74

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Determination of Uranium Isotopes in Environmental Samples Using Different Analytical Techniques: A Comparison

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Abstract

Different analytical methods for different environmental samples (rock, soil, sediment, plant, waste water, ground water and tap water) which have low activity concentrations are developed for the determination of uranium isotopes to be assured of no contamination or pollution of the environment. Using of non-destructive method based on gamma spectrometer and destructive analysis based on alpha spectrometer. Choice of an accurate and precise technique to get better performance and quality is essential for the results assessment and improvement. A set of different matrices of IAEA reference certified samples were used for method verification. Two separation techniques for ^{238}U, ^{234}U and ^{235}U were used; i) UTEVA extraction chromatography which achieved recoveries higher than 50 %, ranged between 59 and 79 % and ii) TOPO solvent extraction which achieved a chemical recovery lower than that obtained by UTEVA for the same matrices ranged from 26 % and 55 %. From the obtained results a significance difference was shown between UTEVA and TOPO techniques.

Keywords; Uranium isotopes, Alpha spectrometry, Gamma spectrometry, Radiochemical procedure

1. Introduction

Uranium is an element of the actinide series, has an atomic number of 92. Uranium in the environment occurs naturally as three radioactive isotopes: ^{238}U (99.27%), ^{235}U (0.72%) and ^{234}U (0.005%), but other isotopes can be synthesized [1]. ^{238}U and ^{235}U radionuclides are the two parent isotopes of the ^{238}U and ^{235}U-series decay chains, and the ^{234}U isotope is the longest-lived daughter of all intermediate nuclides of the ^{238}U-series decay chain [2, 3]. U-series isotopes (^{238}U and ^{234}U) are in secular radioactive equilibrium and their activities are equal. Percent variations in $^{234}U/^{238}U$ activity ratios have been reported in natural terrestrial environments [4-6]

The preferential dissolution of ^{234}U is mainly caused by preferential leaching owing to crystal lattice instability after alpha emission during ^{238}U decay. It can also be caused by the recoil ejection of the ^{234}Th nucleus into the water via the alpha recoil effect or by the etching of alpha recoil tracks [7, 8].

The use of U isotopes has several benefits over traditional geochemical techniques. Uranium is an abundant trace element in natural waters in areas with a predominantly carbonate lithology [9-11]. Therefore, it can be used as an additional tracer to gain more knowledge and understanding of complex karst hydrodynamics. Its isotopic composition varies in such an environment because of the U several processes that cause isotope fractionation effects [12, 13]. Additionally, isotope ratios can be easily measured at high levels of precision and accuracy, which is important for U isotope measurements in karstic waters where U concentrations are low [14-16] Radiometric methods, alpha and gamma spectrometry, and inductively coupled plasma mass spectrometry (ICP-MS), are used to quantify uranium. The detection limit of the method, the amount of sample available, the time available for analyzing the sample, and occasionally the cost of the analysis are all factors that affect the determination method [17].

The determination of man-made and natural radionuclides from environmental samples has been done using high resolution gamma spectrometry. This method has the advantage of being able to determine

many radionuclides in the same sample while also being reasonably straightforward to prepare.

However, as compared to radiometric and mass spectrometric measurements, its detection limit is often higher. These procedures, in comparison to gamma spectrometry, require a significant amount of laboratory effort before the sample is in liquid form and the radionuclides of interest are isolated from other interfering nuclides for measurement [18].

For ^{238}U determination precisely could be using the γ line; 1001.03 keV (0.837 %) of ^{234m}Pa. The most predominant gamma transition 185.7 keV (57.2 %) is preferred to measure the ^{235}U. The reason for the 143.76 keV (10.96 %), 163.33 keV (5.08 %) and 205.31 keV (5.01 %) energy transitions were not commonly used to determine ^{235}U in environmental samples which mainly due to their relatively lower branching ratios compared to 185.7 keV energy transition [19].

Counting rates due to the 143.76 keV, 163.33 keV and 205.31 keV energy transitions would be below the detection limits ranges for the HPGe detector based on average normal ^{235}U concentrations in different environmental samples; Rock, Soil, Sediment, Plant, Waste water, Ground water and Tap water. Radiochemical methods are routinely used in analytical chemistry. They have been developed for measurements in the laboratory, mostly for fundamental research [20]. Radioanalytical techniques have undergone many important developments in recent decades [21] and can easily be adopted to solve many problems of samples with a high degree of accuracy, precision, sensitivity and selectivity [22].

