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Uranium Analysis in Aqueous Samples by Selective Extraction and Photon-Electron Rejecting Alpha Liquid Scintillation (PERALS®) Spectrometry

Hyun-Sang Shin, Myung-Ho Lee, Geun-Sik Choi, and Chang-Woo Lee
Korea Atomic Energy Research Institute
150 Dakjin-dong, Yusong-gu, Taejon 305-353, Korea
hyuns@nanum.kaeri.re.kr

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Abstract

This work describes the adaptation of extractive scintillation by URAEX™ with a photon-electron rejecting alpha liquid scintillation (PERALS®) spectrometer to the analysis of uranium in aqueous samples. The extraction efficiency of the system was evaluated under varing chemical conditions including pH, and sample-cocktail volume ratio. Isotopic information from the PERALS® spectrum of natural uranium was obtained using a curve fitting routine. Comparisons of the result with that obtained from alpha spectrometry method using ion implanted silicon detector showed good agreement.

Key Words : uranium isotopes, extractive scintillator, PERALS® spectrometry, alpha spectrometry

1. Introduction

Determination of uranium concentration and ^{234}U to ^{238}U activity ratios in environmental water samples is important in constructing the geochemical balance of these radionuclides and understanding their behaviour in the environment, and also concerned with radiation safety and monitoring [1-2]. Several techniques are usually used for the determination of low activities of uranium in the environmental samples. These techniques include radiochemical methods, fluorometry, mass spectrometry etc.. The mass spectrometer provides high sensitivity in the measurement of uranium isotopes of ^{234}U and ^{238}U having long decay times [3]. Its high cost, however, make it difficult to use the equipment for the analysis of environmental samples. Alpha spectrometry with semiconductor detectors is another sensitive technique commonly used for uranium determination [4-5]. Unfortunately, its use requires complicated sample preparation procedures prior to counting in vacuum, including steps such as preparation of thin and homogeneous sources, elimination of other interfering alpha emitters etc.. In addition, low counting efficiency due to the self-absorption of alpha emitters in the sample matrix results in poor counting statistics, which necessitates long

counting times for the determination of the low activities [5-6].

A number of studies have demonstrated in recent years that alpha-liquid scintillation by PERALS® spectrometry provides an attractive method for measuring alpha particle activity. These studies have found that the technique offers almost 100% counting efficiency, no self-absorption effect and high reproducibility [7-10]. The PERALS® spectrometer was specially designed for the detection of alpha particles in the presence of beta/gamma background [9-10]. Additionally, liquid-liquid extraction combined with the measurement of alpha particles can eliminate many quenching problems by extracting the nuclide of interest into the organic phase of a non-mixable cocktail [11-12]. Therefore, by using appropriate extractive scintillator with PERALS® spectrometer, one can easily perform an element-specific and quantitative separation and a subsequent assay in a relatively short period of time.

In the present work, uranium in aqueous samples was extracted by URAEX™ containing tertiary amine as a extractant and its activity was determined by PERALS® spectrometry. The extraction efficiency by URAEX™ was evaluated as a function of solution pH, Na_2SO_4 concentrations and sample-cocktail volume ratio in order to determine the optimum condition for maximum uranium extraction and minimum extraction of other alpha-emitters such as thorium and radium. We also compared the procedure with a alpha spectrometric technique with traditional radiochemical separation. Emphasis was given to the elaboration of a optimum procedure for the rapid and easy determination of uranium in the aqueous samples by PERALS® method and comparison of the procedure with that of a alpha spectrometry.

2. Experimental

2.1. Chemical Reagent

As an uranium extractive scintillator, UREAX™ purchased from ETRACK (East Tennessee Radiometric Chemicals) laboratories, Inc. was used in these studies. The extractive scintillator contains a tertiary mixed alkyl amine as the extractant, and 2-(4' -biphenylyl)-6-phenyl-benzoxazole (PBBO) as the scintillator in toluene. Naphthalene is also included to improve energy and pulse shape resolution [13]. The stock solution of uranium (240 ppm) was prepared by dissolving accurately weighed $U(NO_3)_2 \cdot 6H_2O$ (99.99%, Aldrich, Co) in double deionized water. The uranium concentration in the stock solution was checked by ICP-AES (JY50P, Jovin Yvon) prior to use. Tracer solutions of ^{226}Ra, ^{229}Th and ^{232}U were obtained from Isotope Products Laboratory. An aliquot of the solutions was separately delivered in glass vial and evaporated by concentrated sulfuric acid until fuming stops. The residues of each isotope were then diluted with double deionized distilled water to obtain stock solution of each isotope. The activity of the isotopes was checked by alpha spectrometric method prior to use. All other reagents were of analytical grade and purchased from Aldrich and Merk, and they were used without further purification.

