

## Concentrations of Arsenic in Brackish Lake Water: Application of Tristimulus Colorimetric Determination

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The evaluation of a simple and rapid tristimulus colorimetric method for the determination of arsenic in brackish waters and its application to brackish water samples taken from brackish Lake Nakaumi are described. The determinations of arsenic in brackish water samples were made satisfactorily independent of sample salinity. By applying this method to lake water samples, the distributions and behaviors of arsenic in the lake and their controlling factors were clarified, such as seasonal variations of arsenic and the effect of a typhoon.

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### Introduction

Arsenic occurs naturally in the environment as both inorganic and organic chemical species. In natural water, predominant forms are arsenite [arsenic(III)] and arsenate [arsenic(V)]. Generally, arsenic(V) dominates in oxic water, while arsenic(III) is more likely to occur in anoxic water. The redox environment in water systems is one of the factors that control the oxidation states of arsenic. The oxidation states of arsenic are related to the toxicity, and also its behavior in aquatic systems.<sup>1-3</sup>

Determinations of arsenic in water samples have been conventionally made by some spectrometric techniques, such as atomic absorption spectrometry (hydride generation-AAS,<sup>4-9</sup> graphite-furnace AAS,<sup>10</sup>) inductively coupled plasma-atomic emission spectroscopy,<sup>4,5</sup> and spectrophotometry by a silver diethyldithiocarbamate method.<sup>4,5</sup> These methods for the determination of arsenic have been used indoors in most laboratories, and are very expensive and highly skillful regarding operation and maintenance. However, simple and rapid methods for the determination of trace amounts of arsenic in environmental water samples are useful in field work.<sup>11</sup> As a simple, rapid and sensitive method for field work, we have developed a visual and tristimulus colorimetric determination of trace inorganic arsenic [total of arsenic(III) and arsenic(V)] in environmental water samples by improving the Gutzeit method,<sup>11</sup> which is based on the reaction of arsine gas with mercury(II) bromide.

In the present study, the determination of trace inorganic arsenic [total of arsenic(III) as arsenite and arsenic(V) as arsenate] in water samples by the tristimulus colorimetric method<sup>12</sup> was evaluated concerning its application to real water samples containing various salinities (brackish water samples) by comparing with the conventional method (hydride generation-AAS).<sup>9</sup> Also, the vertical distribution and behavior

of arsenic in a brackish lake and their controlling factors were clarified from the results of the determination of arsenic in the lake water samples taken in the period of May, 2003 to August, 2005.

### Experimental

#### Reagent and apparatus

An arsenic(III) standard solution (1000 mg/l) was prepared by dissolving 0.1320 g of diarsenic trioxide, As<sub>2</sub>O<sub>3</sub> (Kanto Chemicals, Tokyo) in 10 ml of a 1 M sodium hydroxide solution, diluting it with water and then adding 10 ml of 2 M hydrochloric acid, and diluting to 100 ml with distilled deionized water. An arsenic(V) standard solution (1000 mg/l) was prepared by dissolving 0.2403 g of potassium dihydrogen arsenate, KH<sub>2</sub>AsO<sub>4</sub> (Wako Pure Chemicals, Tokyo) in water, adding 10 ml of 2 M hydrochloric acid, and diluting to 100 ml with deionized water. Their working standards were prepared by appropriate dilution of the stock solutions. A mercury(II) bromide solution was prepared by dissolving 5 g of mercury(II) bromide, HgBr<sub>2</sub> (Kanto Chemicals, Tokyo) in 99.5% ethanol, and diluting to 100 ml with ethanol. A rosaniline chloride solution (0.001%) was prepared by dissolving 0.001g of rosaniline chloride (Kanto Chemicals, Tokyo) in 99.5% ethanol, and diluting to 100 ml with ethanol. Artificial seawater (salinity 34 psu) was prepared by dissolving NaCl (23.477 g), MgCl<sub>2</sub> (4.981 g), Na<sub>2</sub>SO<sub>4</sub> (3.917 g), CaCl<sub>2</sub> (1.102 g), KCl (0.664 g), NaHCO<sub>3</sub> (0.192 g), KBr (0.096 g), H<sub>3</sub>BO<sub>3</sub> (0.026 g), SrCl<sub>2</sub> (0.024 g), and NaF (0.003 g) in 1 kg of water, according to the Lyman and Fleming's procedure.<sup>13</sup> Artificial brackish water samples (salinity 5, 10, 15, 20, 25, and 30 psu) were prepared by diluting artificial seawater (salinity 34 psu) with water. All of the reagents used were of analytical grade, and were arsenic free.

