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STABILITY OF BIS(TRI-N-BUTYL TIN) OXIDE
IN SEDIMENT EXTRACTS

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**PRESERVATION OF ORGANICS. PART IV
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IN SEDIMENT EXTRACTS**

by

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MANAGEMENT PERSPECTIVE

Concern about bis(tri-n-butyltin)oxide (TBTO) pollution in the aquatic environment has resulted in the monitoring of water, sediment and fish samples for TBTO. To develop sediment extract reference samples fortified with TBTO as QC samples for evaluating the laboratory performance in interlaboratory studies, considerable in-house investigation for the preparation and stability of TBTO in the fortified sediment extracts was carried out. Results indicated that the TBTO in sediment extract was stable for a minimum of four months either stored at 4°C or 25°C in the dark. This study will provide the necessary background information for designing and conducting interlaboratory QA studies for research and monitoring of TBTO.

Dr. J. Lawrence
Director
Research and Applications Branch

PERSPECTIVE GESTION

Vu la crainte des conséquences de la pollution du milieu aquatique par l'oxyde de bis(tri-n-butylétain) (TBTO), un contrôle a été entrepris des teneurs en ce composé présentes dans des échantillons d'eaux, de sédiments et de poissons. Maintes recherches maison ont été réalisées sur la préparation et la stabilité d'échantillons à matrice d'extraits de sédiments enrichis de TBTO, de façon à mettre au point des échantillons de référence de ce type pour fins de contrôle de la qualité. Les résultats obtenus ont montré que le TBTO est stable dans des extraits de sédiments pour au moins quatre mois lorsqu'ils sont conservés à une température de 4 °C ou de 25 °C en l'absence de lumière. La présente étude fournira les renseignements nécessaires à la conception et à l'exécution d'études interlaboratoires d'AQ en matière de détection et de dosage du TBTO.

M. J. Lawrence (Ph. D.)

Directeur

Direction de la recherche pure et appliquée

ABSTRACT

This report summarizes the results for the preparation and stability of sediment extracts fortified with bis(tri-*n*-butyltin)oxide (TBTO). The analysis of TBTO in sediment extracts involved solvent exchange, chemical derivatization with ethyl Grignard reagent and analysis of the resulting ethyl derivative (ethyl-tributyltin) by GC/AAS. Stability of TBTO in sediment extracts was investigated under two storage conditions, namely 4°C and 25°C in the dark. Analytical results indicated no degradation of TBTO occurred in the two fortified sediment extracts for a minimum of 4 months.

RÉSUMÉ

Ce rapport est le résumé des résultats obtenus lors d'études sur la préparation et la stabilité de l'oxyde de bis(tri-*n*-butylétain) (TBTO) dans des extraits de sédiments enrichis. Le dosage du TBTO dans des extraits de sédiments fait intervenir un échange de solvant, une réaction de Grignard avec un halogénure d'éthylmagnésium et le dosage du dérivé formé (le tri-*n*-butyléthylétain) par CPG/SAA. La stabilité du TBTO dans des extraits de sédiments a été étudiée pour deux températures d'entreposage, soit à 4 °C et à 25 °C, en l'absence de lumière. Les résultats des dosages montrent que, dans ces conditions, le TBTO présent dans les extraits de sédiments enrichis ne s'est aucunement dégradé pendant au moins quatre mois.

1.0 INTRODUCTION

Tributyltin compounds (TBTs) are the principal butyltin compounds that are widely used as industrial biocides. Their use in antifouling paint formulation on ships, boats and docks has raised many environmental concerns because of the release of highly toxic tributyltin species (Bu_3Sn^+) into the aquatic environment. Bis(tri-n-butyltin)oxide (TBTO) is the most commonly used compound for these purposes (1). The occurrence and fate of TBTO and other butyltin compounds and inorganic tin in water, sediment and biota samples have been studied extensively (2,3). Routine monitoring of sediment samples for these butyltin species and inorganic tin is particularly important, since the sediments are considered as a sink as well as a source for toxic contaminants in water.

To develop sediment extract reference samples as QC samples to evaluate the laboratory performance for analysis of TBTO in sediments, considerable in-house investigation into the preparation and stability of TBTO in sediment extract is required before interlaboratory studies could be initiated. Thus in this study, the stability of bis(tri-n-butyltin)oxide in fortified sediment extracts in acetone over a period of 4 months was investigated.

