A Rapid Method for Determination of Uranium, Americium, Plutonium and Thorium in Soils Samples

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Abstract. A simple and fast method for actinides determinations in soils samples is described. Uranium, plutonium, americium and thorium are separated using UTEVA and TRU Eichrom® Resins. The sample is traced with uranium 232, plutonium 242 and americium 243, and then is digested with a mixture of nitric, hydrofluoric and perchloric acids in a sealed bomb with Teflon® at 150°C during 4 hours. The solution is transferred into a Teflon® beaker with graphite base and evaporated to near dryness. Nitric acid is added several times in order to eliminate the hydrofluoric acid and then is evaporated to dryness to eliminate perchloric acid. The residue is dissolved in nitric acid and aluminum nitrate solution. Then ferrous sulfamate and ascorbic acid are added. The sample solution is passed through the UTEVA® Resin column. The loading and rinsing effluent is reserved for the subsequent americium and plutonium separation. The UTEVA® Resin column is rinsed several times in order to eliminate polonium, since ²¹⁰Po interfere in the uranium measurement by alpha spectrometry. Thorium and neptunium are eluted with hydrochloric and oxalic acids. The uranium is eluted with diluted hydrochloric acid. The reserved solution for the americium and plutonium separation is passed through the TRU® Resin column. The americium is eluted from TRU® with hydrochloric acid and the plutonium is eluted with ammonium oxalate. The actinides are electrodeposited on stainless steel disc and measured by alpha spectrometry. Several standard samples were analyzed and their results are presented.

1. Introduction

For identification and quantification alpha emitters radionuclides it is necessary to separate and purify from each other in order to obtain highly accurate results. A rapid and reliable determination is a desirable and necessary option in most of the radiochemical analysis.

Current techniques for sample dissolution and for actinides separation and purification, include leaching with strong acids, microwave digestion, precipitation, solvent extraction, ion exchange and extraction chromatography. In the following method, a proper combination of some of these techniques, allows to obtain a very good separation of U, Th, Pu y Am into four spectroscopically distinct groups. The total dissolution of soil samples is necessary to improve the U quantification. The elimination of some steps, like precipitation and solvent extractions, permits an important reduction of the time required for the analysis. Using only two extraction chromatography columns, Eichrom® UTEVA and TRU [1,2], permits a significant reduction of acids volumes and their concentration.

2. Procedure

Pre-packed UTEVA and TRU Eichrom® Resin columns were used for all tests. Reference soils (QAP and IAEA) and tracer solutions of uranium-232, plutonium-242 and americium-243 were used in the testing procedures.

The used recipient for sample dissolution was a sealed bomb with Teflon®. This is an appropriate hermetic recipient sealed of Teflon with an O’Ring® of Viton®.

The following method was developed through a series of experiences that included:
- Different methods for soil samples dissolution
- Different sizes of soil samples.
- Tests with and without calcium oxalate precipitation in the sample preparation
- Different techniques to resolve the problem of interference of polonium-210 with uranium-232 tracer.
2.1. Sample preparation

A 0.5g of soil sample was placed in the recipient of Teflon®. Uranium-232, plutonium-242 and americium-243 were added as tracers. Then, 8 ml of HNO₃(c), 12 ml of HF(c) and 2 ml of HClO₄(c) were added to the sample. The recipient was hermetically closed and the sample was digested at 150°C for about 5 hours.

The obtained solution was transferred to a Teflon® baker with graphite base and was evaporated to near dryness. The residue was dissolved in 5 ml of HF(c) and evaporated to near dryness again. The last step was repeated until no evidence of Si was in the sample. 10 ml of HNO₃(c) were added and evaporated to dryness in order to eliminate the HF. The residue was dissolved in the minimum necessary amount of (3M HNO₃ + 1M Al(NO₃)₃). Usually, 13-15 ml are necessary for total dissolution.

3 ml of ferrous sulfamate 0.6M and 200 mg of ascorbic acid were added to the sample solution. It was allowed to stand for 5 minutes prior to load onto columns.

