APPLIED ORGANOMETALLIC CHEMISTRY, VOL. 6, 351–356 (1992)

Selective determination of trace arsenic and antimony species in natural waters by gas chromatography with a photoionization detector

Masahiro Yamamoto, Shigeru Tanaka* and Yoshikazu Hashimoto
Faculty of Science and Technology, Keio University, Hiyoshi, kouhoki-ku, Yokohama-shi 223, Japan

Traces amounts of arsenic and antimony in water samples were determined by gas chromatography with a photoionization detector after liquid-nitrogen cold trapping of their hydrides.

The sample solution was treated with sodium hydroborate ($NaBH_4$) under weak-acid conditions for arsenic(III) and antimony(III) determination, and under strong-acid conditions for arsenic(III + V) and antimony(III + V) determination.

Large amounts of carbon dioxide (CO_2) and water vapor obscured determination of arsine and stibine. Better separation from interference could be achieved by removing CO_2 and water vapor in two tubes containing sodium hydroxide pellets and calcium chloride, respectively.

The detection limits of this method were 1.8 ng dm^{-3} for arsenic and 9.4 ng dm^{-3} for antimony in the case of 100-cm^3 sample volumes. Therefore, it is suitable for determination of trace arsenic and antimony in natural waters.

Keywords: Photoionization detector, gas chromatography, hydride generation, arsenic, antimony, arsine, stibine, natural waters

INTRODUCTION

It has been reported that arsenic and antimony in natural waters exist in various oxidation states arsenic(III), arsenic(V), antimony(III), antimony(V)), and that their concentrations are very low e.g. *ca.* 1000 ng dm^{-3} for arsenic[1] and *ca.* 200 ng dm^{-3} for antimony.[2] The behavior of arsenic and antimony in natural water depends on their chemical forms. For example, while arsenic(V) and antimony(V) are the thermodynamically stable chemical forms in water,[3,4] arsenic(III) and antimony(III) are reduced from arsenic(V) and antimony(V), respectively, by phytoplankton.[5] Thus, selective determination of arsenic and antimony species is very important for studying their cycles in the environment.[4,6]

Hydride generation atomic absorption spectrometry (HG AA) has been used for selective determination of arsenic and antimony species in natural waters. However, this method could not be adapted for simultaneous determination of arsenic and antimony. Vien and Fry[7] and Cutter *et al.*[8] reported simultaneous determination of arsenic and antimony in natural waters by hydride generation gas chromatography (HG GC) with a lamp-type photoionization detector.

In this study, a simultaneous and selective determination of arsenic and antimony species in natural waters was improved by using HG GC with a helium discharge-type photoionization detector.

EXPERIMENTAL

Reagent

A standard solution (1000 μg cm^{-3}) of arsenic(III) was prepared by dissolving 1.330 g of arsenic(III) trioxide in 20 cm^3 of 1 mol dm^{-3} sodium hydroxide solution and diluting to 1000 cm^3. A standard solution (1000 μg cm^{-3}) of arsenic(V) was prepared by dissolving 2.529 g of potassium arsenate in water and diluting to 1000 cm^3. A standard solution (1000 μg cm^{-3}) of antimony(III) was prepared by dissolving 2.478 g of antimonyl potassium tartrate in water and diluting to 1000 cm^3. A standard solution (1000 μg cm^{-3}) of antimony(V) was prepared by dissolving 2.222 g of potassium pyroantimonate acid in hydrochloric acid and diluting to 1000 cm^3. Potassium dihydrogen citrate solution (1.6 mol dm^{-3}) was prepared by dissolving 94.39 g potassium dihydrogen citrate and 20.63 g sodium hydroxide in water and diluting to 250 cm^3. Potassium iodide solution