In order to carry out this study, the method of analysis for butyltin species in sediments using GC/AAS and chemical

derivatization with Grignard reagent developed by Chau et al. (4) was modified for the determination of TBTO in sediment extracts.

2.0 **EXPERIMENTAL**

2.1 Standards and Reagents

Bis(tri-n-butyltin)oxide, ethylmagnesium bromide and tropolone were all obtained from Aldrich (Milwaukee, Wisconsin). All solvents were pesticide grade from Caledon (Georgetown, Ontario). The TBTO standard solution was prepared by dissolving an appropriate amount of TBTO in methanol to give a solution of 1.0 mg/mL as tin.

2.2 Preparation of Sediment Extracts

Two sediments were taken from the left over bulk sediments of CRM SC-1 and LE-1 previously collected from Lake St. Clair and Lake Erie, respectively. The procedure for the preparation of bulk sediment extracts for toxic organic contaminants developed by Chau et al. (5) was followed. Briefly, five subsamples each of 200 g freeze-dried sediment was extracted with 500 mL of acetone in a 2 L Erlenmeyer flask by stirring vigorously with a magnetic stirrer for 2 h. The supernatant solution was filtered through a solvent-washed Celite 545 column under vacuum and the eluate was collected in a 500 mL round-bottomed flask. The sediment was then re-extracted with another

500 mL of acetone. The combined extracts for each subsample were evaporated to about 100 mL with a 3-stage Snyder column. The concentrated sediment extracts from 5 subsamples were combined in a 500 mL volumetric flask and made to volume with acetone. One mL of the this concentrated extract is equivalent to 2 g of sediment.

The sediment extract was then stored in a freezer at -20°C for at least one week after which it was filtered through a 0.45 µm filter to remove particulates and precipitates formed during cold storage. The clear sediment extract was made up to 500 mL with additional acetone to compensate for any loss of solvent during the filtration step. The final sediment extract was then stored in a refrigerator at 4°C in the dark until ready for the preparation of the fortified sediment extract samples.

2.3 Fortification of Sediment Extract Samples for Stability Study

A 100 µg Sn/mL TBTO working standard in acetone was prepared by diluting appropriate amount of the 1000 µg Sn/mL TBTO standard with acetone. For the preparation of the fortified sediment extract at 1.0 µg Sn/mL TBTO level, one mL of 100 µg Sn/mL TBTO working standard was diluted to 100 mL with sediment extract (SC-1 or LE-1) in acetone. In order to monitor the stability of TBTO in sediment extracts at specific period and to correct for the variation of the instrument stability, a 1.0 µg

Sn/mL TBTO standard solution in acetone was prepared. All prepared standard and sediment extract samples were thoroughly mixed and placed in a refrigerator at 4°C in the dark overnight to achieve equilibrium. A series of standard and fortified sediment extracts were prepared by transferring about 1.5 mL aliquot of solution into GC sample vials and sealed with teflon caps. A total of about 60 subsamples was prepared for each standard and sediment extract. All subsamples of standard solution were stored in a refrigerator at 4°C in the dark. Thirty subsamples of the two fortified sediment extracts were stored in a refrigerator at 4°C in the dark together with standard solutions and another 30 subsamples were stored at 25°C in the dark.

After a certain storage period, four replicates of subsample were taken from each group for the determination of TBTO by a modified procedure for sediment extracts as described in section 2.4.

2.4 Determination of TBTO in Sediment Extracts

A modified procedure of the method of Chau et al. (4) was used to study the stability of TBTO in fortified sediment extracts. The subsample was allowed to reach room temperature and one mL of sample was transferred into a 15 mL graduated centrifuge tube. An aliquot of 5 mL 0.5% tropolone in hexane and about one mL of iso-octane as keeper were added for the solvent exchange procedure.

The contents were thoroughly mixed and evaporated to about 2 mL in a vortex evaporator at room temperature under vacuum. To ensure complete removal of acetone, the solvent exchange procedure was repeated with a further addition of 5 mL hexane. The final solution was made up to exactly 5 mL with hexane. An aliquot of 2 mL of hexane solution was then transferred into another 15 mL graduated centrifuge tube for chemical derivatization with ethyl Grignard reagent. In this case, 0.5 mL of ethylmagnesium bromide in tetrahydrofuran was added to the hexane solution and the mixture was mixed thoroughly with a vortex mixer and allowed to react for at least 10 min for complete alkylation. Excess ethylmagnesium bromide was destroyed with 5 mL 0.5 N H_2SO_4 . The hexane phase was stored in a small GC vial containing approximately 0.1 g of anhydrous Na_2SO_4 for the determination of TBTO by GC/AAS.

