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Determination of Uranium in Aqueous Samples by Photon-Electron Rejecting Alpha Liquid-Scintillation (PERALS®) Spectrometry

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Abstract

A method for measuring uranium isotopes in water samples by selective and quantitative extraction by URAEX™ and alpha counting by PERALS® spectrometer has been studied. The extraction efficiency of the system was evaluated under varying 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 resul with that obtained from alpha spectrometry methods using ion implanted silicon detector showed good agreement.

1. Introduction

Determination of uranium concentration and $^{234}U/^{238}U$ activity ratios in environmental water samples is important in the field of radiation safety and monitoring [1]. Several techniques including radiochemical methods, fluorometry, mass spectrometer etc. are usually used for the determination of low activities o uranium in the environmental samples.

Recently, PERALS® spectrometry (acronym for photon-electron rejecting alpha liquid scintillation) was developed by the Oak Ridge Detector Laboratory (ORDELA, Inc.,). The PERALS® spectrometer was specifically designed for the detection of alpha particles in the presence of beta/gamma background [2]. In its current configuration, the technique uses a nearly total rejection of beta/gamma emission (99.9%) by incorporating of electronic pulse-shape discrimination (PSD). Additionally, liquid-liquid extraction approach is combined with the measurement of alpha particles and eliminate many quenching problems by extracting the nuclide of interest into the organic phase of a non-mixable cocktail [3].

The purpose of this study is to elaborate a rapid and simple method fo uranium determination in the aqueous samples using URAEX™ extraction from water samples followed by counting the alpha particles by PERALS® spectrometer. The extraction efficiency by URAEX™ was evaluated in the presence of potential chemical interference, chloride ion and nitrate ion and experiment on the optimum pH and sample-cocktail volume ratio were carried out. Additional studies have been conducted to determine the optimum conditions for quantitative uranium extraction while extracting a minimum amount of some other alpha-emitters such as radium and thorium.

2. Experimental

2-1. Chemical reagent

As an uranium extractive scintillator, UREAX™ purchased from ETRAC (East Tennessee Radiometric Chemicals) laboratories, Inc. is used in these studies. The extractive scintillator contains tertiary amine (MG > 300) as the extractant, and 2-(4'-biphenylyl)-6-phenyl-benzoxazole (PBBO) as the scintillator in toluene. The stock solution of uranium was prepared by dissolvin accurately weighed $U(NO_3)_2$ $6H_2O$ (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 Laboratories. All other reagents were of analytical grade and purchased from Aldrich and Merk

2-2. Apparatus

An ORDELA model 8100 AB PERALS® spectrometer was used in the measurement. The instrument is capable of rejecting more than 99.9 % of beta- and gamma-events and has alpha-counting efficiency of 99 % when pulse-shape discriminator (PSD) is properly adjusted. 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 detailed description of experimental procedure and condition have been well described in our previous paper [4].

2-3. Preparation of test solutions and uranium extraction using URAEX™

For studies of the extraction dependence on various parameters, test solutions (100 mL except in the case of aqueous volume dependence studies) were prepared in double deionized distilled water with desired amounts of acid radionuclides, sodium sulfate and test anions. The pH was adjusted to the desired value with either 6.0 M NaOH solution or 6.0 M NH4OH solution. The prepared solution (100 mL) was transferred to a 250 mL glass separator funnel and add 1.0 g of sodium sulfate to convert the sample solution to a sulfate system. The 1.5 mL of extractive scintillator (URAEX™) was then added to the funnel for uranium extraction. After shaking the mixed solution on a mechanical shaker (Model VS-8480SR, Vision scientific. Co.) for 5 min., the funnel was allowed to stand undisturbed for 30 minutes so that the phase could separate. The 1.0 mL of the organic phase was pipetted and transferred into a

10 mm × 75 mm borosilicate glass culture tube, and then sparged for 3 minutes with toluene-saturated argon prior to counting in the PERALS® spectrometer.

2-4. Sample preparation for uranium extraction from a groundwater

For uranium analysis in environmental water samples, the sample is required to be treated properly for uranium extraction. The proposed procedure for water sample is as follows: acidify 500 mL aliquot of water with 5mL concentrated H_2SO_4. Heat the solution to boiling on a hot plate and boil gently for 5-10 minutes to drive off radon (Rn) and to destroy any bicarbonate ion (HCO_3^-) present. Reduce the heat and evaporate until the volume is around 100 mL. Cool to room temperature and control to the proper sample conditions in pH and sodium sulfate concentration, and extract uranium in the aqueous phase using URAEX™. ^{232}U isotope was added to the original water samples prior to prior treatment to determine its chemical recovery yield.