2.2. Instruments

PERALS® spectrometry: An ORDELA model 8100 AB PERALS® spectrometer was used in the measurement and the schematic diagram of the counting system is presented in Fig. 1 [9].

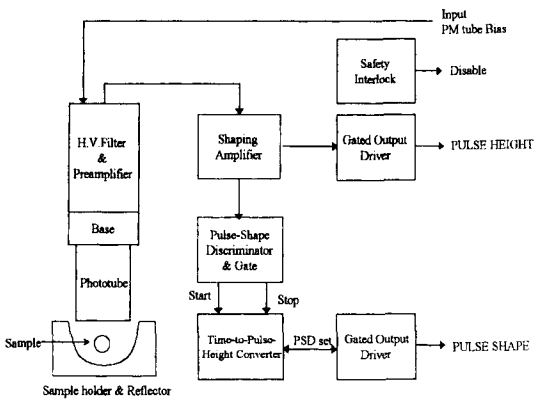

Fig. 1. Schematic Diagram of the PERALS® Spectrometor System

The counting system consists of a sample holder in a hemispherical chamber and reflector, a PM tube, a preamplifier, a shaping amplifier, and a pulse-shape discriminator. The sample chamber was filed with silicon fluid (polysiloxanes with 50 centistokes, Dow Coning® 200 Fluid) having similar refractivity to 10D × 75H mm borosilicate glass culture tube and high transmittance for ultraviolet. Alpha particles, as well as beta particles and gamma radiation produce light in the liquid scintillation solution of a sample placed in the sample holder/reflector assembly. This light is collected by the PMT that, in turn, produces a pulse with an amplitude proportional to the amount of light collected. Each input pulse to the system generates an amplified voltage pulse for pulse-height analysis and a pulse-shape signal with a voltage proportional to the time length of the incoming pulse. The PSD analyzes the pulse-shape voltages and generates a gating signal for only the alpha-induced light pulses which decay and return to zero more slowly than beta- or gamma-induced pulses. Energy calibration of the multichannel analyser was performed with a ^{226}Ra (4.78 MeV) standard sample containing its alpha daughters, ^{222}Rn (5.49 MeV), ^{214}Po (6.00 MeV) and ^{218}Po (7.69 MV).

pH measurement and alpha spectrometry: pH measurement was made using a glass electrode (Metrohm, Type 6.0202.100) coupled to a digital pH meter (Metrohm, Type 632). For complementary measurement and for comparisons, alpha spectrometer (Model 676A, EG&G ORTEC) with ion implanted surface barrier detector of 450 mm^2 active area was used. The detector was lodged in a vacuum chamber ($<10^{-2}$ torr) coupled to a low noise preamplifier system and a multichannel analyzer. Energy calibration of the detector was performed with a mixed standard source (^{239}Pu: 5.16 MeV, ^{241}Am: 5.48, ^{244}Cm: 5.81 MeV) obtained from Isotope Products Laboratory. The sample-detector distance was fixed as 10 mm, which give a 20 ± 1 % of alpha counting efficiency. Energy resolution of this detector was 25 KeV (FWHM) for the 5,486 MeV alpha particles of ^{241}Am. The detailed description of experimental procedure and condition has been described in our previous paper [14].