2.5 Gas Chromatography-Atomic Absorption Spectroscopy (GC/AAS)

The GC-AAS system has been described in a previous publication (4). Briefly, a Hewlett-Packard 5880A equipped with a direct injection port and a 30 m x 0.53 mm i.d. SPB-1 wide bore capillary column (Supelco) was interfaced through a 1 m x 0.53 mm stainless steel transferline to a Perkin Elmer model 4000 AAS equipped with a quartz furnace atomizer. The following GC conditions were used. Injection port was 110°C; transferline temp., 150°C; initial column temp., 90°C; initial time, 0 min., oven temp.

program rate, 18°C/min to 200°C and held at 200°C for 2 min. Carrier gas was N₂ with flow rate of 10.5 mL/min. A 10 µL aliquot was injected. The following AAS conditions were used. The quartz furnace temperature was 850° - 900°C; Furnace gases, H₂, 84 mL/min; air, 21 mL/min. The 224.6 nm Sn line was generated by an Electrodeless Discharge Lamp operated at 8 W. Deuterium background correction was used and peak areas were measured with a HP 3392A integrator.

3.0 RESULTS AND DISCUSSION

3.1 Determination of TBTO in Sediment Extracts

Various methods have been developed for the speciation of butyltin in sediments. In general, it involved an extraction procedure (e.g. extraction, concentration, derivatization and cleanup) followed by speciation and determination using tandem analytical systems (e.g. GC/ECD, GC/FPD, GC/AAS, GC/AES and GC/MS) (6). In the extraction of bis(tri-n-butyltin)oxide from water with 0.5% tropolone in hexane and derivatization with ethylmagnesium bromide, we have noticed that the recovery of TBTO was not quantitative and reproducibility was poor when acetone was present in the extraction system. The calculation of absolute recovery was based on comparison with the standard prepared in iso-octane and diluted with 0.5% tropolone in hexane without carrying out the extraction procedure. TBTO is an ionic compound, its quantitative extraction from aqueous medium with nonpolar solvent such as hexane

required the presence of tropolone. However, in an aqueous medium in the presence of a water miscible polar solvent such as acetone, the efficiency of extraction of TBTO into tropolone/ hexane was low presumably due to the competition between acetone and hexane. In order to have complete extraction, longer extraction time may be required. In addition, Grignard reagent can react with water, alcohol and ketone (7), and direct alkylation of Grignard reagent with TBTO in sediment extract in acetone is not suitable. The removal of acetone from the sediment extract is essential. Therefore a solvent exchange process is recommended. The detailed analytical procedure has been described in section 2.4.

To validate the modified method with authentic samples, SC-1 and LE-1 sediment extracts were used. Analysis of the original sediment extracts indicated that they were free from any butyltin compounds. In this recovery study, sediment extract was fortified at three concentration levels, namely 1.0, 0.5 and 0.1 μg Sn/mL TBTO. Table 1 presents the recovery of TBTO in two sediment extracts. The recovery of TBTO was obtained by four replicate analyses of fortified sediment extract. As shown in Table 1 for the two sediment extracts studied, recoveries of TBTO at all three levels were close to quantitative, within the experimental error. Overall, average recovery for all three fortified levels was 104.2% and 98.0% for SC-1 and LE-1, respectively. The precision of the method based on four replicates for the three fortified levels, expressed as relative standard deviation (RSD), ranged from 4.2 to

6.5% and from 6.9 to 12.9% for SC-1 and LE-1 sediment extracts, respectively. Overall, the average RSD for all three fortified levels was 5.6% and 9.7% for SC-1 and LE-1 sediment extract, respectively.