Alpha spectrometry is a convenient technique to determine the activity concentration of uranium isotopes in environmental samples and provides an accurate determination of isotopic activity ratios. Sample pretreatment, radiochemical separation, preparation of a thin alpha source by electrodeposition or micro-precipitation, and high-resolution counting are all steps in the alpha spectrometric measurement of uranium isotopes. Uranium is commonly separated radio-chemically by liquid-liquid extraction, ion exchange, and extraction chromatography [23, 24].

Through the objectives of this study, the development of the radio analytical methodology for the determination of the uranium isotopes by alpha spectroscopy includes the improvement of accuracy of the results and the achievement of high chemical yield and lower uncertainties by following the ISO-17025 guidance and quality assurance parameters in radio-analysis.

In this study soil samples, ground water and tap water samples were analyzed to determine uranium isotopes using gamma spectrometry and alpha spectrometry. U isotopes activities determined by gamma spectrometry were compared with that determined by alpha

spectrometry through. The method validation was demonstrated using IAEA certified reference samples.

Material and method

Samples Collection

In this study, the authors were concerned with determination of rapid and low-cost method for uranium isotopes analysis, so different types of soil and plants were chosen. The analyzed samples were selected from CLERMIT library, where the Egyptian Radiological Maps were studied. The samples collected were prepared in the suitable containers and kept for different uses. We have 12 soil samples, 3 plant samples, 5 ground water and 5 tap water samples were selected randomly for the application of different methods. Soil and plant samples were crushed to (100 mesh) and were dried in an oven at 105 °C for 24 h for complete removing of any organic matter present. The samples were transferred to special tight polyethylene plastic containers and left for four weeks to reach radioactive equilibrium. Water samples were collected and transferred into special tight polyethylene plastic containers.

Gamma spectrometric (HPGe-detector)

In this study, we used high purity germanium detector with 40 % efficiency and 2.0 keV energy resolutions at 1.33 MeV photons of ^{60}Co, shielded by 4 mm Pb, 1 mm Cd and 1 mm Cu was used. HPGe detector equipped with Canberra Genie 2000 software for Gamma Acquisition and Analysis. The average counting time interval for all samples was about 80,000 seconds [25]. Geometric efficiency of the detector was determined and verified using IAEA certified reference.

The activity of ^{234}U was determined using gamma rays released at energies of 53.2 and 120.9 keV. The activity concentration of ^{230}Th was determined using the emitted gamma-ray at 67.7 keV. After subtracting the 185.7 keV of ^{235}U, the 186.1 keV from ^{226}Ra's gamma-ray emission was used to calculate its accurate activity concentration [26, 27]. ^{214}Pb's activity concentration was measured at 241.9, 295.2, and 351.9 keV, while ^{214}Bi and ^{210}Pb's activity concentrations were measured using 609.3 and 46.5 keV, respectively [28]. No self-absorption correction was applied.

Alpha Spectrometry

Silicon-surface barrier detector 450 mm^2 CANBERRA model 7401/7401VR was used for determine of uranium isotopes ^{238}U, ^{234}U and ^{235}U activity concentrations. The spectrometer resolution is 19 keV FWHM at 5.486 Mev of ^{241}Am. Calibration and efficiency of the detector were attained using a standard mixed alpha source; ^{241}Am, ^{239}Pu and ^{244}Cm with known activity (1 kBq). There are different methods for uranium separation from sample matrix. Some of them are based on precipitation, liquid-liquid extraction, ion exchange, and chromatography [29]. Spectral analysis was obtained by means of Canberra Genie 2000 software for Acquisition and Analysis.

In the present work, the activity concentration of uranium isotopes in different environmental samples using extraction chromatography with TOPO [30, 31] and UTEVA [32] were obtained and compared to establish an accurate and rapid method in the Central Laboratory for Environmental Radioactivity Measurements Inter-comparison and Training (CLERMIT). Both methods were verified using Reference Certified Materials.

Classical method (TOPO method)

Sample preparation

To obtain precise and accurate data on the U isotopes in the analyzed samples, it is necessary to completely separate the uranium isotopes from transuranium elements with the extraction chromatography method [33]. TOPO was the first extraction chromatography separation method used in the CLERMIT till year 2015. Sample preparation is carried out in order to homogenize the sample and prepare it for chemical processing. Each sample is crushed (to a depth of 2 mm) and well combined. The crushed sample is dried in a drying oven at 105°C until its weight remains constant. The dried sample is ashed with Conc. HNO_3 (1-2 mL) at 550 °C to produce organic carbon oxidation. The ash was weighed (about 5 g of soil ash and 1 g of granite ash) and then the ^{232}U tracer (100 mBq) was added. A digestion and dissolution of material by a medium heating at 70-80 °C, a mixture of both nitric and hydrofluoric acids (40:10 mL) was used the residue is dissolved in 8 M HNO_3 and then the sample solution was heated for 30 minutes while increasing the volume to 100 mL **(Figure 1) [30].**

