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RAPID FLOTATION SEPARATION AND ATOMIC ABSORPTION SPECTROMETRIC DETERMINATION OF ARSENIC IN NATURAL WATERS*

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INTRODUCTION

Arsenic is a naturally occurring element and can be found at the 1 μg/l level in natural water samples. It is important to develop a rapid and accurate method of determining arsenic (Ⅲ, Ⅴ) in natural waters in various fields including environmental chemistry, limnology, marine biology and agriculture owing to its severe toxicity.

In general, for an accurate determination of arsenic in natural waters, preconcentration is needed in order to achieve the necessary sensitivity.

In previous papers (Nakashima 1978, 1979 a), a flotation technique (De Carlo and Zeitlin 1981; Hiraide and Mizuike 1977; Hiraide et al. 1976; Mizuike and Hiraide 1982) in which the precipitate of hydrated iron (Ⅲ) oxide is floated with the aid of surfactant and small air bubbles was used for the preconcentration of arsenic in natural waters. Subsequently, the determination of arsenic by hydride generation and atomic absorption spectrometry was performed.

In the procedure described previously (Nakashima 1978, 1979 a), the preconcentration by flotation was carried out on aliquots of natural waters, filtered through 0.45 μm Millipore filters after the addition of 10ml of hydrochloric acid per 1000ml of sample immediately after collection.

However, in the procedure of the prefiltration of water samples, filtration for larger sample volumes is sometimes time-consuming because the filter is clogged with suspended solids present in natural waters.

Therefore, for the more rapid determination of arsenic in natural waters, the flotation cell used in the previous papers (Nakashima 1978, 1979 a) was improved. In the procedure of separation of arsenic from natural water samples by employing the new cell, arsenic coprecipitated with hydrated iron (Ⅲ) oxide was floated with suspended solids without prefiltration of samples. As a result, good agreement has been obtained between

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the values obtained by this method and by the method previously described (the flotation method using natural water samples filtered through 0.45 μm Millipore filters, after the addition of hydrochloric acid to the water samples immediately after collection).

Therefore, it is clear that this method is more rapid than the method described previously (Nakashima 1978, 1979 a) for the determination of arsenic in natural water samples.

This paper describes a rapid and convenient method for the separation and determination of arsenic in natural waters.

EXPERIMENTAL

1. *Apparatus*

The flotation cells used in this work are shown in Fig. 1. The specific components and the schematic diagram of the experimental sys-

