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Determination of uranium isotopes (^{234}U, ^{238}U) and natural uranium (U-nat) in water samples by alpha spectrometry

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ABSTRACT

Background: Due to the potential public health effects of releases of uranium to the environment, isotopic determination and measurement of this radionuclide in environmental samples is very important. Achieving this goal, monitoring program for this radionuclide seems necessary and is applied in many countries.

Materials and Methods: The uranium was separated from the water samples using anion exchange resin (Dowex 1×8 Cl^- form) and then purified by electrodeposition or co-precipitation method with Lanthanide fluorides such as Lanthanum fluoride (LaF_3) and finally the prepared source it is counted by Alpha spectrometry.

Results: The activity of ^{234}U, ^{238}U and natural uranium (U-nat) in 4 water samples, sent by Analytical Quality Control Services (AQCS) center of International Atomic Energy Agency (IAEA), were determined and the results were compared with the AQCS laboratories data. The ranges of measured activities for low and high activity samples were from 3.217×10^{-3} to 597 Bq/kg respectively.

Conclusion: Since the results were relatively close to the AQCS data, the applied procedure seems to be proper for isotopic uranium determination. It was observed that in case of low activity level samples, preparing source by co-precipitation method showed more accurate results.

Key words: *Uranium isotopes, activity, anion exchange resin, source preparation, electrodeposition, co-precipitation, alpha spectrometry.*

INTRODUCTION

Uranium is the heaviest element present in almost all minerals, rocks, sand, soil and is important because of its chemical and radiotoxicity. Natural uranium can be detected in low concentrations in nearly all materials from the environment. In radiochemical equilibrium, it consists of the isotopes ^{234}U, ^{235}U and ^{238}U with the activity ratio of 1:0.0462:1, corresponding to a mass ratio of .0054:0.711:99.2836 percent. All of these three nuclides are alpha emitters, which have a particular biological effectiveness (Pimple *et al.* 1991).

Radioactive nuclides from uranium and its decay series enter the human body mainly through food and drinking water (Bansal *et al.* 1992). Water comes into contact with several minerals under the earth's surface, and uranium is transferred to water by its leaching action. Water consumed by livestock and used for irrigating purposes can also be a source of this radionuclide. Sea water can be a contamination source for sea foods. Water from streams, lakes and ponds should also be considered as a source of contamination. (IAEA Technical Report series No.295). So, determination of this radionuclide in water has a great importance.

Determination of uranium isotopic composition in the environmental matrices such as soil, sediment, water, air particles, vegetation and

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bioassay samples, by Alpha spectrometry require very high degree of chemical purification (Gavinini *et al.* 1981).

In the literature, many radiochemical procedures for uranium determination are described. One of these methods, published in Health and Safety Laboratory (HASL) was taken and optimized for isotopic determination of uranium in water samples.

MATERIALS AND METHODES

Sample conditioning

Four water samples were sent by AQCS in which two samples were synthetic with low salinity (IAEA- 423 and IAEA-098), while one was natural with high salinity (IAEA-426) and the last one was synthetic with high salinity (IAEA-430). From activity point of view, two of them were high activity (IAEA-098 and IAEA-423) one was medium activity (IAEA-430), and the last one (IAEA-426) was low activity level (table 1).

According to AQCS report, the natural samples were collected from different locations in Austria and Poland in 2001 and the synthetic samples were tap water from Seibersdorf laboratories diluted by deionized water and spiked with known amounts of a certified standard solution containing natural uranium.

Samples conditioning were done according to following steps (HASL, 2000):

a. Acidifying sample to pH = 2 by nitric acid.
b. Adding exact amount of ^{232}U tracer solution in order to measure chemical recovery.

Table 1. ^{238}U, ^{234}U and U-nat concentrations in water samples.