Sample Digestion, Separation and Purification

The sample was dissolved in 40 ml of 65 % HNO_3, 15 mL of 37 % HCl and 10 mL of 40 % HF acids. Uranium in the dissolved sample solution was extracted with 25 mL of 0.2 M TOPO/Cyclohexane (Trioctyl-phosphine oxide). The uranium of the organic phase was stripped to the aqueous phase using 1 M NH_4 F/0.1 M HCl (add 3.71 g of NH_4F to 100 mL 0.1 M HCl), 0.8 mL to 99.2 mL of distilled water) and then purified by washing three times with 9 mL of $CHCl_3$. The obtained uranium (^{+6}U) was reduced again to the tetravalent state (^{+4}U) by adding 5 mL of a reducing agent ($TiCl_3$). The solution is co-precipitated by LaF_3 (25 mg/mL of La $(NO_3)_3$ with HF 40 %). The solution at room temperature was centrifuged at 3500 rpm for 15 minutes and then was dissolved in hot boric acid (saturated solution) and HNO_3. The uranium was re-oxidized to the hexavalent state by adding H_2O_2. The solution was evaporated to dryness and the residue was dissolved in 10 mL of 9 M HCl, and then passed through a conditioned anion exchange resin column (Dowex 1x8 Cl^- form). 0.5 M of HNO_3 was passed through the column to eluted Uranium. The eluted U was evaporated to dryness in a crystallizing dish using 1 mL of concentrated HCl **(Figure 1) [32].** Distilled water was used as a blank sample, as it was free as possible of chemical or radioactive impurities. For

method verification, IAEA-326 Soil, IAEA-375 Soil and IAEA-300 Sediment were analyzed.

Modified method (UTEVA method)

Sample preparation and **digestion**

The soil samples were homogenized and prepared for the subsequent chemical processing. Each sample was crushed (≤ 2 mm) and mixed well. The crushed samples were dried at 105 °C in drying oven until arrived to constant weight. The samples were ashed with conc. HNO_3 (1-2 mL) to oxidize all the organic carbon at 550 °C overnight. 1.52 g of the sample was weighted into a 250 mL Teflon beaker glass beaker. The soil samples were acidified with 10 mL conc. HNO_3. A known amount of ^{232}U tracers (100 mBq) was added to monitor the chemical yield. Add about 10 mL of conc. HNO_3 and 5 mL of conc. HCl then heated for about 3 hours and left-over night. The supernatant was discarded by decantation and the precipitate was separated by centrifugation. The white precipitate was then dissolved in conc. HNO_3 and evaporated till dryness [34].

The water samples were acidified with 3 mL conc. HNO_3 and heated up to 80 °C with stirring. A known amount of ^{232}U tracers was added to monitor the chemical yield (All time; the amount of tracer added depending on the expected activity of analyte in the analyzed sample). About 0.5 ml of 1.25 M Ca $(NO_3)_2$ was added into the sample and heated up with stirring. Then 1 mL of 3.2 M $(NH_4)_2HPO_4$ was added for uranium co-precipitated in the form of $(Ca_3(PO_4)_2)$. Concentrated ammonia was added to adjust pH (pH = 9). The precipitate was left to settle down overnight. The supernatant was discarded by decantation and the precipitate was separated by centrifugation from 2-3 times until ammonia odor is volatized (at 3500 rpm for 5 minutes in each). The white precipitate was then dissolved in concentrated $HNO3$ and evaporated till dryness.

The plant samples were homogenized and prepared for the subsequent chemical processing. Each sample was crushed (≤ 2 mm) and mixed well. The crushed sample was dried at 110 °C in drying oven until its weight remained constant. 1 g of the sample was weighted into a 250 mL Teflon beaker. The plant samples were acidified with 8-10 mL conc. HNO_3. A known amount of ^{232}U tracer was added to calculate the chemical yield. Add 6 mL of conc. HNO_3 and 1 mL of H_2O_2 and evaporated till dryness.