3.2 Stability Study

In common practice, sediment extract samples are kept in a refrigerator at 4°C in the dark until analysis, but there is no published experimental data on the analyte's storage stability in any given solvent. In this study, the effect of storage conditions on the TBTO in sediment extracts prepared in acetone was investigated. Acetone was chosen as the solvent for sediment extract samples because of its solubility for coextractives. Thus coextractives in sediment extract samples would not be precipitated out during the long-term storage period which could affect the integrity and homogeneity of samples. Fortified SC-1 and LE-1 sediment extracts were stored in the dark at 4°C and 25°C and removed for recovery determination at 5 storage times; namely, shortly after fortification (0 time), 2 weeks, 1 month, 2 months and 4 months. Results of recovery of TBTO are tabulated in Tables 2 and 3. In all cases, recoveries are quantitative within experimental errors ($\pm 10\%$). It shows no significant difference for recovery of TBTO between two storage conditions for the two sediment extracts studied. Typical results of TBTO in standard solution and sediment extract are shown in Figures 1 and 2. The

chromatogram from sediment extract indicates that it is identical to that in standard solution. In conclusion, no degradation was found during the storage times up to 4 months for the two sediment extracts studied at two storage conditions, i.e. 4°C and 25°C. The results of this study provide the necessary background information for designing and conducting interlaboratory QA studies for research and monitoring of TBTO.

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Table 1. Mean recoveries and precision of TBTO from fortified sediment extracts.
(No. of replicates = 4)

Level of fortification	Mean rec. \pm S.D., %	RSD, %
<u>SC-1 Sediment Extract</u>		
$\mu\text{g/mL}$		
1.0	98.7 \pm 6.4	6.5
0.5	105.4 \pm 6.4	6.1
0.1	108.6 \pm 4.6	4.2
Avg. rec.	104.2 \pm 5.8	5.6
<u>LE-1 Sediment Extract</u>		
1.0	101.2 \pm 7.0	6.9
0.5	101.6 \pm 9.3	9.2
0.1	91.3 \pm 11.8	12.9
Avg. rec.	98.0 \pm 9.4	9.7

Table 2. Stability of TBTO at 4°C in two fortified sediment extracts.

Storage time (Months)	No. of detns.	Mean rec. \pm S.D., %	RSD, %
<u>SC-1 Sediment Extract</u>			
0	4	98.7 \pm 6.4	6.5
1/2	4	103 \pm 6.0	5.8
1	4	96.0 \pm 3.0	3.1
2	4	106 \pm 3.0	2.8
4	4	103 \pm 11.0	10.7
<u>LE-1 Sediment Extract</u>			
0	4	101.2 \pm 7.0	6.9
1/2	4	97.0 \pm 4.0	4.1
1	4	107 \pm 5.0	4.7
2	4	109 \pm 2.0	1.8
4	4	99.0 \pm 3.0	3.0

Table 3. Stability of TBTO at 25°C in two fortified sediment extracts.

Storage time (Months)	No. of detns.	Mean rec. \pm S.D., %	RSD, %
<u>SC-1 Sediment Extract</u>			
0	4	98.7 \pm 6.4	6.5
1/2	4	105 \pm 3.0	2.9
2	4	96.0 \pm 1.0	1.0
4	4	95.0 \pm 9.0	9.5
<u>LE-1 Sediment Extract</u>			
0	4	101.2 \pm 7.0	6.9
1/2	4	110 \pm 5.0	4.5
1	4	105 \pm 3.0	2.9
2	4	96.0 \pm 15.0	15.6
4	4	101 \pm 6.0	5.9

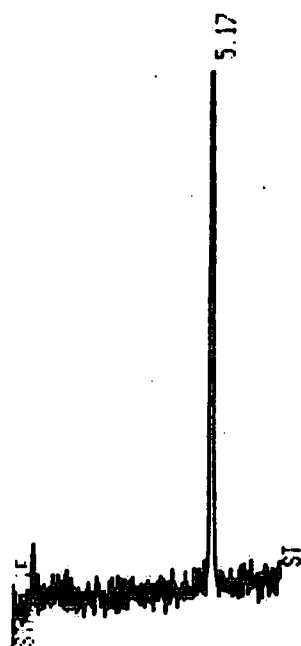


Figure 1. Chromatogram showing ethyl derivative of TBTO in a standard solution.

