

A new method for determination of uranium isotopes in water, vegetation and soil by alpha spectrometry

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Abstract. A new and accurate method for determination of uranium isotopes (^{238}U , ^{234}U and ^{235}U) in environmental samples by alpha spectrometry has been developed. Uranium is preconcentrated from filtered water samples by coprecipitation with iron (III) hydroxide at pH 9-10 using ammonia solution and the precipitate is dissolved with HNO_3 and mineralised with H_2O_2 and HF ; uranium in biological samples is ashed at 600°C , leached out with Na_2CO_3 solution and mineralised with HNO_3 , HF and H_2O_2 ; uranium in soil samples is melted with Na_2CO_3 and Na_2O_2 at 600°C and leached out with HCl , HNO_3 and HF . The mineralised or leaching solution in 2 M HNO_3 is passed through a Microthene-TOPO (tri-octyl-phosphine oxide) column; after washing uranium is directly eluted into a cell with ammonium oxalate solution, electrodeposited on a stainless steel disk and measured by alpha spectrometry. The lower limits of detection of the method are 0.37 Bq kg^{-1} (soil) and 0.22 mBq l^{-1} (water) for ^{238}U and ^{234}U and 0.038 Bq kg^{-1} (soil) and 0.022 mBq l^{-1} (water) for ^{235}U if 0.5 g of soil and 1 litre of water are analysed. Five reference materials supplied by IAEA have been analysed and reliable results are obtained. The average uranium yields for waters, mosses, lichens and sediments are $74.5\pm 9.0\%$, $80.5\pm 8.3\%$, $77.8\pm 4.9\%$ and $89.4\pm 9.7\%$ respectively.

1. INTRODUCTION

Increased public attention to the radioactive waste disposal practices, and especially military's use of depleted uranium (DU) and the potential public health effects of releases of uranium to the environment, have made accurate and reliable methods for the determination of uranium isotopes (^{238}U , ^{234}U and ^{235}U) in various environmental, geological and biological samples increasingly important. Alpha-spectroscopy [1-6] and inductively coupled plasma-mass spectrometry [7,8] are the common techniques that measure uranium isotopes and both can detect low uranium level (below ng l^{-1}), but extensive sample preparation procedures are required to achieve accurate results. As far as only α -spectroscopy method is concerned, it has an advantage of low cost and can widely be used in routine analysis.

In this paper, a new, simple and accurate method is presented to determine the isotopic composition of uranium in water, vegetation and soil samples by α -spectrometry for environmental monitoring. Typical analytical characteristics and applicability of the method are studied.

2. EXPERIMENTAL

2.1 Apparatus and reagents

The uranium sources were counted by alpha spectrometry (Canberra, U.S.A.) with a counting efficiency of 31.2% and a background of $\leq 2 \cdot 10^{-6}\text{ s}^{-1}$ in the interested energy region. The electrodeposition apparatus (model PL320QMD, England) was used with perspex cells of 25 mm internal diameter and stainless-steel disks of 20 mm diameter. Chromatographic columns were 150 mm long and 9 mm internal diameter. ^{232}U or ^{236}U standard solution, Microthene (microporous polyethylene, 60-140 mesh), tri-octyl-phosphine oxide (TOPO, 99%) and reference materials were supplied by Amersham (G. B.), Ashland (Italy), Fluka (Switzerland) and IAEA (Vienna) respectively. FeCl_3 was used to prepare the carrier solution for uranium in water sample and all other reagents were analytical grade (Merck, Germany).

2.2 Column preparation

A solution (50 ml) of 0.3 M TOPO in cyclohexane was added to 50 g of Microthene; the mixture was stirred for several minutes until homogeneous and was then evaporated to eliminate cyclohexane at 50 °C. The porous powder thus obtained contained about 10.4% TOPO. A portion (1.6 g) of the Microthene-TOPO powder, slurred with 3 ml concentrated HCl and some water, was transferred to a chromatographic column; after conditioning with 30 ml of 2 M HNO₃, the column was ready for use.

