Thorium Coprecipitation Method for Spectrophotometric Determination of Arsenic(III) and Arsenic(V) in Groundwaters

Yuzo TAMARI, Nobuki YAMAMOTO, Haruo TSUJI and Yuzuru KUSAKA

Department of Chemistry, Faculty of Science, Konan University, Higashinada, Kobe 658, Japan

A new coprecipitation method for the spectrophotometry of arsenic(III) and arsenic(V) in groundwater has been developed. Arsenic(III) and arsenic(V) were coprecipitated with thorium(IV) hydroxide from 1000 ml of groundwater at pH 9. The precipitate was centrifuged and then dissolved with hydrochloric acid. Arsenic(III) was spectrophotometrically determined by the usual silver diethyldithiocarbamate (Ag-DDTC) method after generating the arsenic to arsine with sodium tetrahydroborate under masking the thorium with EDTA-NaF at pH 6. From another portion of the same groundwater, both arsenic(III) and arsenic(V) were determined by the Ag-DDTC method after reducing all the arsenic to arsine with sodium tetrahydroborate at pH less than 1 in the presence of the EDTA-NaF. The concentration of arsenic(V) was obtained by subtracting that of arsenic(III) from the total for arsenic.

Keywords Arsenic, coprecipitation, thorium hydroxide, groundwater, spectrophotometry, silver diethyldithiocarbamate

Arsenic in fresh water is distributed in a wide range of concentrations; *e.g.* in Japan, 0.01–13.9 ppb in rain water¹, 0.25–7.7 ppb in river water¹, and 30–3950 ppb in hot spring water.¹ Groundwater and river water are useful for life: both are utilized for drinking or industry. It is our concern to know the concentration of arsenic in drinking water, since arsenic was recognized as being an essential trace element for both humans and other animals in 1975.² We have investigated for the vertical concentration of arsenic with its oxidation state and for the sedimentation process of the element in a reservoir used for drinking water.³ We have also investigated the arsenic content of rocks and rock-forming minerals in order to study the dissolution effect of arsenic from rocks⁴ and the origin of arsenic in water.

Arsenic has been determined by using solvent extraction methods; the extraction of an arsenic(V)-molybdate complex, $H_7[As(Mo_2O_7)_6]^5$, into 1-butanol^{6,7} or methyl isobutyl ketone⁷ from acidic solutions, or generally by measuring the absorbance of Molybdenum Blue⁷ produced by the reduction of the complex in acidic media. For a determination of trace arsenic (III and V) in water samples, this Molybdenum Blue method or the Ag-DDTC method described in this abstract has been applied after preconcentration with the precipitation of a thionalide arsenic(III) complex⁸, or after coprecipitation of both arsenic with iron(III) hydroxide^{9,10} and zirconium(IV) hydroxide.¹¹ In the iron(III) hydroxide coprecipitation method, however, the purification of the iron(III) reagent used, the aging for

precipitation, and the adjustment of the different pH for the quantitative collection⁹ of arsenic(III and V) are required. Since we have found that all the arsenic were collected with thorium(IV) hydroxide formed at pH 9, we have developed a new coprecipitation method for arsenic. We have spectrophotometrically determined the ppb levels of respective arsenic in groundwater using the Ag-DDTC method. This thorium(IV) hydroxide coprecipitation method has been applied for the collection of uranium¹² in seawater and selenium¹³ in sea- and groundwaters. The thorium- and zirconium-coprecipitation methods are superior to the iron method in that there are no requirements regarding the purifications of both the reagents used as precipitants and of the aging for precipitation, due to the low arsenic content of the reagents and to the probably rapid reaction between arsenic (III and V) and both the hydroxide formed, respectively. However, the thorium method is recommended rather than the zirconium one since there is almost a 100% recovery for respective arsenic(III) and arsenic(V), whereas there is an 85% recovery for arsenic(III) with the zirconium method. In a groundwater sample, we compared each arsenic value determined by the proposed method with that by the zirconium method.

Experimental

Reagents

Highly pure water, distilled twice and doubly deionized, was used throughout the present work.

A standard 1000 mg/l stock solution of arsenic(III) was prepared by dissolving 0.1320 g of arsenic trioxide with 10 ml of a 1 M sodium hydroxide solution, diluting it with water, adding 10 ml of 2 M hydrochloric acid, and then making up to 100 ml with water.

A standard 100 mg/ml stock solution of arsenic(V) was prepared as follows. To 10 ml of the stock solution of arsenic(III) in a beaker add 5 ml of concentrated nitric acid and 1 ml of 6 M hydrochloric acid; dry up it on a water bath; and then dissolve the residue with water to 100 ml.