2.2. Actinides separation and purification

The soil solution was passed through the UTEVA column. The resin was rinsed with 20 ml of 3 M HNO₃. The loading and washing solutions were collected and reserved to pass through the TRU column. This solution is named “second loading” and contains Pu, Am and small traces of Th. It is important not to let it stand more than 3 hours until TRU loading.

The medium was changed passing through the UTEVA column 5 ml of 9M HCl. Th was eluted with 20 ml of (5M HCl + oxalic acid 0.05 M) and saved for the subsequent electrodeposition. Finally, U was eluted using 20 ml of 0.01M HCl and reserved for polonium elimination and electrodeposition.

The second loading solution was passed through the TRU column.

In order to oxidize the possible Pu³⁺ to Pu⁴⁺, 5 ml of (3 M HNO₃ + 0.1 M NaNO₂) was passed through the TRU resin. Am was eluted using 3 ml of 9M HCl and 20 ml of 4 M HCl, and this eluate was reserved for the subsequent electrodeposition.

To eliminate possible contamination with small traces of Th, the TRU resin was rinsed with 8 ml of (4 M HCl + 0.01 M HF).

Pu was eluted with 20 ml of ammonium bioxalate 0.1 M and reserved for electrodeposition.

2.3. Polonium removal

It was observed that small traces of polonium are eluted with uranium, even though the first rinse with 3M HNO₃. Since alpha particle energies of ²¹⁰Po and ²³²U are similar, and impossible to resolve spectroscopically, the remaining polonium must be removed previous to electrodeposition.

The uranium eluate was evaporated to dryness and dissolved in HCl (c); 0.5 g of hydrazine dichlorohydrate was added and let it stand for 10 minutes, to reduce Po⁴⁺. The solution was evaporated to dryness and was maintained at 250°C for about 4 hours in order to remove the PoCl₂. To assure the total elimination of polonium and the hydrazine decomposition, the residue was subjected to 500°C in a furnace for 8 hours. Uranium was dissolved in HNO₃ (c) and prepared for electrodeposition.

The procedure chart of this method is shown in figure 1.
0.5 g soil
+ $^{232}$U, $^{242}$Pu, $^{243}$Am
+ 8 ml HNO$_3$ (c)
+ 12 ml HF(c)
+ 2 ml HClO$_4$ (c)

Hermetic Teflon Recipient

150 °C x 5 h

Soil solution
- Si removal
- HF removal
- Loading solution:
  13-15 ml [HNO$_3$ 3 M + Al(NO$_3$)$_3$ 1M]
  + 3 ml ferrous sulfamate 0.6 M
  + 200 mg ascorbic acid

2 - Loading solution for UTEVA

1- Conditioning: 5 ml HNO$_3$ 3 M

3- Washing: 30 ml HNO$_3$ 3M

4- 5 ml HCl 9M

5- Th elution: 20 ml (HCl 5M + Oxalic Acid 0.05M)

6- U elution: 20 ml de HCl 0.01 M

I- Conditioning:
  5 ml HNO$_3$ 3 M

(4+5) Th

(6) U

II- (2+3) Loading solution for TRU

III - Pu oxidation: 5 ml(HNO$_3$ 3M+NaNO$_2$ 0.1 M)

IV- Am elution: 3 ml HCl 9M + 20 ml HCl

V – Th washing: 8 ml (HCl 4M + HF 0.01 M)

VI- Pu elution: 20 ml ammonium bixalate 0.1 M

(II+III) – Discard

IV - Am

(V) – Discard

VI - Pu

FIG. 1. Procedure chart
2.4. Electrodeposition

The actinides were electroplated on stainless steel discs, in ammonium sulphate media at pH 2.5, during 2 hours, according to the habitual technique used in the laboratory [3]. The discs were previously electropolished with a mixture of sulphuric and phosphoric acids, in order to achieve better peaks resolution in the spectra. The electroplated actinides were measured by alpha spectrometry.