Sample separation and purification

The UTEVA was preconditioned twice with 5 mL of 3 M HNO_3 at a flow rate of ~8 drops/min. The samples then were dissolved by 3M HNO_3/1M Al $(NO_3)_3$. The dissolved sample was transferred onto a preconditioned UTEVA column. The column was washed with 20 mL of 3 M HNO_3, 5 mL of 9 M HCl, and 20 mL of 5 M HCl with 0.05 M oxalate to remove the interfering radionuclides of Th, Np and Pu. U isotopes were eluted with 15 mL of 1 M HCl in a clean

beaker, and the eluated sample was evaporated to dryness. To destroy any possible organic residue that might co-elute from the resin, the dry residue was digested three times with a mixture of HNO₃ and H₂O₂ before electro-deposition (**Figure 1**). For method verification, IAEA-2011-04 Soil, IAEA-315 Sediment and water samples IAEA-CU-2010-03, IAEA-420, IAEA 421 and IAEA-330 were analyzed.

Source preparation

The electrodeposition technique was applied for source preparation. The electrodeposition cell is composed of Teflon, which acts as an electrical insulator and prevents radioactive adsorption on the electrolyte along the wall. A platinum wire spiral serves as the cell's anode. The stainless-steel screw cap acts as a cathode and retains the stainless-steel disc that is used for deposition. The exposed cathode area is 3.14 cm² and the cell height is 34 mm, which is large

enough to hold roughly 10 mL of electroplating solution without losing anything during the electroplating process. The ammonium format (ammonium oxalate, ammonium chloride, ammonium sulfate, or mixtures of these electrolytes) is used to electroplate the uranium. Because it is faster and less sensitive to experimental variations and contaminants in the electrolyte, ammonium oxalate was used. The eluted uranium is transferred from the crystallization dish to the electrolysis cell using 1 mL of 6 M HCl and 10 mL of 3.7 % Ammonium oxalate in HCl. After 3 hours of electrolysis at 500 mA (0.5 A), 1 mL of ammonia solution (NH₄OH with 25 % concentration) is added to increases OH⁻ concentration which prevents re-dissolution of the hydroxide from the cathode surface. After one minute, the electrolysis current is cut off. The source then measured by alpha spectrometry [35].
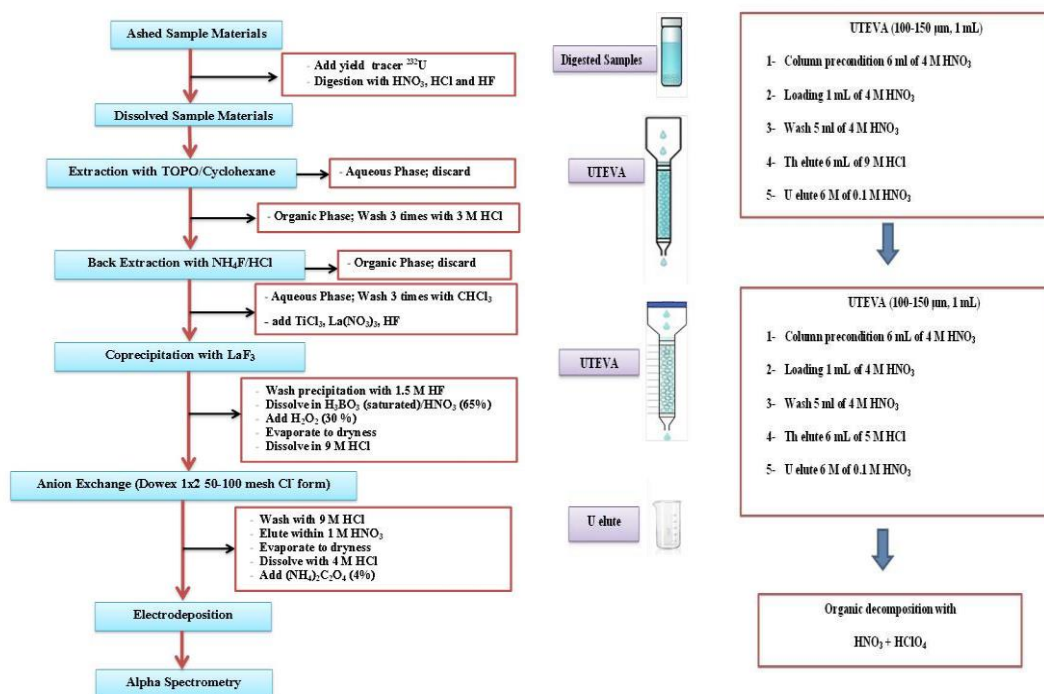

Figure 1. Flow chart of TOPO and UTEVA for U-Isotopes Radiochemical Procedure.

Activity calculation

All calculations of this study were done using Geni-2000 and Apex-Alpha reported. The total procedure efficiency is calculated from the ^{232}U tracer peak as:

$$\eta_t = \frac{N_{(tracer)}}{A_{(tracer)}.t_c} \quad (1)$$

where n_t is the total efficiency, N_{tracer} is the counts in the tracer peak, A_{tracer} is the activity of the tracer peak and t_c is the counting time.