A tristimulus colorimeter (Spectrophotometer CM-2600d, Minolta, Tokyo) was used for measuring the color intensity of the arsenic test spot. An arsine gas generation apparatus (Sibata Scientific Technology, Tokyo) was used to generate arsine gas.

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Table 1 Recovery of arsenic added to artificial seawater and brackish water samples

Sample	As(III) added/ $\mu\text{g l}^{-1}$	As(V) added/ $\mu\text{g l}^{-1}$	Found/ $\mu\text{g l}^{-1}$	Recovery,		RSD ( $n = 5$ ), %
				$\mu\text{g l}^{-1}$	%	
Distilled water	20.0	0	19.2	19.2	96	4.9
	10.0	10.0	19.6	19.6	98	4.8
	0	20.0	20.0	20.0	100	3.0
Artificial brackish water (Salinity, 15.0 psu)	20.0	0	18.7	18.7	94	4.5
	10.0	10.0	19.8	19.8	99	5.8
Artificial seawater (Salinity, 31.0 psu)	0	20.0	18.3	18.3	92	3.4
	20.0	0	18.2	18.2	91	5.3
Brackish lake water (Salinity, 20.9 psu)	10.0	10.0	18.3	18.3	92	5.5
	0	20.0	19.6	19.6	98	4.5
Brackish lake water (Salinity, 30.4 psu)	0	0	4.7	—	—	4.0
	5.0	5.0	13.9	9.2	92	5.2
Brackish lake water (Salinity, 30.4 psu)	0	0	3.0	—	—	6.3
	5.0	5.0	12.9	9.9	99	6.8

### Sampling

Brackish water samples were taken at two sampling sites, the center area (St. 4; water depth, *ca.* 7 m) and dredged region (St. 12; water depth, *ca.* 16 m) in the brackish Lake Nakaumi, Japan, during the period of May, 2003 to August, 2005. Lake Nakaumi is located on the boundary between Shimane and Tottori Prefectures. From the late spring until autumn, stable strata of water are usually formed in the lake, due to the sinking of seawater into the hypolimnion and the introduction of river water (freshwater) into the epilimnion. A halocline existed at 3–4 m water depth at St. 4 and also at St. 12. Usually, from early summer to late autumn epilimnion water was oxic and hypolimnion water was anoxic, and an oxic/anoxic interface was formed at *ca.* 4 m water depth at St. 12 because of strong stagnation formation in the hypolimnion.<sup>14</sup>

After collecting water samples from various water depths, they were brought back to the authors' laboratory and filtered; then, arsenic (total of arsenic(II) and arsenic(V)) was determined by the tristimulus colorimetric method after collecting arsenic on a test paper.<sup>12</sup>

### Procedure for the collection and determination of arsenic

The preparation of a mercury(II)-impregnated paper (test paper) was made as follows. A square paper (18 mm  $\times$  18 mm in size; No. 51A, Toyo-Roshi, Tokyo) was dipped in a mercury(II) bromide solution and air-dried in a dark place. Then, this paper was dipped into a 0.001% rosaniline chloride solution and air-dried in a dark place. The test paper was used to collect arsine generated from sample solutions containing arsenic within 48 h.

Arsine generation and its collection on a test paper were made using an arsine generation apparatus, as previously described.<sup>12</sup> The test paper was set between the joints of the upper and lower tubes, which were connected with a rubber stopper plugged tightly in the upper side of a glass bottle (sample container).

A sample solution (15 ml) was taken into the sample container. To the solution, 0.1 g of potassium iodide, 0.1 g of tin(II) chloride, 1.0 g of zinc sand, and finally 4.0 ml of 6 M hydrochloric acid were added successively. After the resulting solution was allowed to stand for 30 min to generate arsine from its solution containing arsenic(III) and/or arsenic(V), the test paper was removed from the apparatus. A yellow, brownish-yellow, or brownish spot was produced on the test paper according to the concentration of arsenic [total of arsenic(III)