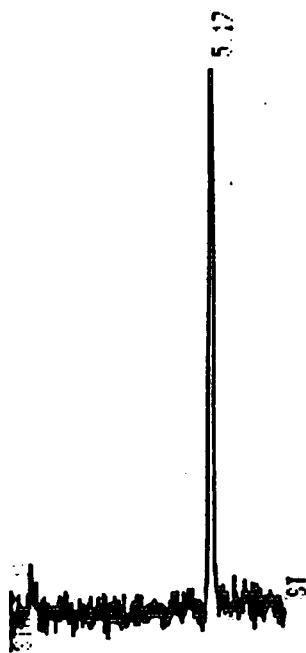
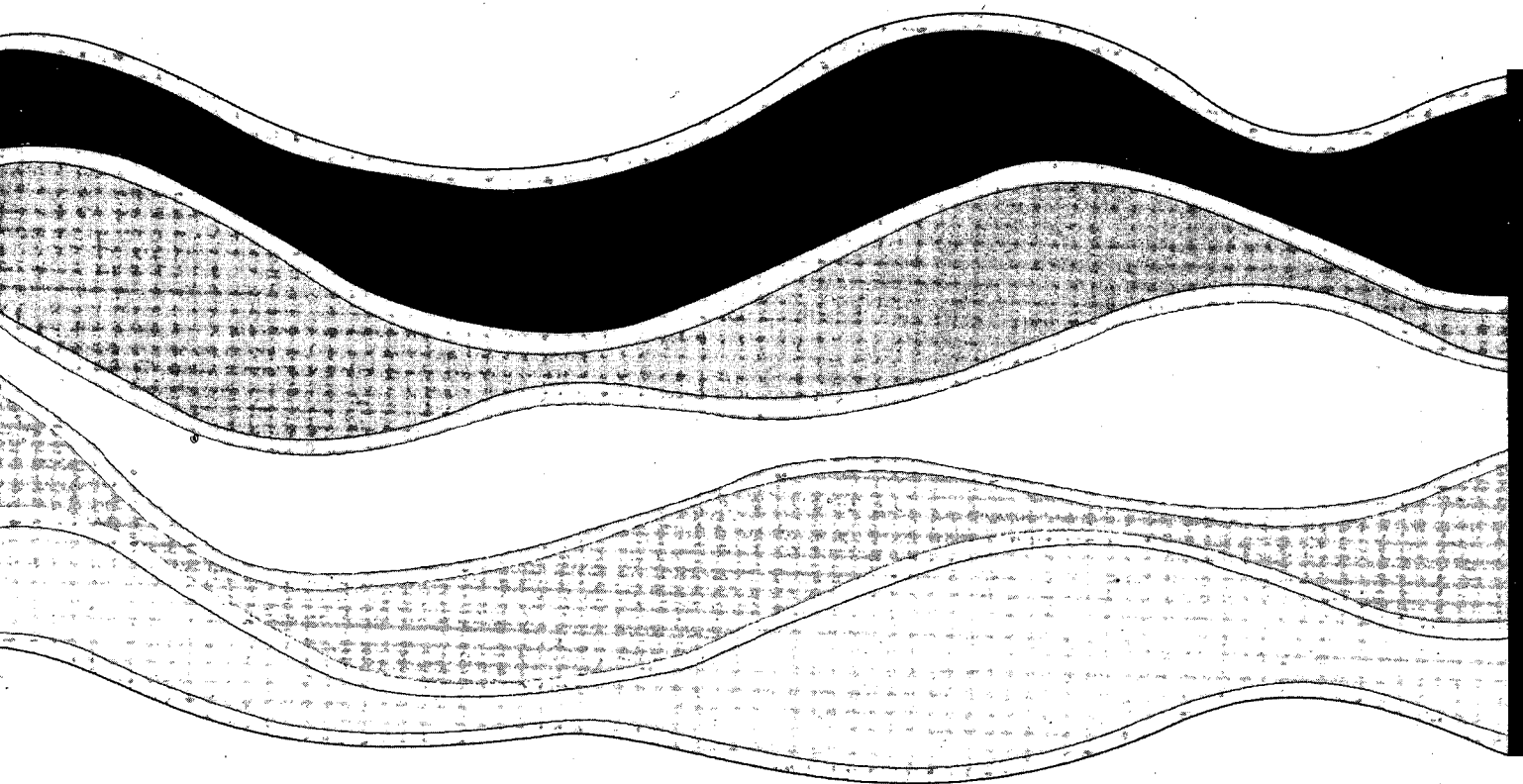


Figure 2. Chromatogram showing ethyl derivative of IBTO in a sediment extract sample (LE-1) stored for one month at 4 C in the dark.

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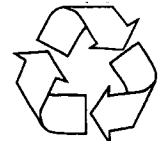


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