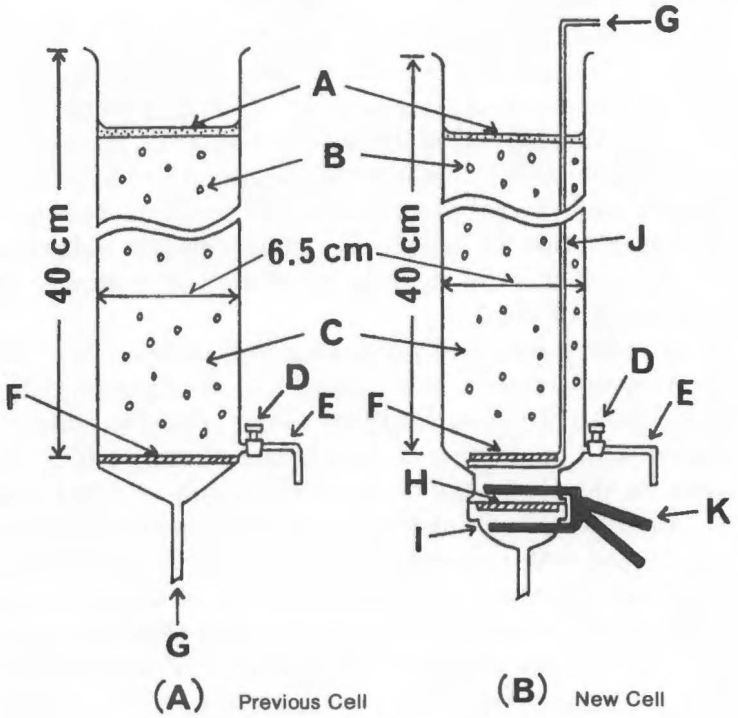

FIG. 1. Flotation cell for preconcentration of arsenic.
A, Foam layer containing hydrated iron (Ⅲ) oxide and arsenic; B, Bubble; C, Sample solution; D, Cock; E, Drain pipe; F, Sintered-glass disk (porosity 4); G, Air; H, Millipore filter (pore size: 0.4 μm; diameter: 47mm); I, Millipore stopper; J, Bubbler; K, Millipore clamp.

tem employed in this work have been previously described (Nakashima 1978, 1979 a) except for the flotation cell (B) shown in Fig. 1. Figure 1 (A) shows the flotation cell described previously (Nakashima 1979b, c, 1980, 1981). The cell was composed of a glass cylinder, 40×6.5cm i. d., fitted with a sintered-glass filter (No. 4) to generate small air bubbles. A side arm was added near the bottom of the cell to drain the mother liquor rapidly after the flotation.

Figure 1 (B) shows the new cell used in this work. It has a side arm near the bottom of the cell and a flange at the bottom of the cell. This cell is connected to the lower part of Millipore filter funnel assembly (filter: 0.45 μm pore size, 47mm diameter). Air is passed through a custom-made bubbler (No. 4 -sintered glass disk) which has been put into the flotation cell and the precipitate of the hydrated iron (Ⅲ) oxide floats.

2. *Reagents*

All reagents were of analytical-reagent grade except for sodium dodecyl sulfate (sudium lauryl sulfate) and sodium oleate. Aqueous reagents were prepared in deionized, distilled water. Stock solutions (1 mg/ml) of As (Ⅲ) and As (V) were prepared from diarsenic trioxide (As_2O_3) and sodium arsenate ($Na_2HAsO_4 \cdot 7\,H_2O$), respectively, and arsenic standard solutions were freshly prepared by diluting stock solutions before use.

An iron (Ⅲ) solution (5 mg Fe/ml) was prepared from ammonium iron (Ⅲ) sulfate. A sodium dodecyl sulfate solution (1 mg/ml) was prepared by dissolving sodium dodecyl sulfate (powder, extra-pure reagent, Wako Pure Chemicals, Osaka) in 99.5% (v/v) ethanol. A sodium oleate solution (1 mg/ml) was prepared by dissolving sodium oleate (powder, extra-pure reagent, Wako Pure Chemicals) in 99.5% (v/v) ethanol with magnetic stirring. A potassium iodide solution (20%w/v) was prepared by dissolving in water. A sodium tetrahydroborate solution (5 %w/v) in a 0.1M sodium hydroxide solution was freshly prepared.

3. *Procedure for the flotation step*

The procedure for the separation using the flotation cell shown in Fig. 1 (B) is as follows: Ten ml of hydrochloric acid per liter of natural water samples was added immediately after collection in the field. The 1000-ml sample of fresh water (500ml for sea water) was placed in a beaker without prefiltration, and 2 ml of iron (Ⅲ) solution was added. The pH of the solution was adjusted to 8.0-8.5 (or 3.8-4.2) with aqueous ammonia to precipitate hydrated iron (Ⅲ) oxide, and the mixture was stirred for about 15min. One ml (2 ml for sea water) of sodium dodecyl sulfate solution and 1 ml of sodium oleate solution were added to the beaker. The