3. Results and Discussion

3-1. PERALS® spectrum of uranium isotopes

Fig. 1 shows a pulse shape spectrum of PERALS® from the extraction of the sample solution containing depleted 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 signal of beta/gamma-events can effectively be rejected by adjusting the PSD level properly between the two peaks. Fig. 2 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 $^{234}U/^{238}U$ activity ratio to be analyzed. The resulting spectrum were fit using commercially available non-linea least squares fitting program (Peak Fit 4.0, *Jandal*) and give the value of $^{234}U/^{238}U$ activity ratio, 0.35/0.65. The reduce of the higher energy peak for ^{234}U

indicates that the uranium sample is depleted in the lighter isotopes $^{234, 235}U$. The concentration of each uranium isotope can then be easily calculated with the count rate measured for overall peaks of the spectrum.

3-2. Study of the extraction of uranium by URAEX^{TM}

Effect of pH on extraction: Solutions (100 mL) containing depleted uranium were prepared at the pH range from 0.4 to 6.0 and extracted using 1.5 mL URAEX^{TM} to determine the percentage of recovery as a function of pH. The result is presented in Fig. 3. The uranium recovery obtained at pH range from 1.5 to 2.5 is quantitative within experimental uncertainty as near 100%. 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 [5], which result in decreasing of uranium partition coefficient between URAEX^{TM} containing tertiary amine as a extractant and aqueous solution.

Aqueous phase volume : In order to determine optimum volume of aqueous phase for the direct extraction with URAEX^{TM}, the percentage of uranium 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 1.7 ± 0.1. The uranium recovery obtained at less than 100 mL of aqueous volume was quantitative within experimental uncertainty and its average value is 98.2 ± 4.5 %, but there is observed a significant decrease at greater than 100 mL.

Interference of NO_3^- *and* Cl^- *on extraction* : The effects of nitrate and chloride anions on uranium extraction by the use of URAEX^{TM} are tested for potential interferences on the extraction system. The anions are commonly used to acidify environmental water samples to avoid adsorption of actinides on the walls of the container used for sampling. They are also known to be mos ubiquitously present in the ground water [6].

For this, solutions (100 mL) containing depleted uranium and different amounts of NaCl and $NaNO_3$ added were separately prepared at pH 1.7 ± 0.1 and extracted using 1.5 mL URAEX^{TM}. The experimental results are shown in Fig. 4. Extraction efficiency decreased as concentration of chloride or nitrate anions in the sample solution was increased. With NaCl in the system, the extraction efficiency decreases by almost 47% between 200 and 3000 ppm. For $NaNO_3$, more significant decrease is seen at levels higher than 50 ppm indicating that the presence of nitrate provides more pronounced detrimental effects on the extraction system. Such a dramatic decrease of the extraction efficiency by the use of URAEX^{TM} in the presence of nitrate anion is probably due to the formation of nitrate complexes with U(VI) which are weakly absorbed by the tertiary amines, which effect on the extractive distribution coefficient of the extraction [7]. For the quantitative extraction of uranium under the higher anion concentrations (> 1000 ppm for Cl^-, and > 200 ppm fo NO_3^-), therefore, it should be recommended that converting the system to sulfate media.

Effect of thorium and radium on uranium extraction: The influence of thorium and radium concentrations on the uranium extraction by the use of URAEX^{TM} was studied, because of the two ions are ubiquitously found in natural water samples and it can be extracted by amine-based extractant [8]. For these studies, each solution (100 mL) containing ^{229}Th and ^{226}Ra, with known activities, were separately prepared at pH 2.0 ± 0.1 and extracted using 1.5 mL URAEX^{TM}. The percentage recovery of ^{229}Th and ^{226}Ra extracted by the use of URAEX^{TM} from the solution was measured just as the percentage of uranium extracted has been measured. The results show that the percentages of the thorium and radium extracted were found to be about 0.3 ± 0.2 % and 0.7 ± 0.2 % respectively, while that of the uranium was 99.2 ± 4.1 %. 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 equation [9]. For this, the blank sample was prepared by only mixing 100 mL double deionized distilled water containing 1.0 g sodium sulfate at pH 1.7 and UREAX^{TM} (1.5 mL). Resulting MDA value obtained with T = 200 min was 3.2 mBq/L. Lower MDA value can be obtained with increasing the counting time: With counting time of 500 min, the value was 1.1 mBq/L.

3-4. Application of the PERALS$^{®}$ technique to environmental water samples and comparison with alpha spectrometry

The analysis procedures established in this study were applied to groundwater samples (100 mL) spiked with ^{232}U as a yield tracer, prior to extraction. Three batch of groundwater samples from the same source are obtained for this study. Detailed sample preparation procedure is described earlie part in this paper. The sample solution pH was then adjusted to 1.7 ± 0.1 and 1.0 g of sodium sulfate was added. Pulse height spectrum of ^{232}U, ^{234}U and ^{238}U from the PERALS$^{®}$ spectrometer was obtained by counting for 200 min., and then deconvoluted into three area of the isotopes using the curve fitting program as shown in Fig. 5. Percentage recovery of each of the spiked samples was calculated with the measured activities of ^{232}U, and estimated to be 73.4 ± 3.2 %. The reduced recovery of uranium in the groundwater sample may result from the interferences of the anions present in the groundwater. The ^{234}U/^{238}U activity ratio (1.207) of uranium in the sample was also measured from the fitted deconvolution curves, and the concentrations of each isotope can thus be determined.

