ANALYTICAL SCIENCES FEBRUARY 2005, VOL. 21

Indirect Determination of Uranium by the On-line Reduction and Fluorimetric Detection of Cerium(III)

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A novel flow injection method has been developed for the indirect determination of uranium by the on-line reduction and subsequent fluorimetric detection of cerium(III). A sample solution containing uranium(VI), prepared as a sulfuric acid solution, was injected into a sulfuric acid carrier solution and passed through a column packed with metal bismuth to reduce uranium(VI) to uranium(IV). The sample solution was merged with a cerium(IV) solution to oxidize uranium(IV) to uranium(VI) and the cerium(III) generated was then monitored fluorimetricaly. The present method is free from interference from zirconium, lanthanides, and thorium, and has been successfully applied to the determination of uranium in monazite coupled with an anion-exchange separation in a sulfuric acid medium to eliminate iron(III). The sample throughput was 25 per hour and the lowest detectable concentration was 0.0042 mg l^{-1}.

(Received September 27, 2004; Accepted November 8, 2004)

Uranium is now used mainly as fuel in nuclear power stations, and some uranium compounds are also used as catalysts and staining pigments. It is brought into the environment as a result of leaching from natural deposits, release in mill tailings, emission from the nuclear industry, the combustion of coal and other fuels, and the use of phosphate fertilizer that contains uranium. Various flow injection (FI) methods have so far been developed for the determination of uranium in diverse samples.

Most of the reported FI methods have employed spectrophotometry to detect uranium using sensitive chromogenic reagents. Among the typical chromogenic reagents used are Arsenazo III, 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP), Chromazurol S (CAS), and 4-(2-pyridylazo)-resorcinol (PAR). Theses reagents are not selective for uranium, *e.g.*, they also react with zirconium, thorium, and lanthanides to form colored complexes, and require some measures to overcome interferences from other metals. For example, the determination of uranium in samples containing both uranium and thorium with Arsenazo III was based on two injections per sample; in the first the sample was reduced in a lead mini-column [U(VI) → U(IV)] and the obtained signal was due to the total amount of thorium and uranium in the sample; the second injection was performed while avoiding the reduction step, the obtained signal thus being mainly due to the thorium content in the sample.[1] Trace uranium in geological samples was determined by on-line levextrel CL-5209 resin separation and preconcentration, and spectrophotometry with Arsenazo III using diethylenetriaminepentaacetic acid (DTPA) and sodium fluoride as masking reagents.[2] Although Br-PADAP has a greater tolerance to iron(III), and has found wide applications as a very sensitive reagent in the spectrophotometric determination of uranium(VI), *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) was essential as a masking reagent to determine uranium in leach liquor samples with Br-PADAP.[3,4] When uranium was determined with CAS in the presence of thorium, interference from thorium was eliminated by the use of ethylenediaminetetraacetic acid (EDTA) as a masking reagent.[5] Uranium in tin tailings was determined with PAR using *trans*-1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA), sodium fluoride, or sulfosalicylic acid to mask the interfering ions.[6] The spectrophotometric determination of uranium in rock and water samples required an in-valve column containing Duolite C-225(H) resin for preconcentration and separation, and detection with PAR using triethanolamine and CyDTA as masking reagents.[7]

Because the fluorimetry of uranium in solutions is not sensitive, laser-induced fluorimetry was applied to the determination of uranium in percentage or mg ml^{-1} in test samples prepared from concentrates and other uranium-rich materials.[8] When uranium in waste water was determined with conventional fluorimetry, it was first concentrated from sample solutions prepared as 0.03 mol l^{-1} in EDTA, 0.06 mol l^{-1} in tartrate, and 0.05 mol l^{-1} in fluoride (pH 9.3) on a silica-gel column, and then eluted with a mixture of 1.33 mol l^{-1} sulfuric and phosphoric acids to be detected by a fluorimeter.[9]

Inductively coupled plasma mass spectrometry (ICP-MS) is increasingly selective toward heavier elements, and hence has recently been used as a detection technique in flow injection analysis to determine trace concentrations (sub-ppm) of uranium. Uranium in urine and blood samples was determined by ICP-MS without any sample preparation[10] or ICP-MS coupled with extraction chromatography with UTEVA™ (a commercially available resin for extraction chromatography) after microwave digestion.[11] However, the determination of uranium in natural water samples required on-line separation and preconcentration to remove the potentially interfering