Isotope and sample code	**Sample activity**	**Sample salinity**	**Sample structure**	**Chemical recovery (%)**	**Activity (Bq.kg^{-1}) (AQCS)**	**Activity (Bq.kg^{-1}) (Obtained)**	**Uncertainty (Bq.kg^{-1}) (AQCS)**	**Uncertainty (Bq.kg^{-1}) (Obtained)**
U-238(423)	High activity	Low salinity	Synthetic	67	0.238	0.1898	0.0012	0.0134
U-238(426)	Low activity	High salinity	Natural	22	0.026	0.02935	0.0072	0.004788
U-238(430)	Medium activity	High salinity	Synthetic	34	0.077	0.08296	0.0012	0.006541
U-238(098)	High activity	Low salinity	Synthetic	79	486	596.767	1.5	39.876
U-234(423)	High activity	Low salinity	Synthetic	67	0.239	0.1853	0.0017	0.0131
U-234(426)	Low activity	High salinity	Natural	22	0.09	0.1096	0.019	0.0125
U-234(430)	Medium activity	High salinity	Synthetic	34	0.088	0.09854	0.0017	0.007563
U-234(098) (Standard)	High activity	Low salinity	Synthetic	79	468	572.395	2.3	38.356
U-nat(423)	High activity	Low salinity	Synthetic	67	19.17*	15.26*	0.096*	1.523*
U-nat(426)	Low activity	High salinity	Natural	22	2*	2.363*	0.56*	0.4762*
U-nat(430)	Medium activity	High salinity	Synthetic	34	6.21*	6.667*	0.098*	0.733*
U-nat(098)	High activity	Low salinity	Synthetic	79	39200*	47960*	120*	4539*

*The natural uranium unit (U-nat) is in µg/kg.

c. Evaporating to dryness.
d. Converting system to nitric form by adding concentrated HNO_3 and evaporating to dry (two times).
e. Converting system to chloride form by adding concentrated HCl and evaporating to dry (two times).
f. Dissolving the residue in about 50 ml of 7N HCl.

In case of high salinity samples, the following procedures were added after b step:

1) Adding known amount of Fe^{+3} carrier solution to the sample.
2) Adjusting the pH of solution to 9-10 by adding ammonia solution. At this pH uranium will participate with iron hydroxide $\{Fe\,(OH)_3[U]\}$ (Bishop *et al.* 1978).
3) The precipitation was centrifuged and dissolved in concentrated HNO_3.

Then the next steps of sample conditioning (d, e and f) were repeated for high salinity samples, as well.

Uranium separation

There are different methods for uranium separation from sample matrix. Some of them are based on extraction with special organic solvents such as TOPO (Trioctylphosphinoxide) (Pimple e*t al.* 1992) and TIOA (Triisooctylamine) (Parsa 1992).

The other method uses anion exchange resin to separate uranium (HASL 2000, Takada *et al.* 1983, Jiang *et al.* 1986, Parsa 1992). In the present work, the latter method was selected for uranium separation. The anion exchange resin was Dowex 1×8 (Cl^-, 100-200 mesh). A column containing about 10 ml resin was prepared and preconditioned with 250 ml of 7N HCl .The sample, which was in form of 7N chloride (1-f), passed through the column. After passing the sample solution, 200 ml of 7N HCl passed through the column in order to eliminate Thorium (Th) (Alpha energies of ^{228}Th (5.42 MeV) and ^{232}U (5.32 MeV) were closed together so the existence of Th could cause some interferences in determination uranium therefore it should be eliminated. Uranium (with iron) was eluted from the column by passing 150 ml of 0.1N HCl. In order to separate iron from uranium (in case of those samples containing iron), the obtained solution was dried and made into 30 ml 8N hydrochloric acid. Iron was extracted using 30 ml Di-iso-butyl ketone into the organic phase (Takada *et al.* 1983).

Radiochemical purification of the uranium fraction

There were two main methods for Radiochemical purification or source preparation in Alpha emitters analysis process. These were: 1- Electrode position and 2- Co-precipitation by the lanthanide fluorides. Electrode position was chosen for three samples (IAEA098, IAEA423 and IAEA 430) in which uranium was deposited on stainless steel plates using a constant electrical current (Talvitie 1972, ASTM, C1284).

The co-precipitation method was applied for IAEA 426 samples (this sample was natural with low activity sample) which electrode position did not lead to good results for that.

This method was based on co-precipitating of uranium with lanthanum fluoride and filtering the precipitate with a membrane filter (Pimple *et al*. 1992, Parsa 1992, HASL 2000).

