Determination of Methyltins by a Hydridization Solvent Extraction Method

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Abstract : Analytical methods for the determination of methyltins in aqueous solutions were investigated. Methyltins ($(CH_3)_nSn^{(4-n)+}$) were derived to hydrides ($(CH_3)_nSnH_{(4-n)}$) using sodium borohydride and extracted with benzene. Various factors related to hydridization and extraction were studied, and the optimum analytical conditions were established. Each methyltin in 50 ml of aqueous solution could be detected in the range of 0.5-250 μg as Sn using a gas chromatography-flame photometric detector (tin selective detector).

Key phrases : methyltins, determination of methyltins, monomethyltin, dimethyltin, trimethyltin, G.C.-F.P.D.

Introduction

Increasing of usage of organotin compounds in industry has caused worldwide environmental pollution[1)-4)] and method for trace level determination of these compounds is needed. Analytical methods for n-butyltin compounds in the environment have been thoroughly studied[2),3),5)-8)] and environmental monitoring of the substances has been carried out in many countries because of their high toxicity to aquatic organisms[9),10)].

In recent years, it has been discovered that methyltin compounds are produced from inorganic tin in the environment[3),4),11)-28)]. Trimethyltin compounds exhibit toxic action on the central nervous system of mammals[29)-32)], and genotoxicity of dimethyltin or trimethyltin compounds with several short term screening methods has also been reported[33)-37)]. Accordingly, methods for determi nation of methyltins for various environmental samples is required.

For the detection of methyltin compounds, the analytical methods used for n-butyltin compouds were applicable[3),4),38)-50)]. However, some special equipment and analytical procedures are required to detect volatile methyltins at trace levels. For example, a hydride generator and a cold purge trap are necessary for efficient determination of methyltin hydrides and carful temperature regu-

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lation of the cold purge trap is necessary to identify each methyltin accurately based on its retention time[41].

Matthias et al.[51] analyzed butyltin compounds using a simultaneous hydridization/extraction method with gas chromatography-flame photometric detection (G.C.-F.P.D.). The authors modified their analytical methods for the analysis of mono-, di- and trimethyltins. Various analytical conditions, such as the volume of the separatory funnel, the shaking time, the amount of sodium borohydryde and the pH of the solution were investigated. As a result, we found that volatile methyltins could be extracted quickly by benzene as methyltin hydrides and detected in the range of 0.5-250 μg as Sn in 50ml aqueous solution by G.C.-F.P.D. (tin selective detector).

Materials and Methods

1) Chemicals

Methyltin trichloride (Aldrich), dimethyltin dichloride (Kanto Chemical Co.) and trimethyltin chloride (Kanto Chemical Co.) were used as standards. Sodium borohydride solution (Kishida Chemical Co.) to derive methyltin hydrides was prepared fresh for each experiment. Pesticide residue analysis grade benzene was purchased from Hayashi Pure Chemical Co.. Tetrabutyltin (Merck)-benzene solution (5 μg as Sn/ml) was used as the internal standard. Extracted benzene solution was dehydrated with sodium sulfate anhydrous (Kishida Chemical Co.). 0.1N or 1N HCl and NaOH solutions were used to adjust the pH of sample solutions. All reagents were of analytical grade.

2) Simultaneous hydridization/extraction

50 ml of standard mixture containing 5 μg as Sn of each methyltin chloride (CH_3SnCl_3, $(CH_3)_2SnCl_2$, $(CH_3)_3SnCl$) was prepared. These solutions were adjusted to pH 2.5-3, and 10 ml of benzene and 4 ml of 4 % $NaBH_4$ solution was added to a 100 ml separatory funnel. The separatory funnel was capped tightly and shaken by a shaker for 10 min. The benzene layer was removed, dried over sodium sulfate anhydrous, and analyzed by G.C.-F.P.D..

