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Determination of Mono-, Di-, and Tri-Butyltin Compounds in Seawater of Several Bays in Korea

Hwa-Seon Choi, Ee-Yol Kwon, and Dong-Sup Lee[*][†]

Department of Chemistry, Hanyang University, Seoul 133-791
[†]Department of Chemistry, Korean Sahmyook University,
Chung Ryang POB 118, Seoul 130-650. Received October 1, 1992

The method of study describes the determination of the nanogram amounts of mono-, di-, and tri-butyltin compounds in sea water. The procedure is based on 1) the conversion of tin compounds to non-ionic species by sodium tetraethyl borate as an alkylation reagent, 2) one-step ethylation and 3) extraction. No further purification or concentration of the extract was required before GC-FPD (Flame Photometric Detector). The detection limits for mono-, di,- and tri-butyltin were 12.50, 6.02, and 4.19 ng/L. The linear range (0-120 ng/L) was solely dependent on the detector response height. Sea water samples ($n=24$) were obtained from Masan Bay, Busan, Ullsan, Gunsan, Sockcho, Yeasu, Donghae, Inchun, Kanghwa, and Ahsan in Korea. The samples were collected between June, 1992 to July, 1992 and the distribution of monobutyltintrichloride (MBTC), dibutyltindichloride (DBTC), and tributyltinchloride (TBTC) in sea water was recorded. The concentrations of butyltin compounds in seawater were found to be in the range of N.D. (not detected)-61.93 ng/L for MBTC, N.D.-32.16 ng/L for DBTC, and N.D.-55.76 ng/L for TBTC.

Introduction

The production of butyltins has continuously increased on a worldwide basis in the last several decades (from under 5,000 tones in 1955 to at least 35,000 tones in 1992), due to the antifouling agent in paints for boats, submerged marine structure, and stabilizers for polyvinylchloride.

These butyltins chemicals have very high toxicity for some non-target species, particularly in estuaries near bays.[1] The toxicity of butyltine compounds is depend on the number of alkyl groups, of which alkyl group's number 3 and 4, are the most toxic.[2] Environmental degradation causes stepwise loss of organic groups from the Tin atom, which results in a variety of species, whith less toxicity. The toxicity of an individual species and the probability that a compound will be incorporated in the food chain is dependent on the nature of the alkyl group. Butyltins antifouling paints (TBT) have disturbed oyster farming.[3] Advance effects on growth and calcifications have been observed[4] and it is suspected that the fecundity of adult oysters has been affected.[5] Among the most visible effects is shell deformation of the oyster *Crassostrea virginica* and development of male sexual organs in the female dogwhelk *Nucella Lapillus*.[6] Pacific oyster reproduction is inhibited at areas with concentrations, about 20 ng/L for TBT.[7] Recently regulations in some countries require the limiting of TBT levels to no more than 1 ng/L in coastal sea water.

Current techniques for analysizing butyltins compounds in sea water are based in the use of chromatography with pre-column derivatization step,[8-12] ether by hydride generation[13] or by Grignard alkylation.[14] These techniques are time consuming and not entirely reliable. These procedures must be carried out in a clean, dry organic solvent and requires final clean-up and concentration. Hydride generation of volatile organotin compounds has been performed directly in aqueous environments, using sodium tetrahydro borate. However, organotin hydride compounds are very unstable and very volatile so that this lead to a loss of compounds and consequent underestimation of concentration. Therefore, sodium tetraethyl borate was used in this work for alkylation step.[15] Ethylation and extraction requires only one flask during the operation. The technique is as easy and quick as that use of sodium borohydrate and provides the same advantages as for alkyl derivative from the Grignard reaction. The reserches survey the principal bays of Korea and made a minute study for Masan Bay, by this method. The results are presented in Tables 1 and 2.

Experimental Section

Apparatus. A Hewlett Packard 5890II Gas Chromatogra-

*To whom correspondence should be address.