2.3 Preliminary tests

2.3.1 Leaching

Leaching uranium from the residue obtained from water or biological samples by mineral acid is not a problem as most of the uranium compounds in such media are in soluble forms. On the contrary, leachability of uranium from soil is variable and largely depends on its own set of well-defined properties or compositions of the mineral. Although ²³²U or ²³⁸U is often used to trace the uranium recovery in most of the procedures, the accurate results can be obtained by the yield correction only when a complete isotope exchange between the added uranium tracer and uranium in the sample is achieved. Unfortunately, complete uranium exchange during soil analysis is not achievable in many procedures if a special treatment of the sample is not involved. For instance, in a reference material (IAEA-135 Sediment) supplied by IAEA two recommended ²³⁸U values were given, one (13 Bq kg⁻¹) obtained from normal leaching method and another (30 Bq kg⁻¹) from total dissolution (or gamma spectrometry) method. After careful evaluation of the two values, it is concluded that one obtained from total dissolution method is believable and so-called "normal leaching" provided an abnormal value probably due to existence of 50% refractory uranium compound in the sample. Therefore, in order to get accurate results the mineralization or leaching techniques used in an analytical procedure become very critic.

In this paper, IAEA-326 Soil, IAEA-327 Soil and IAEA-315 Sediment have been chosen to examine the leaching efficiency by four different leaching techniques. (a) 0.5 g soil sample was ashed in a muffle at 600 °C for 6 h and transferred to a teflon beaker with some water and HNO₃, 0.03 Bq of ²³²U, 5 ml of concentrated HNO₃, HCl, 40% HF each and 1 ml of 30% H₂O₂ were added. Leaching and evaporation were carried out at 250 °C. Before dry, the sample was further attacked with a 10 ml of aqua regia and 5 ml of 40% HF. The residue was changed into nitric form by two time evaporations with 4 ml concentrated HNO₃ and the further uranium separation step was the same as the recommended procedure. (b) Other operation was same as (a), but after aqua regia and HF treatment, the sample was further attacked by 10 ml of 72% HClO₄. (c) The operation was similar to (b) and the only different is that the sample was further attacked by 1 g boric acid and some water instead of 10 ml of 72% HClO₄. (d) 0.5 g of soil sample and 2 g Na₂O₂ were added to a platinum crucible containing 2 g sodium carbonate. The crucible with cover was then put in a muffle at 600 °C for 10-15 min. The melted sample was cooled at room temperature and transferred to a teflon beaker by water and HNO₃. The next leaching and separation was same as (a). The obtained results show that (1) first three leaching methods, so-called conventional methods, seem much less efficient with a leaching efficiency values from 51.4% to 63.3% and can lead to wrong results during analysis, and (2) method (d) is the most efficient leaching method with a quantitative leaching efficiency of 98.7±2.8%. The basic principle of method (d) is to remove uranium from soils in a form of water-soluble uranyl carbonate complexes.

2.3.2 Uranium elution

In a literature 1 M (NH₄)₂CO₃ was used for uranium elution from Microthene-TOPO column, then (NH₄)₂CO₃ was eliminated from the eluant by evaporation [6]. In order to simplify the procedure, 0.025 and 0.05 M (NH₄)₂C₂O₄ was tested as eluant for uranium, with the advantage that the eluant can directly be used for electrodeposition. The results show that both eluants are effective, but in the recommended

procedure 0.025 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is used. The elution curve shows that a 30 ml volume is sufficient to elute most of the uranium.

2.4 Recommended Procedures

2.4.1 Preconcentration of uranium in sea and fresh water

Forty mg of Fe^{3+} (40 mg $\text{Fe}^{3+} \text{ ml}^{-1}$) as carrier, 0.03 Bq of ^{232}U as tracer and 20 ml of concentrated HNO_3 are added to one litre of filtered water sample. After boiling for 30 min, the solution is removed to an electric-magnetic stirrer and adjusted to pH 9.5-10 with concentrated ammonia solution to coprecipitate uranium with iron (III) hydroxide. The solution is stirred for another 30 min and the precipitate is allowed to settle down for at least 4-6 h and preferable overnight. The supernatant is carefully siphoned off and the hydroxide slurry is centrifuged at 4000 rpm. The supernatant is discarded, the precipitate is dissolved with 5 ml of concentrated HNO_3 and a few drops of 40% HF and 30% H_2O_2 , and transferred to a 150 ml beaker. The obtained solution is evaporated to incipient dryness and the residual is dissolved with 2 ml of concentrated HNO_3 , 13 ml of water and a few drops of 40% HF by heating. Further separation is carried out following the uranium determination procedure given below.