3) G.C. systems

a) G.C.-F.P.D. system

We modified the G.C. analytical method of Gilmoure et al.[42] to clearly separate each methyltin hydride. G.C.-F.P.D. conditions were as follows; Instrument : Hitachi 163 with F.P.D. (detection wave length : 585-610 nm), glass column: 3 mm x 3 m, column packing : 10 % SP2100 + 3 % SP2401 on Supelcoport 80-100 mesh, carrier gas : N_2 1.2 kg/cm^2, gas supporting flame : H_2 1.5 kg/cm^2, O_2 0.4 kg/cm^2, N_2 0.25 kg/cm^2, column temperature : 50 ℃ for 7 min followed by 50-230 ℃ at 20 ℃/min, detector temperature: 280 ℃, injection temperature: 280 ℃.

b) Gas chromatography-mass spectrometry (G.C.-M.S.) system

G.C.-M.S. system was used only for the confirmation of each methyltin, because the sensitivity of G.C.-M.S. system for methyltins detection was lower than that of the G.C.-F.P.D. system. G.C-M.S. conditions were as follows; instrument: JEOL JMS-D300, glass column: 2 mm x 3 m, column packing: 10 % SP2100 + 3 % SP2401 on Supelcoport 80-100 mesh, carrier gas: He_2 0.8 kg/cm^2, column temparature : 60 ℃ for 6 min and 60-230 ℃ at 20 ℃/min, detector temperature : 280℃, injection temperature: 280 ℃. ionization voltage: 20 eV, ionization current: 100 μA.

Results and Discussion

1) Hydridization of methyltin chlorides

The standard mixture was extracted with and without $NaBH_4$ and analyzed with a G.C-F.P.D. system. The results are shown in Fig.1.

No peak was detected from the benzene solution without $NaBH_4$. Three peaks were detected from the benzene sample with $NaBH_4$, and peaks 1, 2, and 3 were identified as CH_3SnH_3, $(CH_3)_2SnH_2$ and $(CH_3)_3SnH$, respectively, by a G.C.-M.S. system as shown in Fig.2.

The average retention time and standard deviation (n=10) for each methyltin by our G.C.-F.P.D. system are shown in Table 1.

The standard deviation of the retention time for each methyltin hydride was very small.

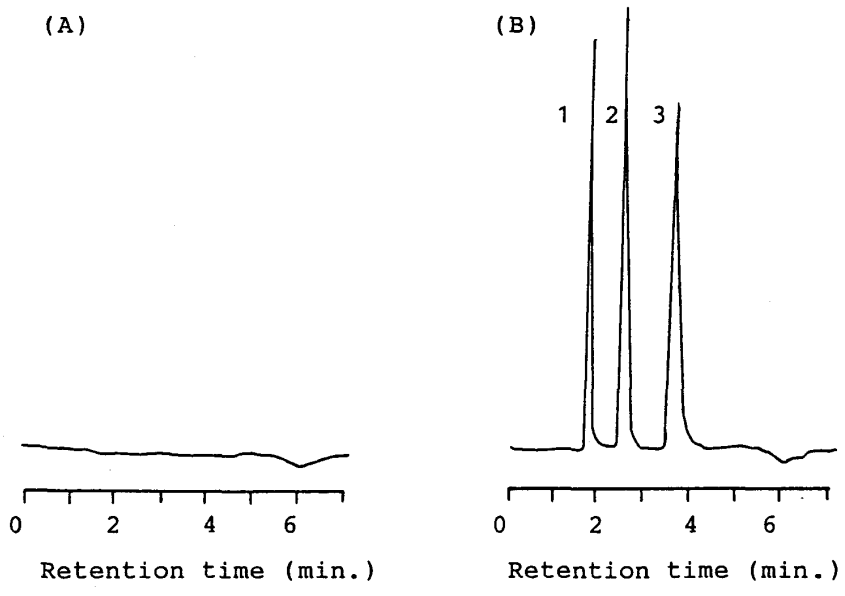

Fig.1 : G.C.-F.P.D. Chromatograms of Benzene Extracts (A) : without $NaBH_4$, (B) : with $NaBH_4$