Distribution of Butyltin Compounds

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Table 1. Concentrations (ng/L) of MBT, DBT, and TBT in Sea-water Samples Collected from Several Bays

Sample	MBT	DBT	TBT
Masan	61.93	10.16	9.80
Gunsan	33.74	14.30	N.D.
Sockcho	N.D.	13.74	N.D.
Donghae	N.D.	N.D.	7.64
Pusan	N.D.	32.16	55.76
Ullsan	N.D.	25.26	8.90
Yeasu	N.D.	N.D.	N.D.
Inchun	10.42	30.65	22.32
Ahsan	N.D.	22.35	12.65
Kanghwa	5.98	11.86	10.52

N.D.= not detected.

Table 2. Concentrations (ng/L) of MBT, DBT, and TBT in Sea-water Samples Collected from Masan Bays (ng/L)
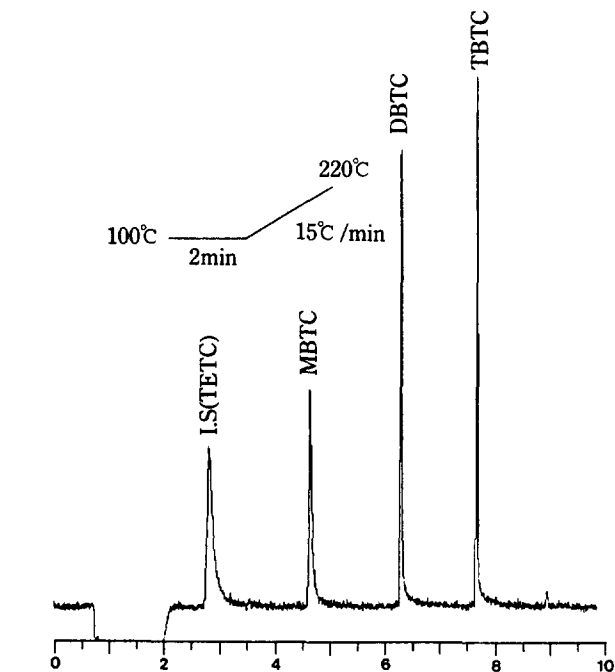
Sample		MBT	DBT	TBT
Masan	1	61.93	10.16	9.80
	2	39.57	12.03	6.44
	3	24.72	10.39	5.30
	4	30.09	12.05	3.26
	5	22.91	8.70	4.86
	6	23.49	8.74	4.82
	7	14.79	N.D.	4.08
	8	17.49	6.47	3.70
	9	30.37	7.54	5.70
	10	31.18	15.67	15.06
	11	16.33	7.46	7.44
	12	20.78	5.98	6.58
	13	23.86	7.95	8.30
	14	17.41	5.64	6.22
	15	21.35	5.88	N.D.
	16	12.73	7.70	N.D.

N.D.= not detected.

phy (GC) was fitted with a split/splitless injector, fused silica capillary column (Ultra-1, 25 m, 0.32 mm, *i.d.*, film thickness 0.52 μm) and a flame photometry detector. The apparature was operated with a 610-nm cut-off interference filter at a temperature of 250℃, using hydrogen and air flow rates of 45, and 35 psi/cm² respectively. The injection port temperature was set at 220℃ and Helium (20 psi/cm²) served as carrier gas using a splitless mode (70 sec). As a nitrogen gas was served, there was a drift in the baseline when a temperature program was used. This drift cause a decrease in the reproducibility of signals. For this reason, helium was selected for this experiment.

The column temperature was programmed at 100℃, 2 min and heated to 220℃, rates 15℃/min. A typical chromatogram of organotin standard is shown in Figure 1, and retention times are 2.80 min for internal standard, TETC, 4.62 min for MBTC, 6.25 min for DBTC, and 7.68 min for TBTC.