0268-2605/92/040351-06 $08.00

Received 25 February 1992

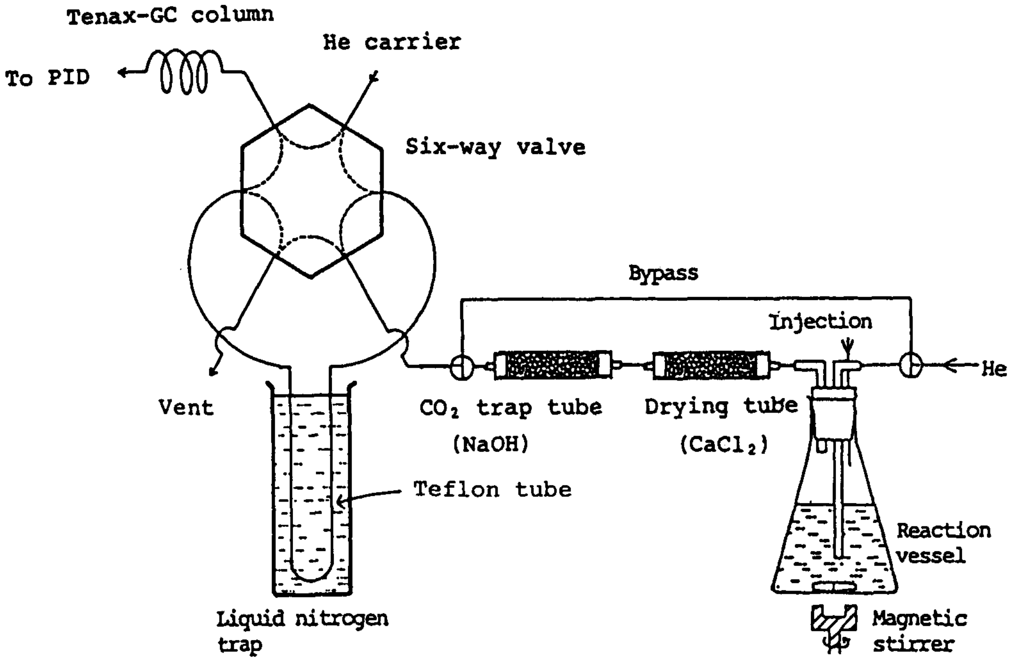

Figure 1 Schematic diagram of analytical system for arsenic and antimony.

(2 mol dm^{-3}) and sodium tetrahydroborate ($NaBH_4$) solution were made fresh daily. All solutions were prepared with distilled deionized water.

Apparatus

A schematic diagram of the analytical system for arsenic and antimony is shown in Fig. 1. It consists of a reaction vessel, drying tube, carbon dioxide (CO_2) trap tube, six-way valve, liquid-nitrogen cold trap, gas chromatograph and photoionization detector. The reaction vessel was a 200-cm^3 flask, combined with a silicon-rubber cork and stainless-steel needle for injection of sodium tetrahydroborate solution. The drying tube and CO_2 trap tube were Pyrex glass tubes (150 mm long, 17 mm i.d., 20 mm o.d.) packed with calcium chloride and sodium hydroxide pellets, respectively. A Teflon tube (400 mm long, 2 mm i.d., 3 mm o.d.) placed in a Dewar flask filled with liquid nitrogen was used as a cold trap for collection of arsine and stibine. The gas chromatograph/photoionization detector (GC/PID) consisted of a helium discharge type (Hitachi G-3000). The GC column was a Teflon tube (2 m long, 2 mm i.d., 3 mm o.d.), and the packing material was Tenax-GC (60/80-mesh).

Table 1 Analytical conditions for determination of arsenic(III), antimony(III), arsenic(III + V) and antimony(III + V) in natural waters

	As(III), Sb(III)	As(III + V), Sb(III + V)
$NaBH_4$	5 wt %, 1 cm^3	8 wt %, 5 cm^3
HCl	—	12 mol dm^{-3}, 10 cm^3
Potassium citrate*	1.6 mol dm^{-3}, 1 cm^3	—
Potassium iodide	—	2 mol dm^{-3}, 2 cm^3
Reaction time	5 min	3 min
Sampling volume	100 cm^3	100 cm^3

* Buffer.

Table 2 Ionization potential

	Ionization potential (eV)
Arsine (AsH_3)	10.06
Stibine (SbH_3)	9.51
H_2O	12.61
CO_2	13.78
N_2	15.59
O_2	12.07

Procedure

The sample solution was placed in the reaction vessel, the system was flushed with helium gas for 2 min to replace air, and the solution was agitated with a magnetic stirrer. Then, the Teflon tube was placed in liquid nitrogen and $NaBH_4$ solution was injected into the reaction vessel to generate arsine and stibine from the sample solution. The generated arsine and stibine were carried through the drying tube and the CO_2 trap tube and collected in the Teflon tube in liquid nitrogen. After generation of arsine and stibine, the six-way valve was turned to the column/injection position and the liquid-nitrogen Dewar flask was removed, and then the arsine and stibine collected in the Teflon tube were carried into the gas chromatograph.