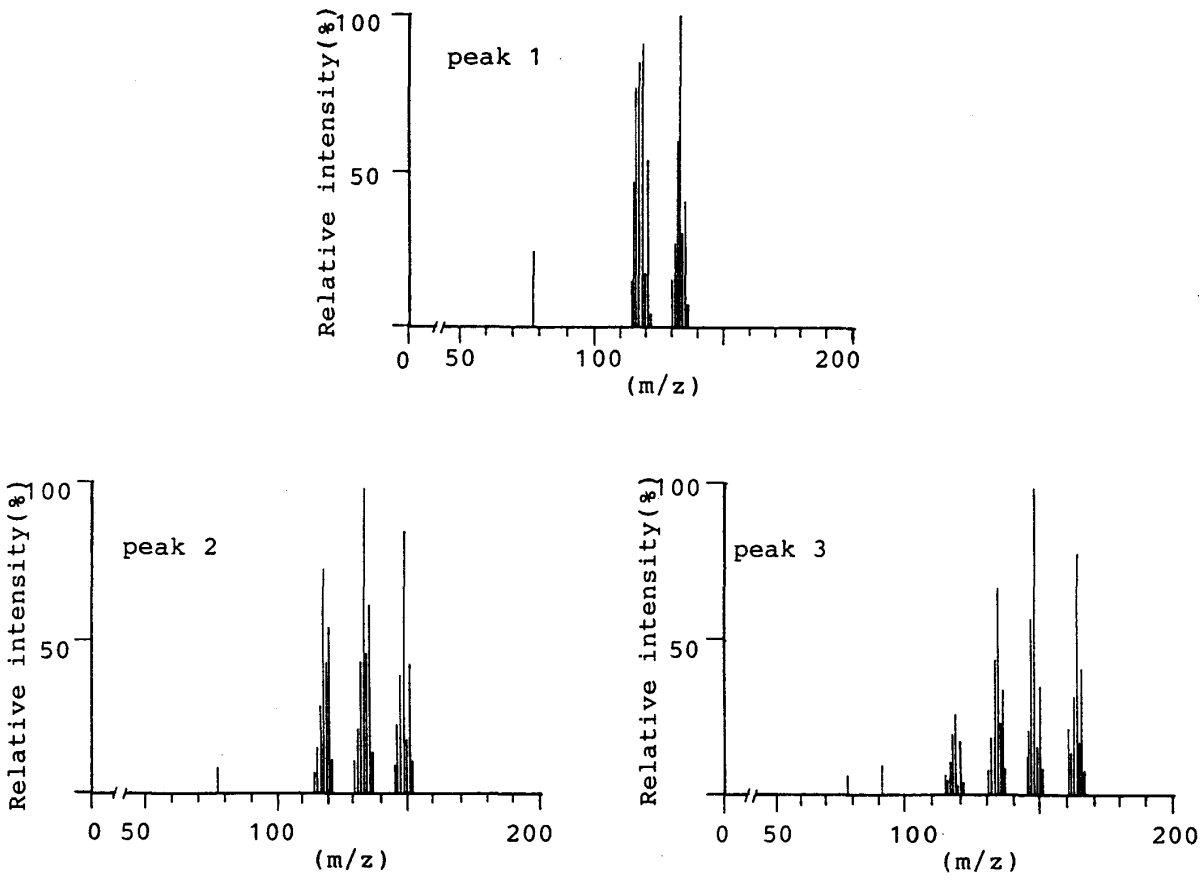

Fig.2 : Mass Spectra of Each Peak

Table 1. Retention Time for Each Methyltin Hydride

(n=10)

Methyltin hydride	Retention time (min.)
CH_3SnH_3	1.74 ± 0.03
$(CH_3)_2SnH_2$	2.52 ± 0.06
$(CH_3)_3SnH$	3.83 ± 0.12

2) Investigation of extraction conditions

1 ml of tetrabutyltin (5 μg as Sn/ml)-benzene solution as the internal standard was added to 4 ml of extracted benzene solution, and the extraction efficiency of methyltin halides was shown as the relative ratio to tetrabutyltin.

a) Volume of separation funnel

The extraction efficiency of 100 and 300 ml of separatory funnels was compared. The experiment was repeated 4 times and the results are shown in Table 2. The efficiency of extraction was represented as the relative ratio (sample peak area/Bu_4Sn peak area), because methyltin hydrides are very volatile and labile compounds, and standard methyltin hydrides could not be obtained.

