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PRESERVATION OF ORGANICS, PART V STABILITY OF BUTYLTIN SPECIES IN SEDIMENT EXTRACTS

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MANAGEMENT PERSPECTIVE

Concern about organotins pollution in the aquatic environment has resulted in the monitoring of water, sediment and fish samples for butyltins. To develop sediment reference samples fortified with butyltins as QC samples for evaluating laboratory performance in interlaboratory studies, considerable in-house investigation for the preparation and stability of butyltins in the fortified sediment extracts was carried out. Results indicated that the Bu_3Sn^+ and Bu_2Sn^{2+} in sediment extracts were stable for a minimum of five months either stored at 4°C or 25°C in the dark while $BuSn^{3+}$ showed that it was degraded by debutylation when the storage period was more than two months. This stability study provides the basic background information for the design and conduct of interlaboratory QA studies for butyltin species in sediment extracts.

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PERSPECTIVE-GESTION

Devant l'inquiétude que suscite la pollution du milieu aquatique par des composés organiques de l'étain, on a procédé au dosage des butylétains dans des échantillons d'eau, de sédiments et de poissons. Afin de préparer des échantillons étalons de sédiments additionnés de butylétains, qui serviront d'échantillons de CQ lors de l'évaluation de la performance des laboratoires d'analyse dans le cadre d'études interlaboratoires, la Direction a procédé à des études exhaustives sur la préparation et la stabilité des butylétains ajoutés à des extraits de sédiments. Selon les résultats obtenus, le Bu_3Sn^+ et le Bu_2Sn^{2+} présents dans des extraits de sédiments sont stables pendant au moins cinq mois lorsqu'ils sont entreposés à 4 °C ou à 25 °C à l'obscurité, alors que le $BuSn^{3+}$ est dégradé par débutylation lorsque la durée d'entreposage dépasse deux mois. Les résultats obtenus au cours de cette étude sur la stabilité constituent des informations de base qui serviront lors de la conception et de l'exécution d'études d'AQ interlaboratoires applicables aux butylétains dans des extraits de sédiments.

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ABSTRACT

This report summarizes the results for the preparation and stability studies of sediment extracts fortified with three butyltin species; namely, tributyltin, dibutyltin and monobutyltin. Stability of butyltins in sediment extracts was investigated under dark storage conditions at 4°C and 25°C. Analytical results indicated that no degradation of tributyltin and dibutyltin species occurred in the two fortified sediment extracts for a period of up to five months, while the analysis of monobutyltin showed that it was degraded by debutylation when the storage period was more than two months. The extent of degradation for monobutyltin was not significantly different with two sediment extracts of different matrices under the same storage conditions. However, the degradation under 4°C and 25°C temperatures had half-lives of five and three months, respectively. To extend the storage time for the monobutyltin in sediment extracts, storage of the samples at -20°C in the dark may be required.

RÉSUMÉ

On résume dans ce rapport les résultats obtenus au cours d'études sur la préparation et la stabilité d'extraits de sédiments auxquels trois butylétains, soit le tributylétain, le dibutylétain et le monobutylétain, ont été ajoutés. On a étudié la stabilité des butylétains dans des extraits de sédiments entreposés à l'obscurité à des températures de 4 °C et de 25 °C. Selon les résultats d'analyse, le tributylétain et de dibutylétain n'étaient pas dégradés dans deux extraits de sédiments additionnés de ces composés pendant une période pouvant atteindre cinq mois, tandis que le monobutylétain était dégradé par débutylation lorsque la période d'entreposage dépassait deux mois. La quantité de monobutylétain dégradé n'était guère différente dans deux extraits de sédiments possédant des matrices différentes et entreposés dans les mêmes conditions. Toutefois, les demi-vies de dégradation étaient de cinq mois et de trois mois à des températures de 4 °C et de 25 °C respectivement. Il sera peut-être nécessaire, pour prolonger la durée d'entreposage du monobutylétain dans des extraits de sédiments, de conserver les échantillons à l'obscurité à une température de -20 °C.

1.0 INTRODUCTION

Tributyltin has been found in many harbour locations because of its use as an antifouling agent in ship paint formulations (1,2). Tributyltin (Bu_3Sn^+) degrades under environmental conditions to dibutyltin (Bu_2Sn^{2+}) and monobutyltin ($BuSn^{3+}$) species, and eventually to tin(IV) species, with tributyltin being the most toxic form to aquatic organisms. In addition, dibutyltin is used as a poly(vinylchloride) stabilizer. Thus, over the past several years, various analytical methods have been developed for the monitoring of butyltin species in water, sediment and biota samples (2-4).