Alpha spectrometry and calculations

The measurement of ^{234}U, ^{238}U and were performed using passive implanted silicon surface barrier detector, 450 mm^2 Active area, 100 µm depletion depth and Alpha resolution of 35 keV (FWHM) connected to multichannel analyzer model 35 plus was manufactured by Canberra. Alpha spectrum of these isotopes is shown in figure 1.

Concentration levels of ^{234}Uand ^{238}U were calculated based on the known tracer (^{232}U), added to each sample. The ratio of the alpha peak areas after necessary correction for background and tailing was taken to be equal to the ratio of disintegration rates.

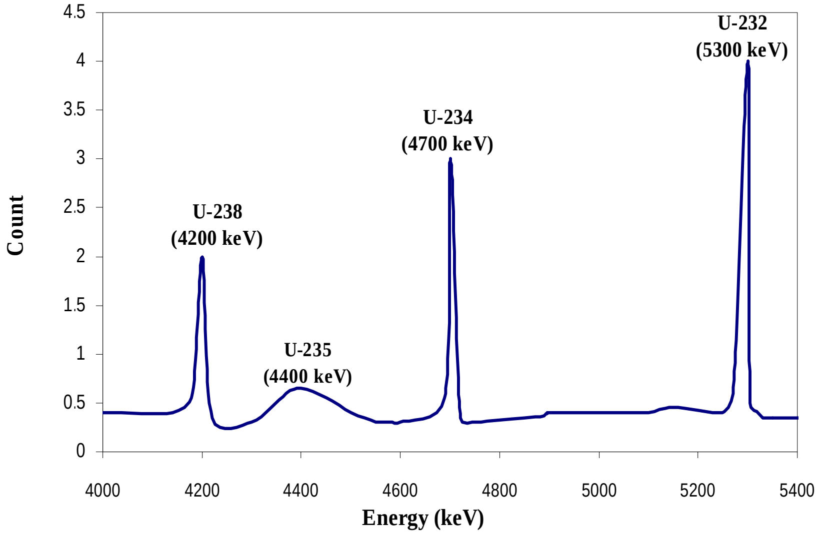

Figure 1. Typical alpha spectrum of uranium isotopes.

Calculations

- ∗ The formula applied to calculate the activity of each radionuclide is as follows:

$$\alpha\left({}^{238}U_{or}{}^{234}U\right)=\left[\frac{N_{({}^{238}U_{or}{}^{234}U)}}{N_{{}^{232}U}}\right]\times A_{({}^{232}U)}\times M^{-1} \qquad \textbf{(1)}$$

Where:

α (^{238}U or ^{234}U)= Concentration level of ^{238}U in the sample (Bq.kg^{-1}).

N (^{238}U or ^{234}U) = Net counts in the ^{238}U or ^{234}U peak.

N $^{232}{}_{U}$ = Net counts in the ^{232}U peak.

A $_{(}{}^{232}{}_{U)}$ = Concentration level of tracer added to the sample(Bq).

M = Mass of the sample (kg).

- ∗ The formula used for calculation of Recovery factor (chemical yield) is as follows:

$$R_f\% = \frac{N_{{}^{232}U}}{E_{ff}\times T\times A_{({}^{232}U)}}\times 100 \qquad \textbf{(2)}$$

Where:

R$_f$ = Recovery factor or chemical yield.

E$_{f\,f}$ = Counting efficiency (calculated by standard Pu-239 source).

T= Counting time (second).

A $_{(}{}^{232}{}_{U)}$ = Concentration level of tracer added to the sample (Bq).

- ∗ The formula used for calculation of Minimum Detection Activity (for 95% degree of confidence level) is as follows:

$$MDL = \frac{1.96\times\sqrt{N_{BG}}}{E_{ff}\times T\times R_f\times M} \qquad \textbf{(3)}$$

Where:

N$_{BG}$ = Background counts in each peak region.

R$_f$ = Recovery factor or chemical yield.

E$_{ff}$ = Counting efficiency (calculated by standard Pu-239 source).

T= Counting time (second) and

M = Mass of the sample (kg).