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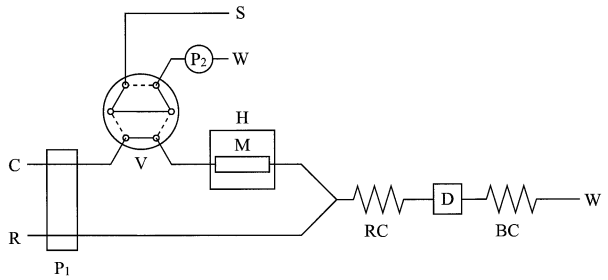

Fig. 1 Schematic diagram of the flow injection system used. C, carrier solution (0.3 mol l^{-1} sulfuric acid); R, 5×10^{-5} mol l^{-1} Ce(IV) solution (0.1 mol l^{-1} sulfuric acid); V, injection valve; P_1, P_2, pump; S, sample (100 µl); H, heater (85°C) ; M, Bi-reduction column (30 cm × 2 mm); RC, reaction coil (50 cm); D, spectrofluorometer; W, waste; BC, back pressure coil (0.5 mm × 5 m).

matrix, columns packed with activated alumina,[12] TRU™ (a commercially available resin for extraction chromatography),[13] UTEVAT™,[14] newly synthesized chitosan resins,[15] or a chelating disk[16,17] having been used.

The present work was undertaken to develop a selective flow injection method of analysis for the determination of uranium in the presence of thorium and lanthanides. The developed analytical method here measures the fluorescence of cerium(III) in order to determine uranium indirectly, and is free from interference from zirconium, rare earths and thorium, allowing us to determine uranium in monazite coupled with a simple anion-exchange separation of iron(III). The lower detection limit is 0.0042 mg l^{-1} and the sample throughput is 25 per hour.

Experimental

Reagents

All chemicals used were of analytical reagent grade. Distilled-deionized water was used after further purification by a Milli-Q® Ultra pure water purification system (Millipore, Bedford, USA).

A uranium(VI) stock solution of 1000 mg l^{-1} was prepared by dissolving an appropriate amount of uranylnitratehexahydrate (Kanto Chemicals, Tokyo) in 0.1 mol l^{-1} nitric acid. Working uranium(VI) solutions were prepared daily by diluting proportionally the stock solution with 0.3 mol l^{-1} sulfuric acid.

A cerium(IV) stock solution was prepared by dissolving prescribed amount of cerium(IV) sulfate tetrahydrate (Kanto Chemicals, Tokyo) in 0.1 mol l^{-1} sulfuric acid.

To prepare a reduction column, bismuth shots (99.999%, Wako Chemicals, Tokyo) were crushed, sieved to collect 250 to 300 µm pieces and packed in a 30 cm × 2 mm i.d. polytetrafluoroethylene (PTFE) column plugged at the ends with cotton.

A strongly basic anion-exchange resin (Bio-Rad AG 1, X-8, 100 to 200 meshes, chloride form (Bio-Rad Labs., CA, USA)) was used for a column-separation procedure. A glass column of 10-mm inner diameter was packed with 1 g of the anion-exchange resin and conditioned with 20 ml of 0.1 mol l^{-1} sulfuric acid before use.

Instrumentation

A block diagram of the flow injection analysis system used is shown in Fig. 1. The system was constructed with 0.5-mm i.d. PTFE tubing. A double plunger pump Sanuki DMX2000 (Sanuki Kogyo, Tokyo) was used for propelling the carrier and cerium(IV) solutions. A peristaltic pump (Perista Mini Pump SJ1211 (Atto, Tokyo)) was used for filling a sample solution to a six-way loop injection valve. A Model S3370 spectrofluorimetric detector (Soma Optics, Tokyo) was used to monitor cerium(III).

Recommended procedure

About 100 µl of a sample solution prepared as 0.3 mol l^{-1} in sulfuric acid was injected into the carrier solution, 0.3 mol l^{-1} sulfuric acid (0.75 ml min^{-1}), and passed through a bismuth column to reduce uranium(VI) to uranium(IV). The sample solution was then merged with a 5×10^{-5} mol l^{-1} cerium(IV) solution (0.1 mol l^{-1} in sulfuric acid) (0.75 ml min^{-1}) to oxidize uranium(IV) to uranium(VI), and the fluorescence of the generated cerium(III) was monitored at 350 nm (excitation wavelength: 260 nm). The obtained signal was fed directly to a pen recorder, and the average of the peak heights, measured triplicate for each sample, was used for quantification.

Analysis of monazite

About 0.1 g of a powdered monazite sample was decomposed according to a procedure described in a previous paper.[18] The sample solution was made up as a 20-ml solution of 0.3 mol l^{-1} sulfuric acid.