In order to assist project managers and regulating bodies under the Canadian Environmental Protection Act (CEPA), and to ensure the validity of analytical data, we are developing sediment extract quality control reference materials for evaluating laboratory performance of butyltin analysis in sediments. The use of sediment extracts as QC samples would eliminate the variation of sample extraction procedures used for sediment analysis. Considerable in-house investigation for the preparation and stability of butyltin species in sediment extracts was required before interlaboratory studies can be initiated. In Part IV of the preservation and stability studies, we have reported the stability of Bis(tri-n-butyltin)oxide in fortified sediment extracts. In the present study, we have extended investigation to tributyltin,

dibutyltin and monobutyltin species in fortified sediment extracts.

2.0 EXPERIMENTAL

2.1 Materials

Tributyltin chloride, dibutyltin dichloride, monobutyltin trichloride, tetraethyltin, ethylmagnesium bromide in tetrahydrofuran and tropolone were obtained from Aldrich Chemicals (Milwaukee, Wisconsin). All solvents were pesticide grade from Caledon (Georgetown, Ontario). Other apparatus has been described in a previous report (5).

2.2 Extraction, Fortifications, Subsampling and Storage

The protocol for the preparation of sediment extract has been described in the previous reports (5,6). The sediment extracts (SC-1) and (LE-1) used for the study of stability of bis(tri-n-butyltin)oxide were also employed in the present investigation. A mixture of three butyltin species; namely tributyltin, dibutyltin and monobutyltin species with concentrations of 100.0 μg Sn/mL, each, in acetone was prepared for the use of spiking and for the preparation of mixed calibration standard. An appropriate amount of the above mixed standard was spiked into SC-1 and LE-1 sediment extracts, respectively, and made up to 100 mL with respective sediment extracts, to give a concentration of 1.0 μg Sn/mL for the butyltin species. In order

to monitor the stability of butyltin species in sediment extracts at specified periods, and to correct for the variation of the instrument stability, a mixed standard of concentration 1.0 μg Sn/mL was also simultaneously prepared. All prepared standard and sediment extract samples were thoroughly mixed and stored at 4°C, to achieve further equilibrium. Series of subsamples of standard solution and fortified sediment extract samples were prepared by transferring approximately 1.5 mL aliquot into a 1.5 mL GC sample vial and sealing with a teflon-faced cap. A total of about 60 subsamples were made for each 100 mL standard solution and sediment extracts. All subsamples of standard solution were stored in a dark refrigerator at 4°C. The subsamples of sediment extracts were likewise split into two groups, with one group stored at 4°C in the dark, and the other at 25°C in the dark.

2.3 Analytical Procedure

After the storage time had elapsed, four replicates of subsamples from standard solution and sediment extracts were analyzed for butyltin species, by a modified procedure for sediment extract as described in the previous report (5). Briefly, the subsample was brought to room temperature and exactly one mL of aliquot was transferred into a 15 mL graduated centrifuged tube. An aliquot of 5 mL 0.5% tropolone in hexane and about 1 mL iso-octane as keeper were added for the solvent exchange procedure for removal of acetone in the mixed solution. 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 butyltin species by GC/AAS.

For GC-AAS analysis, a Hewlett-Packard 5880 A GC 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 mode 4000 AAS equipped with a quartz furnace atomizer. The following GC conditions were used: injection port, 110°C; transferline temperature, 150°C; initial column temperature, 90°C; initial time, 0 minutes; oven temperature program rate, 18°C/minute to 200°C and held at 200°C for 2 minutes. Carrier gas was N_2 with a flow rate of 10.5 mL/min. A 10 μL aliquot was injected. The following AAS

conditions were used: the quartz furnace temperature, 850-900°C; furnace gases, H_2, 84 mL/min, air, 21 mL/min. The 224.6 nm Sn line was generated by an Electrodeless Discharge Lamp operated at 8W. Deuterium background correction was used and peak areas were measured with a HP 3392A integrator.

3.0 RESULTS AND DISCUSSION

Tables 1 and 2 indicate recoveries of the 3 butyltins from the fortified sediment extract samples following varying lengths of storage time, at storage conditions of 4°C and 25°C, respectively. Before fortification, these two sediment extracts showed no detectable amounts of butyltins.