2.3. Preparation of Test Solution and Extractive Procedure Using URAEX™

For studies of the extraction dependence on various parameters, test solutions (100 *ml*) except in the case of aqueous volume dependence study were prepared in double deionized distilled water with desired amounts of acid, radionuclides, Na_2SO_4 and test anions. The pH was adjusted to the desired value with either 6.0 M H_2SO_4 solution or 6.0 M NH_4OH solution. The prepared solution was transferred to a 250 *ml* glass separatory funnel and 1.5 *ml* extractive scintillator, URAEX™, added to the

funnel. After shaking the mixed solution on a mechanical shaker (Model VS-8480SR, Vision scientific. Co.) for 5 minutes, the funnel was allowed to stand undisturbed for 30 minutes so that the phases could separate. The aqueous (lower) phase was drained off from the funnel and 1.0 *ml* of the organic phase was transferred to a 10D × 75H mm borosilicate glass culture tube. The culture tube containing sample was closed with a rubber septum (Adrich Co.) and purged with dried, toluene-saturated argon(99.9%) for 3 minutes prior to counting in the PERALS® spectrometer.

2.4. Sample Preparation for Uranium Extraction from Natural Waters

For uranium analysis in ground and drinking water samples, the sample is required to be treated properly prior to extraction. Briefly, an aliquot of water sample (generally, 500~1,000 *ml*) was transferred into a beaker and acidified with 5 *ml* concentrated H_2SO_4 instead of HNO_3 or HCl. In our preliminary study, it was observed that the presence of the anions (NO_3^-, Cl^-) has very detrimental effect on the extraction of uranium by tertiary amine, which agree well with other literature [15]. After covering the beaker with a watchglass, the solution was heated on a hot plate and boiled gently for 5 ~ 10 minutes to drive off radon(Rn) and to destroy any bicarbonate ion (HCO_3^-) present. The solution was then evaporated with reduced heat until the volume becomes around 100 *ml*. After cooling to room temperature, the solution was controlled to the sample conditions in pH 1.7 and 1.0 g/100 *ml* Na_2SO^4 concentration for uranium extraction using URAEX™. ^{232}U isotope can be added to the original water samples prior to the sample treatment to determine its chemical recovery.

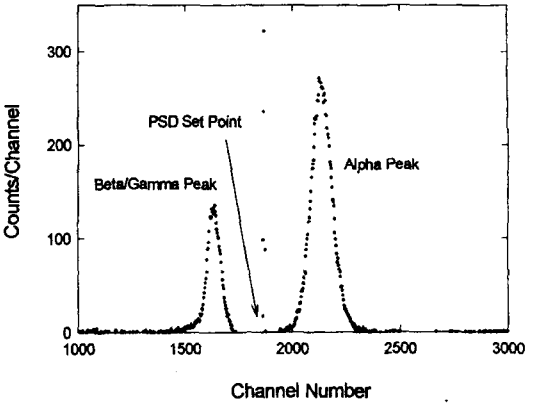

Fig. 2. PERALS® Pulse Shape Spectrum of the Depleted Uranium Sample, Which was Obtained at 2.3 of PSD Level

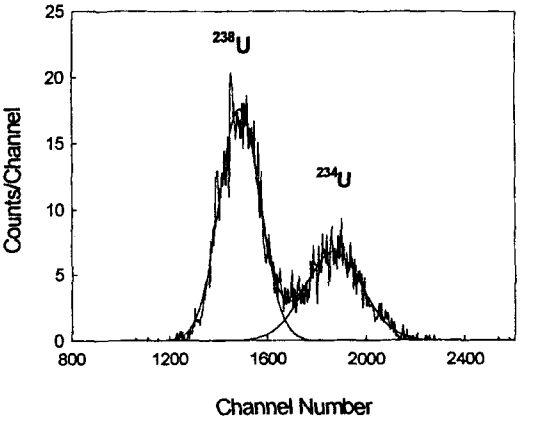

Fig. 3. PERALS® Pulse Height Spectrum of the Depleted Uranium Sample Showing 4.20 MeV Peak of ^{238}U and the 4.76 MeV Peak of ^{234}U

3. Results and Discussion

3.1. PERALS® Spectrum of Uranium Isotopes

Fig. 2 shows a pulse shape spectrum of

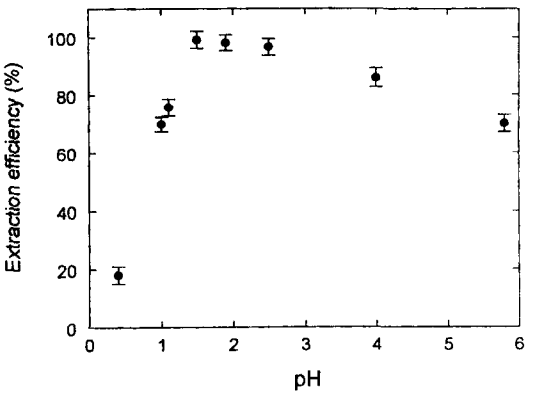

Fig. 4. Variation of Uranium Extraction Efficiency with pH of the Sample Solution