Reagent. Dibutyltindichoride (DBTC) and tributyltinch-

Figure 1. A typical Chromatogram of organotin standards, Concentration (80 ng/L as Sn).
Column; Ultra-1 (Cross-Linked Methyl Silicon), 25 m×0.32 mm×0.52 μm film. Carrier; He. Oven; Temperature program list above. Injection; Splitless (70 sec), 5 μl. Detector; FPD.

loride (TBTC) were purchased from Aldrich Chemical, Inc., triethyltinchloride (TETC) from Merck, monobutyltintrichloride (MBTC) from Johnson Mattey Alfa Products, GmbH, Germany. These standard were used without further purification. Ethanolic stock solutions, containing 1,000 ppm as tin, were prepared monthly in a 100 m*l* hypo-vial at 4℃. Working solutions were prepared daily from this stock solution. Sodium tetraethyl borate was obtained from Johnson Matthey Alfa Product GmBH, Germany. Solutions were daily prepared by dissolving 0.2 g in 10 m*l* of deionized water. Ethanol of HPLC grade, and hexane of UV grade were obtained from American Burdick Jackson. All glasswares were cleaned with detergent, rinsed in deionized water, then 10% nitric acid and soaked with this medium overnight before being rinsed in deionized water.

Samples. The location of sampling stations is shown in Figures 2 and 3. Surface sea water samples were collected from June, 1992 to July, 1992 in 1,000 m*l* polycarbonate 'Nalgene' bottles, which had been cleaned with detergent, rinsed in deionized water, then left in a 10% nitric acid bath overnight. The collected samples were analyzed before 2 days.

Ethylation/Extraction. When NaBEt₄ (Sodium tetraethyl borate) was used as ethylation reagent, ethylation/extraction of organotin compounds could be performed in sea water in a one step procedure. A 250 cm³ borosilicate volumetric flask was used for this operation. Sea water (250 cm³), hexane (1 cm³), and sodium tetraethyl borate (1 cm³, 0.2 g/10 cm³) were added successively, vigorous swirling was obtained by magnetic stirring (2,000 rpm for 1 hr). The swirling was stopped and then the organic phase transferred into a vial for injection into the GC-FPD (Gas Chromatography-
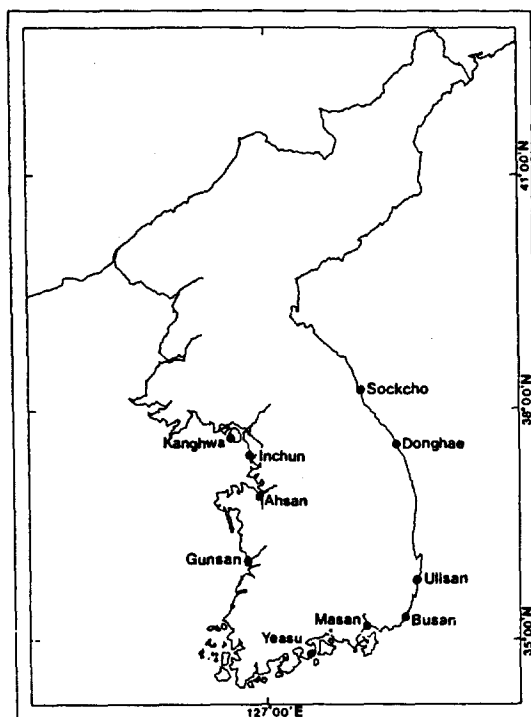
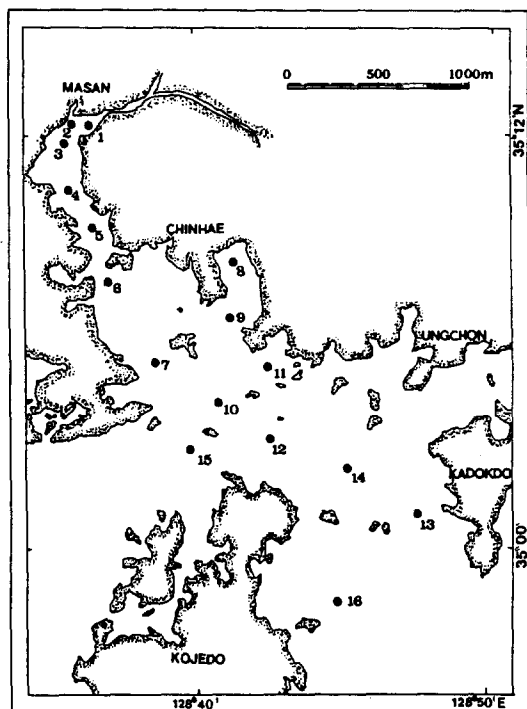**Figure 2.** The location of principal Bays.