The activity concentrations of ^{238}U, ^{235}U, and ^{234}U are calculated through two main equations as follows;

i) Calculation of the tracer yield (Y_{tracer}),

$$Y_{tracer} = \frac{N_{tracer} - N_{Background}}{t \times A_{tracer} \times eff} \quad (2)$$

where N_{tracer} is the count of the tracer used, ($N_{Background}$) is the background count, t is the counting time (s), A_{tracer} is the activity (Bq) of the tracer and (eff) is the efficiency of the detector (%)

ii) Calculation of the final activity concentration of uranium ($A_{Nuclide}$),

$$A_{Nuclides} = \frac{N_{Nuclide} - N_{Background}}{M \times t \times Y_{tracer} \times eff} \quad (3)$$

where $N_{Nuclide}$ is the count of the studied nuclide, $N_{Background}$ is the background count, t is the counting time (s), m is the mass of the sample (kg) and eff is the efficiency of the detector.

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Egypt. J. Chem. **65,** No. SI:13B (2022)

iii)The combined standard uncertainty was calculated through equations as follows; the combined relative uncertainty of A at the end of sampling can be obtained from equation **4;**

$$\frac{u_{(A)}}{A} = \sqrt{\left(\frac{u(C_T)}{C_T}\right)^2 + \left(\frac{u(V_T)}{V_T}\right)^2 + \left(\frac{u(P_{\alpha A})}{P_{\alpha A}}\right)^2 + \left(\frac{u(P_{\alpha T})}{P_{\alpha T}}\right)^2 + \left(\frac{u(m_s)}{m_s}\right)^2 + \left(\frac{u(y)}{y}\right)^2 + \left(\frac{u(f_3)}{f_3}\right)^2}$$
(4)

Where, VT is the volume of tracer (mL).

Where
$$y = \frac{R_{GA} - R_{BA}}{R_{GT} - R_{BT}} - q_1 \qquad (5)$$

iv) Calculation of MDA (minimum detectable activity) of ^{232}U, ^{234}U and ^{238}U based on their blank counts and its relation to the radiometric yield obtained:

$$MDA = \frac{2.71 + 4.65*\sqrt{B}}{\varepsilon*P_\alpha*t_B*S*R} \qquad (6)$$

Where B is the total counts of the region of interest (ROI) of the energy line of interest in the blank sample.

A blank sample was prepared with the same method as the real sample to control that no radioactivity was left in the electro-deposition cell. The lower limits of detection of ^{238}U, ^{234}U and ^{235}U are 1.1 mBq.kg^{-1}, 0.96 mBq.kg^{-1} and 1.2 mBq.kg^{-1} respectively.

Results

Gamma spectrometric (HPGe-detector)

Results obtained with gamma spectrometry on soil, sediment, plant and water samples were obtained and summarized in Table 1. ^{226}Ra (U-series) was determined via ^{214}Pb (295.2 and 351 keV) and ^{214}Bi (609.3, 1120.3 and 1764.5 keV). The ^{238}U was determined via ^{234}Th (63 and 92 keV), ^{234m}Pa (766 and 1001keV) and ^{230}Th (67.7 keV) [19]. ^{234m}Pa can be successfully used when measuring samples with medium to high uranium concentration [32]. The 93 keV peak suffers overlap of ^{228}Ac 93 keV X-ray peak. ^{234}U was hardly detected due to its low emission probability for direct gamma rays (53.2 keV and 120.9 keV). ^{235}U determination is affected by ^{226}Ra which often can't be suppressed (185.7 keV) and was hardly detected through 143.8, 163.4 and 205.3 keV. From the data obtained, the activity concentration measured by gamma spectrometry demonstrated that it is a valid for uranium in soil and sediment samples. However, when the activity of the sample (water and plant) to be measured is less than its gamma spectrometry MDA, another technique should be used.