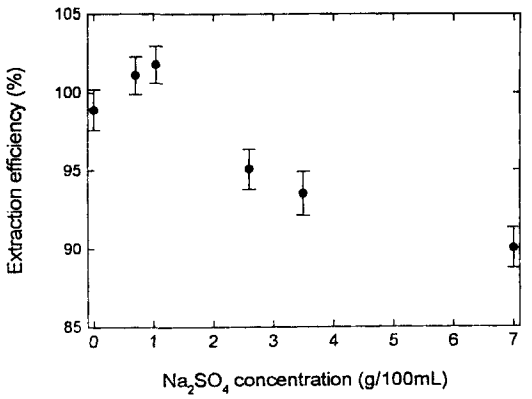

Fig. 5. Variation of Uranium Extraction Efficiency with the Amount of Na_2SO_4 Added in the Sample Solution

PERALS® from the extraction of the sample solution (20 *ml*) containing uranium at a concentration of 24 ppm. Two peaks, alpha (right) peak and beta/gamma (left) peak, being completely separated are appeared on the spectrum. It shows that the unwanted signals of beta and gamma events can effectively be rejected by adjusting the PSD level properly between the two peaks. Fig. 3 illustrates a pulse height spectrum of ^{234}U and ^{238}U in the sample solution, which was obtained at PSD set point of 2.3. The spectrum has a sufficient resolution for the ^{234}U to ^{238}U activity ratio to be analyzed. The resulting spectrum were fit using commercially available non-linear least squares fitting program (Peak Fit 4.0, *Jandal*) and give the value of ^{234}U to ^{238}U activity ratio, 0.55 ± 0.02. The reduction of the higher energy peak for ^{234}U indicates that the uranium sample is depleted in the lighter isotopes ^{234}U, ^{235}U. The concentration (Bq) of each uranium isotope, ^{238}U or ^{234}U, can then be easily calculated from the count rate measured for overall peaks of the spectrum.

3.2. Study of the Extraction of Uranium by URAEX™

Effect of pH on extraction: Solutions (100 *ml*) containing the depleted uranium, with known activity (5.94 Bq for ^{238}U), were prepared at the pH range from 0.4 to 6.0 and extracted using 1.5 *ml* URAEX™ to determine the percentage of recovery as a function of pH. The result is presented in Fig. 4. The uranium recovery obtained at pH range from 1.5 to 2.5 is quantitative as near 98 ± 1 % within experimental uncertainty. The recovery yield began to decline at a pH 1.5 and dramatic decrease in the recovery yield between pH value of 0.4 and 1.5 are observed (Fig. 1). The result is probably due to the forming of stronger complex of bisulfate with amine than dose the sulfate [15-16], which result in decreasing of uranium partition coefficient between URAEX™ containing tertiary alkyl amine compound as a extractant and aqueous solution.

The amount of Na_2SO_4 added in solution: Solutions (100 *ml*) containing the depleted uranium and different amounts of Na_2SO_4 were

Table 1. Extraction of Uranium at pH 1.7±0.1 as a Function of Aqueous Phase Volume

Aqueous volume (*ml*)	Organic volume (*ml*)	Added Na_2SO_4 (g)	U extracted[a] (%)
10	1.5	1.0	101.3 ± 5.0
20	1.5	1.0	103.1 ± 5.1
50	1.5	1.0	102.2 ± 4.5
100	1.5	1.0	100.8 ± 5.2
200	1.5	1.0	87.8 ± 4.9
500	1.5	1.0	75.3 ± 4.7
1000	1.5	1.0	48.8 ± 4.3

[a]quoted uncertainties are 2σ

prepared at pH 1.7 ± 0.1 and extracted using 1.5 *ml* URAEXTM. The amount of Na_2SO_4 added in the solution was increased up to 7.0 g, as shown in Fig. 5. The result shows that optimum additions of Na_2SO_4 for the extraction are found to be around 1.0 g at pH 1.7 ± 0.1, in which the recovery yield was 101.3 ± 4.8 %. The value is apparently higher than that of the solution measured without addition of Na_2SO_4, which indicating that the process of uranium extraction by the use of URAEX™ is preferred in sulfate system [12].

