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Determination of inorganic arsenic and organic arsenic compounds in marine organisms by hydride generation/cold trap/gas chromatography–mass spectrometry

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The behavior of arsenite, methylarsonic acid, dimethylarsinic acid, trimethylarsine oxide, dimethyl-R-arsine oxides, and trimethyl-R-arsonium compounds (R = carboxymethyl, 2-carboxyethyl, 2-hydroxyethyl) toward sodium borohydride and hot aqueous sodium hydroxide was investigated. The arsines obtained by sodium borohydride reduction of the undigested and digested solutions were collected in a liquid-nitrogen cooled trap, separated with a gas chromatograph, and detected with a mass spectrometer in the selected-ion-monitoring mode. The investigated arsenic compounds were stable in hot 2 mol dm^{-3} sodium hydroxide except arsenobetaine [trimethyl(carboxymethyl)arsonium zwitterion] that was converted to trimethylarsine oxide, and dimethyl(ribosyl)arsine oxides that were decomposed to dimethylarsinic acid. Hydride generation before and after digestion of extracts from marine organisms allowed inorganic arsenic, methylated arsenic, arsenobetaine, and ribosyl arsenic compounds to be identified and quantified. This method was applied to extracts from shellfish, fish, crustaceans, and seaweeds.

Keywords: Arsenic, arsine, methylarsine, dimethylarsine, trimethylarsine, arsenocholine, dimethyl(ribosyl)arsine oxide, arsenobetaine, marine organisms, hydride generation–gas chromatography–mass spectrometry (GC MS)

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INTRODUCTION

Marine organisms frequently contain arsenic in high concentrations. Much of the arsenic is present in organic forms[1–4] that are water- or lipid-soluble.[5–10] One of the water-soluble organic arsenic compounds, arsenobetaine [$(CH_3)_3As^+CH_2COO^-$], was isolated from the western rock lobster and structurally characterized in 1977.[11] Subsequently, arsenobetaine was found in several marine animals.[12–24] Arsenocholine [$(CH_3)_3As^+CH_2CH_2OH$],[25–27] dimethyl(2-hydroxyethyl)arsine oxide [$(CH_3)_2AsO(CH_2CH_2OH)$],[28] and dimethyl(ribosyl)arsine oxides[29–32] are other water-soluble organic arsenic compounds identified in marine organisms. The distribution and concentrations of these arsenic compounds must be known, before the metabolic pathways and the accumulation of arsenic in marine ecosystems can be understood. The identification and quantification of organic arsenic compounds in marine organisms were generally carried out with complicated techniques after laborious purification of extracts. A rapid and more direct technique would considerably speed up analytical investigations.

Braman *et al.*[33] reduced inorganic and methylated arsenic compounds in aqueous solution with sodium borohydride [$NaBH_4$] to arsine and methylarsines. The arsines were separated according to their boiling points and detected by atomic absorption spectrometry. This hydride generation technique has been widely used for the separation and identification of arsenic compounds that can be reduced to volatile arsines. Edmonds and Francesconi[34] found that the arsenic compounds in extracts from marine organisms are

reduced by sodium borohydride to dimethylarsine and timethylarsine after (but not before) digestion of the extracts with aqueous sodium hydroxide. Arsenic compounds in the urine and plasma of mammals exposed to inorganic arsenic could be reduced to arsines after alkaline digestion.[35] Often, the arsines are collected in cold traps[35,36] before transportation to detectors such as atomic emission spectrometers, atomic absorption spectrometers and GC MS.[36,37]

In this paper, a method for the determination of organic arsenic compounds in marine organisms is described consisting of digestion of the sample with 2 mol dm^{-3} aqueous sodium hydroxide, reduction with sodium borohydride, cryogenic trapping of the arsines, gas chromatographic separation of the arsines, and detection by selected-ion-monitoring mass spectrometry.

EXPERIMENTAL

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected.

^1H and ^{13}C NMR spectra were recorded on a JEOL JMN-FX100 NMR spectrometer (^1H, 100 MHz; ^{13}C, 25 MHz) and a Bruker-AAM400 NMR spectrometer (^1H, 400 MHz; ^{13}C, 100 MHz) in D_2O with sodium 3-(trimethylsilyl)propionate-d_4 (TSP) as the internal standard. The chemical shifts are given as δ values from TSP. The following abbreviations are used: s, singlet; d, doublet; t, triplet; q, quartet.

The high-resolution fast atom bombardment mass spectra (HR FAB MS) were taken on a JEOL JMS-DX300 mass spectrometer equipped with a fast atom bombardment ion source and xenon atoms at 6 keV as reported by Kaise *et al.*[24]

Reagents

Arsenic(III) and arsenic(V) standard solutions were prepared by dissolving arsenic trioxide [As_2O_3] and sodium arsenate (Na_2HAsO_4; Mallinckrodt), respectively, in distilled water. Methylarsonic acid [$CH_3AsO(OH)_2$; MAA] was obtained from Ventron Corp. as the disodium salt and was recrystallized from methanol. Dimethylarsinic acid [$(CH_3)_2AsOOH$; DMAA] was recrystallized from aqueous ethanol. Trimethylarsine oxide [$(CH_3)_3AsO$; TMAO] synthesized from trimethylarsine (Tri Chemical Corp.) by oxidation with 5% hydrogen peroxide[38] was recrystallized from benzene.