A working solution of standard arsenic(III) and arsenic(V) (containing 10 µg of respective arsenic per 5 ml) was prepared by diluting the stock solution with water.

A thorium 10 mg/ml solution was prepared by dissolving 2.38 g of thorium(IV) nitrate tetrahydrate (Wako Pure Chemical Industries, Ltd., Osaka, Japan) in water containing 2 ml of 6 M hydrochloric acid and then diluted to 100 ml with water. The thorium solution was used without any purification.

Silver diethyldithiocarbamate (Ag-DDTC) in chloroform was prepared by dissolving 0.25 g of Ag-DDTC (Dojin Chem. Labo., Kumamoto, Japan) and 0.05 g of brucine dihydrate in chloroform purified by distillation, and by diluting to 100 ml with chloroform.

A 4%(w/v) sodium tetrahydroborate (STB) solution was prepared by dissolving 0.8 g of STB (Wako Pure Chemical Industries) with water and diluting to 20 ml with water. The freshly prepared STB solution was used for experiments.

A tris buffer (pH 6) solution was prepared by dissolving 7.57 g of tris(hydroxymethyl)aminomethane hydrochloride (Sigma Chemical Co. Ltd., U.S.A.) in 10.3 ml of 6 M hydrochloric acid, and then diluted to 25 ml with water. For experiments, use a solution diluted to 1/50 with water.

A solution of EDTA-NaF (0.2 M each) was prepared by dissolving 74.5 g of disodium EDTA dihydrate and 8.4 g of sodium fluoride in water, then diluting to 1000 ml with water.

All other reagents and solutions were of the highest purity available, and were used without further purification.

Apparatus

A spectrophotometer (Model 100-10, Hitachi Ltd.) and a pH meter (Model M-8) equipped with a glass electrode were used.

The same experimental apparatus used for generating and collecting arsine (shown in a paper by the authors¹¹⁾) was used.

Recommended procedure

Coprecipitation of arsenic(III) and arsenic(V). To a beaker containing 1000 ml of water add about 2 ml of concentrated hydrochloric acid to adjust the pH to about 1. Add 7.5 ml of thorium solution and then 25% aqueous ammonia dropwise, to be adjusted to the

pH 9. After allowing to stand for about 1 h at room temperature, discard the supernatant of the solution. Transfer the residual precipitate to a centrifugal tube (50-ml volume) with a stopper, centrifuge the tube at 2500 min⁻¹ for 20 min, and then discard the supernatant solution.

Determination of arsenic(III). Dissolve the precipitate of thorium(IV) hydroxide in the tube with 1 ml of 6 M hydrochloric acid, and transfer the solution in the tube to a conical flask (100-ml volume). Add 11 ml of an EDTA-NaF solution and 2 ml of a tris buffer solution into the flask, adjust the resulting solution to pH 6 with aqueous ammonia, and then dilute it with water to about 50 ml. Settle the flask into a water bath controlled at 25°C, and add dropwise 3 ml of STB solution (0.3 ml/min) from a funnel attached with the flask. Flow argon (60–100 ml/min) into the flask through the funnel, and collect generated arsine in 5 ml to Ag-DDTC solvent. Measure the absorbance at 540 nm in the solvent, and determine the concentration of arsenic(III) by comparing it with those of standards.

Determination of arsenic(V). Dissolve another precipitate of thorium(IV) hydroxide in a centrifugal tube with 1 ml of 6 M hydrochloric acid. Transfer the solution to a conical flask (100-ml volume), add 1 ml of EDTA-NaF, adjust the pH of the solution to less than 1 with hydrochloric acid, and then dilute to about 50 ml with water. The next procedure is the same as that of the determination of arsenic(III). Since the total amounts of arsenic are determined in this procedure, obtain the concentration of arsenic(V) by subtracting that of arsenic(III) from the total amounts of arsenic.

Results and Discussion

Effect of amounts of thorium on the coprecipitation of arsenic

As shown in Fig. 1, arsenic(III) and arsenic(V) were almost quantitatively coprecipitated with thorium(IV) hydroxide formed at pH 9 in 1000 ml of water, when 70–80 mg of thorium was used. Accordingly, we decided on the addition of 75 mg of thorium as being optimum.

Effect of pH on the coprecipitation of arsenic

Arsenic(III) and arsenic(V) were quantitatively recovered from 1000 ml of water adjusted to pH 8–10 in the presence of 75 mg of thorium, as can be seen in Fig. 2. From this result, the coprecipitation at pH 9 was recommended.