2.4.2 Leaching of uranium from biological samples (vegetables, mosses and lichens etc.)

One or two grams of dried sample are put in a 30 ml of ceramic crucible and ashed in muffle at 600 °C for 14 h; after cooling 0.4 g Na_2CO_3 , 0.03 Bq of ^{232}U and some water are added to the crucible to remove uranium from the residue in a water-soluble form by heating for 1-2 h. Then the sample is transferred to a 100 ml teflon beaker with some water, 5 ml of concentrated HNO_3 and 40% HF each and 1 ml of 30% H_2O_2 ; mineralization and evaporation are carried out at 250 °C. Before dry, the sample is further attacked with a mixture of 5 ml of concentrated HNO_3 and 40% HF each and evaporated to incipient dryness. 4 ml of concentrated HNO_3 and some water are added to eliminate the remaining HF by heating. Finally the residue is dissolved with 2 ml of concentrated HNO_3 and 10 ml of water and filtered through a 0.1 μm Whatman filter paper together washing with 6 ml of 1 M HNO_3 to a 150 ml beaker.

2.4.3 Leaching of uranium from soil or sediment

Two grams of milled sodium carbonate powder are put in a 30 ml of ceramic or platinum crucible and made into a crucible shape with a smaller crucible. Then, 0.5 g of soil or sediment sample ($\leq 150 \mu\text{m}$) and 2 g Na_2O_2 are added to the sodium carbonate crucible. After mixing well the sample with Na_2O_2 , the crucible with a cover is put in a muffle at 600 °C for 10-15 min. The decomposed sample by fusion is taken out from the muffle, cooled at room temperature and 0.03 Bq of ^{232}U are added. Leaching is carried out by adding some water and sufficient concentrated HNO_3 and the leachate is transferred to a 100 ml teflon beaker. 5 ml of concentrated HNO_3 , HCl and 40% HF each are added to the leachate which is then evaporated to incipient dryness and this step is repeated another two or three times to eliminate most of the silicates. The obtained residue is dissolved again with 5 ml of concentrated HNO_3 and some water and filtered through a 0.1 μm cellulose nitrate membrane filter (Whatman, England) together washing with 10 ml of 2 M HNO_3 to a 150 ml beaker. Some concentrated ammonia solution is added to the beaker to adjust the solution pH to 9.5-10 to coprecipitate uranium with hydroxide which is then centrifuged at 4000 rpm in a 100 ml glass tube. After discarding the supernatant, the precipitate is dissolved with 3 ml of concentrated HNO_3 , 12 ml of water and a few drops of 40% HF by heating and transferred to a 150 ml beaker together washing with 10 ml of 2 M HNO_3 .

2.4.4 Separation and determination of uranium

The obtained leachate solution is passed through a preconditioned Microthene-TOPO column at a flow rate of 0.6-0.8 ml min^{-1} . After washing with 20 ml of 2 M HNO_3 , 50 ml of 1 M HCl and 5 ml of water at

the same flow rate, uranium is eluted with 30 ml of 0.025 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ at a flow rate of 0.1 ml min⁻¹. The first 4 ml of eluant are discarded and the remains are directly collected in an electrodepositing cell. 0.62 ml of 8 M HNO_3 is added to the cell and the solution is adjusted to pH 1.0-1.5 with 1:4 ammonia solutions. Uranium is electrodeposited on a stainless steel disk at a current density of 400 mA cm⁻² for 4 h and counted by alpha spectrometry.

3. RESULTS AND DISCUSSION

3.1 Decontamination from other alpha emitting radionuclides

The decontamination effect of this method from other main alpha emitting actinides, such as natural thorium, plutonium and americium, is verified by analysing the reference material of IAEA-135 Sediment, which contains 36.9 Bq kg⁻¹ of ²³²Th, 213 Bq kg⁻¹ of ²³⁹⁺²⁴⁰Pu and 318 Bq kg⁻¹ of ²⁴¹Am. The obtained decontamination factor (DF) of uranium from thorium is 1114±244, showing that washing the Microthene-TOPO column with 50 ml of 1 M HCl is very effective to eliminate nearly all the natural thorium.

The decontamination effect of the recommended procedure from plutonium is poor (DF=11.2±6.0). However, no interferences from plutonium isotopes are observed for uranium determination in environmental samples, as (1) the plutonium activities due to global fallout of nuclear weapon tests (²³⁹⁺²⁴⁰Pu and ²³⁸Pu: 0.147±0.054 Bq/kg and 0.005±0.002 Bq/kg in cultivated soil, 0.721±0.456 Bq/kg and 0.023±0.014 Bq/kg in uncultivated soil respectively) in such a small quantity of environmental samples (0.5 g soil, 1 litre water) is nearly undetectable [9], and (2) the peaks of the alpha particles of uranium and plutonium isotopes are good enough to be resolved from each other by alpha spectrometry. For the samples containing higher plutonium activities, mainly the soils or sediments contaminated by nuclear facilities or accidents, the decontamination effect from plutonium can be improved by washing the TOPO-Microthene column with 30 ml of 0.025 M $\text{H}_2\text{C}_2\text{O}_4$ +0.15 M HNO_3 at a flow rate of 0.5 ml min⁻¹ before the uranium elution. In this case the uranium yield will remain unchanged, but nearly all the plutonium can be eliminated with a DF of 516±5.

