is a simple, reliable, specific and accurate technique for quantitative determination of ^{238}U . It has no limitations of incomplete sample dissolution or non quantitative chemical yields. Thus, the possible association: INAA - α spectrometry, is a valid option for the demanding task of determining the isotopic composition of uranium in samples with low and very low contents of this element.

The need to perform very long measuring times is a major limitation of α spectrometry, when compared with ICP-OES, which allows

completion of a measurement in a couple of minutes [1], although without considering the step of sample dissolution. Nevertheless, it is not yet possible to detect ^{234}U by ICP – OES, because of its low isotopic abundance. On the other hand, very good high-resolution α spectrometers can be manufactured at significant low prices [15,16] and, consequently, many analytical laboratories can have at their disposal the equipment necessary to process simultaneous batches of several samples.

In conclusion, at the present state of the art and regarding their comparative advantages and disadvantages, α spectrometry and ICP – OES become complementary, rather than competitive.

5. Acknowledgment

The authors wish to thank O. Baltuano and Y. Hernández for the design and manufacturing of the alpha spectrometer used in the present work.

6. References

- [1] Krachler M, Carbol PJ. Anal. At. Spectrom. 2011; 26: 293-299.
- [2] Radenković MB, Cupać SA, Joksić JD, Todorović DJ. Depleted uranium mobility and fractionation in contaminated soil (Southern Serbia). Environ. Sci. Pollut. Res. 2008; 15(1):61-67.
- [3] Salar Amoli HS, Barker J. Accurate determination of uranium in soils using electroplating and closed-vessels microwave digestion methods. Chem. Anal. (Warsaw). 2007; 52:35-41.
- [4] Goldstein SJ, Rodriguez JM, Lujan N. Health Phys. 1997; 72:10-18.
- [5] Bourdon B, Turner S, Henderson GM, Lundstrom CC. Rev. Mineral Geochem. 2003; 52:1-21.
- [6] Fleischer RL, Raabe OG. Geochim. Cosmochim. Acta. 1975; 42: 973-978.
- [7] Serdeiro NH, Marabini S. A Rapid Method for determination of uranium, americium, plutonium and thorium in soil samples. In: 11th International Congress on the International Radiation Protection Association. 2004 May 23-28; Spain: Madrid; 2004.
- [8] Zarki R, Elyahyaoui A, Chiadli A. Appl. Radiat. Isot. 2001; 55:167-174.
- [9] Zarki R, Elyahyaoui A, Chiadli A.

Radiochim. Acta. 2004; 92:161-169.

[10] Lee MH, Kim CJ, Boo BH. Bull. Korean Chem. Soc. 2000; 21, 175.

[11] Bedregal P, Mendoza P, Ubillús M, Montoya E. Nucl. Instrum. Meth. Phys. Res. A. 2010; 622:419-424.

[12] Montoya E, Bedregal P, Mendoza P, Ubillús M, Torres B, Cohen IM. Nucl. Instrum. Meth. Phys. Res. A. 2010; 622:381-384.

[13] Narayanan UI, Mason PB, Zebrowski JP, Rocca F, Iris W. The Quantitative Ion Exchange Separation of Uranium from Impurities. U.S. Department of Energy, New Brunswick Laboratory; 1995 March. Report No. NBL-331.

[14] Galán-López M, Martín-Sánchez A, Tosheva Z, Kies A. Comparisons of LSC and alpha spectrometry methods applied to environmental samples. In: Stanislaw Chalupnik S, Schönhofer F, Noakes J, eds. LSC 2005, Advances in Liquid Scintillation Spectrometry: Proceedings of the 2005 International Liquid Scintillation Conference, Katowice, Poland. 17-21 October, 2005. Tucson: Radiocarbon; 2006. p.165-170.

[15] Baltuano O, Hernandez Y, Mendoza P, Montoya E. A homemade high resolution alpha spectrometer. In press.

[16] Drndarević V. Meas. Sci. Technol. 2008. DOI: 10.1088/0957-0233/19/5/057001.

Table 1. Results of the determination of ^{238}U and ^{234}U .

<i>Sample ID</i>	<i>^{238}U, mg/kg (Estimated relative uncertainty: 10 %)</i>	<i>$^{238}\text{U}/^{234}\text{U}$ activity ratio (Estimated relative uncertainty: 5.1 %)</i>	<i>^{234}U specific activity, Bq/kg</i>	<i>^{238}U specific activity, Bq/kg</i>
M1	9.60	1.07	110 ± 13	120 ± 12
M2	3.70	1.04	44.1 ± 4.0	45.9 ± 5.0
M3	38.4	1.00	480 ± 70	480 ± 70
M4	13.8	0.90	190 ± 20	170 ± 17
M5	17.3	1.07	200 ± 20	210 ± 20
M6	13.4	1.05	160 ± 15	160 ± 17
M7	11.7	0.99	150 ± 15	140 ± 15