2.5. Measurement

The alpha spectrometers used for the measurements were:
1) α Alpha Analyst™ -Canberra and
2) Octete™PC - EG&G Ortec,

equipped with the following detectors:
1) Passivated Ion-Implanted Planar Silicon (PIPS) 900 mm², distance 5 mm (Canberra)
2) Ultra™ Ion Implanted Silicon (EG&G Ortec), 900, 1200 mm², distance 5 mm.

The spectra were analyzed using the software PC-based "PROALFA V.9" developed by A.R.N. personnel [4].

3. Results and discussion

For testing the applicability of the present procedure, some standard soils were analyzed. Their results and the reference values are listed in table I. The analyzed samples were: soil QAP 0203 (QAP 56) EML-USDOE, QAP 0303 (QAP 58) EML-USDOE, and IAEA-135 Sediment. The chemical yields and the minimum detectable amount of each radionuclide are presented in table II.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Value</th>
<th>QAP 0203 (56)</th>
<th>IAEA -135 Sediment</th>
<th>IAEA -135 Sediment</th>
<th>QAP 0303 (58)</th>
<th>QAP 0303 (58)</th>
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<tbody>
<tr>
<td>U-234 (Bq/Kg)</td>
<td>OV</td>
<td>92.6</td>
<td>28.4</td>
<td>28.7</td>
<td>116</td>
<td>115</td>
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<td></td>
<td>RV</td>
<td>93.88</td>
<td>28.3</td>
<td>28.3</td>
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<td>U-238 (Bq/Kg)</td>
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<td>29.5</td>
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<td>120</td>
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<td>RV</td>
<td>96.78</td>
<td>30.0</td>
<td>30.0</td>
<td>125.0</td>
<td>125.0</td>
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<td>U-total (Bq/Kg)</td>
<td>OV</td>
<td>198.3</td>
<td>59.6</td>
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<td>244</td>
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<tr>
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<td>RV</td>
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<td>249.0</td>
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<td>Am-241 (Bq/Kg)</td>
<td>OV</td>
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<td>315</td>
<td>309</td>
<td>15.6</td>
<td>---</td>
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<tr>
<td></td>
<td>RV</td>
<td>10.927</td>
<td>318</td>
<td>318</td>
<td>13.7</td>
<td>13.7</td>
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<td>Pu-238 (Bq/Kg)</td>
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<td></td>
<td>RV</td>
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<td>43</td>
<td>43</td>
<td>22.38</td>
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<tr>
<td>Pu-239+240 (Bq/Kg)</td>
<td>OV</td>
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<td>230</td>
<td>217</td>
<td>23.4</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>RV</td>
<td>19.098</td>
<td>213</td>
<td>213</td>
<td>22.6</td>
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Table II. Chemical Yields and Minimum Detectable Amount

<table>
<thead>
<tr>
<th>Chemical Yield (%)</th>
<th>Minimum Detectable Amount (Bq/Kg)</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>U</td>
</tr>
<tr>
<td>QAP 0203 (56)</td>
<td>68</td>
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<tr>
<td>IAEA -135 Sediment</td>
<td>51</td>
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<tr>
<td>IAEA -135 Sediment</td>
<td>64</td>
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<tr>
<td>QAP 0303 (58)</td>
<td>75</td>
</tr>
<tr>
<td>QAP 0303 (58)</td>
<td>65</td>
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</table>

4. Spectra

The following spectra were achieved applying this procedure.
5. Conclusions

The main advantages of the proposed method are the fast and efficient separation of the actinides, no precipitation is required and low consumption of reagents. The period of time required for the actinides determination is 35-40 hours. It makes possible to determine the activity of uranium, plutonium, americium and thorium in a soil sample without alpha spectral interferences. An additional advantage is the use of lower acid concentrations than the traditional methods. The recoveries are variable depending on the alpha emitter radionuclide and the composition of the soil.

A disadvantage is the high Minimum Detectable Amount, due to the low quantity of soil sample that may be possible to pass through the column without rupture.

This procedure for sequential separation of uranium, thorium, americium and plutonium is easy to apply to other matrixes like, filter and vegetable. If only one of these actinides determinations is required, some steps may be eliminated with care.

6. References