Arsenobetaine [trimethyl(carboxymethyl)arsonium zwitterion] was synthesized according to the procedure of Edmonds *et al.*[11]

Trimethyl(2-carboxyethyl)arsonium zwitterion was synthesized from trimethylarsine and ethyl β-bromopropionate under an atmosphere of carbon dioxide according to the procedure used for arsenobetaine. White crystals were obtained from acetone containing a trace of methanol, mp 178°C. ^1H NMR: 1.85, 9H, s, $(C\underline{H}_3)_3As$; 2.43, 2H, t, $AsC\underline{H}_2CH_2$; 2.61, 2H, t, $CH_2C\underline{H}_2CO$. ^{13}C NMR: 9.60, q, $(\underline{C}H_3)_3As$; 25.3, t, $As\underline{C}H_2CH_2$; 31.6, t, $CH_2\underline{C}H_2CO$; 178.5, s, $CH_2\underline{C}OO$. HR FAB MS *m/z* calcd for $C_6H_{14}O_2As$ $[M+H]^+$: 193.0210; found: 193.0212.

Arsenocholine bromide [trimethyl(2-hydroxyethyl) arsonium bromide] was prepared according to the procedure of Saaman.[39]

Dimethyl(2-carboxyethyl)arsine oxide, dimethyl-(carboxymethyl)arsine oxide and dimethyl(2-hydroxyethyl)arsine oxide were prepared from dimethylarsinic anhydride which was obtained by the reaction of dimethyliodoarsine and aqueous sodium hydroxide,[40] and 3-chloropropionic acid, sodium monochloroacetate, or 2-chloroethanol by a modification of the Wigren method.[41] The products were recrystallized from acetone containing a trace of methanol.

Dimethyl(2-carboxyethyl)arsine oxide: mp 163–166°C. ^1H NMR: 2.09, 6H, s, $(C\underline{H}_3)_2As$; 2.67, 2H, t, $AsC\underline{H}_2C\underline{H}_2$; 2.82, 2H, t, $CH_2C\underline{H}_2CO$. ^{13}C NMR: 16.32, q, $(\underline{C}H_3)_2As$; 28.5, t, $As\underline{C}H_2CH_2$; 30.1, t, $CH_2\underline{C}H_2CO$; 178.3, s, $CH_2\underline{C}OO$. HR FAB MS *m/z* calcd for $C_5H_{12}O_3As$ $[M+H]^+$: 195.0002; found: 194.9998.

Dimethyl(carboxymethyl)arsine oxide: mp 86°C. ^1H NMR: 1.98, 6H, s, $(C\underline{H}_3)_2As$; 2.75, 2H, s, $AsC\underline{H}_2CO$. ^{13}C NMR: 14.9, q, $(\underline{C}H_3)_2As$; 29.3, t, $As\underline{C}H_2CO$; 171.5, s, $CH_2\underline{C}OO$. HR FAB MS *m/z* calcd for $C_4H_{10}O_3As$ $[M+H]^+$: 180.9846; found: 180.9850.

Dimethyl(2-hydroxyethyl)arsine oxide: mp 153–156°C. ^1H NMR: 1.75, 6H, s, $(C\underline{H}_3)_2As$; 2.36, 2H, t, $AsC\underline{H}_2CH_2$; 3.95, 2H, t, $CH_2C\underline{H}_2OH$. ^{13}C NMR: 15.3, q, $(\underline{C}H_3)_2As$; 35.6, t, $As\underline{C}H_2CH_2$; 56.6, t, $CH_2\underline{C}H_2OH$. HR FAB MS *m/z* calcd for $C_4H_{12}O_2As$ $[M+H]^+$: 167.0053; found: 167.0052.

Stock solutions of these arsenic compounds (1000 arsenic $\mu g\ cm^{-3}$) were prepared by dissolving the required amounts in water purified with a Milli-Q system (Millipore Corp). $NaBH_4$ was purchased from Wako Pure Chemical Corp. All other chemicals were of analytical reagent grade.

Apparatus

A JEOL DX300 gas chromatograph–mass spectro-

meter (GC MS) and a DA5000 data system served as detector. The arsines were separated on a glass column (3 m × 3 mm i.d.) packed with 3% silicone OV-17 on 80/100 mesh Chromosorb W (AW, DMCS). The injection port was kept at 100°C and the oven at 50°C. The carrier gas (helium) flowed through the system at 30 cm^3 min^{-1}. The mass spectrometer was operated in the electron impact mode (70 eV), an ion-accelerating voltage of 3.0 kV, and an ion source temperature of 180°C. The arsenic compounds were reduced in a fully automated hydride generation system (Hitachi Model HFS-2). The hydride generator was connected to a stainless-steel U-tube (each arm 15 cm × 6 mm i.d.) packed with quartz wool, wrapped with 4.2 m Nichrome wire (0.35 mm diameter), resistance 15 ohm m^{-1}, and insulated with asbestos ribbon. The tube temperature was measured with a thermocouple. The wire was connected to a variable transformer that allowed the temperature to increase at 200°C/30 s.

The time required for the complete formation of the arsines was monitored with a Hitachi Z-8000 atomic absorption spectrophotometer (193.7 nm) with a heated quartz tube connected to the hydride generation system.

