DETERMINATION OF TRIBUTYLTIN AND TRIPHENYLTIN COMPOUNDS IN ENVIRONMENTAL AND INDUSTRIAL WASTE WATERS BY GAS CHROMATOGRAPHY

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Abstract - Tributyltin (TBT) and triphenyltin compounds (TPT) in environmental and industrial waste waters were determined by gas chromatography with flame photometric detection using triphenyltin chloride (Pe_3SnCl) as a surrogate compound. Recoveries of TBT and TPT from these water samples was 96-108%, respectively and the standard deviations (R.S.D) were 2.2 - 9.8%, 1.4 - 7.4%, respectively. The detection limits were 2 ng/l, for TBT (as tributyltin chloride) and 6 ng/l for TPT (as triphenyltin chloride).

Key words tributyltin and triphenyltin compounds, triphenyltin as surrogate compound, capillary GC-flame photometric detection, propylation with propylmagnesium bromide

TBT and TPT, which exhibit fungicidal activity, have been used as anti-fouling paints for ship hulls and fishing nets or agricultural chemical. The concentration of TBT and TPT in environmental waters or fish and mollusk have been researched [1][2]. The analytical method employed at these programmes have contained a complex procedure and required good skill [3]. Then it is desired to develop simpler and more precise method of TBT and TPT. Many reports have been published concerning determination of TBT and TPT. But only a few papers have been reported concerning simpler and precise method about both of TBT and TPT. In this report, determination of TBT and TPT using Pe_3SnCl as a surrogate compound and with simpler pretreatment was studied.

EXPERIMENTAL

Apparatus A gas chromatograph (Shimadzu GC-9AM) with flame photometric detector (FPD) was used. FPD was equipped with Sn-filter.

Reagents Tributyltin chloride (Bu_3SnCl), triphenyltin (Ph_3SnCl) were obtained from Tokyo Chemical Co. Ltd. Triphenyltin chloride (Pe_3SnCl) was synthesized with reference to the methods by Unger et al [4] and James et al [5]. Propylmagnesium bromide (PrMgBr) in tetrahydrofuran (2 mol/l, Tokyo Chemical Co. Ltd.) was used. Hexane and diethyl ether (pesticides analytical grade) were obtained from Wako Pure Chemical Co. Ltd.

Procedure A volume of water sample (1L), to which 1 ml of Pe_3SnCl solution (0.02 mg/l or 0.1 mg/l) was added, was mixed 10 ml of hydrochloric acid and 20 g of sodium chloride and then extracted twice with 100 (50) ml of hexane. The extract was dehydrated with anhydrous sodium sulfate and concentrated to a small volume (ca. 5 ml) using a rotary evaporator at below 40°C. The concentrate was propylated with 1 ml of PrMgBr solution. Reaction product was passed through sep-pak florisisil column and eluted with 5 (v/v)%-diethyl ether/hexane. The eluate was concentrated to about 0.2 ml. Three microliters was injected to GC for analysis. GC conditions employed were as follows: column; DB-1 (0.53 mm i.d. x 30 m, film thickness 1.5 μm), carrier gas; He (20 ml/min.), make up gas; He (20 ml/min.), column temperature; 80°C (1 min.), 80-160°C (40°C/min.), 160-290°C (10°C/min.) 290°C (3 min.), detector; FPD (Sn-filter, H_2 = 200 ml/min, air = 40 ml/min.), splitless injection, injector temperature; 290°C, Detector temperature; 300°C.

RESULTS AND DISCUSSION

EXTRACTION CONDITION Extraction conditions were studied on acidity and concentration of salt. Figure 1 and 2 show results. There were no loss in concentrating procedure by rotary evaporator and heating under nitrogen stream.

DERIVATIZATION We chose propylation method for derivatization. Gas chromatogram of 20 kinds of organotin compounds (OTC) was shown in Fig. 3. Each peak corresponding to propyl derivatives of OTC were well separated. The reaction times for derivatization was studied at room temperature and 40°C. As shown in Fig. 4, peak responses to propyl-derivatives of TBT and TPT were constant after 10 min. On this basis, propylation was performed for 30 min. at room temperature.