Table 1 Specific activity (mBq.kg^{-1}) of natural radionuclides in the environmental samples using γ-Spectroscopy

Sample code	^{238}U (mBq.kg^{-1})	^{232}Th (mBq.kg^{-1})	^{40}K (mBq.kg^{-1})
Rock 1	2.0616E+07±1030.8E+03	4.94 E+04±4450	5.498 E+05±56 E+03
Rock 2	2.0601.3E+07±1030E+03	4.82 E+04±5.25 E+03	4.647 E+05±42 E+03
Rock 3	0.901167E+07±240E+03	0.7134 E+04±667 E+03	0.647 E+05±22 E+03
Rock4	0.83276E+07±543E+03	2.82 E+04±1.21 E+03	0.789 E+05±32 E+03
SOIL 1	1.9 E+03±0.7 E+03	0.12 E+04±0.5 E+03	0.06 E+05±0.9 E+03
SOIL 2	61.1 E+03±3.0 E+03	0.64 E+04±0.8 E+03	4.607 E+05±9 E+03
SOIL 3	2.15E+04±0.5 E+03	2.6 E+04±0.7 E+03	0.05 E+05±0.6 E+03
SOIL 4	1.2E+04±0.4E+03	3.6 E+04±0.7E+03	3.621 E+05±0.8E+03
Bottom sediments 1	31 E+03±2E+03	1.47 E+04±1.5E+03	2.15 E+05±6E+03
Bottom sediments 2	9.8 E+03±1E+03	1.39 E+04±1.2E+03	1.74 E+05±5.8E+03
Bottom sediments 3	0.87E+04±1E+03	2.31+04±1.5E+03	2.55 E+05±1.9E+03
Bottom sediments 4	0.48E+05±2E+03	2.2 E+04±3E+03	1.89 E+05±0.9E+03
Drainage water 1	< DL	< DL	< D
Drainage water 2	< DL	< DL	< DL
Tap water 1	< DL	< DL	< DL
Tap water 2	< DL	< DL	< DL
Ground water 1	< DL	< DL	< DL
Ground water 2	< DL	< DL	< DL
Plant 1	< DL	< DL	< DL
Plant 2	< DL	< DL	< DL
Plant 3	< DL	< DL	< DL

Alpha spectrometry

UTEVA resin is a specific for the selective separation for all actinides depending on the different acid concentrations used for radionuclide needed, so it was the perfect separation technique for Uranium isotopes separation and measured by alpha-spectrometry (where;U-238 peak at 4.77 mev.,U-234 peak at 4.17 mev. ,U-235 peak at 4.4 mev. and U-232 tracer peak at 5.32 mev.) ;although there is some interfering may be occurred from some elements which affected on the recovery obtained and poor alpha peaks as: i) The presence of any traces of iron (III) may lead to the bad resolution of the alpha peaks. The full width at half maximum (FWHM) of the spectrum peaks is greater than 100 keV, indicating the bad resolution of the spectrum, ii) Samples dissolution and radiochemical separation procedure was not efficient to eliminate all impurities, and this can be noticed from the small peaks appearing after uranium peaks, iii) Radon gas and any organic impurities may affect the electrodeposition of uranium and iv) To obtain precise and accurate data on the U isotopes in the analyzed samples, it is necessary to completely separate the uranium isotopes from trans uranium elements.

Table 2 represented the activity concentrations of ^{238}U, ^{234}U, ^{235}U and their recovery using UTEVA extraction chromatography. Uranium

recoveries were higher than 50 %, ranged from 59 to 79 %. A good chemical recovery (>79 %) was obtained with water samples than that obtained for soil, plant and sediment samples. It may be attributed that both soil, plant and sediments are complex samples to analyze because of present of stable elements which could be interfere in the separation process. Complete decomposition of the soil or sediment or plant sample is important because destruction of soil or sediment or plant matrices facilities the exchange and convert the nuclides to an ionic form [36]. The Minimum detectable activity was calculated and it is 0.00024 mBq.kg^{-1} for ^{238}U, 0.000953 mBq.kg^{-1} for ^{234}U and 0.001987 mBq.kg^{-1} for ^{232}U. For method validated, IAEA Certified Reference Materials with different matrix were used.

TOPO separation technique used for the separation of Uranium isotopes but it had some disadvantages because it talke along time and more and more chemicals; so high coast and chemical yield decreased.

As obtained in table 3, the chemical recovery using TOPO were found to be lower than that obtained by UTEVA for the same matrices (water, sediment, soil and plant) ranged from 26 % to 55 % [34].

Comparison of the methods

The analytical techniques (destructive and non-destructive) were verified using IAEA reference materials. As presented in Table 4, the results were in good agreement with the certified values. The results of IAEA reference samples given by gamma and alpha spectrometers are consistent with the IAEA reported result for soil and sediment samples which reflect the good agreement among the different techniques used. For water and plant samples it was hard to determine the activity concentration of uranium by gamma spectroscopy. It is preferable to use radiochemical separation of uranium isotopes followed by alpha spectrometry measurements. Gamma spectrometry is a practical method for soil and sediment samples as a rapid method and to consume time, efforts and cost.