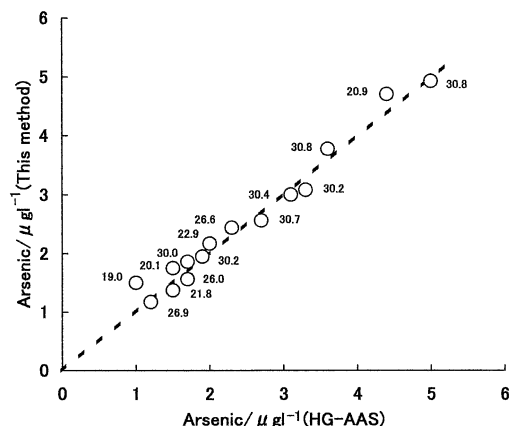


Fig. 1 Correlation between the arsenic concentrations in brackish water samples, obtained by the tristimulus colorimetric method (this method) and by hydride generation-AAS (HG-AAS). The value attached to the respective plotted mark (O) denotes the salinity (psu) of the respective brackish water sample determined by both methods. The brackish water samples were taken from brackish Lake Nakaumi.

and arsenic(V)]. The developed color intensity was measured by tristimulus colorimetry, as described in a previous paper.<sup>12</sup> The color spot on a test paper was stable for periods of at least one month in a dark place.

## Results and Discussion

### Evaluation of tristimulus colorimetric method for the measurements of arsenic in brackish water

**Effect of sample volume.** In the tristimulus colorimetric method developed previously, the calibration curves for arsenic(III) and arsenic(V) in 15 ml of the sample volume are in fair agreement with each other, and are linear up to 30  $\mu\text{g/l}$ . The determination limit for arsenic was 1.0  $\mu\text{g/l}$  using 15 ml of the sample solution. In this study, the effect of the sample volume on this determination was examined using arsenic(V). The color intensity developed on a test paper increased proportionally with increasing sample volume up to at least 30 ml. This was due to quantitative arsine generation from a sample solution and its quantitative collection on the test paper. When 30 ml of the sample solution was used for the determination of arsenic, the color intensity was two-times that obtained from 15 ml of a sample solution containing the same concentration of arsenic. The determination limit for arsenic was 0.5  $\mu\text{g/l}$  using 30 ml of the sample solution.

**Application to brackish water.** Seawater and brackish water, which is a mixture of seawater and freshwater, contain various cations such as  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{K}^+$  and  $\text{Sr}^{2+}$  ions, and anions such as  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ , and  $\text{Br}^-$  ions at high concentration levels. The effect of the salinity on arsenic determination by the tristimulus colorimetric method was examined in detail using artificial seawater (salinity, 34.0 psu) and artificial brackish water with salinities of 5.0, 10.0, 15.0, 20.0, 25.0, 30.0 psu, which contained either 20.0  $\mu\text{g/l}$  of arsenic(III) alone, 10.0  $\mu\text{g/l}$  of arsenic(III) and 10.0  $\mu\text{g/l}$  of arsenic(V), or 20.0  $\mu\text{g/l}$  of arsenic(V) alone. In these examined solutions, the recoveries of arsenic(III) and arsenic(V) were in the range of 95 to 102%, independent of the salinity.

The recovery and reproducibility of arsenic were examined using distilled water, artificial brackish water, and real brackish lake water, to which arsenic(III) and/or arsenic(V) were added.

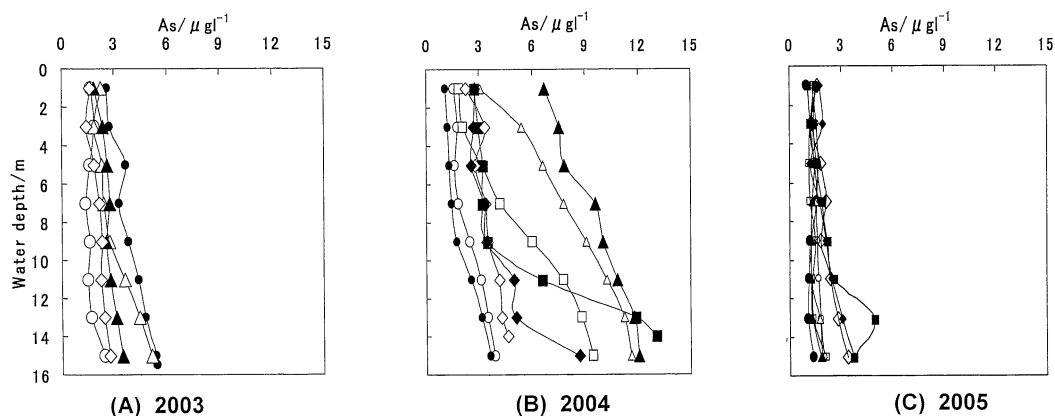


Fig. 2 Vertical distribution of arsenic at St.12 in brackish Lake Nakaumi. Sampling dates are as follows: (A) (○) May 12, (●) Jul. 24, (△) Aug. 19, (▲) Sep. 26, (◇) Oct. 20 in 2003; (B) (○) Jun. 28, (●) Jul. 12, (△) Aug. 24, (▲) Sep. 27, (□) Oct. 15, (■) Oct. 25, (◇) Nov. 15, (◆) Dec. 7 in 2004; (C) (○) Jan. 24, (●) Mar. 14, (△) Apr. 18, (▲) May 16, (□) Jul. 5, (■) Jul. 25, (◇) Aug. 8, (◆) Aug. 22 in 2005.