The gas flow rates of helium stripping gas, helium carrier gas and helium discharge gas were $50\,cm^3\,min^{-1}$, $30\,cm^3\,min^{-1}$ and $40\,cm^3\,min^{-1}$, respectively. The GC column temperature was 90 °C. The GC injector and detector temperatures were 130 °C. An integrator (Hitachi D-2500 type) was used for data calculation.

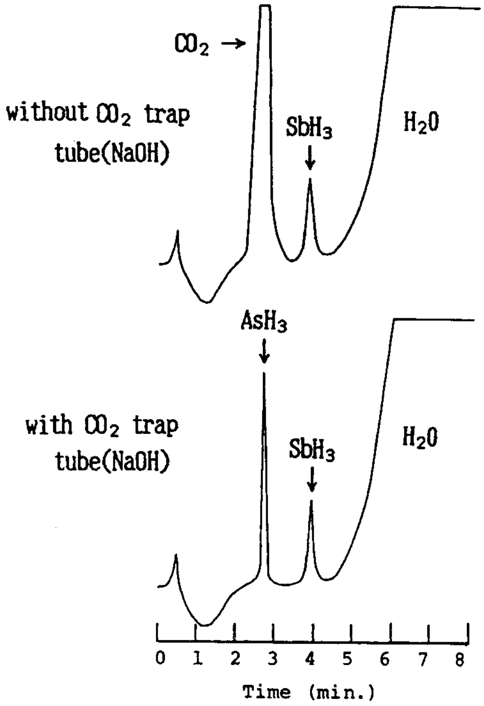

Figure 3 Effect of CO_2 trap (sodium hydroxide) on elimination of CO_2.

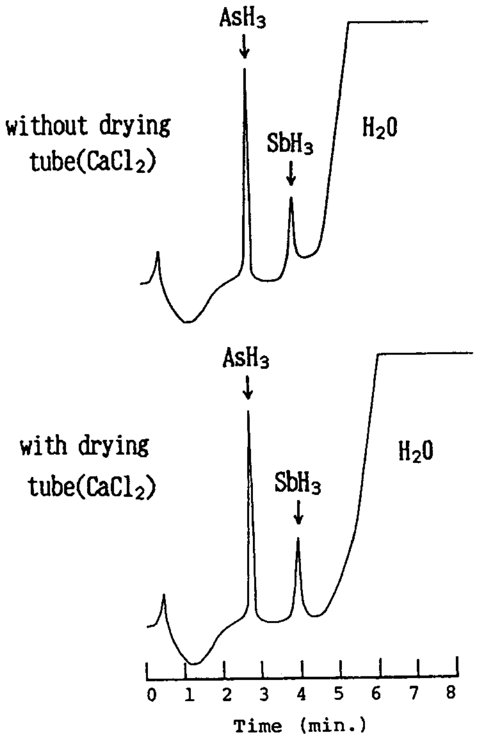

Figure 2 Effect of drying tube (calcium chloride) on elimination of water.

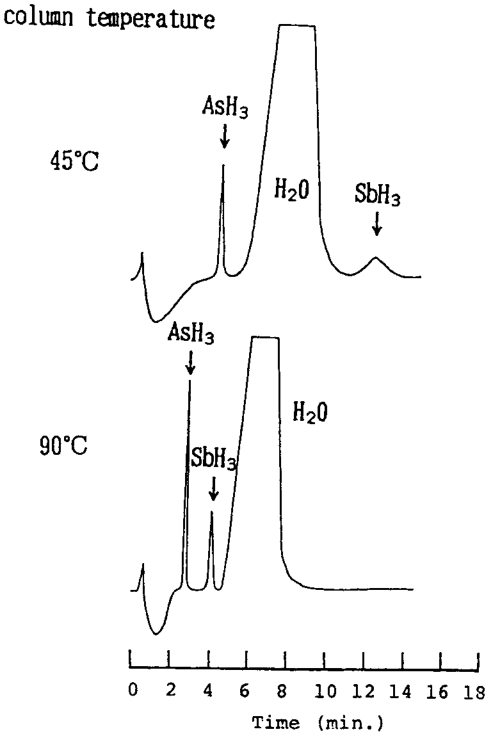

Figure 4 Effect of GC column temperature on separation of arsine (50 ng) and stibine (50 ng).