Operating procedure

The marine biological sample (5–10 g) was suspended in aqueous methanol (70% v/v, 30 cm^3) and homogenized. The homogenate was diluted with methanol to 50 cm^3. After centrifugation, the supernatant (1 cm^3) was transfered into a polymethylene-pentene tube. Aqueous sodium hydroxide solution (2.0 mol dm^{-3}, 10 cm^3) was added. The mixture was heated in a water bath at 85°C for 3 h. The digest was neutralized with dilute hydrochloric acid and diluted to 20 cm^3 with water. The solution (3 cm^3) was introduced into the arsine generator. Hydrochloric acid (0.6 mol dm^{-3}) and sodium borohydride (2.0 g per 100 cm^3 of 0.2 mol dm^{-3} aqueous sodium hydroxide) solution were continuously pumped through the mixing coil at 6 cm^3 min^{-1}.

The U-tube was precooled for 2 min with liquid nitrogen and then the generated arsines were collected in the U-tube for 30 s. The coolant was then removed and the U-tube heated at 200°C to transfer the arsines into the GC MS for selective ion monitoring (SIM) at m/z 76 for AsH_3, 78 for AsH_3, 90 for CH_3AsH_2, 90 for $(CH_3)_2AsH$, 103 for $(CH_3)_3As$, and 120 for $(CH_3)_3As$.

RESULTS AND DISCUSSION

Hydride generation system

The apparatus for the fully automated, continuous reduction of arsenic compounds is a modification of the system reported by Yamauchi and Yamamura (Fig. 1).[42] The formation of arsines was complete within 25 s after the sample had been mixed with the sodium borohydride solution (Fig.2). The arsines were collected in the quartz wool-filled, liquid nitrogen-cooled U-tube for 30 s after the mixing and were subsequently flashed into GC MS. Carbon dioxide and water that accompanied the arsines were also trapped in the cooled U-tube. Sodium hydroxide, calcium chloride and magnesium perchlorate were previously used for removing water and carbon dioxide,[33] larger quantities of which might interfere with the determination of the arsines. These reagents absorb not only water and carbon dioxide but also some of the arsines. Alternately, water vapor was removed by passage of the gas

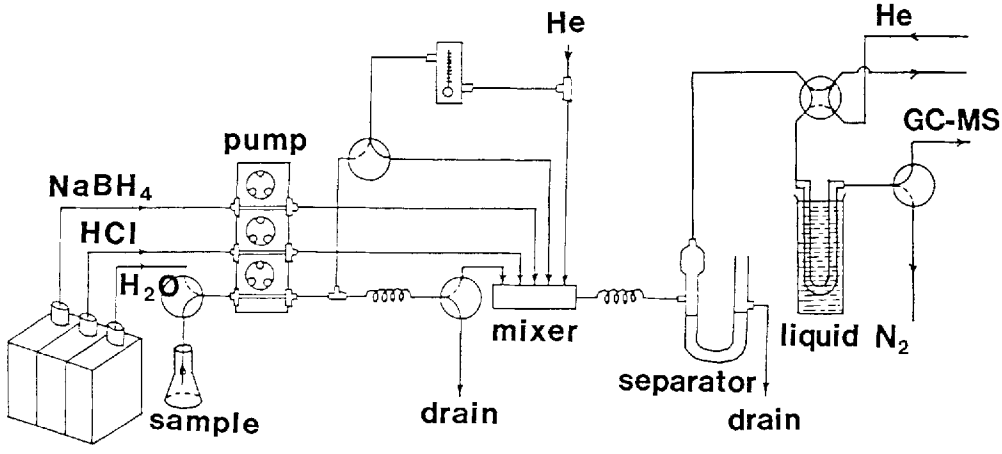


Figure 1 The hydride generation and cold-trap system for the generation and collection of arsines.

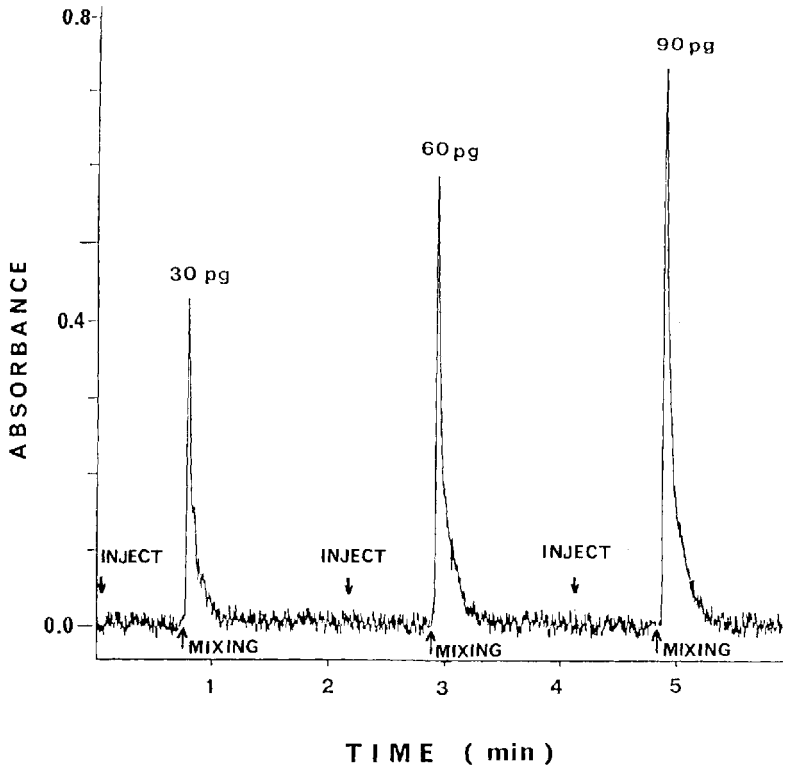


Figure 2 Generation time of arsine. The standard solutions of arsenite (30, 60, or 90 pg arsenic/3 cm^3) were injected into the arsine generation system and were then mixed with aqueous sodium borohydride. Monitored by atomic absorption spectrophotometer (AA) with a heated quartz tube at 193.7 nm.