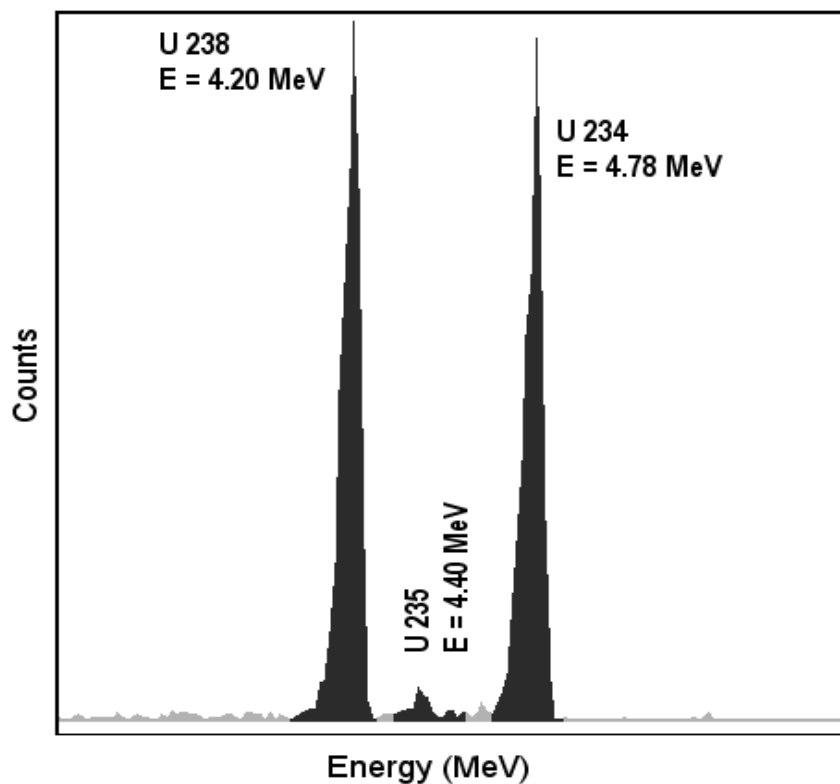


Figure 1. Alpha spectrum of the sample M5, counted for 235600 s. The net peak areas for ^{238}U and ^{234}U are respectively 1411 and 1323 counts, with negligible background. Both axes are in linear scale.

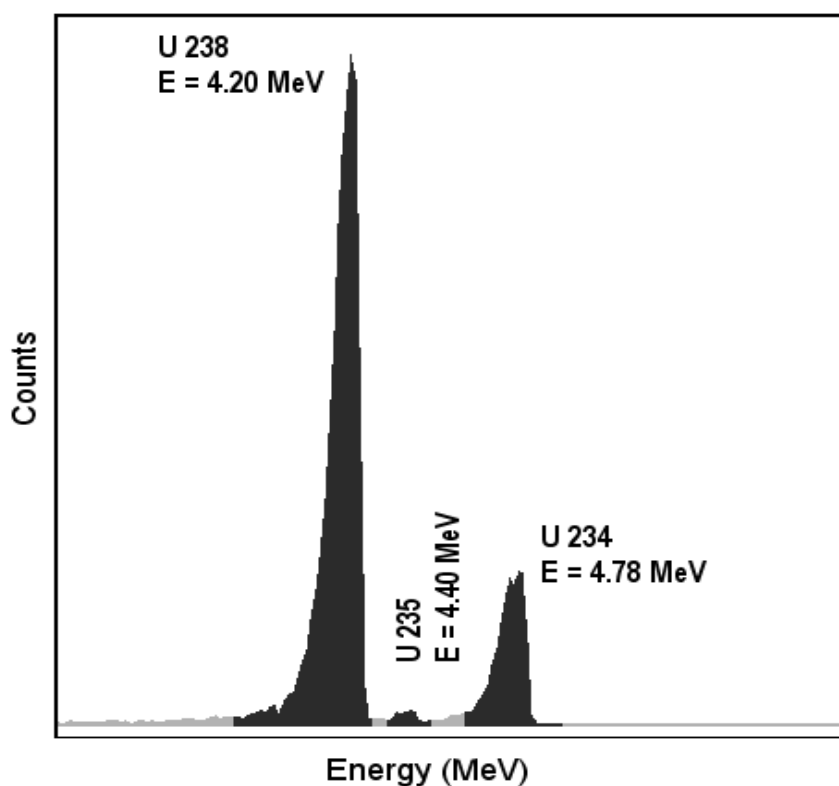


Figure 2. Alpha spectrum of uranium from a commercial atomic absorption standard solution, counted for 153000 s. The net peak areas for ^{238}U and ^{234}U are respectively 11486 and 2496 counts. Both axes are in linear scale.