Figure 3. The location of sampling station in Masan Bay.

Flame Photometric Detector). The efficiency of the procedure was checked, using a triethyltinchloride as an internal standard. Recovery from spiked reference sea water was equal to external calibration concentration using the same procedures. The percentage recoveries of butyltin compounds are ranged from 91.62 to 102.64% (at, 80 ng/L) for MBTC, DBTC, and TBTC in spiked sea water.

Table 3. Concentrations (ng/L) of DBT, and TBT in Seawater Samples America, Europe and Japan.

Location	Country	DBT	TBT
Tokyo Bay (1986)	Japan	N.D.-120	N.D.-280
Chesapeake Bay (1987)	USA	N.D.-300	N.D.-1,000
San Diego Bay (1986)	USA	N.D.-440	N.D.-930
Honolulu Harbor (1989)	USA		N.D.-380
Ala wai Harbor (1989)	USA		100-210
Pearl Harbor (1989)	USA		N.D.-20
California (1987)	USA		
Crescent City, Bayside Marina		40	440
Bodege Bay, Masons Marina		40	70
Stockton, Tower Park		N.D.	N.D.
Ventura Harbor		90	190
Arcachon (1987)	France		100-300
Brixham Harbor (1985)	England		230-560
Torquay Harbor (1985)	England		150-200
Sutton Harbor (1985)	England		850-880
Plymouth offshore (1985)	England		<100
Falmouth (1985)	England		130

N.D.=not detected. From reference number #14.

Results and Discussion

The method proposed the possibility of utilizing alkylation and extraction simultaneously. The statistical detection limits were 4.19-12.50 ng/L. The Grignard reaction has usually been used for organotin alkylation. But his method involves many steps (extraction, drying, alkylation, concentration). Therefore, It is time consuming and costly, and reliability and accuracy may be decrease. Hydride generation of volatile organotin derivatives has been performed directly in aqueous phase using sodium tetrahydroborate. However, organotin hydride derivatives are not really stable, so that contamination can be underestimated.

The ethylation by NaBEt₄ (sodium tetraethyl borate) in the aqueous phase was used in this paper. The concentration distribution of butyltin compounds in sea water were found to be in the range of N.D. (Not Detect)-61.93 ng/L for MBTC, N.D.-31.16 ng/L for DBTC, and N.D.-55.76 ng/L for TBTC.

These survaying datas are introduce that seawaters in principal bays in Korea are not serious contaminate than other nations, like a Table 3.

pH Effect on Ethylation Yield. For the purpose of preserving natural properties, acid was not added to the samples to obtain natural sea water (pH=7.8-8.2). However, the addition of alkaline sodium tetraethyl borate increased the pH of the samples. It was necessary to check the true pH effect on ethylation reaction. The result were shown in Figure 4. The pH effects was in the 2.0-7.2 range with the best response at pH>7.