By comparing the two radiochemical separation techniques (TOPO and UTEVA), it is clear that the recovery, time consuming task and analytical cost it is confirmed that UTEVA is a powerful method. Therefore, separation methods based on UTEVA extraction chromatography are preferable.

Table 2 Uranium isotopes activities (mBq.kg^{-1}) in some selected Environmental samples using UTEVA resin and their corresponding recoveries

Sample code	^{238}U(mBq.kg^{-1})	^{234}U(mBq.kg^{-1})	^{235}U(mBq.kg^{-1})	Chemical Recovery %
Rock 1	2.12E+07 ± 11.1 E+03	2.25E+07 ± 10.1 E+03	1.25E+06 E+03	61
Rock 2	2.51E+07 ± 12.1 E+03	2.59E+07 ± 10.1 E+03	1.50E+06 E+03	67
SOIL 1	2.51E+4 ± 1.3 E+03	1.72E+4 ± 1.1 E+03	< DL	59
SOIL 2	3.15E+4 ± 1.9 E+03	1.87E+4 ± 1.3 E+03	< DL	65
Bottom sediments 1	2.03E+4 ± 3.7 E+03	2.06E+4 ± 3.0 E+03	< DL	64
Bottom sediments 2	1.63E+4 ± 4.9 E+03	1.59E+4 ± 4.8 E+03	< DL	68
Tap water 1	2.7E-02 ± 0.2 E+03	4.9E-02 ± 0.2 E+03	< DL	70
Tap water 2	8.9E-01 ± 0.1 E+03	1.3E+00 ± 0.1 E+03	< DL	69
Ground water 1	1.5E+00 ± 0.1 E+03	1.5E+00 ± 0.1 E+03	< DL	79
Ground water 2	5.7E-01 ± 0.1E+03	5.7E-01 ± 0.1 E+03	< DL	72
Plant 1	3.37E-03 ± 0.002E+03	1.18E-02 ± 0.005 E+03	< DL	70

Table 3 Uranium isotopes activities (mBq.kg^{-1}) in some selected environmental samples using TOPO resin and their corresponding recoveries

Sample code	^{238}U(mBq.kg^{-1})	^{234}U(mBq.kg^{-1})	^{235}U(mBq.kg^{-1})	Chemical Recovery %
Rock 3	1.02278E+07±675E+03	9715.4 E+03±667 E+03	276.3 E+03 ± 150.1 E+03	55
Rock 4	0.94278E+07±885E+03	0.95375 E+07 ± 840E+03	0.02418E+07±134.6E+03	49
SOIL 3	2.26 E+04 ± 0.2E+03	18800 ± 500	< DL	40
SOIL 4	1.31 E+04 ± 0.4E+03	8800 ± 500	< DL	36
Bottom sediments 3	0.981E+04 ± 1.1E+03	7740 ± 870	< DL	38
Bottom sediments 4	0.559 E+05 ± 5.9E+03	49200 ± 110	< DL	46
Drainage water 1	56 ± 5	85 ± 6	< DL	54
Drainage water 2	97 ± 5	129 ± 6	< DL	48
Plant 2	1.8E+03 ± 0.43E+03	3.12 E+03 ± 570	< DL	44
Plant 3	4.39E+03 ± 0.85E+03	5.66 E+03± 980	< DL	26

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Egypt. J. Chem. **65,** No. SI:13B (2022)

Table 4 Results of Uranium isotopes Activities (mBq.kg⁻¹) in Some Selected IAEA Certified Reference Samples

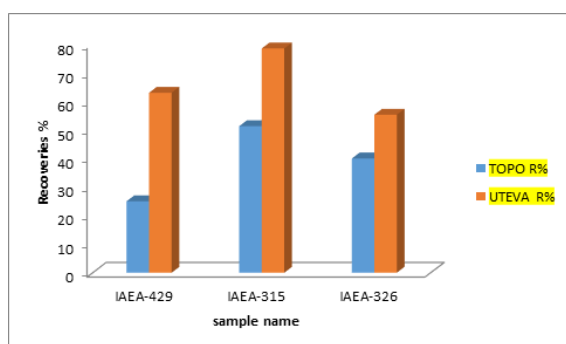| Samples	γ-Spectroscopy	Alpha Spectrometry								certified value	
		TOPO				UTEVA					
		^{238}U	^{234}U	^{235}U	R%	^{238}U	^{234}U	^{235}U	R%	^{238}U	^{234}U
IAEA-CU 2010-03	< DL	--	--	--	--	0.327	0.463	ND	97.5	0.31	0.47
IAEA-420	< DL	--	---	--	--	0.038	0.040	ND	68.4	0.036	0.045
IAEA-421	< DL	--	--	--	--	0.045	0.049	ND	86.5	0.041	0.050
IAEA-429	< DL	0.0076	0.007	0.0007	25	0.0156	0.0309	N. D	63	0.058	0.046
IAEA-315	19.2 ± 0.9	14.6	13.8	ND	51.3	15.909	17.518	1.850	78.5	17.6	17.8
IAEA-326	29.9±1.4	32.0± 1.4	31.4±3.4	ND	40	25.3± 2.9	24.08±3	15.2±2.1	55.3	29.4	27.9
IAEA-2011-04	30.8±2.3	--	--	--	--	23.572	26.649	7.974	69	27	26.4
IAEA-430	< DL	0.0715	0.077	ND	--	--	--	--	--	0.077	0.088
IAEA-375	19.7±0.9	13.2	13.9	ND	--	--	--	--	--	24.4	25
IAEA-330	< DL	-	-	-		0.87	1.09	N.D	80	0.95	1.02