Aqueous phase volume : In order to determine the optimum volume of aqueous phase for the direct extraction with URAEX™, the percentage of uranium (^{238}U) extracted into the extractive scintillator was measured as a function of aqueous phase volume. For this, organic phase volume is fixed at 1.5 *ml* and aqueous phase volume was varied from 10 *ml* to 1000 *ml*. In each case the aqueous phase pH was adjusted to 1.7 ± 0.1 and the 1.0 g Na_2SO_4 was added to the solution. As a result, the uranium obtained at less than 100 *ml* of aqueous volume was quantitative within experimental uncertainty, but there is observed a significant decrease at greater than 100 *ml*. The results are presented in Table 1.

Effect of thorium and radium on uranium extraction: In the experimental conditions described above, the influence of thorium and radium concentrations on the uranium extraction by the use of URAEX™ was evaluated, because of the two ions are ubiquitously found in natural water samples and could be extracted by amine-based extractant [12, 17]. For this study, each solution (100 *ml*) containing ^{229}Th and ^{226}Ra, with known activities, was separately prepared at pH 1.7 ± 0.1 and extracted using 1.5 *ml* URAEX™. The percentage recovery of ^{229}Th and ^{226}Ra was then measured just as the percentage of uranium extracted has been measured. The results show that the percentage of the thorium and radium extracted were found to be less than 0.3±0.1 % and 0.5±0.2 % respectively, while that of uranium was near 100 %. The results indicate that interference from thorium and radium is practically negligible for the extraction conditions established in this work for uranium analysis.

3.3. Evaluation of Minimum Detectable Activity

Minimum detectable activity (MDA) of the proposed method was evaluated using Currie

Table 2. Comparison of the Proposed Extractive Procedure Using PERALS® and Alpha SpectromeTry with Ion Implanted Silicon Detector for the Determination of the Uranium Activity in Water Samples

Sample	Technique	Sample volume (*l*)	Preparation time (h)	Measurement time (min.)	Activity of U isotopes[c] (Bq/ *l*)	MDA[d] (mBq/ *l*)
Ground water	PERALS®	0.5	3	200	0.110 ± 0.004[a] 0.134 ± 0.004[b]	3.22
	Alpha Spec.	5.0	72	200	0.106 ± 0.003[a] 0.129 ± 0.004[b]	0.55
Drinking water	PERALS®	1.0	4	200	0.035 ± 0.003[a] 0.059 ± 0.003[b]	1.90
	Alpha Spec.	10.0	72	200	0.033 ± 0.003[a] 0.060 ± 0.003[b]	0.39

[a]the value represents ^{238}U activity, [b]the value represents ^{234}U activity, [c]quoted uncertainties are 2σ
[d]the MDA value was obtained from the background count rate measured in the region of the ^{234}U and ^{238}U peaks

equation [18]:

$$MDA(Bq/L) = \frac{4.65 \times \sqrt{C_B}}{V \times \varepsilon \times 60 \times T} \quad (1)$$

where V is the volume of sample (*l*), T (min) the sample measurement time (which is the same as for the background), ε the efficiency and C_B is the background counts using a radiochemical blank. The blank sample was prepared by extracting only 100 *ml* double deionized distilled water containing 1.0 g Na_2SO_4 at pH 1.7 with UREAX™ (1.5 *ml*). Resulting MDA value obtained with T = 200 minutes was 3.22 mBq/ *l* . The lower MDA value can be obtained with increasing the counting time: With counting time of 500 min, the value was lowered to 1.80 mBq/ *l* .