Americium will not remain on the TOPO-Microthene column at the acidity of 1-2 M HNO_3 or HCl, therefore, the obtained DFs from americium are $\geq (1.75\pm 0.92)\times 10^4$. The same DFs can also be achieved for curium, which shows a similar chemical behaviour to americium.

3.2 Quality control

Soil or sediment samples are the most complex and representative matrices of environmental samples, of which the chemical compositions are different one from another. In order to check the adaptability of the recommended procedure, five reference materials supplied by IAEA have been tested and the results are listed in Table 1. The uncertainties given for individual analysis in the Table are 1σ , which are estimated from the uncertainties associated with the tracer (²³²U) activity, the addition of the tracer to the sample, counting statistics and the weighing of the sample. It is shown that except for IAEA-315 Sediment the obtained ²³⁸U and ²³⁴U mean values in all samples are in good agreement with the recommended or information values with relative errors < 10%, especially if the confidence intervals are taken into account. Higher values are obtained for IAEA-315 Sediment, but this does not imply any fault from the procedure; on the contrary, the higher values could be more believable due to the very good leaching efficiency. The IAEA-135 Sediment sample has been tested for six times and the obtained ²³⁸U and ²³⁴U concentrations are 29.1±0.8 Bq kg⁻¹ and 27.7±1.2 Bq kg⁻¹ respectively; therefore, the accuracy and precision of the method are -3.0% and 2.7% for ²³⁸U and -2.1% and 4.3% for ²³⁴U respectively. The fact confirms that the recommended procedure for uranium isotope determination gives reliable results.

3.3 Application of the method

Some environmental samples have been analysed. The average uranium yields are $74.5 \pm 9.0\%$ for waters, $80.5 \pm 8.3\%$ for mosses, $77.8 \pm 4.9\%$ for lichens and $89.4 \pm 9.7\%$ for sediments. The high and stable yields in these matrices show the wide adaptability of the procedure. The uranium isotope concentrations in these matrices will be published elsewhere in detail [10].

The most important application of the method was carried out during UNEP (United Nations Environment Programme) scientific mission to Kosovo in 2000 to assess the impact of militarily used depleted uranium on the environment and human health [11]. More than 300 samples have been analysed including water, vegetable, moss, lichen and soil. Elevated ^{238}U , ^{234}U , ^{235}U and ^{236}U activities have been found in many of the samples, especially in soils. The contamination factors of ^{238}U , ^{234}U , and ^{235}U in some Kosovo soils are as high as 2237, 296 and 696 respectively if compared with their background level (^{238}U : 26.7 Bq kg^{-1} ; ^{234}U : 25.4 Bq kg^{-1} ; ^{235}U : 1.29 Bq kg^{-1}). Moreover, the ^{236}U activities in some Kosovo soils are as high as 358 Bq kg^{-1} , which are not detectable in normal environmental soils. As it is well known, soil is the most complex and difficult medium for uranium isotope determination in the environmental samples due to containing refractory uranium compounds, but the recommended procedure conquered the difficulty and assure to give accurate and reliable results. Therefore, UNEP highly commented the method that "the best results for ^{238}U and ^{234}U was achieved by a laboratory that prepared the sample by melting with $\text{Na}_2\text{CO}_3 + \text{Na}_2\text{O}_2$ before leaching".

3.4 Lower limits of detection

Taking into account the 3σ of the blank count rates, the counting efficiencies of the instruments, the radiochemical yields and the sample quantity, the lower limits of detection of the method are 0.37 Bq kg^{-1} (soil) and 0.22 mBq l^{-1} (water) for ^{238}U and ^{234}U , and 0.038 Bq kg^{-1} (soil) and 0.022 mBq l^{-1} (water) for ^{235}U if 0.5 g of soil and 1 litre of water are analysed.