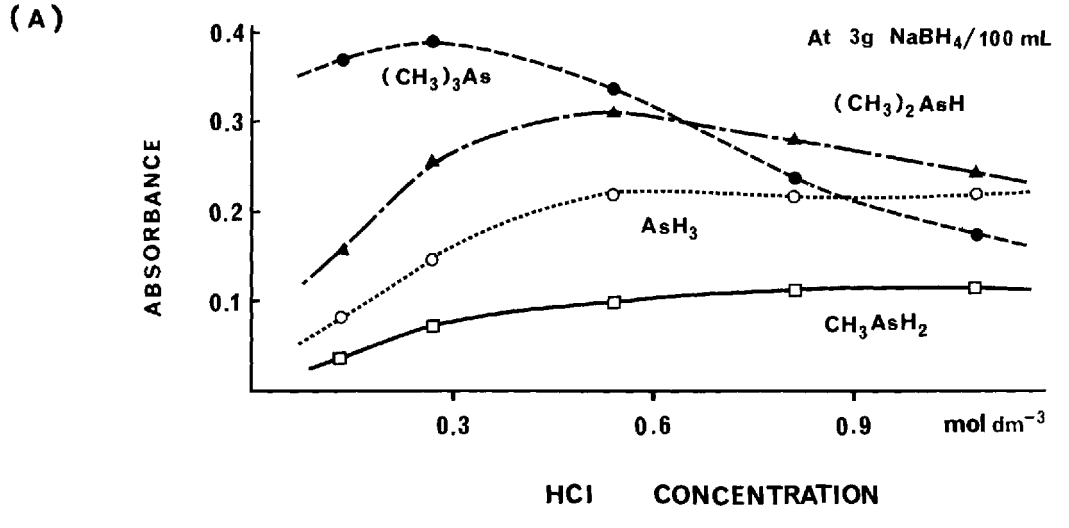


Figure 3(A) Effect of HCl concentration on the yield of generated arsines.

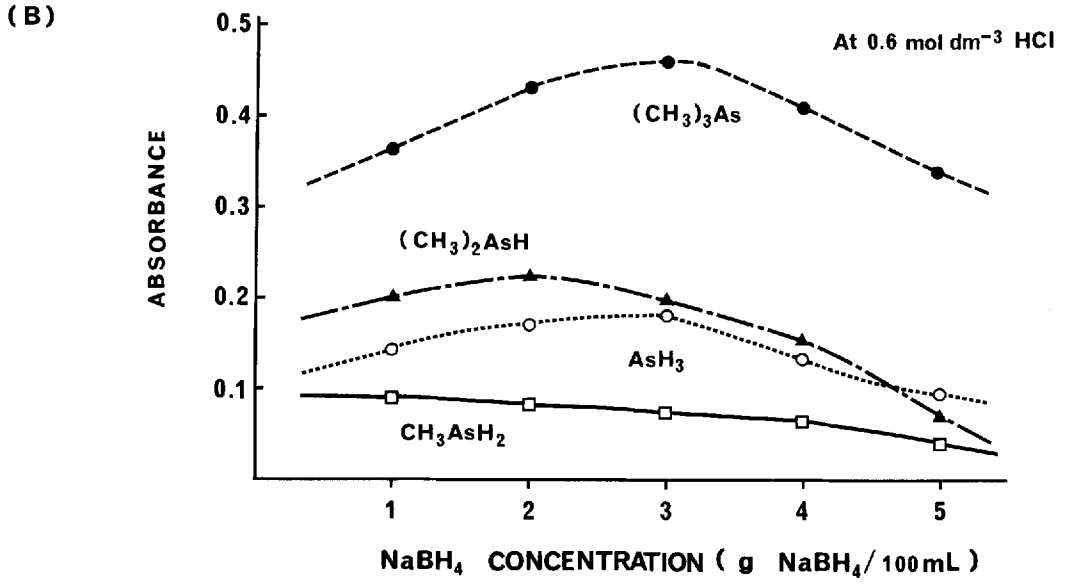


Figure 3(B) Effect of $NaBH_4$ concentration on the yield of generated arsines. Monitored by AA with a heated quartz tube at 193.7 nm.