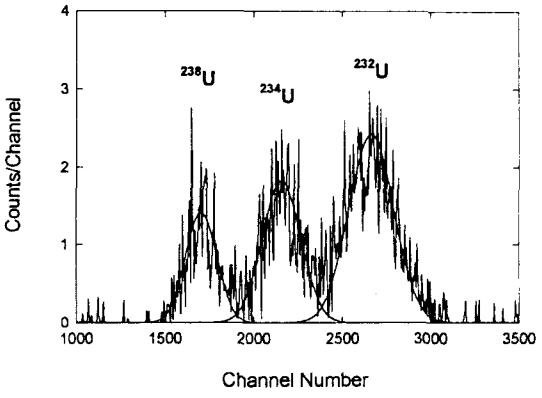

Fig. 6. Weighted Non-linear Least Squares Fit of a PERALS® Spectrum of the Natural Uranium Extracted from a Groundwater Sample Containing ^{234}U, ^{238}U, and ^{232}U Added as a Yield Tracer

3.4. Application to Environmental Water Samples

The analysis procedures established in this study were applied to the ground water and bottled drinking water samples spiked with ^{232}U as a yield tracer, prior to extraction. Duplicated ground water (500 *ml*) and bottled drinking water samples (1,000 *ml*) from the same source were obtained for this study. Detailed sample

preparation procedure is described earlier in this paper. The sample solution pH was adjusted to 1.7 ± 0.1 and 1,0 g of Na_2SO_4 was added to the solution. Pulse height spectrum of ^{232}U, ^{234}U and ^{238}U from the PERALS® spectrometer was obtained by counting for 200 minutes, and then deconvoluted into three area of the isotopes using the curve fitting program as shown in Fig. 6. Percentage recovery of each of the spiked samples was calculated with the measured activities of ^{232}U, and estimated to be 88 ± 4 % for the ground water samples and 95 ± 4 % for the bottled drinking water samples, respectively. The error associated with calculated average values is corresponding to 95.5 % confidence level of the mean. The ^{234}U to ^{238}U activity ratio (1.22 ± 0.04) of uranium in the ground water sample was measured from the fitted deconvolution curves, and the concentrations of each isotope can thus be determined. ^{235}U isotope information, however, could not be ascertained because of the current resolution limitation of the PERALS® spectrometer.

3.5. Comparison of PERALS® with Alpha Spectrometric Methods

The uranium analysis for the ground water and bottled drinking water samples was also carried out by traditional alpha spectrometric method with ion implanted silicon detector, and the result obtained is compared with that of PERALS® spectrometry. The radiochemical procedure used in the alpha spectrometric method, involving the steps of direct evaporation, solvent extraction, ion-exchange separation and electrodeposition, has been described in detail elsewhere [14]. Results for the samples using the two methods are given in Table 2. Two methods give similar results, but PERALS® uses a lower sample volume and shorter times of sample preparation. Approximately 72 hours per sample were required, using the alpha spectrometric method, to chemically process the ground water samples. At 200 minutes of counting time per sample, MDA on the order of 0.55 mBq/ l for the isotopes of uranium (^{234}U and ^{238}U) was obtained. The chemical recoveries for the ground water and drinking water samples were similar to each other and were in the range of 60 to 70 %. In contrast, the PERALS® extraction procedure required only 3 hours per sample to completely prepare the ground water sample for counting. Each sample was counted for 200 minutes to achieve the uranium MDA of 3.22 mBq/ l . Similar results were also observed in the comparative experiment performed with bottled drinking water samples (see Table 2)

4. Conclusions

A rapid and easy method for the determination of total uranium activity and ^{234}U to ^{238}U activity ratios in aqueous sample by PERALS® spectrometry has been established. This method combines chemical separation and sampling preparation into a single step with the use of an extractive scintillator, URAEX™, containing tertiary alkyl amine as the extractant. It was found that near 100% of uranium was selectively and quantitatively extracted from aqueous solutions at pH 1.7 ± 0.1, while below 0.7% of thorium and radium are extracted. The method provides results which are comparable to a traditional radiochemistry technique using alpha spectrometry with semiconductor detector. The PERALS® procedure required only 6.5 hours per sample, while the alpha spectrometric technique required approximately 75 hours per sample for complete separation and obtaining similar counts for the uranium isotopes (^{234}U and

^{238}U). The established procedure is thus suitable for the low level uranium determination in environmental samples and can be considered as an alternative tool to the conventional alpha spectrometry methods. However, it should be noted that PERALS® method could not ascertain ^{235}U isotope information because of its poor resolution limitation compare with that of the radiochemical method.

Acknowledgement

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