Time Effect on the Ethylation/Extraction Step. Ethylation of butyltin ions occurred in the water phase and could proceed rapidly in the water phase. However, TBTC and DBTC were already soluble in the organic phase before ethylation. The duration and mixing efficiency of this step must be adequate to obtain the complete ethylation required.
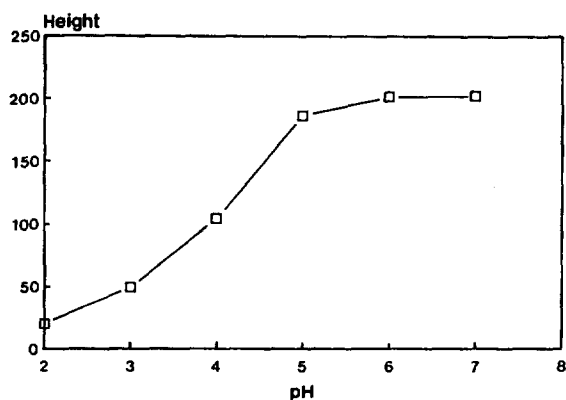
Distribution of Butyltin Compounds

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Figure 4. pH effect on signal response height for butyltin compounds.
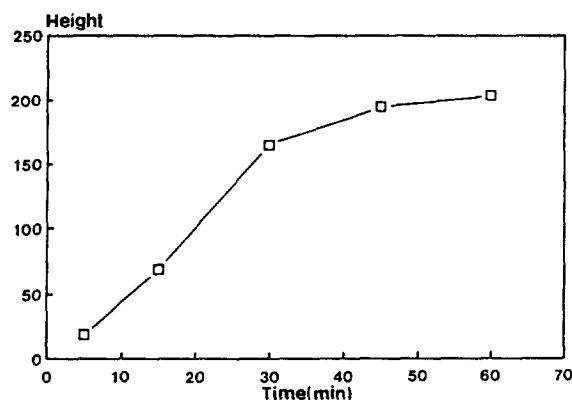

Figure 5. Time effect on signal response height for butyltin compounds.

Therefore, signal response height depended on reaction time. This ethylation reaction time checked, using a mixture of MBTC, DBTC, TBTC and TETC in deionized water. The results are shown in Figure 5. The steady state of time effect was reached in one hour under mixed condition. Lower time reactions did not reach complete ethylation.

Calibration and Detection Limit. The calibration curves for the butyltin compounds studied using peak heights had a linear range (0-120 ng/L). The determinations were carried out with external calibration for MBT, DBT,
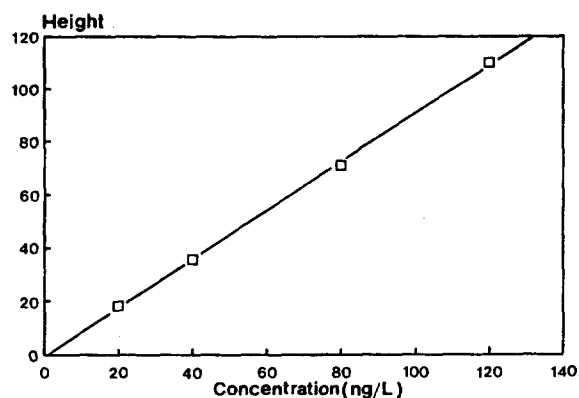

Figure 6. Calibration curve for TBTC.

Table 4. Statistical Detection Limit and Correlation Coefficient of organotin Compounds

Compound	Detection Limit (ng/L)	Correlation Coefficent
MBT	12.50	0.9971
DBT	6.02	0.9993
TBT	4.19	0.9997
TET	5.02	0.9995

TBT and TET, which improves the precision shown in Figure 6. The statistical detection limits (3σ of blank) are also shown in Table 4. The solutions were analyzed at least six times with reative standard deviations lower than 5% (MBT 3.80%, DBT 1.08%, TBT 2.19%, and TET 0.88%), when peak height was used. The response of the detector using peak areas were usually greater than 5% (TET 6.36%). Because, tin compounds were gave some peak tailing, which had effect on calibration. For this reason peak height was used throughout.