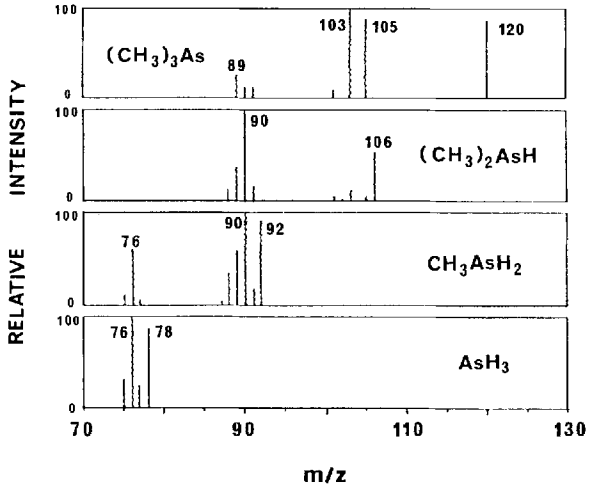


Figure 4 The mass spectra of trimethylarsine, dimethylarsine, methylarsine, and arsine at an ion accelerating voltage of 3.0 kV and an ion source temperature of 180°C.

stream through a U-tube cooled with dry ice–acetone or ice–sodium chloride. This U-tube became often clogged.[33] Odanaka *et al.*[36] trapped the arsines in n-heptane cooled with dry ice–acetone. Aliquots of the heptane solutions were then injected into the GC MS. The quartz wool-filled U-tube in the system shown in Fig. 1 did not become clogged, because only small amounts of carbon dioxide and water reached the U-tube during the short collected time of 30 s. The effects of the concentrations of hydrochloric acid and sodium borohydride on the reduction of arsenic compounds were explored by many investigators.[36,37,42] We found the optimal concentrations for the determination of inorganic and methylated arsenic compounds to be 0.6 mol dm^{-3} for hydrochloric acid and 2.0 g per 100 cm^3 for sodium borohydride in 0.2 mol dm^{-3} aqueous sodium hydroxide (Fig. 3).

GC MS measurements

The arsines were separated by gas chromatography and identified and quantified by GC MS in the selected-ion-monitoring (SIM) mode. The electron-impact mass specta (Fig. 4) of arsine, methylarsine, dimethylarsine, and trimethylarsine contain peaks corresponding to molecular ions and fragment ions formed by loss of hydrogen atoms or methyl groups from the molecular ions. The peaks corresponding to the most abundant ion in each spectrum were used for selected-ion monitoring: 76 $[M-2]^+$ and 78 $[M]^+$ for arsine, 90 $[M-2]^+$ for methylarsine, 90 $[M-CH_3-1]^+$ for dimethylarsine, 103 $[M-CH_3-2]^+$ and 120 $[M]^+$ for trimethylarsine.

Silicone OV-17 is better as the liquid phase for the chromatographic separation of the four arsines than OV-1, OV-101, PEG-20M, or DC-550. The retention times of the arsines increase with their boiling points.[33] The SIM chromatograms for the arsines are shown in Fig. 5. The calibration curves of peak area versus amount of arsenic for arsine and trimethylarsine

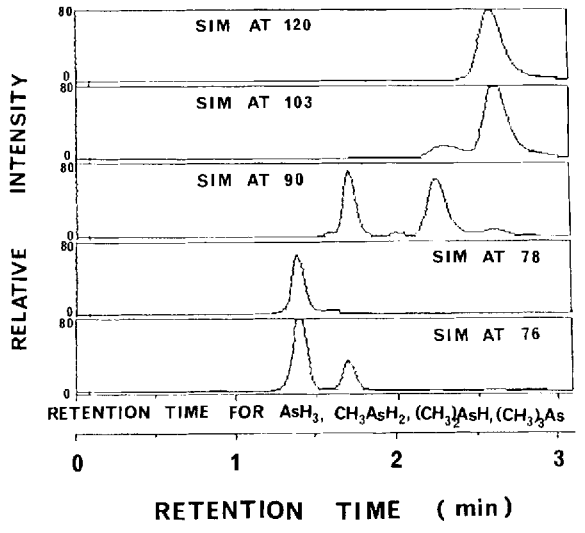


Figure 5 The SIM chromatograms of arsine, methylarsine, dimethylarsine, and trimethylarsine (10 ng arsenic each) after introduction of a solution containing arsenite, methylarsonic acid, dimethylarsinic acid, and trimethylarsine oxide into the hydride generation system.

were linear from 0.3 ng to 300 ng of arsenic (Fig. 6). The other calibration curves of methylarsine and dimethylarsine were also linear. The detection limit is 0.1 ng arsenic g^{-1} of biological sample.

Alkaline digestion of arsenic compounds

Hot aqueous sodium hydroxide converted arsenobetaine to trimethylarsine oxide (Scheme 1) that was subsequently reduced to trimethylarsine by sodium borohydride. The quantitative conversion of arsenobetaine to trimethylarsine oxide required 2 mol dm^{-3} sodium hydroxide and 3 h of heating (Fig. 7). Heating arsenobetaine with acid and adding sodium borohydride to the resulting mixture did not produce any trimethylarsine.