contents of the beaker (excluding the stirring bar) were transferred to the flotation cell and the residue in the beaker was washed into the cell using three small portions of water. Air was passed through at 20ml/min from the sintered-glass disk (No. 4) of the bubbler for about 2 min to obtain complete mixing and to float the precipitate. Most of the mother liquor was drained from the side arm by opening the cock on the drain pipe. After the cock had been closed, the residual mother liquor was sucked off through the Millipore filter. The precipitate adhering to the wall of the cell and the bubbler was washed down by spraying with water, and then the precipitate was washed with 30ml of water. A 8–ml portion of 6 M hydrochloric acid was added to the cell to dissolve the precipitate. The filtrate was collected by suction in a 20-ml volumetric flask, the Millipore filter was washed with water, the washings were added to the flask, and the mixture was diluted to 18ml with water. One ml of potassium iodide solution was added into the flask prior to analysis and the mixture was diluted to volume (20ml) with water.

4. *Procedure for the atomic absorption measurement*

The procedure for the atomic absorption spectrometric determination of arsenic after the separation was almost the same as the determination of arsenic described previously (Nakashima 1979 a). A calibration curve using 2.4M hydrochloric acid solutions containing 1 mg/ml of iron (Ⅲ), 1 % of potassium iodide and 0–0.10 μg/ml of arsenic (Ⅲ) is linear within the above range of arsenic concentration. The atomic absorption equipment was operated under the following conditions: wavelength, 193.7nm; lamp current, 14mA; gas-flow rates, nitrogen 1.0, hydrogen 1.0, and auxiliary nitrogen 6.0 l /min; spectral bandwidth 1 nm. The long tube system of 60cm was used in the atomic absorption units.

RESULTS AND DISCUSSION

The recovery rates for arsenic using this preconcentration method were investigated. Solutions (1000ml) at pH 3.8–4.2 or pH 8.0–8.5 containing 10mg of iron (Ⅲ), 1 ml of sodium dodecyl sulfate solution, 1 ml of sodium oleate solution, and 0.2–1.0 μg of arsenic (Ⅲ) were analyzed by the proposed method using the flotation cell (B) shown in Fig. 1. The results are shown in Table 1. Recoveries of the arsenic added were greater than 95% in all instances. The blank value throughout the whole analytical process was less than 5 ng As/ l . It is clear that arsenic in 1000 ml of water samples can be quantitatively recovered by the proposed method using the flotation cell (B) newly developed.

To investigate the applicability of this method to the separation and

TABLE 1. Recovery of arsenic added to water*

pH of sample solution for coprecipitation and flotation	Added** (μg)	Recovery (%)
3.8–4.2	0.2	95, 100
	0.4	96, 95
	0.6	99, 97
	0.8	98, 99
	1.0	98, 96
8.0–8.5	0.4	98, 95
	0.6	97, 100
	1.0	98, 98

These recoveries were examined by the flotation separation method using the flotation cell (B).

* Solution containing 10mg of iron (Ⅲ); volume, 1000ml.

** Added as As (Ⅲ).

determination of arsenic in natural waters, the analyses of arsenic in tap, well, river and sea water samples were carried out by the proposed method without prefiltration and the previous method with prefiltration. As can be seen in Table 2, good agreement of the arsenic results was obtained irrespective of whether the samples were prefiltered through 0.45 μm Millipore filters, or not.

The pervious method described the procedures for the flotation separation and determination of arsenic by atomic absorption spectrometry following arsine generation. However, it had a disadvantage of

TABLE 2. Determination of arsenic in natural water samples

Sample	Sample volume (ml)	SS* (mg/l)	pH**	Arsenic content (μg/l)	
				Without prefiltration***	With prefiltration****
Tap water	1000	<0.5	8.0–8.5	1.04, 1.07	1.06, 1.11
Well water	1000	<0.5	8.0–8.5	0.22, 0.22	0.22, 0.20
River water 1	1000	7.2	8.0–8.5	1.14, 1.16	1.07, 1.11
River water 2	1000	6.1	3.8–4.2	1.20, 1.22	1.20, 1.16
			8.0–8.5	1.23, 1.20	1.22, 1.21
Sea water 1	500	1.2	8.0–8.5	1.64, 1.60	1.60, 1.59
Sea water 2	500	8.2	8.0–8.5	1.66, 1.68	1.62, 1.64

* Suspended solids remained on a 0.45 μm Millipore filter.