Table 2. Effect of Separatory Funnel Volume

(n=4)

Volume	Methyltin	Relative ratio*
100 ml	CH_3Sn^{3+}	0.359 ± 0.023
	$(CH_3)_2Sn^{2+}$	0.871 ± 0.153
	$(CH_3)_3Sn^{+}$	1.143 ± 0.140
300 ml	CH_3Sn^{3+}	0.254 ± 0.045
	$(CH_3)_2Sn^{2+}$	0.688 ± 0.046
	$(CH_3)_3Sn^{+}$	1.021 ± 0.088

*Relative ratio = (sample peak area)/(Bu_4Sn peak area)

The extraction efficiency with the 100 ml of separatory funnel was better than that of the 300 ml funnel. Methyltin hydrides may be more effectively trapped with smaller head space of separatory funnel.

b) Shaking time

Experiments were performed with shaking times of 3 and 20 min. Each experiment was repeated 4 times and results are shown in Table 3.

Lower extraction efficiency for mono- and dimethyltin was observed at 20 min shaking time compared to 3 min of shaking time. Extraction efficiency of trimethyltin was not influenced by shaking time.

Table 3. Effect of Shaking Time

(n=4)

Volume	Methyltins	Relative ratio*
3 min.	CH_3Sn^{3+}	0.429 ± 0.110
	$(CH_3)_2Sn^{2+}$	0.792 ± 0.093
	$(CH_3)_3Sn^{+}$	1.007 ± 0.130
20 min.	CH_3Sn^{3+}	0.369 ± 0.083
	$(CH_3)_2Sn^{2+}$	0.364 ± 0.079
	$(CH_3)_3Sn^{+}$	1.010 ± 0.063

*Relative ratio = (sample peak area)/(Bu_4Sn peak area)

c) Amount of $NaBH_4$

The amounts of $NaBH_4$ were varied from 10 mg (1 ml of 1 % solution), 40 mg (4 ml of 1 % solution), 80 mg (2 ml of 4 % solution), 160 mg (4 ml of 4 % solution), 240 mg (6 ml of 4 % solution) and 320 mg (8 ml of 4 % solution). Each experiment was carried out twice and the average was calculated. The results are shown in Fig. 3.

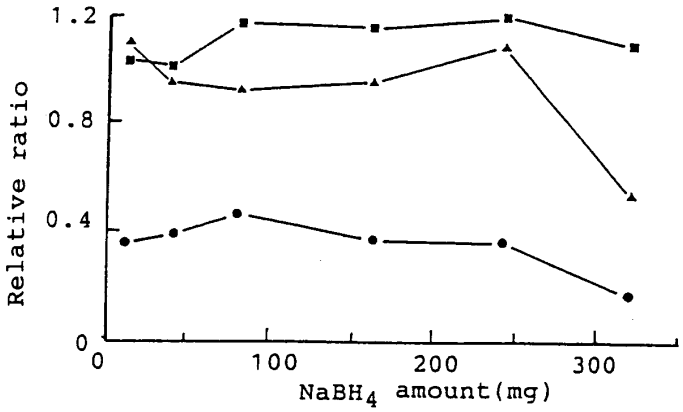

Fig.3 : Effect of $NaBH_4$ Amount
(●) : methyltin chloride, (▲) : dimethyltin dichloride,
(■) : trimethyltin chloride

When the amount of $NaBH_4$ exceeded 240 mg, the extraction efficiency decreased.

d) The pH of the solution

The pH of the sample solution was adjusted to various values. The experiment was carried out

twice and the average was calculated. The results are shown in Fig. 4.