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Table 1. ^{238}U , ^{234}U and ^{235}U concentrations (in Bq kg⁻¹ dry weight) in some IAEA reference materials.

| Sample code | W _{U5} * g | U yield % | Recommended value (confidence interval) | | | Experimental value | | | | |
|-------------------|------------------------|--------------|--|------------------|------------------|--------------------|------------------|------------------|---------------------------------|---------------------------------|
| | | | ^{238}U | ^{234}U | ^{235}U | ^{238}U | ^{234}U | ^{235}U | $^{234}\text{U}/^{238}\text{U}$ | $^{235}\text{U}/^{238}\text{U}$ |
| IAEA-135 Sediment | 0.5443 | 82.4 | 30(27-36.5)* | 28.3(20.9-32)* | 1.05(0.65-1.3)* | 28.6±1.1 | 27.1±1.0 | 1.63±0.20 | 0.947 | 0.057 |
| IAEA-135 Sediment | 0.5355 | 63.1 | 30(27-36.5)* | 28.3(20.9-32)* | 1.05(0.65-1.3)* | 27.7±1.2 | 26.7±1.2 | 1.43±0.22 | 0.965 | 0.052 |
| IAEA-135 Sediment | 0.5634 | 97.3 | 30(27-36.5)* | 28.3(20.9-32)* | 1.05(0.65-1.3)* | 29.8±1.1 | 29.8±1.1 | 1.36±0.17 | 1.00 | 0.046 |
| IAEA-135 Sediment | 0.5745 | 92.3 | 30(27-36.5)* | 28.3(20.9-32)* | 1.05(0.65-1.3)* | 29.4±1.0 | 26.7±1.0 | 1.42±0.17 | 0.907 | 0.048 |
| IAEA-135 Sediment | 0.5713 | 70.8 | 30(27-36.5)* | 28.3(20.9-32)* | 1.05(0.65-1.3)* | 28.9±1.2 | 28.5±1.2 | 1.54±0.22 | 0.988 | 0.054 |
| IAEA-135 Sediment | 0.5913 | 77.3 | 30(27-36.5)* | 28.3(20.9-32)* | 1.05(0.65-1.3)* | 30.0±1.1 | 27.1±1.0 | 1.47±0.19 | 0.905 | 0.049 |
| IAEA-315 Sediment | 0.5179 | 92.4 | 17.6(16.1-18.5) | 17.8(16.6-20.0) | 0.84(0.65-1.20) | 19.5±0.9 | 20.3±0.9 | 0.89±0.16 | 1.04 | 0.046 |
| IAEA-315 Sediment | 0.5968 | 84.5 | 17.6(16.1-18.5) | 17.8(16.6-20.0) | 0.84(0.65-1.20) | 19.7±0.7 | 19.4±0.7 | 1.01±0.14 | 0.989 | 0.052 |
| IAEA-368 Sediment | 0.5077 | 80.1 | 31(25-33) | 35.7(21.5-44.8)* | 1.9(1.6-2.6)* | 34.1±1.2 | 37.7±1.3 | 1.71±0.20 | 1.10 | 0.050 |
| IAEA-368 Sediment | 0.5070 | 80.3 | 31(25-33) | 35.7(21.5-44.8)* | 1.9(1.6-2.6)* | 31.8±1.1 | 36.6±1.3 | 1.52±0.19 | 1.15 | 0.048 |
| IAEA-326 Soil | 0.5023 | 63.1 | 29.4(28.1-30.7) | 27.9(26.5-29.3) | 1.48(1.21-1.75) | 28.5±1.3 | 27.9±1.4 | 1.45±0.25 | 0.926 | 0.051 |
| IAEA-326 Soil | 0.4998 | 85.5 | 29.4(28.1-30.7) | 27.9(26.5-29.3) | 1.48(1.21-1.75) | 29.1±1.5 | 26.4±1.2 | 1.06±0.25 | 0.958 | 0.036 |
| IAEA-326 Soil | 0.5036 | 68.5 | 29.4(28.1-30.7) | 27.9(26.5-29.3) | 1.48(1.21-1.75) | 29.0±1.3 | 26.4±1.5 | 1.25±0.23 | 0.911 | 0.043 |
| IAEA-327 Soil | 0.5408 | 76.9 | 32.8(31.4-34.2) | 31.9(30.4-33.4) | 1.43(1.22-1.64) | 30.0±1.3 | 29.0±1.2 | 1.65±0.24 | 0.967 | 0.055 |
| IAEA-327 Soil | 0.5113 | 89.1 | 32.8(31.4-34.2) | 31.9(30.4-33.4) | 1.43(1.22-1.64) | 31.2±1.1 | 31.0±1.1 | 1.25±0.17 | 0.993 | 0.040 |

*: Sample weight for uranium analysis.

*: Information value.