For the SC-1 fortified sediment extract samples, as shown in Table 1, the average recoveries of Bu_3Sn^+ stored at 4°C in the dark were between 91 and 108% over the 5-month study period and the relative standard deviations of the four replicates were below 10% in most cases. Similarly, for the LE-1 sediment extract samples, the average percentage recovery fell between 104 and 109%, with the relative standard deviations below 12%. During the study period, there was no continuous decline in recovery for Bu_3Sn^+, as all observed values fell within the experimental error of ±10%. This suggests that no degradation had occurred for Bu_3Sn^+ under this storage condition. These results are in accordance with those obtained in the previous study for TBTO in sediment extracts (5).

For the storage condition of 25°C in the dark, (Table 2), generally similar results were observed for Bu_3Sn^+. At the end of the study period (month 5), both the sediment extract samples showed slightly low recoveries, which were still within the experimental error of ±10%. Thus, the results obtained using two fortified sediment extracts with different matrices indicated that Bu_3Sn^+ was stable over a 5-month period when the samples were stored in the dark either at 4°C or 25°C.

For the Bu_2Sn^{2+} in the fortified sediment extract samples, as shown in Tables 1 and 2, the average recoveries were between 92 and 109%, except for the two cases with recoveries below 90% at the 25°C storage condition. However, no continuous decline in recoveries was observed in the two sediment extracts under both storage conditions. Thus, Bu_2Sn^{2+} in sediment extracts was stable at least for a period of five months. The precision of four replicates, expressed as relative standard deviation, was below 15% in most cases. In general, when compared with the analysis of Bu_3Sn^+ determination, the precision of Bu_2Sn^{2+} was less than that of Bu_3Sn^+.

For the results of $BuSn^{3+}$ in sediment extract samples, as indicated by Tables 1 and 2, for up to 2 months of storage period, there was no decline in observed recoveries for both storage conditions for the two sediment extract samples. In addition, no degradation product of Sn(IV) was observed in the analysis.

Typical results of butyltins in standard solution and sediment extract are shown in Figure 1. The chromatogram from sediment extract indicated that it was identical to that of the standard solution. However, when the subsamples of LE-1 sediment extract stored at 25°C in the dark for the period of month 3 were analyzed, the chromatogram from sediment extract was found to contain an additional peak, while the peak area for $BuSn^{3+}$ was substantially decreased, as shown in Figure 2. It was obvious that $BuSn^{3+}$ had undergone degradation. The additional peak was identified as Et_4Sn [formed by chemical derivatization of Sn(IV) with ethylmagnesium bromide] by the retention time of pure Et_4Sn, as shown in Figure 3. Thus, it was evident that $BuSn^{3+}$ in sediment extract underwent debutylation reaction to Sn(IV) during long-term storage. It should be noted that fortified sediment extract samples were not spiked with tropolone during the storage period, and that the degradation product Sn(IV) could be complexed by naturally occurring organic ligands such as humic and fulvic acids (HA and FA) which were present in the extracts. Thus, Sn(IV)-HA and/or Sn(IV)-FA could be dissolved in the extracts and subsequently reacted with Grignard reagent (ethylmagnesium bromide) during chemical derivitization to give tetraethyltin as identified in Figure 2. As can be seen from Table 1, for example, at the third month of 25°C dark storage, the loss of $BuSn^{3+}$ (39%) corresponded to an increase in Sn(IV) (44%) in the SC-1 sediment extract. However, in the experiment with longer storage period, the amount of $BuSn^{3+}$ continuously decreased but a corresponding amount of

Sn(IV) was not recovered. The apparent contradiction of these results may be due to precipitation of Sn(IV) from solution, or reduction by HA and/or FA to Sn(II), which did not react with the Grignard reagent during chemical derivitization. The exact reason was not clear. However, $BuSn^{3+}$ was not stable in sediment extracts under long-term storage. Overall, the extent of the degradation pattern for the two sediment extracts with different matrices was not significantly different. In contrast, for both the sediment extracts, the extent of degradation of $BuSn^{3+}$ under 25°C storage was more than that under 4°C storage condition.