A 5-ml aliquot of the sample solution was loaded on the anion exchange column at a flow rate of 1 ml min^{-1}, and the column was washed with 40 ml of 0.1 mol l^{-1} sulfuric acid. Then, uranium adsorbed on the column was eluted with 20 ml of 1 mol l^{-1} hydrochloric acid at a flow rate of 1 ml min^{-1}. The effluent was collected in a 50-ml beaker and evaporated nearly to dryness. About 3 ml of nitric acid and 2 ml of 3 mol l^{-1} sulfuric acid were added and heated on a hot plate until dense fumes of SO_3 appeared to destroy fluorescent contaminants introduced from the ion-exchange resin. The wall of the beaker was rinsed with water and heated again until dense fumes of SO_3 appeared. The sample solution was transferred into a 20-ml volumetric flask and diluted to the mark with water, and then subjected to determination of uranium by flow injection analysis (see *Recommended procedure*).

Results and Discussion

Principle of indirect fluorometric determination of uranium

Uranium(VI) shows weak fluorescence in aqueous solutions and its direct measurement is not practical for the determination of uranium. Therefore, the fluorescence of cerium(III), which is generated by the reaction of cerium(IV) with uranium(IV), was used to detect uranium more sensitively. In this work, uranium(VI) in samples was reduced to uranium(IV) by a mini-column packed with metal bismuth, and then uranium(IV) was oxidized to uranium(VI) by a reaction with cerium(IV) in the flow system. The fluorescence of the generated cerium(III) was monitored at 350 nm to determine uranium.

Effect of the sulfuric acid concentration used as a carrier solution

The effect of the sulfuric acid concentration in the carrier solution was investigated over the concentration range of 0.1 to 0.5 mol l^{-1}. The slope of the calibration graph (unit: cm ppm^{-1}) exhibited a maximum at around 0.3 mol l^{-1}. Furthermore, noisy signals were obtained at a higher concentration of sulfuric acid. Hence, a 0.3 mol l^{-1} sulfuric acid solution was used as a carrier solution hereinafter.

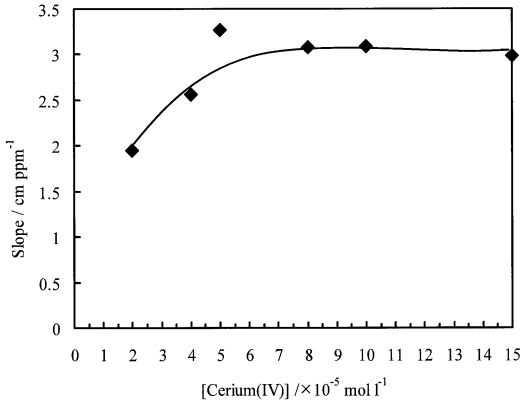

Fig. 2 Effect of the Ce(IV) concentration on the slope of the calibration graph. Bismuth column, 10 cm × 2 mm (85°C); total flow rate, 2 ml; reaction coil, 100 cm; carrier solution, 0.3 mol l^{-1} sulfuric acid.

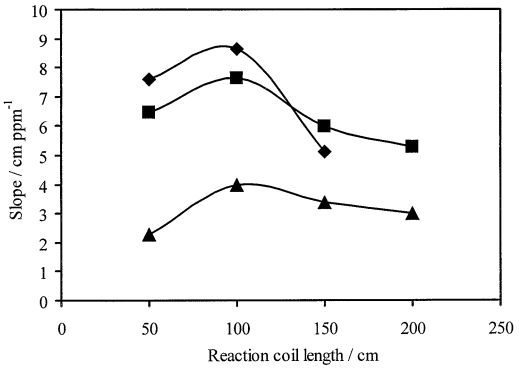

Fig. 3 Effect of the reaction coil length and the flow rate on the slope of the calibration graph. Bismuth column, 10 cm × 2 mm (85°C); [Ce(IV)], 2 × 10^{-5} mol l^{-1}; carrier solution, 0.3 mol l^{-1} sulfuric acid. Total flow rate: ◆, 1 ml min^{-1}; ■, 1.5 ml min^{-1}; ▲, 2 ml min^{-1}.

Effect of the cerium(IV) concentration

The effect of the concentration of cerium(IV) solution was studied over the range of 2 × 10^{-5} to 1.5 × 10^{-4} mol l^{-1} to ensure the oxidation of uranium(IV). All of the cerium(IV) solutions tested were prepared as 0.1 mol l^{-1} in sulfuric acid. The results are given in Fig. 2. The slope of the calibration graph increased with the concentration of cerium(IV), and reached a maximum at 5 × 10^{-5} mol l^{-1}, and then remained almost constant. Since the concentration of sulfuric acid at higher than 0.1 mol l^{-1} in the cerium(IV) solution did not affect the slope of the calibration graph, the cerium(IV) solution was prepared as 5 × 10^{-5} mol l^{-1} in cerium(IV) and 0.1 mol l^{-1} in sulfuric acid.