RESULTS AND DISCUSSION

Selective hydride generation

Andreae *et al.*[3,4] reported the effects of pH of the reaction solution on hydride generation for arsenic and antimony. Under weak-acid conditions, arsenic(III) and antimony(III) were reduced in a solution buffered at pH 5.9 with potassium dihydrogen citrate, but no reduction of arsenic(V) and antimony(V) took place under these conditions. Under strong-acid conditions, while arsenic(V) was reduced to arsine, antimony(V) was not sufficiently reduced. However, 100% of antimony(V) was reduced to stibine by addition of potassium iodide as a prereduction reagent.

Analytical conditions used for selective hydride generation are shown in Table 1. In the case of simultaneous determination of arsenic(III) and antimony(III), 1 cm^3 of 1.6 mol dm^{-3} potassium dihydrogen citrate was added to 100 cm^3 of sample solution to adjust the pH to 5.9, and then 1 cm^3 of 5 wt % $NaBH_4$ was injected into the reaction vessel. On the other hand, in the case of the simultaneous determination of arsenic(III + V) and antimony(III + V), 10 cm^3 of 12 mol dm^{-3} HCl and 2 cm^3 of 2 mol dm^{-3} KI were added to 100 cm^3 of sample solution, and then 5 cm^3 of 8 wt % $NaBH_4$ was injected.

Chromatographic separation

The principle of photoionization detection is as shown in Eqn [1],

$$R + h\nu \rightarrow R^+ + e^- \qquad [1]$$

and it is therefore a use of the phenomenon that a molecule R is ionized by radiation of ultraviolet light whose energy is more than the ionization potential (energy). The photoionization detector (PID) in this study is a helium discharge type, the UV source is a discharge in helium gas. Table 2 shows the ionization potentials of the major products of the hydride generation (HG) reaction. As the energy of the UV source of the helium discharge type is from 11.27 eV to 20.66 eV, arsine (IP 10.0 V) and stibine (IP 9.58 eV) can be ionized for detection. On the other hand, ionization potentials of by-products of the HG reaction such as CO_2 (IP 13.78 eV) and H_2O (IP 12.61 eV) are less than that of the UV source, and they can be also detected. Therefore, they must be removed or separated from arsine and stibine. In the gas chromatographic separation, the stibine peak was a shoulder on the foot of a large water peak when a drying tube as shown in Fig. 2 was not used. Therefore, a calcium chloride drying tube was used between the reaction vessel and the CO_2 trap tube, so that stibine could be separated from water. When a glass U-tube immersed in dry ice–2-propanol was used as a drying tube, the amount of water trapped was not enough to separate stibine completely from water.

Table 3 Instrumental operating conditions for gas chromatography with photoionization detection

Helium flow rate	
Carrier gas	30 cm^3 min^{-1}
Discharge gas	40 cm^3 min^{-1}
Column temperature	90 °C
Injector temperature	130 °C
Detector temperature	130 °C
Column	Teflon column 2 mm i.d. × 3 mm o.d. × 2 m
Packing material	Tenax-GC 60/80

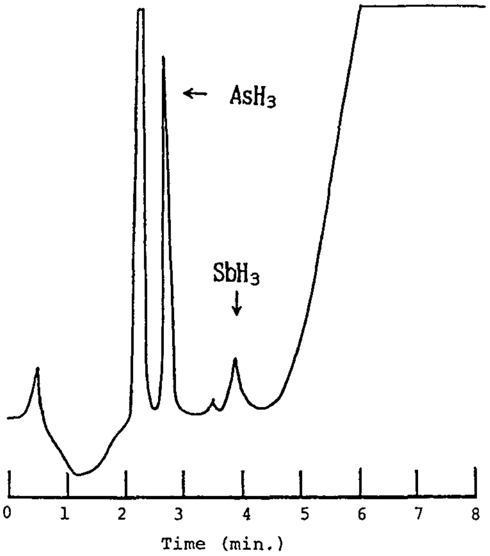

Figure 5 Typical chromatogram of arsine and stibine in seawater sample. (The first peak may be H_2S.)