Arsenite, methylarsonic acid, dimethylarsinic acid and trimethylarsine oxide were found to be stable in hot aqueous sodium hydroxide. Although trimethyl(carboxymethyl)arsonium zwitterion (arsenobetaine) was quantitatively converted to trimethylarsine oxide, only 23% of trimethyl(2-carboxyethyl)arsonium zwitterion decomposed under the same conditions (Table 1). Arsenocholine, which was identified in shrimp, did not form trimethylarsine oxide on treatment with base. Dimethyl(2-carboxyethyl) arsine oxide, dimethyl(carboxymethyl)arsine oxide and dimethyl(2-hydroxyethyl)arsine oxide were not decomposed by hot aqueous sodium hydroxide. Dimethylarsine could not be detected after reduction of the reaction mixtures with sodium borohydride (Table 1). The reduction of methanol extracts of *Hizikia fusiforme*, *Laminaria japonica* and *Penaeus semisulcatus* with sodium borohydride produced neither dimethylarsine nor trimethylarsine. However,

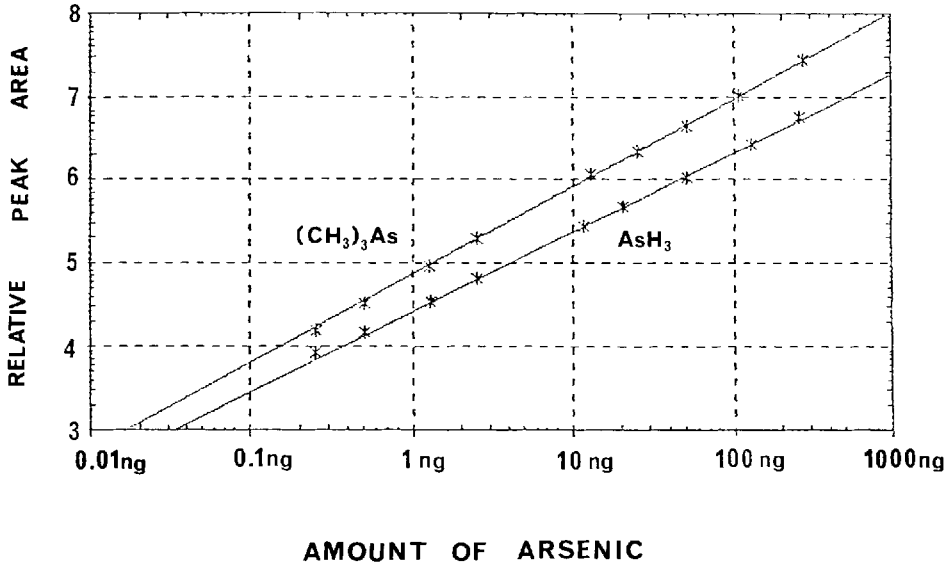
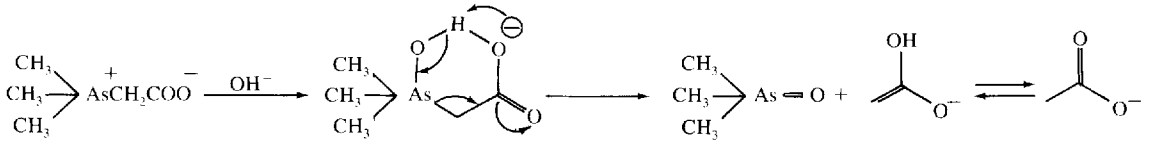


Figure 6 Calibration curves for arsine (*m/z* 76) and trimethylarsine (*m/z* 103).



Scheme 1

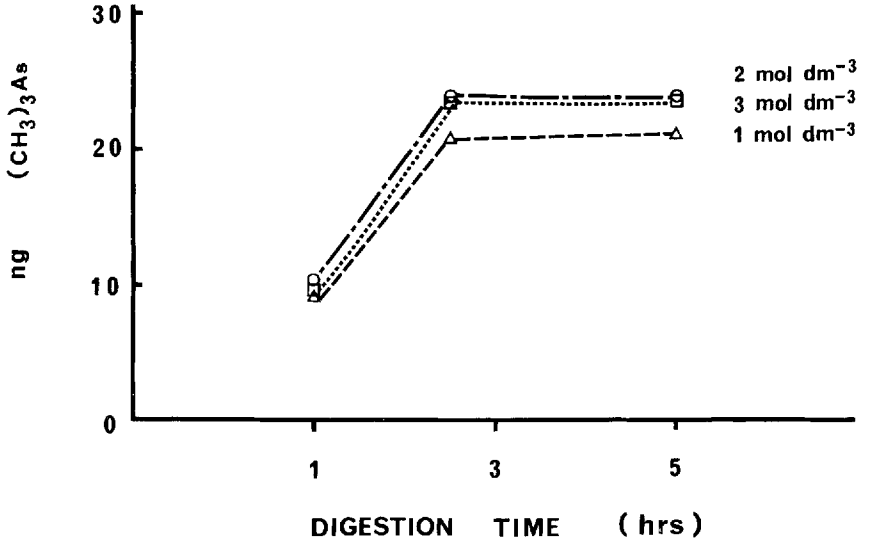
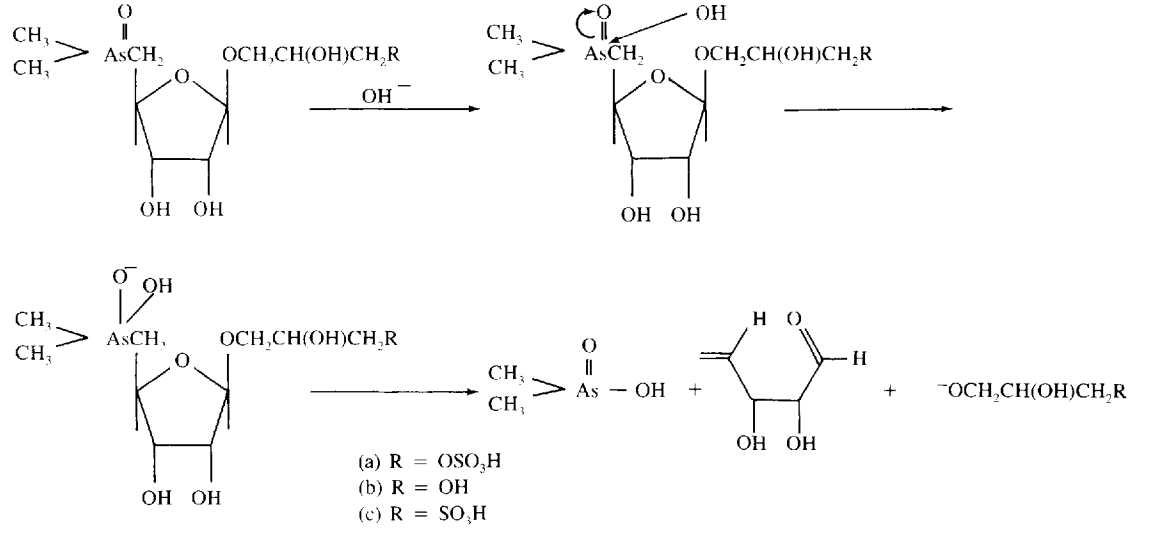