4.0 CONCLUSION

In conclusion, as expected from the molecular structure, $BuSn^{3+}$ was less stable than the corresponding Bu_3Sn^+ and Bu_2Sn^{2+} species. $BuSn^{3+}$ was degraded in sediment extracts under 4°C and 25°C storage conditions. On the other hand, the other two butyltin species were stable in sediment extracts at 4°C and 25°C for up to the investigated period of 5 months. Based on this stability study, monobutyltin was not stable for long-term storage in sediment extracts even at a low storage condition at 4°C. The extent of degradation for $BuSn^{3+}$ was not significantly different with two sediment extracts of different matrices under the same storage condition. However, to estimate approximately the extent of the degradation for $BuSn^{3+}$ in sediment extracts under different storage conditions, namely 4°C and 25°C in the dark, the half-life

of $BuSn^{3+}$ was determined graphically by plotting the percentage of the remaining test chemical in the sediment extract against time (i.e. the half-life is the storage time at which the remaining concentration of test chemical is equal to one-half of the original concentration of test chemical). $BuSn^{3+}$ was degraded in sediment extracts under 4°C and 25°C storage conditions with half-lives of about five and three months, respectively. To retard the degradation and extend the storage life of monobutyltin in sediment extracts, storage of the samples at -20°C in the dark may be required.

5.0 REFERENCES

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Table 1. Mean % recoveries of butyltins in fortified sediment extracts, stored at 4°C in the dark.

Parameter	Month 0		Month 1		Month 2		Month 3		Month 4		Month 5	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
SC-1 Sediment Extract												
Bu_3Sn^+	103	6	105	10	91	6	108	9	103	21	104	7
Bu_2Sn^{2+}	95	11	94	16	95	2	106	9	92	12	105	8
$BuSn^{3+}$	103	8	102	7	101	1	84	9	80	9	52	5
Sn(IV)	0	0	0	0	0	0	9	2	0	0	0	0
LE-1 Sediment Extract												
Bu_3Sn^+	104	11	105	12	100	14	109	6	109	12	104	11
Bu_2Sn^{2+}	98	9	103	7	112	1	107	3	101	20	107	9
$BuSn^{3+}$	97	5	99	1	96	1	88	2	73	16	46	9
Sn(IV)	0	0	0	0	0	0	9	1	0	0	0	0

Table 2. Mean % recoveries of butyltins in fortified sediment extracts, stored at 25°C in the dark.

Parameter	Month 0		Month 1		Month 2		Month 3		Month 4		Month 5	
	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.	Mean	S.D.
SC-1 Sediment Extract												
Bu_3Sn^+	103	6	101	1	100	7	106	9	108	13	89	1
Bu_2Sn^{2+}	95	11	100	7	106	10	105	3	81	22	109	14
$BuSn^{3+}$	103	8	97	7	97	7	61	6	14	3	22	4
Sn(IV)	0	0	0	0	0	0	44	8	4	0	0	0
LE-1 Sediment Extract												
Bu_3Sn^+	104	11	115	19	97	16	101	9	109	15	94	8
Bu_2Sn^{2+}	98	9	97	4	88	2	104	6	93	13	104	10
$BuSn^{3+}$	97	5	98	4	102	4	59	8	40	10	21	5
Sn(IV)	0	0	0	0	0	0	48	2	4	0	0	0