Fig. 1 Effect of concentration of sodium chloride on recovery of tributyltin chloride and triphenyltin chloride

Fig. 2 Effect of concentration of hydrochloric acid on recovery of tributyltin chloride and triphenyltin chloride (NaCl:2(w/v)%)

Fig. 3 Gas chromatogram of propyl derivatives of organotin compounds

Peaks — (1) trimethylpropyltin, (2) dimethyldipropyltin, (3) tetraethyltin, (4) methyltripropyltin, (5) diethyldipropyltin, (6) tetrapropyltin, (7) tripropylbutyltin, (8) dipropyldibutyltin, (9) propyltributyltin, (10) tetrabutyltin, (11) tripropylphenyltin, (12) tripropyloctyltin, (13) propyltripentyltin, (14) dipropyldiphenyltin, (15) dipropyldicyclohexyltin, (16) dipropyldioctyltin, (17) propyltriphenyltin, (18) propyltricyclohexyltin, (19) propyltrioctyltin, (20) tetraphenyltin. The amount of organotin compounds were about 2 ng, except that of tetrapropyltin was about 4 ng.

Fig. 4 Reaction time of propyl derivatives of tributyltin and triphenyltin

A: room temperature; B: 40°C

Recovery and Precision Results of recovery test were shown in Table 1. Recovery of TBT and TPT from these water samples was 96 - 104%, 96 - 108%, respectively. Repeated analysis showed that the precision of the method is good with the standard deviations (R.S.D.) 2.2 - 9.8%, 1.4 - 7.4 %, respectively. The detection limits were 2 ng/l for TBT (as tributyltin chloride) and 6 ng/l for TPT (as triphenyltin chloride). Both recovery and precision were improved by addition of the surrogate compounds.

TABLE 1. Recovery of tributyltin (TBT) and triphenyltin (TPT) from environmental and industrial waste waters

Sample	Added ng	Found $\pm$ S.D. ^{a)} ng	Recovery ^{b)} %	R.S.D. ^{c)} %	A.S.C. ^{d)} ng
Distilluted Water					
TBT	0	N.D. ^{e)}			
	10	9.7 $\pm$ 0.6	96.9	5.7	20
TPT	0	N.D. ^{e)}			
	30	29.6 $\pm$ 1.4	98.6	4.7	20
TBT	0	N.D. ^{e)}			
	10	10.0 $\pm$ 0.4	100.0	4.4	100
TPT	0	N.D. ^{e)}			
	30	30.7 $\pm$ 1.0	102.4	3.3	100
TBT	0	N.D. ^{e)}			
	100	95.7 $\pm$ 4.9	95.7	5.1	100
TPT	0	N.D. ^{e)}			
	300	319.0 $\pm$ 19.2	106.3	6.0	100
TBT	0	N.D. ^{e)}			
	1000	997 $\pm$ 33	99.7	3.3	100
TPT	0	N.D. ^{e)}			
	3000	3216 $\pm$ 77	107.2	2.4	10
River Water					
TBT	0	1.6 ^{f)}			
	10	11.6 $\pm$ 0.4	99.7	3.5	20
TPT	0	N.D. ^{e)}			
	30	32.3 $\pm$ 0.4	107.6	1.4	20
TBT	0	N.D. ^{e)}			
	100	98.4 $\pm$ 2.2	98.4	2.2	100
TPT	0	N.D. ^{e)}			
	300	296.0 $\pm$ 5.5	98.7	1.9	100
Sea Water					
TBT	0	1.8 ^{f)}			
	10	11.8 $\pm$ 1.0	100.4	9.8	20
TPT	0	4.0 ^{f)}			
	30	33.7 $\pm$ 0.7	99.0	2.5	20
TBT	0	N.D. ^{e)}			
	100	96.3 $\pm$ 4.0	96.3	4.2	100
TPT	0	N.D. ^{e)}			
	300	292.5 $\pm$ 21.5	97.5	7.4	100
Pharmaceutical factory					
TBT	0	N.D.			
	100	103.9 $\pm$ 2.2	103.9	2.2	100
TPT	0	N.D.			
	300	316.4 $\pm$ 9.0	105.4	2.8	100
Ship building					
TBT	0	8.3 ^{f)}			
	10	18.1 $\pm$ 0.7	98.4	7.3	20
TPT	0	26.9 ^{f)}			
	30	55.7 $\pm$ 1.6	96.1	5.6	20
TBT	0	N.D. ^{e)}			
	100	104.3 $\pm$ 3.7	104.3	3.5	100
TPT	0	34.0 ^{f)}			
	300	352.8 $\pm$ 23.4	106.3	7.3	100
TBT	0	8 ^{f)}			
	1000	1033 $\pm$ 28	102.6	2.7	100
TPT	0	27 ^{f)}			
	3000	3155 $\pm$ 111	104.2	2.2	100

a) standard deviation; b) average of five runs; c) relative standard deviation; d) added amount of surrogate compound; e) not detected; f) average of two runs

Interference Gas chromatograms of water sample were shown Fig.5.
No severe interference peaks were present in the gas chromatograms.

Fig.5 Gaschromatogram of environmental and industrial waste waters
A:standard solution, B:river water, C:sea water,
D:ship building factory

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