- ∗ The relations used for measuring natural uranium (U-nat) concentration are as follows:

$$Conc.({}^{238}U_{or}{}^{234}U)(\mu g.kg^{-1}) = \frac{\alpha({}^{238}U_{or}{}^{234}U)(Bq.kg^{-1})}{SA_{{}^{238}U_{or}{}^{234}U}(Bq.mg^{-1})}\times 1000(\mu g.mg^{-1}) \qquad \textbf{(4)}$$

$$Conc.(U-nat)(\mu g.kg^{-1}) = Conc.({}^{238}U)(\mu g.kg^{-1}) + Conc.({}^{234}U)(\mu g.kg^{-1}) \qquad \textbf{(5)}$$

Where:
α (^{238}U or ^{234}U)= Concentration level of ^{238}U in the sample.
Conc.(^{238}U or ^{234}U) = Weighting concentration of ^{238}U or ^{234}U.
SA = Specific activity which for ^{238}U and ^{234}U is 12.4 and 231585 Bq.mg^{-1} respectively (HASL,300).

RESULTS

The results are shown in table 1. Two sets of results were compared together using two tests suggested by AQCS for evaluating accuracy and precision. These tests are:

1. Accuracy test: The results were passed if:

$$\left|Value_{AQCS} - Value_{Analyst}\right| \le 3.29\times\sqrt{Unc._{AQCS}^{2} + Unc._{Analyst}^{2}} \qquad \textbf{(6)}$$

Where:
Value $_{AQCS}$: Sample activity pronounced by AQCS
Value $_{Analyst}$: Sample activity obtained by analyst (our experiment)
Unc. $_{AQCS}$: Uncertainty pronounced by AQCS
Unc. $_{Analyst}$: Uncertainty of analyst

2. Precision test: This test depends on activity level. The results were passed if:

$$\sqrt{\left(\frac{Unc._{AQCS}}{Value_{AQCS}}\right)^{2}+\left(\frac{Unc._{Analyst}}{Value_{Analyst}}\right)^{2}}\times 100\% \qquad \textbf{(7)}$$

(a) < Or = 40% for Low activity samples
(b) < Or = 30% for Medium activity samples
(c) < Or = 15% for High activity samples

The comparison results are shown in table 2. As it is observed in this table, more than 80% of our results are acceptable for accuracy and also half of them for precision.

DISCUSSION

It seems that diminished precision is because of high uncertainty in determination of tracer solution activity (The activity of ^{232}U tracer

Table 2. Comparing the obtained results with AQCS results using accuracy and precision tests.

Isotope and sample code	$\lvert Val_{AQCS}-Val_{Analyst}\rvert$	$3.29\times[(Unc_{IAEA})^2+(Unc_{Ana})^2]^{1/2}$	Accuracy	$[(Unc_{IAEA}/ Val_{AQCS})^2 + (Unc_{Analyst}/ Val_{Analyst})^2]^{1/2} \times 100\%$	Comparing with activity	Precision
U-238 (423)	0.05	0.044	F	0.07	0.035	P
U-238 (426)	0.003	0.018	P	0.32	0.0104	F
U-238 (430)	0.006	0.021	P	0.08	0.0231	F
U-238 (098)	111	131.09	P	0.07	72.9	P
U-234 (423)	0.05	0.043	F	0.07	0.036	F
U-234 (426)	0.02	0.047	P	0.24	0.036	F
U-234 (430)	0.01	0.024	P	0.08	0.0132	F
U-234 (098)	104	125.96	P	0.07	70.2	P
U-nat(423)	3.91	5.00	P	0.10	2.87	P
U-nat(426)	0.36	0.97	P	0.34	0.8	P
U-nat(430)	0.46	2.39	P	0.11	1.863	P
U-nat(098)	8760	14928.09	P	0.09	5880	P

P: Passed, F: Failed

solution should be determined by a reference laboratory such as AQCS) but because of some problems it was determined and also some systematic errors occurred in counting process.

The method can be used for determination of uranium isotopes in all environmental samples by making little changes mainly in sample conditioning (step1). The experiences showed that in case of natural, low level activity samples, co-precipitation method (for source preparation) leads to better results than electrodeposition. So, for these types of samples the former method has been suggested.

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