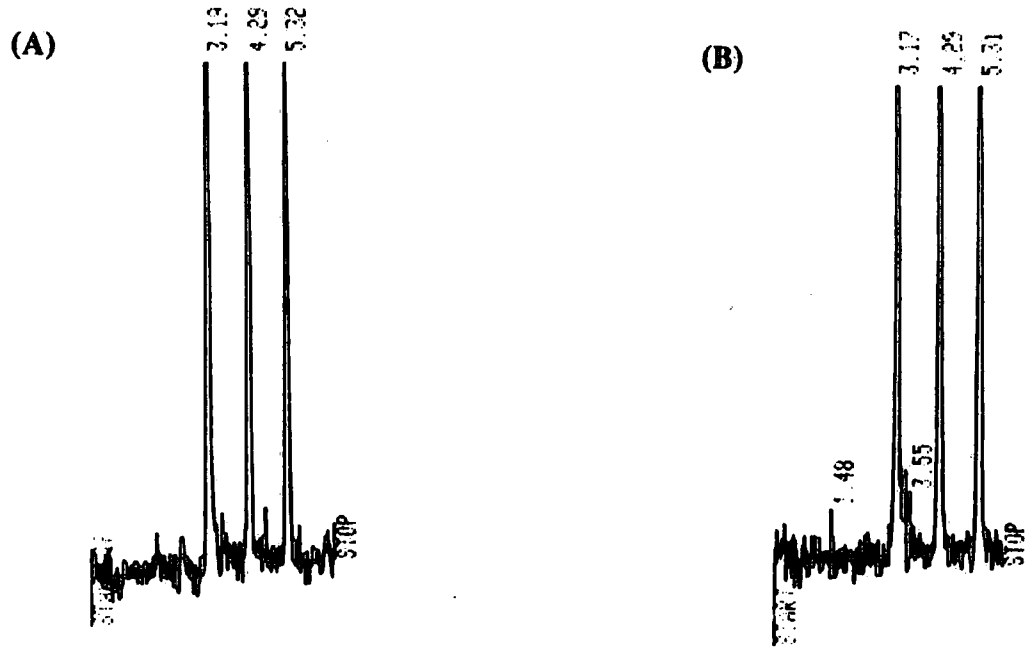

Figure 1. Chromatograms showing ethyl derivative of $BuSn^{3+}$,Bu_2Sn^{2+} and Bu_3Sn^{+} in a mixed standard solsution (A) and a fortified LE-1 sediment extract stored at 25°C in the dark for 1 month (B).

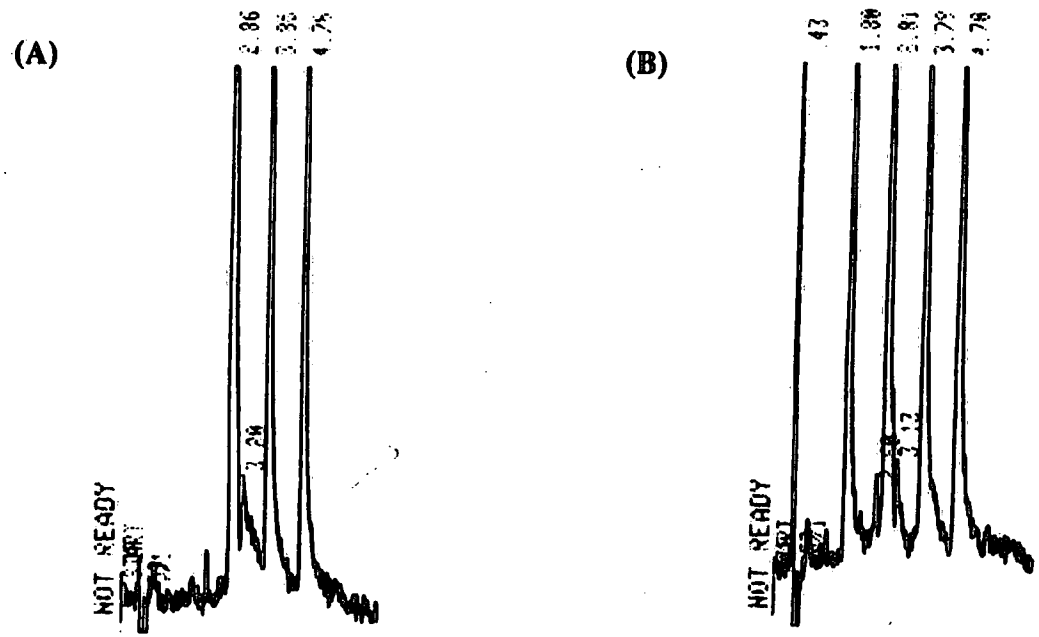

Figure 2. Chromatograms showing ethyl derivatives of $BuSn^{3+}$, Bu_2Sn^{2+} and Bu_3Sn^{+} in a mixed standard solution (A) and a fortified LE-1 sediment extract stored at 25°C in the dark for 3 months (B).

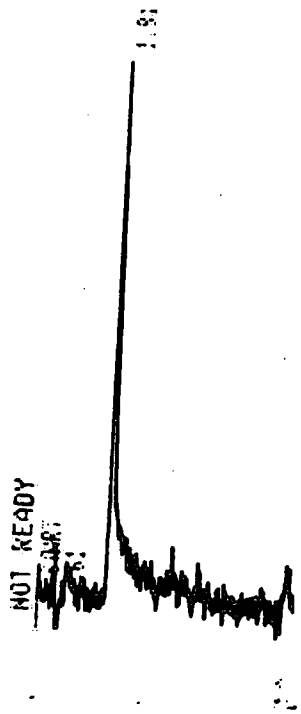

Figure 3. Chromatogram showing tetraethyltin (or formed by chemical derivatization of Sn(IV) with ethylmagnesium bromide) in a standard solution.

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