As shown in Fig. 3, a large CO_2 peak obscured the determination of arsine without a CO_2 trap tube. A CO_2 trap tube packed with NaOH pellets was used prior to the cold trap, so that most CO_2 was eliminated from the gas stream. A separation among arsine, stibine and the above interferences could be achieved by using both the $CaCl_2$ drying tube and the CO_2 trap tube packed with NaOH

Table 4 Recoveries of arsenic(V) and antimony(V) added to natural waters

	Arsenic(V)			Antimony(V)		
	Added (ng)	Found (ng)	Recovery (%)	Added (ng)	Found (ng)	Recovery (%)
Seawater (Antarctic Ocean)	0	114	—	0	45.0	—
	20	135	105	20	63.4	92
River water (Tamagawa)	0	68.5	—	0	28.3	—
	20	88.5	100	20	49.7	107
Rainwater (Yokohama)	0	54.6	—	0	16.3	—
	20	75.9	107	20	37.8	108

Table 5 Analytical results for arsenic(III), arsenic(V), antimony(III) and antimony(V) in natural waters

	Arsenic(III) (ng dm^{-3})	Arsenic(V) (ng dm^{-3})	Antimony(III) (ng dm^{-3})	Antimony(V) (ng dm^{-3})
Seawater (Antarctic Ocean)	5.0	1140	<9.4	450
River water (Tamagawa)	456	229	<9.4	283
Rainwater (Yokohama)	71	475	<9.4	163

pellets. Significant loss of arsine and stibine were not found to be caused by using these tubes.

The effect of GC column temperature on the separation between arsine and stibine is shown in Fig. 4. Below 45 °C, stibine eluted after H_2O and its peak was broad and not suitable for determination of trace antimony. On the other hand, above 90 °C, stibine eluted before H_2O and its peak was sharp and suitable for determination of trace antimony. The GC column temperature was selected at 90 °C. The GC operating conditions are shown in Table 3. As shown in Fig. 5 (a typical chromatogram of a seawater sample), arsine and stibine could be separated from undesirable by-products in a natural sample.

Calibration curves were linear to 1000 ng for both arsenic and antimony. Detection limits of this method were 0.18 ng for arsenic and 0.94 ng for antimony.

Recovery test

In order to evaluate this method, 20 ng of arsenic(V) and antimony(V) were added to 100 cm^3 of the natural waters (seawater, river water, rainwater) and these samples were analyzed under the conditions described in Table 1 and Table 3. As shown in Table 4, the recoveries of arsenic(V) and antimony(V) were almost 100% and no significant interferences were found.

Analytical results

The analytical results for arsenic and antimony species in natural waters by this method are shown in Table 5. Dissolved arsenic was mainly present at arsenic(V) in seawater, and present as arsenic(III) and arsenic(V) in river water and rainwater. Most dissolved antimony was present as antimony(V) in all samples. These results by this method are in good agreement with values determined by HG/AA.

CONCLUSION

Arsenic and antimony in natural waters were simultaneously determined by a combination of the hydride generation method and gas chromatography using photoionization detector. A good chromatographic separation among arsine, stibine and interferences could be achieved by removing CO_2 and water vapor in two tubes containing sodium hydroxide pellets and calcium chloride.

Detection limits of this method were 1.8 ng dm^{-3} for arsenic and 9.4 ng dm^{-3} for antimony for a 100-cm^3 sample volume. These are sufficient for determination of trace amounts of arsenic and antimony species in natural waters.

Acknowledgements The authors are thankful to Dr S Toda for his kind suggestions.

REFERENCES

1. Tanaka, S, Nakamura, M, Kishi, Y and Hashimoto, Y *Kōgai to Taisaku*, 1986, 22: 524
2. Tanaka, S, Nakamura, M, Yokoi, H, Yumura, M and Hashimoto, Y *Bunseki Kagaku*, 1986, 35: 116
3. Andreae, M O *Limnol. Oceanogr.* 1979, 24: 440
4. Andreae, M O, Asmode, J, Foster, P and Van't Dack, L *Anal. Chem.* 1981, 53: 1766
5. Sanders, J G and Widom, H L *Environ. Coast. Mar. Sci.*, 1980, 10: 555
6. Tanaka, S, Nakamura, M, Kishi, Y and Hashimoto, Y *Nippon Kagaku Kaishi*, 1986, 5: 727
7. Vien, S H and Fry, R C *Anal. Chem.* 1988, 60: 465
8. Cutter, L C *Anal. Chem.*, 1991, 63: 1138