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Comparison of acid leaching and fusion techniques to determine uranium in soil samples by alpha spectrometry

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HIGHLIGHTS

- Acid leaching and fusion techniques compared to determine uranium in soil samples.
- Tel 02 IAEA 2011, Tel 03 IAEA 2012, IAEA 375 standard samples prepared and analyzed.
- Better results by fusion dissolution but more impurities than acid leaching.
- Uncertainty budget prepared.
- Recoveries between 60% and 75% for acid leaching and between 70% and 90% for fusion dissolution.

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ABSTRACT

Dissolution of radionuclides of interest is an indispensable first step in the alpha spectrometric analysis of soil samples. In this study a uranium recovery method for the analysis of uranium isotopes in soil samples is presented. Two different soil sample dissolution techniques were used: digestion in open beaker and fusion. The results of these techniques were compared. Two proficiency test samples and one reference material prepared by the IAEA were analyzed. Better results were obtained by fusion dissolution technique but impurities were higher than with acid leaching. Results of two techniques were more or less similar within the uncertainty limits. The detection limit ($a^{\#}$) was evaluated as part of the quality control.

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1. Introduction

Sample dissolution and radiochemical separation are long time-consuming steps in the analysis of alpha emitting nuclides by alpha spectrometry with semiconductor detectors. Measurement time can also be very long for low activity samples. At present, most laboratories prefer simple, fast (short steps, less chemicals and commercial resin columns) and accurate methods. In the radiochemical analysis of solid samples, samples need to be dissolved completely by applying fusion, dry/wet ashing, leaching techniques separately or in some combination (Torre Pérez et al., 2013). Organic matters are eliminated and adsorbed radionuclides were taken into solution by ashing (Vintro and Mitchell, 2000; Selvig et al., 2005; Boyd et al., 1981). According to previous studies, dry ashing, wet digestion and fusion techniques are sufficient to completely solubilize samples and additional steps sometimes need to be used in the case of samples containing actinides which are in the mineral lattice of soil and sediment (Vintro and Mitchell, 2000; Selvig et al., 2005). Wet ashing is a practical method to be applied in soil

samples with low organic content in cases where wet digestion is used (Yamato, 1982; Sekine et al., 1987). Whereas, fusion technique is practical for samples that are difficult to dissolve in acids such as soils, sludges, silicates, and some metal oxides (Gascoyne and Larocque, 1984; Milliard et al., 2011). In this study, wet digestion and fusion dissolution were applied to three different soil samples for the determination of ^{234}U and ^{238}U in well characterized materials provided by International Atomic Energy Agency (IAEA TEL 2011-02, IAEA TEL 2012-03 and IAEA 375).

After sample dissolution, actinides were separated by commercial resin columns. Then the actinide of interest was deposited on a suitable substrate prior to measurement by alpha spectrometry. In order to minimize energy degradation and self-absorption effect, sources should be thin and uniform (Jung-Suk et al., 2013; Crespo, 2012). Therefore electro-deposition technique was used for source preparation.

2. Experimental

2.1. Instrumentation

The massic activities of uranium radioisotopes were determined by using an alpha-particle spectrometer from Canberra model USA model: Alpha Analyst Integrated Alpha Spectrometer containing

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Passivated Implanted Planar Silicon (PIPS) detector with an active surface area of 450 mm². The energy calibration of the spectrometer was performed by using electroplated mixed alpha standard sources containing ²³⁸U: 1.70 Bq (±2.8%), ²³⁴U: 1.69 Bq (±2.8%), ²³⁹Pu: 1.64 Bq (±2.8%), ²⁴¹Am: 1.83 Bq (±2.8%) with an active surface diameter of 17.2 mm supplied from Eckert & Ziegler Isotope Products. The thin sources of uranium for alpha-particle spectrometry measurement were prepared by electrodeposition on a stainless steel disc. An electro-deposition cell assembly consisting of disposable plastic vial, cap assembly containing stainless steel for plating planchet (cathode) and platinum electrode (anode) combined with power supply was used to accumulate uranium on stainless-steel disc of 17.2 mm in diameter.

2.2. Reagents and tracer

All reagents used in this study were of analytical grade and used without further purification. Prepacked column of UTEVA resin (100–150 µ particle size) was supplied from Eichrom Technologies, Inc. The ²³²U tracer solution with a massic activity of (38.22 ± 0.15) kBq g⁻¹ (*k*=1) was obtained from NIST SRM 4324B. The tracer solution was diluted with 2 M HNO₃ for reducing the massic activity approximately to 0.1 Bq g⁻¹.

2.3. Fusion digestion

Firstly, 2 g portion of sample was taken from the stock soil sample whose humidity was already determined at 85 °C and put into a carbon crucible. Uranium-232 tracer was added to the sample in crucible in order to trace sample and then the sample was ashed at 600 °C in a programmable electric muffle furnace for about 9 h. 15 mL of concentrated HF is added to dissolve silicates and then the ashed sample was evaporated gently to dryness on a hot plate. After reaching to dryness, Na₂CO₃, K₂CO₃ and H₃BO₃ in equivalent amounts (1:1:1) were added to the sample (EPA, 2012). Then the sample was incubated in an electric muffle furnace preheated to 800 °C until the sample became to a fluidal form. This took about 10–15 min. This fusion cake was solubilized by boiling in dilute nitric acid until dryness on a hot plate. After dissolution and evaporation steps the residue was ready for chemical separation of uranium.