Effect of EDTA-NaF to mask thorium

In the presence of 75 mg of thorium(IV) ions, arsenic(III) was not sufficiently reduced to arsine in a pH 6 solution, but was quantitatively reduced in the presence of more than 2 ml of an EDTA-NaF solution as masking the thorium. This result is shown in Fig. 3. For the determination of arsenic(III) in actual groundwater, however, more than 11 ml of the masking solution

Fig. 1 Effect of the amount of thorium on the coprecipitation of arsenic. Arsenic(III) 10 μ g or arsenic(V) 10 μ g was coprecipitated from 1000 ml of water at pH 9.

Fig. 2 Effect of the pH on the coprecipitation of arsenic. Arsenic(III) 10 μ g or arsenic(V) 10 μ g was coprecipitated with 75 mg of thorium from 1000 ml of water.

Fig. 3 Effect of the EDTA-NaF used to mask thorium. Arsenic(III) 10 μ g or arsenic(V) 10 μ g was determined in the presence of 75 mg of thorium. ●: Arsenic(III) 10 μ g was determined after coprecipitating it from 1000 ml of groundwater collected in Suma, Kobe.

are required, as is also shown in Fig. 3. In the groundwater (collected in Suma) used, Ca^{2+} 30 ppm, Mg^{2+} 5 ppm, Na^+ 25 ppm, K^+ 1.6 ppm, HCO_3^- 170 ppm, Cl^- 19 ppm, SO_4^{2-} 40 ppm, SiO_2 20 ppm, D. O. 7.1 ppm and pH 6.3 were contained, and the concentrations of sulfate and chloride ions tend to be higher than those of general groundwater.¹⁴ Under inadequate addition, such as 2 ml of EDTA-NaF to the groundwater in Suma, rich sulfate seems to form another complex of thorium(IV) sulfate¹⁵ instead of thorium(IV)-arsenate and -arsenite complexes. Accordingly, the addition of 11 ml of the solution for arsenic(III) is recommended for actual groundwater analysis.

As shown in Fig. 3, arsenic(V) was quantitatively reduced to arsine at pH less than 1 in the absence and in the presence of within 2 ml of EDTA-NaF solution. More than 2 ml of the masking solution, however, inhibited the generation of arsine, since the excess addition brought about a white precipitate of the EDTA-NaF at this pH. Accordingly, the addition of 1 ml of

Table 1 Recoveries of arsenic(III+V) from distilled water and groundwater

As found/ μ g		Recovery, %	
As(III)	As(V)	As(III)	As(V)
Distilled water (1000 ml)			
As(III) 10.0 μ g added			
10.1		101	
9.86		98.6	
9.53		95.3	
9.65		96.5	
		Av. 97.9 $\pm$ 2.5	
As(III) 10.0 μ g and As(V) 10.0 μ g added			
	9.89		98.9
	9.85		98.5
	9.81		98.1
	9.76		97.6
		Av. 98.3 $\pm$ 0.56	
Groundwater (1000 ml)			
As 0 μ g added			
0	0		
As(III) 10.0 μ g added			
9.37		93.7	
9.44		94.4	
9.61		96.1	
9.58		95.8	
		Av. 95.0 $\pm$ 1.1	
As(III) 10.0 μ g and As(V) 10.0 μ g added			
	9.60		96.0
	9.59		95.9
	10.9		109
	10.1		101
		Av. 101 $\pm$ 6.2	

Arsenic(V) amounts were obtained by subtracting As(III) from total amounts of As(III)+As(V). Groundwater used was collected in Suma, Kobe.

Table 2 Comparison of analytical values of arsenic(III+V) in groundwater by this and another method¹¹

As(III), ppb	As(V), ppb
This method	
0.72	3.21
0.61	3.02
0.64	2.94
Av. 0.66±0.06	Av. 3.06±0.14
Zirconium coprecipitation method ¹¹	
N.D.	3.00
N.D.	3.02
N.D.	2.94
	Av. 3.02±0.16

N.D.: not detected. Groundwater used was collected from a shallow well in Nishinomiya, Hyogo Pref.

the solution is recommended for arsenic(V) analysis.

Analytical recovery of arsenic

Table 1 lists the recoveries of arsenic(III) and arsenic(V) in the recommended procedure. From 1000 ml of a distilled water sample, 97.9±2.5% of arsenic(III) and 98.3±0.6% of arsenic(V) were satisfactorily recovered. Also, from 1000 ml of groundwater collected in Suma, Kobe, 95±1.1% of arsenic(III) and 101±6.2% of arsenic(V) were recovered. The relative standard deviations for all the recoveries were in the range (approximately 0.6–6%) for both arsenic values.