The uranium analysis for the groundwater 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 co-precipitation, solvent extraction, ion-exchange separation and electrodeposition, has been described in detail elsewhere [4]. Results for the samples using the two methods are given in Table 1. Two methods give similar results, but PERALS® uses a lower sample volume and shorter times of sample preparation and measurement.

4. Conclusion

A rapid and easy method for the determination of total U activity and $^{234}U/^{238}U$ 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™. Uranium of near 100 % was selectively and quantitatively extracted from the aqueous solutions at pH 1.7 while below 1.0 % of thorium and radium are extracted. The method provides results that are comparable to a traditional radiochemistry technique. The PERALS® procedure required only 6.5 hours per ground water sample, while the radiochemistry technique required approximately 89 hours per the ground water sample for complete separation and counting. 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.

Acknowledgements.

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References

1. J. D. J. Kronfeld, Hydrologic investigation and the significance of $^{234}U/^{238}U$ disequilibrium in the ground waters of central Texas, pH. D. Dissertation, Rice University, Houston (1974).
2. W. J. McDowell, "Photon/electron-rejecting alpha liquid scintillation (PERALS)spectrometry: A review," *Radioact. Radiochem.*, 3, 26 (1992).
3. Y. Dazhu, Z. Yongjun, and S. Mobius, "Rapid method for alpha counting with extractive scintillator and pulse shape analysis," *J. Radioana Nucl. Chem.*, 147, 177 (1991).
4. M. H. Lee and M. Pimpl, "Development of a new electrodeposition method for Pu-determination in environmental samples," *Appl. Raiat. Isot.* 49, 875 (1999).
5. J. D. leyba, H. S. Vollmar, R. A. Fjeld, T. A. Devol, D. D. Brown, and J. R. Cadieux, "Evaluation of a direct extraction/liquid scintillation counting technique for the measurement of uranium in water," *J. Radioanal. Nucl. Chem.* 194, 337 (1995).
6. P.C. Jay and J. M. Judd, Determination of common anion concentration in surface and groundwater samples by eluent-suppressed ion chromatography AECL-8576, Chalk River, AECL (1985)
7. J. Korkish, Modern methods for the separation of rare metal ions Pergamon Press, Hungary (1969).
8. V. G. Escobar, F. V. Tome, J. C. Lozano, and A. M. Sanchez, "Extractive procedure for uranium determination in water samples by liquid scintillation counting," *Appl. Radiat. isot.*, 49, 875 (1998).
9. L. Currie, "Limits for qualitative detection and quantitative determination," *Anal. Chem.*, 40, 586 (1968).

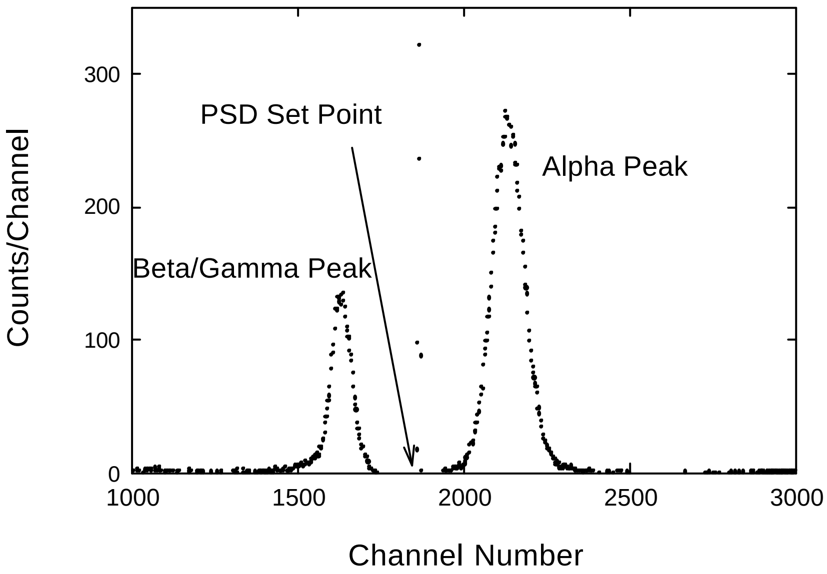

Fig. 1. PERALS pulse shape spectrum of the depleted uranium sample, which was obtained at 2.3 of PSD level