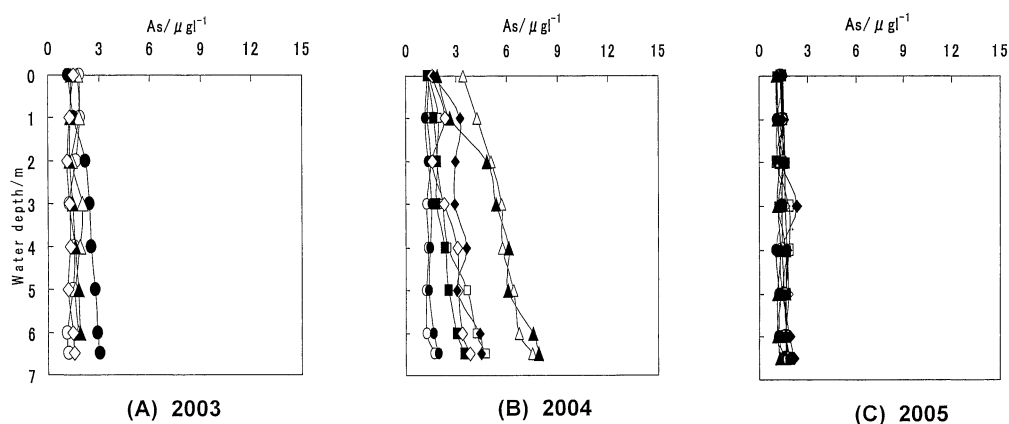


Fig. 3 Vertical distribution of arsenic at St. 4 in brackish Lake Nakaumi. Sampling dates are as follows: (A) (○) May 12, (●) Jul. 24, (△) Aug. 19, (▲) Sep. 26, (◇) Oct. 20 in 2003; (B) (○) Jun. 28, (●) Jul. 12, (△) Aug. 24, (▲) Sep. 27, (□) Oct. 15, (■) Oct. 25, (◇) Nov. 15, (◆) Dec. 7 in 2004; (C) (○) Jan. 24, (●) Mar. 14, (△) Apr. 18, (▲) May 16, (□) Jul. 5, (■) Jul. 25, (◇) Aug. 8, (◆) Aug. 22 in 2005.

As shown in Table 1, arsenic (arsenic(III) and/or arsenic(V)) was recovered quantitatively from these solutions (recovery: 91–100%), and their relative standard deviations (RSD) ranged from 3.0 to 6.8%. Thus, the tristimulus colorimetric method is sufficiently applicable to environmental waters, such as brackish waters and seawaters besides river waters (freshwater).

Furthermore, the tristimulus colorimetric method was compared with hydride generation-AAS by determining arsenic in the same brackish lake water samples having various salinities. Figure 1 shows the correlation between arsenic concentrations obtained by the tristimulus colorimetric method (this method) and hydride generation-AAS (HG-AAS).<sup>9</sup> The arsenic concentrations and salinities in the lake water samples ranged from 1 to 5  $\mu\text{g/l}$  and from 19 to 31 psu, respectively. The obtained determination values by the tristimulus colorimetric method agreed very closely with those by hydride generation-AAS, independent of the salinity. This fact supports the idea that the tristimulus colorimetric method can compare with the hydride generation-AAS in the determination of arsenic in brackish water samples having various salinities.

*The concentrations of total inorganic arsenic in brackish waters of Lake Nakaumi*

*Vertical distribution of arsenic.* Arsenic in the brackish water

of Lake Nakaumi was determined by the tristimulus colorimetric method. The analytical results are given in Figs. 2 and 3 as the vertical distributions of arsenic changing with seasons at St. 12 and St. 4, respectively. The vertical distributions of arsenic and their trends at St. 4 and at St. 12 are fairly similar to each other, although both sampling sites were different in the water depth.