The relative standard deviation (RSD) was 0.88% for internal standard TET. Reproducibility was lower for MBT (RSD 3.80%), probably because of lower peak height as compared with di-, and tri-butyltin compound.

The reproducibility test was performed, using a mixture of MBT, DBT, TBT, and TET. Six replications at concentrations of 80 ng/L as tin in deionized water were used. The results are listed in Table 5.

Table 5. Peak Height (area) Reproducibility Test for TET, MBT, DBT, and TBT in Standard Deionized Water (80 ng/L)

Sample	TET		MBT		DBT		TBT	
1	20.49	(1506.25)	33.80	(1217.88)	64.03	(1534.15)	72.73	(1392.32)
2	20.02	(1499.94)	32.79	(1280.14)	64.49	(1448.35)	71.65	(1367.20)
3	20.12	(1277.66)	30.98	(1191.58)	63.02	(1491.22)	72.39	(1354.81)
4	20.41	(1490.47)	31.15	(1203.62)	62.76	(1492.58)	68.50	(1338.12)
5	20.36	(1455.37)	31.20	(1218.32)	62.96	(1512.42)	71.97	(1320.27)
6	20.29	(1532.45)	30.92	(1189.65)	63.32	(1562.35)	72.41	(1403.21)
Mean	20.28	(1460.36)	31.81	(1217.87)	63.43	(1506.85)	72.61	(1362.66)
SD	0.18	(92.93)	1.20	(33.35)	0.68	(39.31)	1.57	(31.64)
RSD	0.88	(6.36)	3.80	(2.74)	1.08	(2.61)	2.19	(2.32)

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A Green's-Matrix Approach to Chemisorption

Yun Hee Jang and Hojing Kim*

Department of Chemistry, Seoul National University, Seoul 151-742
Research Institute of Molecular Sciences, Seoul National University, Seoul 151-742
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A self-consistent-field Green's matrix method for the calculation of electronic properties of chemisorbed system is devised and applied to the methanol on copper(110) surface. The method is based on CNDO Hartree-Fock approximation. Contour integration in the complex energy plane is used for an efficient calculation of the charge-density bond-order matrix. The information on each fragment prior to chemisorption is efficiently used and a small number of iterations are needed to reach the self-consistency. The changes of density of states and other quantities of methanol due to chemisorption are consistent with reported experimental results.

Introduction

Electronic processes in chemisorption and catalytic action of metal surfaces play fundamental roles in chemistry and chemical industry. Until now, two calculational methods have commonly been used to address problems of this nature: cluster method and slab method. Cluster method models a surface as a group of a few atoms. This permits direct use of highly developed computer programs of quantum chemistry. Since chemisorption is known to be a local phenomenon and an adsorbate is coupled to only a few atoms near the chemisorption site,[1,2] this approach to chemisorption is reasonable. However, the convergence of the results with cluster size is left open to question.[3,4] Slab method(band calculation) simulates the solid with a finite number of layers having two-dimensional periodicity. This method takes a surface as infinite periodic repetitions of a unit cell. However, since the perturbation due to chemisorption breaks the translat-ional symmetry of the surface and the complexity grows rapidly with the number of atoms in the unit cell, the slab calculation for chemisorbed system is a complicated problem requiring larger unit cell, especially in a low coverage.[3,5,6]

The Green's function, which has been used in mathematics and physics to solve an inhomogeneous differential equation in terms of the solution of corresponding homogeneous equation,[7] permits the study of a complicated perturbed system by representing it as a relatively simple unperturbed system plus a small perturbation.[8] The Green's-function approach to a local perturbation in a periodic system was originated by Koster and Slater and by Anderson,[9,10] and it was further developed by Callaway and Hughes.[11] An LCAO matrix form of this method was investigated by Pantelides.[12,13] The self-consistent field treatment was given by Feibelmann in density-functional formalism[3,8] and by Ladik and Seel in Hartree-Fock scheme.[14,15]

We apply the self-consistent field Green's-function app-