Figure 7 Time dependence of the formation of trimethylarsine through the treatment of arsenobetaine with aqueous sodium hydroxide at 85°C.



Scheme 2

Table 1 Arsines[a] generated from aqueous solutions of synthetic arsenic compounds by sodium borohydride reduction at pH 1 before and after treatment of the solutions with hot 2 mol dm^{-3} sodium hydroxide

Compound	Arsenic[b] before digestion/after digestion with NaOH (%)			
	AsH_3	CH_3AsH_2	$(CH_3)_2AsH$	$(CH_3)_3As$
Arsenite	100/99.8	0/0	0/0	0/0
Methylarsonic acid	0/0	100/98	0/0	0/0
Dimethylarsinic acid	0/0	0/0	100/99.1	0/0
Trimethylarsine oxide	0/0	0/0	0/0	100/99.1
Dimethyl(carboxymethyl)arsine oxide	0/0	0/0	0/<0.1	0/0
Dimethyl(2-carboxyethyl)arsine oxide	0/0	0/0	0/<0.1	0/0
Dimethyl(2-hydroxyethyl)arsine oxide	0/0	0/0	0/<0.1	0/0
Trimethyl(carboxymethyl)arsonium zwitterion (arsenobetaine)	0/0	0/0	0/<0.1	0/99.8
Trimethyl(2-carboxyethyl)arsonium zwitterion	0/0	0/0	0/0	0/22.8
Trimethyl(2-hydroxyethyl)arsonium bromide (arsenocholine)	0/0	0/0	0/0	0/0.8

[a] The arsines were detected by gas chromatography–mass spectrometry (selected-ion-monitoring mode). [b] An amount of arsenic compound corresponding to 100 μg arsenic was used in each experiment.

Table 2 Arsine, methylarsine, dimethylarsine and trimethylarsine identified in methanol extracts of marine organisms after alkaline digestion[a]

Organism	Arsenic (μg g^{-1}) as:				
	AsH_3	CH_3AsH_2	$(CH_3)_2AsH$	$(CH_3)_3As$	Total arsenic[b]
Shell fish					
Batillus cornutus	0	0.03	0.13	1.29	1.64
Crassostrea gigas	0	0	0.17	6.15	9.95
Mytilus edulis	0	0	0.07	2.01	4.36
Kellettia lischkei	0	0.07	1.32	90.39	125.92
Fish					
Engraulis japonica	0	0.05	0.01	2.01	2.33
Sardinops melanosticta	0	0.01	0.01	4.07	4.51
Stephanolepis cirrhifer	0	0	0.04	2.81	4.35
Crustacea					
Penaeus semisulcatus	0	0	0	3.42	3.45
Panulirus japonicus	0	0	0.14	42.22	62.01
Plagusia dentipes	0	0	0.15	44.99	46.87
Seaweeds					
Laminaria japonica	0	0	36.48	1.07	49.76
Hizikia fusiforme	1.47[a]	0	33.01	3.86	41.31

[a] Reduction of the undigested extract from *Hizikia* gave 1.5 μg arsenic g^{-1} in the form of AsH_3. No other arsines were detected in any of the other undigested extracts.

[b] Total arsenic was determined by a fully automated hydride generation system and atomic absorption spectrophotometry with a heated quartz tube at 193.7 nm after the samples were digested with a mixture of nitric, sulfuric and perchloric acids.

after alkaline digestion of the extracts and reduction of the digests, dimethylarsine and trimethylarsine were formed (Table 2). The behavior of synthetic arsenic compounds toward aqueous sodium hydroxide and sodium borohydride suggests that the trimethylarsine is derived from arsenobetaine in the marine organisms. Dimethylarsine detected after digestion and reduction of extracts of seaweeds is probably formed by decomposition of dimethy(ribosyl)arsine oxides (Scheme 2). These arsenoriboses were discovered by Edmonds and co-workers[29–32] in marine organisms.