As can be seen from Fig. 2, which shows the concentrations of arsenic at St. 12, in winter and spring of 2003 and 2005, except for 2004, the arsenic concentrations were low, 1–4  $\mu\text{g/l}$ , in both the epilimnion (water depth above 4 m) and the hypolimnion (water depth below 4 m). In summer and autumn the arsenic concentrations were low, 1–3  $\mu\text{g/l}$ , in the epilimnion, while they increased substantially to 3–6  $\mu\text{g/l}$  in the hypolimnion. These high concentrations of arsenic in the hypolimnion, which were found to be in an anoxic aqueous environment, may have been caused by the release of arsenic(III) from the lake bottom sediment.<sup>2</sup> However, in August and September of 2004, arsenic concentrations were extremely high in both the epilimnion and the hypolimnion, and in October and December they were still very high in the bottom water. During these months, five typhoons directly hit this area. Therefore, these extremely high concentrations of arsenic may be due to a great discharge of arsenic into the lake water from the lake bottom, resulting from

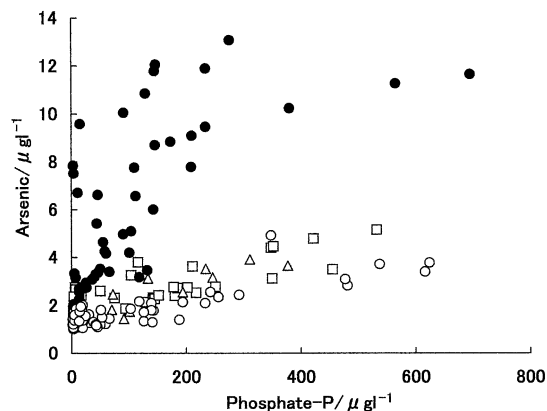


Fig. 4 Relation between the concentrations of arsenic and phosphate-phosphorus at St. 12 in brackish Lake Nakaumi. Sampling dates are as follows: (□) May. – Oct. in 2003, (△) Jun. – Jul. in 2004, (●) Aug. – Dec. in 2004, (○) Jan. – Aug. in 2005.

resuspension of the bottom sediment disturbed by the typhoons.<sup>15</sup> Similar phenomena of vertical distributions and extremely high concentrations of arsenic were also observed at St. 4, as can be seen from Fig. 3.

*Relation between the concentrations of arsenic and phosphate-phosphorus.* The present authors have already found the distribution of phosphate-phosphorus and its trend in Lake Nakaumi,<sup>16</sup> which were very similar to those of arsenic found in this study. That is, in summer the concentrations of phosphate-phosphorus were low and almost constant in the epilimnion, and remarkably increased with the water depth in the hypolimnion, although in the winter the concentrations were very low and constant, independent of the water depth. Therefore, in this study the phosphate-phosphorus concentrations at St. 12 and St. 4 were also determined spectrophotometrically,<sup>4</sup> and the relation between the arsenic and phosphate-phosphorus concentrations was examined. The relation at St. 12 is shown in Fig. 4. A similar relation between arsenic and phosphate-phosphorus to that at St. 12 was also observed at St. 4. An approximately linear relationship exists between the concentrations of arsenic and phosphate-phosphorus in the period of 2003 to 2005, except during the period of August to December, 2004. This finding suggests that the behaviors of arsenic and phosphate-phosphorus are similar to each other, probably due to the similar chemical nature between arsenic and phosphorus. However, the concentrations of arsenic are remarkably higher than those estimated from the linear relationship with phosphate-phosphorus during the period of August to November, 2004. At Lake Nakaumi, strong winds disturb the bottom sediment followed by the release of chemical species into the hypolimnion from the sediment-water interface, and cause mixing between the hypolimnionic water and the epilimnionic water and bringing the chemical species into the epilimnion from the hypolimnion.<sup>17,18</sup> Hence, due to the strong winds of typhoons, the arsenic in the hypolimnion and the epilimnion may reach high concentrations, as can be seen from Figs. 2 and 3. However, the phosphate-phosphorus in the epilimnion may

decrease to low concentrations as the result of its uptake as a nutrient by phytoplankton. This indicates that the behavior and accumulation of arsenic in closed water environments, like Lake Nakaumi, can be more easily affected by hitting of typhoon than those of phosphate-phosphorus.

Thus, the tristimulus colorimetric method is convenient and useful as a tool for measuring trace amounts of arsenic in environmental waters such as brackish water and seawater as well as natural freshwater. This method has advantages of simplicity, rapidity and sensitivity in the analytical method for field work. From the results of its application to brackish lake-water samples, arsenic was found to be accumulated in closed water environments such as brackish Lake Nakaumi by strong winds from typhoons.

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