2.4. Acid leaching

The soil samples were dried at 85 °C. 2 g of dried sample was put in a porcelain crucible. The soil samples were ashed in a furnace at 600 °C for about 9 h. Dried samples transferred in to a Teflon beaker for dissolution. ²³²U tracer was added to the sample. Then 50 mL of concentrated HNO₃ and 150 mL of concentrated HCl were added in a 1:3 proportion to the sample. Teflon beakers were covered with Teflon watch glass and then the sample was evaporated gently for 4 h. After complete dissolution, the Teflon watch glass was removed and the solution evaporated near to dryness. 50 mL of concentrated HF were added to dissolve silicates and then the ashed sample was evaporated gently to dryness on a hot plate. The evaporation of solutions was performed at 220 °C. Finally, the residue was ready for chemical separation of uranium.

The residues of both methods were dissolved in 15 mL HNO₃ and evaporated to dryness. Dried residue was dissolved with 10 mL of 3 M HNO₃–1 M Al (NO₃)₃. Uranium was purified and isolated radiochemically using UTEVA resin prior to source preparation and measurement by alpha-particle spectrometry (Eichrom, 2001). After separation, uranium was deposited on 17.2 mm diameter stainless-steel discs by electro-deposition technique. In this technique evaporated actinide solution was

dissolved with 2.5 mL 5 wt% NaHSO₄, 2 mL distilled water and 5 mL 15 wt% Na₂SO₄. Then 1 mL of ammonium oxalate was added to the electrolysis cell. Electrodeposition was carried out at 0.75 A for 90 min. and ended after addition of 2 mL 25 wt% KOH. The disc was removed from the cell and rinsed with NH₄OH, ethanol and acetone sequentially. The electroplated disc was dried for 5 min at 200 °C and measured immediately in an alpha-particle spectrometer. The alpha sources were counted for a period of 3–4 days. Chemical recoveries were typically obtained as 60–90%.

3. Spectrometric analysis and calculation of ²³⁸U and ²³⁴U massic activities

The ²³⁸U and ²³⁴U peak areas, in the 4000–4200 keV and 4600–4780 keV energy intervals of the alpha-particle spectrum, were determined and corrected by subtracting the ambient background and reagent background respectively. Ambient background is obtained in the region of the uranium peaks by measuring a clean stainless steel disc under the same conditions. The massic activities of the ²³⁸U and ²³⁴U in soil sample were determined using following equation for dry weight (Gingell and Harwood, 2012; Kanisch, 2004).

$$A = \frac{C_T m_T \left[\frac{C_{GA} - C_{BA}}{C_{GT} - C_{BT}} - q_I \right] \left(\frac{P_{\alpha T}}{P_{\alpha A}} \right)^* \left(\frac{A_w}{D_w} \right)}{m_a * T} \quad (1)$$

where *A* is the massic activity of the analyte (²³⁸U, ²³⁴U) in Bq kg⁻¹, *m_a* is the mass of ashed sample in kg, (*A_w/D_w*) is the ratio of the ashed weight to the dried sample weight. *C_T* is the specific activity of ²³²U tracer in Bq g⁻¹ referred to the date of calibration, *m_T* is the mass of tracer added to the ashed sample in g. *C_{GA}* and *C_{BA}* are gross count of the analyte and blank count of the analyte respectively. *C_{GT}* and *C_{BT}* are gross count of the tracer radionuclide and blank count of the tracer radionuclide respectively. *q_I* isotopic impurity ratio of the analyte in the tracer solution. *P_{αA}* and *P_{αT}* are sum of alpha emission probabilities of those individual alpha lines of the analyte and tracer respectively. *T* is sample count time.

Detection limit was also determined as follows. An uncoated stainless steel electro-deposition disc was put in to a chamber of alpha spectrometer. Then background measurement was carried out for 15 days. The detection limit (*a[#]*) was calculated for ²³⁴U, ²³⁸U by using Eqs. (2)–(4) in accordance with ISO 11929. We assumed *α*=*β* then *k_{1-α}*=*k_{1-β}*=*k*,

$$a^{\#} = \frac{2 \cdot a^* + (k^2 \cdot w) / T_g}{1 - k^2 \cdot \frac{u(w)^2}{w^2}} \quad (2)$$

$$w = \frac{1}{m_s \cdot \epsilon \cdot R} \quad (3)$$

$$a^{\#} = \frac{k_{1-\alpha}}{\epsilon \cdot m_s \cdot R} * \sqrt{\frac{n_0}{T_g \cdot t_0} + \frac{n_0}{t_0 \cdot t_0}} \quad (4)$$

where *n₀* is blank or background counts in region of interest of analyte (counts), *T_g* is the sample counting time (s), *t₀* is counting time of blank (s), *ε* is counting efficiency. *m_s* is mass of sample in kg. *a^{*}* is decision threshold (Bq kg⁻¹). *R* is the chemical recovery of the analyte. *w* is auxiliary parameter in calculation of the detection limit, (kg⁻¹) and *u(w)* is the relative standard uncertainty of *w*. *k_{1-α}*=1.65 is chosen referring to the probability that error of the first kind is not greater than 5%. The detection limit of ²³⁴U and

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