* DL means under detection limit
* IAEA-CU 2010-03, IAEA-420, IAEA-421 and IAEA-430 are water reference material samples.
* IAEA-315 is a marine sediment reference material sample.
* IAEA-2011-04, IAEA-326 and IAEA-375 are soil reference material samples.
* IAEA-330 is a plant reference material sample.

Figure 2. Uranium recoveries for reference material Samples with different matrices using TOPO and UTEVA methods

Finally, we can conclude a comparison between advantages and disadvantages of Gamma spectrometry, Alpha spectrometry using TOPO and Alpha spectrometry using UTEVA for different techniques of different environmental samples as shown in table 5;

Table 5 Comparison between advantages and disadvantages of Gamma spectrometry, Alpha spectrometry using TOPO and Alpha spectrometry using UTEVA

Sample Types	Gamma spectrometry	Alpha spectrometry using TOPO	Alpha spectrometry using UTEVA
Rock	- Detectable and Reliable because it has high activity	- Lower chemical yield - High coast and time consuming	- Higher chemical yield - Rapid - Low coast
Soil	- Detectable and Reliable because it has high activity	- Lower chemical yield - High coast and time consuming	- Higher chemical yield - Rapid - Low coast
Bottom sediment	- Detectable and Reliable because it has high activity	- Lower chemical yield - High coast and time consuming	- Higher chemical yield - Rapid - Low coast
Plant	- Not enough for detection because it has low activity	- Lower chemical yield - High coast and time consuming	- Higher chemical yield - Rapid - Low coast
Drainage water	- Detectable and Reliable because it has high activity	- Lower chemical yield - High coast and time consuming	- Higher chemical yield - Rapid - Low coast
Ground water	- Not enough for detection because it has low activity	- Lower chemical yield - High coast and time consuming	- Higher chemical yield - Rapid - Low coast
Tap water	- Not enough for detection because it has low activity	- Lower chemical yield - High coast and time consuming	- Higher chemical yield - Rapid - Low coast

Conclusion

Several works have dealt with the determination of uranium radioisotopes concentrations in environmental samples. This study was carried out under the Research and Development program in CLERMIT (Central Laboratory of Environmental Radiological Measurements and Intercomparison Training) to implement a precise analytical technique for determination of uranium isotopes in environmental samples with different matrices. Two analytical techniques were used in CLERMIT to determine uranium isotopes; gamma spectrometry and alpha spectrometry. For alpha spectrometry, extraction chromatography using TOPO and UTEVA were

implemented. Isotopic activities ratios of uranium were accurately measured using UTEVA with high recovery (more than 70 %), time reduction and low cost. The method was applied to soils and sediments with pure chemical separation of U from the matrices. Finally we prefer alpha spectrometry than gamma spectrometry in the accurate determination of activity concentrations of uranium isotopes; alpha spectrometry, with a detection limit often 100–1000 times lower than gamma spectrometry, is a very sensitive alternative technique. The efficiency of alpha particle detection depends only on geometric factors and, when a careful radiochemical separation process is carried out, it does not suffer from spectral interference.

However, the overall process is time consuming and impractical for large-scale screening of environmental samples. In addition, radioactive tracers not present in the environment must be used to accurately assess activity.

Gamma Spectrometry is a useful non-destructive method that permits the simultaneous determination of many radionuclides in a bulk sample, without the need for complicated and time-consuming radiochemical separation. However, it is limited by the weak emission probabilities of many potentially useful emission lines, the poor efficiency of HPGe (hyper pure germanium) detectors over a wide energy range, the difficult task of precisely calibrating the efficiency of the detector, and the need to evaluate self-absorption and summation factors.

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