REFERENCES

1. Chapman, A C *Analyst*, 1926, 51: 548
2. Lunde, G *Nature (London)*, 1969, 224: 186
3. Lunde, G *Acta Chem. Scand.*, 1973, 27: 1586
4. Shinagawa, A, Shiomi, K, Yamanaka, H and Kikuchi, T *Bull. Jap. Soc. Sci. Fish.*, 1983, 49: 75
5. Holmes, A D *Ind. Eng. Chem.*, 1934, 26: 573
6. Lunde, G *J. Am. Oil Chem. Soc.*, 1971, 48: 517
7. Lunde, G *J. Am. Oil Chem. Soc.*, 1972, 49: 44
8. Vaskovsky, V E *Comp. Biochem. Physiol.*, 1972, 41B: 777
9. Lunde, G *J. Sci. Food Agric.*, 1973, 24: 1021
10. Kaise, T, Watanabe, S and Ikeda, H *J. Food Hyg. Soc. Japan*, 1980, 21: 58
11. Edmonds, J S, Francesconi, K A, Cannon, J R, Raston, C L, Skelton, B W and White, A H *Tetrahedron Lett.*, 1977: 1543
12. Edmonds, J S and Francesconi, K A *Chemosphere*, 1981, 10: 1041
13. Norin, H and Christakopoulos, A *Chemosphere*, 1982, 11: 287
14. Luten, J B, Riekwel-Booy, G, Van der Greef, J and ten Noever de Brauw, M C *Chemosphere*, 1983, 12: 131
15. Shiomi, K, Shinagawa, A, Yamanaka, H and Kikuchi, T *Bull. Jap. Soc. Sci. Fish.*, 1983, 49: 79
16. Shiomi, K, Shinagawa, A, Azuma, M, Yamanaka, H and Kikuchi, T *Comp. Biochem. Physiol.*, 1983, 74C: 393
17. Shiomi, K, Shinagawa, A, Igarashi, T, Yamanaka, H and Kikuchi, T *Experientia*, 1984, 40: 1247
18. Shiomi, K, Shinagawa, A, Hirota, K, Yamanaka, H and Kikuchi, T *Agric. Biol. Chem.*, 1984, 48: 2863
19. Hanaoka, K and Tagawa, S *Bull. Jap. Soc. Sci. Fish.*, 1985, 51: 681
20. Hanaoka, K and Tagawa, S *Bull. Jap. Soc. Sci. Fish.*, 1985, 51: 1203
21. Maher, W A *Comp. Biochem. Physiol.*, 1985, 80C: 199
22. Hanaoka, K, Fujita, T, Matsuura, M, Tagawa, S and Kaise, T *Comp. Biochem. Physiol.*, 1987, 86B: 681
23. Hanaoka, K, Kobayashi, H, Tagawa, S and Kaise, T *Comp. Biochem. Physiol.*, 1987, 88C: 189
24. Kaise, T, Watanabe, S, Ito, K, Hanaoka, K, Tagawa, S, Hirayama, T and Fukui, S *Chemosphere*, 1987, 16: 91
25. Norin, H, Ryhage, R, Christakopoulos, A and Sandstrom, M. *Chemosphere*, 1983, 12: 299
26. Lawrence, J F, Michalik, P, Tam, G K H and Conacher, H B S *J. Agric. Food. Chem.*, 1986, 34: 315
27. Shiomi, K, Orii, M, Yamanaka, H and Kikuchi, T *Bull. Jap. Soc. Sci. Fish.*, 1987, 53: 103
28. Edmonds, J S, Francesconi, K A and Hansen, J A *Experientia*, 1982, 38: 643
29. Edmonds, J S and Francesconi, K A *Nature (London)*, 1981, 289: 602
30. Edmonds, J S, Francesconi, K A, Healy, P C and White, A H *J. Chem. Soc., Perkin Trans. 1*, 1982, 2989
31. Edmonds, J S and Francesconi, K A *J. Chem. Soc., Perkin Trans. 1*, 1983: 2375
32. Edmonds, J S, Morita, M and Shibata, Y *J. Chem. Soc. Perkin Trans. 1*, 1987: 577
33. Braman, R S, Johnson, D L, Foreback, C C, Ammons, J M and Bricken, J L *Anal. Chem.*, 1977, 49: 621
34. Edmonds, J S and Francesconi, K A *Nature (London)*, 1977, 265: 436
35. Yamauchi, H and Yamamura, Y *Toxicology*, 1985, 34: 113
36. Odanaka, Y, Tsuchiya, N, Matano, O and Goto, S *Anal. Chem.*, 1983, 55: 929
37. Norin, H, Christakopoulos, A, Sandstrom, M and Ryhage, R *Chemosphere*, 1985, 14: 313
38. Merijanian, A and Zingaro, R A *Inorg. Chem.*, 1966, 15: 187
39. Saaman, S. Metallorganische Verbindungen As, Sb, Bi. Band XIII/8. *Houben Weyl Methoden der Organischen Chemie*, George Thieme Verlag, Stuttgart, 1978, p 402
40. Wigren, N *J. Prakt. Chem.*, 1930, 126: 223
41. Wigren, N *J. Prakt. Chem.*, 1930, 126: 246
42. Yamauchi, H and Yamamura, Y *Toxicol. Appl. Pharmacol.*, 1984, 74: 134