** pH of sample solution for coprecipitation and flotation.

*** Values obtained by this method.

**** Values obtained by flotation separation method using the flotation cell (A) and water samples filtered through 0.45 μm Millipore filters.

being time-consuming for the prefiltration process of larger volumes of natural water samples. In the present method, the procedure for the flotation separation can be carried out without prefiltration of natural water samples. Therefore, this method is more rapid and convenient than the previous one.

The use of mixed surfactant (sodium dodecyl sulfate and sodium oleate) was more effective for the flotation of the precipitate in water, particularly in sea water, than that of sodium dodecyl sulfate or sodium oleate alone (Nakashima 1980, 1981). Moreover, when natural water samples were treated, the precipitate of hydrated iron (Ⅲ) oxide added to samples containing suspended solids floated more easily than the precipitate added to samples prefiltered through 0.45 μm Millipore filters.

The arsenic contents obtained by the procedure of the coprecipitation-flotation separation at pH 3.8–4.2 showed good agreement with at pH 8.0–8.5. The flotation of hydrated iron (Ⅲ) oxide at pH 3.8–4.2 offers a useful procedure for the simultaneous separation of hydride-forming elements such as arsenic (Ⅲ, Ⅴ), selenium (Ⅳ), tin (Ⅱ, Ⅳ), bismuth (Ⅲ), and antimony (Ⅲ, Ⅴ) from a large volume of fresh water and sea water, and subsequent atomic absorption measurement in a long absorption tube of the hydrides generated from hydride-forming elements is found to be an accurate method for the determination of above elements. In addition, the advantage of the proposed method at pH 3.8–4.2 is the satisfactory isolation of hydride-forming elements from interfering ions such as nickel (Ⅱ) and copper (Ⅱ) present in water for the atomic absorption determination after the separation (Nakashima 1979 b, c, 1980, 1981).

On the other hand, from the viewpoint of adjusting the pH of sample solutions, it is easier to adjust the pH of the sample to 8.0–8.5 than to 3.8–4.2. Therefore, it is preferable to adjust the pH of the solution to 8.0–8.5 when determining arsenic in natural waters as routine work.

The time required for the preconcentration of arsenic from a 1000-ml volume of solution is about 30–35min per sample including 15min of stirring. However, during the preconcentration period of 15–20min after stirring, stirring of the next sample solution can be carried out. Therefore, in practice, the preconcentration of arsenic from a 1000ml volume of solution can be made at intervals of 15–20min per sample when a number of samples is treated.

The 60cm tube system described in this paper cannot be used with most commercial atomic absorption spectrophotometers. However, the arsenic in a sample solution can also be determined by hydride generation-atomic absorption spectrometry using an electrically or flame-heated silica tube.

SUMMARY

A rapid and accurate method is described for the separation and determination of arsenic in natural waters by using the improved flotation cell. A sub-microgram amount of arsenic (Ⅲ, Ⅴ) in natural water samples (1000ml for fresh water, 500ml for sea water) is coprecipitated with hydrated iron (Ⅲ) oxide at pH 8.0–8.5 or 3.8–4.2 without prefiltration through membrane filters. The precipitate is floated with the aid of mixed surfactant (sodium oleate and sodium dodecyl sulfate) and small air bubbles, then separated and dissolved in dilute hydrochloric acid. The arsenic content is determined by arsine generation using sodium tetrahydroborate and atomic absorption spectrometry. In the analytical process, mean recoveries of 95–100% for arsenic added to water were obtained.

Good agreement of the arsenic values was obtained irrespective of whether the samples were prefiltered through 0.45 μm Millipore filters, or not.

The time required for the preconcentration was 15–20min after 15min stirring.

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