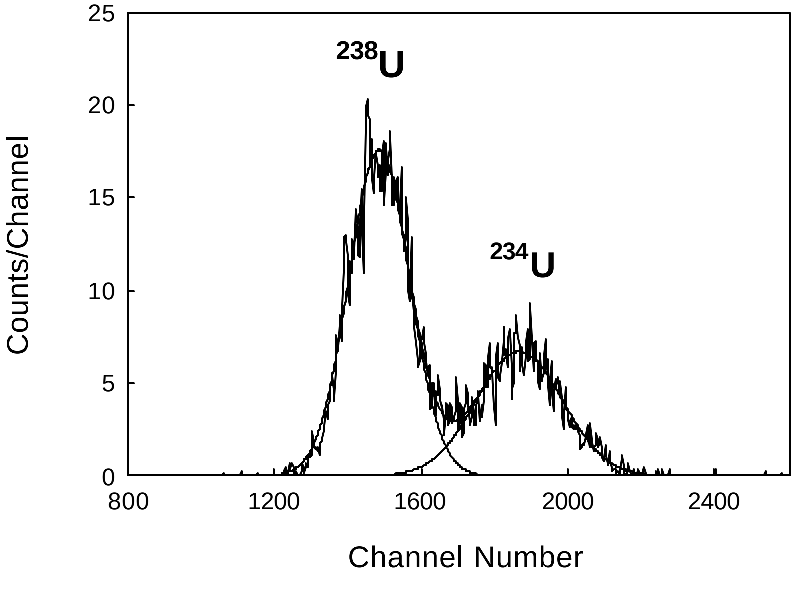

Fig. 2. PERALS pulse height spectrum of the depleted uranium sample showing 4.20 meV peak of ^{238}U and the 4.76 meV peak of ^{234}U

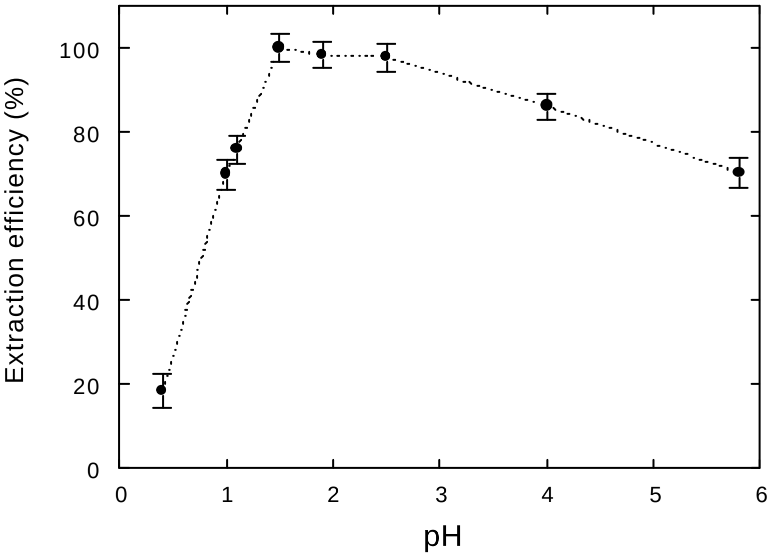

Fig. 3. Variation of uranium extraction efficiency with pH of the sample solution.

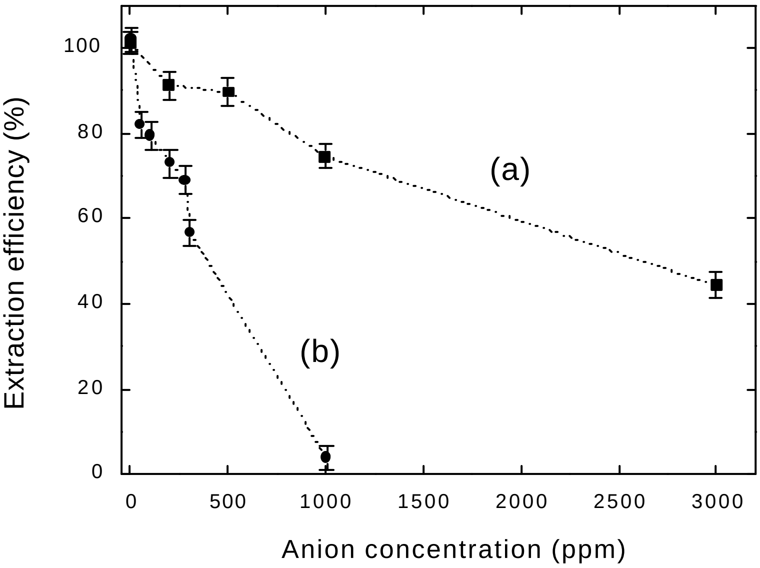

Fig. 4. Variation of uranium extraction efficiency with the (a) chloride and (b) nitrate anion concentration in the sample solution.