Table 2 shows a comparison of the analytical values of arsenic found in the present work with that by the zirconium coprecipitation method.¹¹ The value of arsenic(V) by the proposed method almost agreed with that by the other method. It has been reported¹¹ that the recovery percentage of standard arsenic(III) was 85% when tartaric acid was used for masking zirconium. It was, however, found in the improved zirconium-method¹¹ that the recovery of 95.5±1.6% ($n=3$) of standard arsenic(III) is achieved with an optimum addition of 3 ml of EDTA-NaF solution with tartaric acid.

Arsenic(III), also shown in Table 2, was not detected by the zirconium method (probably due to an insufficient masking action of the tartaric acid used) though it was detected using the proposed method.

Concentration of arsenic in groundwaters

The established method was applied to groundwater samples collected from shallow wells (1–2 m depth), mainly in Nishinomiya area, Hyogo Pref. Table 3 lists analytical values of the arsenic in these samples. In the Nishinomiya area, the average concentration of arsenic(V), 3.3 µg/l, tends to be higher than that of arsenic(III), 0.6 µg/l.

Table 3 Analytical values of arsenic(III+V) in groundwater

Sample	As(III), ppb	As(V), ppb
G.W., K well no.8 ^a	0.57	3.07
G.W., K well no.5 ^a	N.D.	3.38
G.W., K well no.4 ^a	0.76	2.40
G.W., Ky well no.4 ^a	0.57	2.24
G.W., Ky well no.7 ^a	0.76	3.51
G.W., H(S) well no.8 ^a	0.62	2.85
G.W., H(S) well no.5 ^a	N.D.	3.73
G.W., H(S) well no.2 ^a	N.D.	3.40
G.W., H(N) well no.6 ^a	0.53	3.57
G.W., H(N) well no.2 ^a	N.D.	3.11
G.W., H(N) well no.3 ^a	0.62	4.12
G.W., H(N) well no.2 ^a	0.62	3.72
G.W., S(N) well no.1 ^a	0.66	3.90
G.W., S(S) well ^a	0.69	3.35
G.W., K temple ^a	0.59	2.61
G.W., Suma ^b	N.D.	N.D.
G.W., Uzugamori ^b	0.65	N.D.
Sumiyoshi River ^b	N.D.	0.82

G.W., groundwater; N.D., not detected.

a. in Nishinomiya. b. in Kobe.

References

1. National Research Council, "Medical and biological effects of environmental pollutants No. 16, *Hiso*", translated by A. Hisanaga and N. Ichinishi, p. 19, Tokyo-Kagaku-Dojin, 1985.
2. S. Maeda, *Kagaku-no-ryoiki*, **37**, 606 (1983).
3. Y. Tamari, K. Nishimura, H. Tsuji and Y. Kusaka, *Bull. Chem. Soc. Jpn.*, **59**, 2273 (1986).
4. Y. Tamari, K. Nishimura, M. Kitagawa, H. Maki, S. Matsumoto, H. Tsuji and Y. Kusaka, *Mem. Konan Univ. Sci. Ser.*, **34**, 1 (1987).
5. G. Charlot, "Teisei Bunseki Kagaku II", translated by K. Sone and M. Tanaka, p. 411, Kyoritsu Shuppan, Tokyo, 1977.
6. C. Wadeline and M. G. Mellon, *Analyst* [London], **77**, 708 (1952); cited in "Solvent Extraction in Analytical Chemistry" by G. H. Morrison and H. Freiser.
7. "Muki Ohyo Hishoku Bunseki No. 1 (Applied Inorganic Spectrophotometry, in Japanese)", p. 136, Kyoritsu Shuppan, Tokyo, 1973.
8. S. Nakaya, *Bunseki Kagaku*, **12**, 241 (1963).
9. K. Tanaka, *Bunseki Kagaku*, **10**, 612 (1961).
10. E. Kaneko, *Bunseki Kagaku*, **27**, 250 (1978).
11. H. Tsuji, K. Nishimura, Y. Tamari and Y. Kusaka, *Bunseki Kagaku*, **33**, 43 (1984).
12. G. Leung, Y. S. Kim and H. Zeitlin, *Anal. Chim. Acta*, **60**, 229 (1972).
13. Y. Tamari, M. Kitagawa, H. Tsuji and Y. Kusaka, *Bull. Soc. Sea Water Sci. Jpn.*, **42**, 241 (1989).
14. Y. Tamari, H. Tsuji and Y. Kusaka, *Chikyukagaku*, **22**, 139 (1989).
15. Y. Tamari, A. Takada, H. Tsuji and Y. Kusaka, *Anal. Sci.*, **4**, 277 (1988).

(Received January 26, 1989)

(Accepted June 15, 1989)