Effect of the heating temperature of the bismuth column

The efficiency of the bismuth reduction column was presumed to increase with an increase in the temperature. The slope of the calibration graph increased monotonously with increasing heating temperature from 70 to 85°C, as expected. The heating temperature of the bismuth column was maintained at 85°C (the upper limit attained by the bath used). No air bubbles evolved in the flow cell because of the use of a back pressure coil.

In a preliminary experiment, the use of a cooling coil yielded a decrease in the observed peak heights. This is because cooling the sample solution served to slow down the rate of the reaction of uranium(IV) with cerium(IV). Therefore, a cooling coil was not placed after the bismuth column in the FIA system finally established.

Reaction coil length and flow rate of the carrier and cerium(IV) solutions

The effect of the reaction coil length was studied over the range of 50 to 200 cm by keeping the total flow rate at 1.0, 1.5 or 2.0 ml min^{-1}. The flow rates of the carrier and cerium(IV) solutions were adjusted to be the same as each other. The largest slope was observed with a 100-cm reaction coil at every flow rate (Fig. 3). The lower was the flow rate, the larger was the slope. However, a total flow rate of 1.5 ml min^{-1} was employed in subsequent experiments, while considering the sample throughput. The length of the reaction coil finally used was fixed at 50 cm after additional experiments, described below.

Effect of the length of the bismuth column

The influence of the bismuth column length was studied using 10 and 30 cm columns (the inner diameter was kept at 2 mm). A larger slope of the calibration graph was obtained by a 30-cm column, so that the 30-cm bismuth column was employed for further experiments. Here, the effect of the reaction coil length was tested again over the range of 50 to 200 cm, and the order of the slope of the calibration graph observed was 50 cm > 100 cm > 150 cm > 200 cm. This was probably because the 50-cm reaction coil was sufficient, since heating the sample solution at the bismuth column should accelerate the reaction of uranium(IV) with cerium(IV); the increase in the reaction coil length, therefore, resulted in an increasing dispersion of the samples. Accordingly, the 50-cm reaction coil was used hereinafter.

Effect of diverse ions

The effect of diverse ions usually accompanying uranium was examined by using standard solutions of 0.05 or 1 mg U per litter; the obtained results are summarized in Tables 1 and 2.

Zirconium, yttrium, lanthanoids, and thorium even at one hundred-times the uranium concentration did not interfere with the determination of uranium, *e.g.*, the relative errors were less than 5%. These elements are well-known examples that give serious interference to the spectrophotometric determination of uranium. Magnesium and scandium are tolerable at, or less than, the concentration of uranium. The reason why scandium at higher levels interferes with the determination of uranium is not yet clear, but both might be easily separated from uranium by anion exchange in a sulfuric acid medium, even if they are present at higher levels in samples. Iron(III) was reduced by a bismuth column and then reduced cerium(IV) to cerium(III), resulting in profound errors, even at the same concentration levels as those of uranium. Therefore, the anion-exchange separation of iron in sulfuric acid medium was coupled with the present FI method for the determination of uranium in monazite.

Chloride reduced cerium(IV) to cerium(III), yielding marked errors even at concentrations as low as 1 mg l^{-1}. Nitrate might have been reduced in the bismuth column to nitrite, which reduced cerium(IV) to cerium(III).

Determination of uranium in monazite

Monazite is a phosphate of the cerium metals (La, Ce, Pr, Nd, and Sm) and thorium, usually containing grains of rutile, zircon, and various silicates. In advance of applying the present FI method to a real monazite sample, a preliminary investigation was carried out in order to confirm the elimination of iron

Table 1 Effect of diverse ions

Ion	Added/ mg l^{-1}	Uranium			
		Added/ mg l^{-1}	Found[a]/ mg l^{-1}	Added/ mg l^{-1}	Found[a]/ mg l^{-1}
Th(IV)	0.1	0.050	0.051	1.000	1.007
	1		0.051		1.002
	10		0.054		1.004
	100		0.056		0.998
La(III)	0.1	0.050	0.047	1.000	1.015
	1		0.055		1.015
	10		0.053		1.018
	100		0.094		1.056
Eu(III)	0.1	0.050	0.048	1.000	0.992
	1		0.049		1.008
	10		0.050		0.994
	100		0.053		0.997
Zr(IV)	0.1	0.050	0.049	1.000	1.004
	1		0.052		1.003
	10		0.053		1.023
	100		0.040		1.073
Sc(III)	0.001	0.050	0.051	1.000	—
	0.01		0.052		—
	0.05		0.052		—
	0.1		0.054		1.020
	1		0.062		1.030
	10		0.126		1.090
	100		—		1.290
Fe(III)	0.0001	0.050	—	1.000	1.003
	0.001		0.051		1.001
	0.01		0.076		0.999
	0.1		0.316		1.016
	1		—		2.844
Y(III)	0.1			1.000	1.004
	1				1.003
	10				1.023
	100				1.073
Mg(II)	0.1	0.050	0.052	1.000	—
	1		0.083		—
	10		0.096		—

a. Averages of two or three measurements.