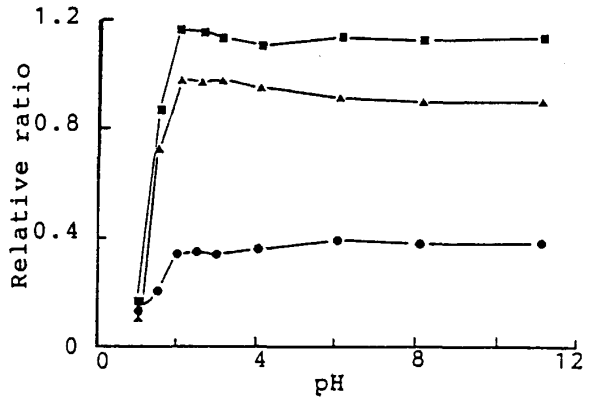

Fig.4 : Effect of pH
(●) : methyltin chloride, (▲) : dimethyltin dichloride,
(■) : trimethyltin chloride

The extraction efficiency decreased at pH 1 and 1.5 Constant extraction efficiencies were observed pH values of 2 or greater.

e) Calibration curves for each methyltin

0.5, 1.25, 2.5, 25, 50 and 250 μg of Sn/50 ml standard mixtures of methyltin chlorides were prepared and analyzed 6 times. The coefficient of variation (C.V.) were calculated and are shown in Table 4 and the calibration curves for those compounds are shown in Fig. 5.

Table 4. Coefficient of Variation (C.V.) Values of Methyltins

(n=6)

Amount	C.V. values (%)		
(Sn μg/50ml)	CH_3Sn^{3+}	$(CH_3)_2Sn^{2+}$	$(CH_3)_3Sn^{+}$
0.5	21.1	21.4	9.0
1.25	22.8	17.2	15.5
2.5	12.0	6.5	6.1
25	21.3	11.2	9.0
50	6.0	3.4	3.4
250	7.8	10.1	11.7

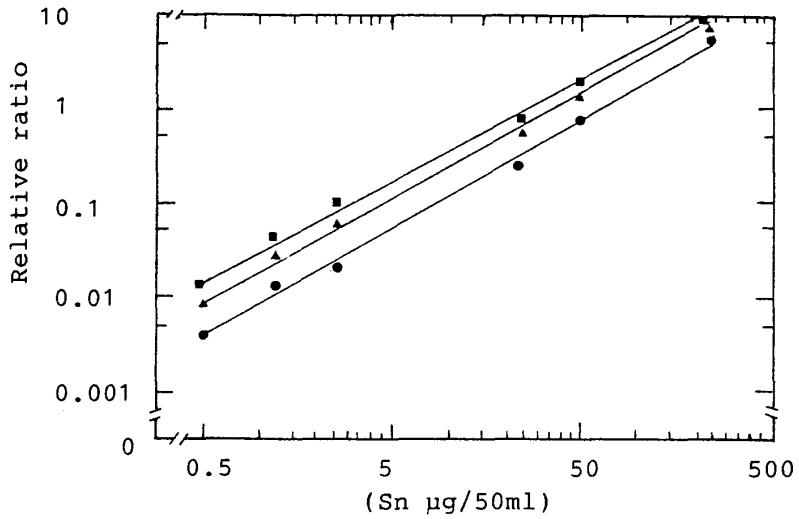

Fig.5 : Calibration Curves for Methyltins
(●) : methyltin chloride, (▲) : dimethyltin dichloride,
(■) : trimethyltin chloride

C.V. values for this analysis were in the range from 3.4 to 22.8 % and a linear relationship was obtained in the range of 0.5-250 μg of Sn/50 ml.

From the obtained C.V. values, we can conclude that our analytical method for methyltin compounds is a reproducible procedure and that this hydridization solvent extraction method enables rapid determination of methyltins in aqueous solutions.

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