Table 2 Effect of anions

Ion	Added/ mg l^{-1}	Uranium			
		Added/ mg l^{-1}	Found[a]/ mg l^{-1}	Added/ mg l^{-1}	Found[a]/ mg l^{-1}
Cl^-	0.1	0.050	0.045	1.000	1.000
	1		0.075		1.874
NO_3^-	0.001	0.050	—	1.000	0.986
	0.01		0.048		1.011
	0.1		0.049		1.011
	1		0.075		1.011
	10		0.053		1.011
	100		0.032		0.926

a. Averages of three measurements.

interference by anion exchange in a sulfuric acid medium using a mock solution prepared as follows: 0.163 mg Mg(II), 0.372 mg Ca(II), 0.423 mg Al(III), 0.462 mg Fe(III), 2.78 mg Y(III), 2.77 mg La(III), 17.7 mg Ce(III), 9.74 mg Th(IV), 0.25 mg U(VI), and 0.388 mmol of phosphate per 25 ml of 0.3 mol l^{-1} sulfuric acid.[18] One milliliter of the mock solution was loaded on the anion-exchange column for each run, and the uranium separated was determined by the proposed FI method. The average recovery of uranium obtained by the three runs was 101%, and the relative standard deviation was 0.96%.

Table 3 Determination of uranium in monazite sample by FIA and ICP-AES

Run	Sample taken/ mg		FIA		ICP-AES	
			U found/ μg	Content in original sample, %	U found/ μg	Content in original sample, %
1	100.0	0	455	0.455	431	0.431
2	100.5	0	473	0.470	430	0.428
3	99.7	0	488	0.489	425	0.426
4	102.5	0	452	0.441	433	0.423
5	72.0	70	428	0.497	421	0.488
6	47.2	70	272	0.429	267	0.417
7	48.0	70	293	0.464	270	0.417
8	51.1	70	308	0.466	299	0.448
9	50.0	70	293	0.447	289	0.438

In a 0.3 mol l^{-1} sulfuric acid medium, the distribution coefficients of uranium(VI) and iron(III) on a strongly basic anion-exchange resin, Bio-Rad AG 1, are about 70 and 3, respectively.[19] Therefore, uranium(VI) was adsorbed on the AG 1 column from 0.3 mol l^{-1} sulfuric acid, and separated quantitatively from iron(III) passing through the column. Scandium(III) was not included in the mock solution, but its distribution coefficient on AG 1 in 0.3 mol l^{-1} sulfuric acid medium was about 4; it would thus be easily separated from uranium(VI). On the other hand, zirconium(IV) was strongly adsorbed on an AG 1 column from 0.3 mol l^{-1} sulfuric acid (distribution coefficient: 150) and co-eluted with uranium(VI) from the AG 1 column. However, the proposed FI method is not disturbed by zirconium(IV) and hence would give accurate results even if the samples might have contained zirconium.

Based on these observations, a monazite sample was analyzed for uranium according to the procedure described in Experimental; the obtained results are listed in Table 3 together with those obtained by ICP-AES. ICP-AES was applied to sample solutions after ion-exchange separation. The results (0.462 ± 0.022%) obtained by the FI method are rather lower than those (0.435 ± 0.022%) obtained by ICP-AES, but a *t*-test revealed that there was no statistical difference between the results obtained using both methods at the 95% confidence level.[20]

Performance of FI system

Under the optimum condition established above, the lower detection limit calculated as the analyte concentration, giving a signal equal to the blank signal plus three standard deviations of the blank,[21] was 0.0042 mg l^{-1}. The calibration graphs of standard uranium(VI) solution *versus* peak height were linear over the ranges of 0.005 to 0.02 mg l^{-1} (r^2 = 0.9986) and 0.2 to 10 mg l^{-1} (r^2 = 0.9997) at high and low sensitivity ranges of the spectrofluorometer, respectively. The relative standard deviation for 22 measurements of 1 mg l^{-1} of uranium(VI) was 0.7%. The sample throughput was 25 per hour.

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