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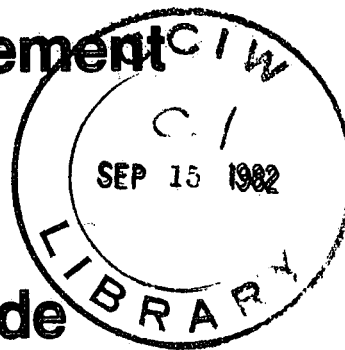


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MICROLAYER OF THE NIAGARA RIVER

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ABSTRACT

Some physical and chemical characteristics of bis (tri-n-butyltin) oxide ("TBTO") are reported which indicate that it may be at least moderately persistent in water and may be bioaccumulated to a moderate degree. The aqueous solubility is 0.5 to 7.5 mg L⁻¹ from pH 5 to 8, the logarithm of the octanol-water partition coefficient at pH 6 is 3.2, and the vapour pressure at 20°C is estimated to be 6.4×10^{-7} mm Hg. TBTO in water in the dark at 20°C is both chemically stable and not subject to volatilization over a period of two months.

INTRODUCTION

Organotin compounds are used in three major ways, viz., as thermal stabilizers for polyvinyl chloride, as catalysts in the production of polyurethane foams, and biocides (1,2). The increasing annual usage of organotins raises the possibility of environmental pollution. Organotins are a class of compounds about which more information is sought under the Environmental Contaminants Act (3) regarding toxicology and environmental fate.

We chose to examine the aquatic fate of butyltins in general, and bis (tri-n-butyltin) oxide (TBTO) in particular. We have recently reported the presence of butyltins in Ontario lakes and rivers (4). Concurrent with our field study is an attempt to estimate the aquatic persistence of TBTO by determining the relative importance of such pathways as volatilization, hydrolysis, photolysis, adsorption to sediments, bacterial degradation, and uptake by biota. This report deals with (i) basic properties such as solubility, octanol-water partition coefficient and vapour pressure, and (ii) the first two pathways described above, viz., volatilization and hydrolysis.

EXPERIMENTAL METHODS

Chemicals

TBTO (97%), dibutyltin dichloride (96.5%), butyltin trichloride (95%), tin (99.99%), 48% HBr and n-pentylmagnesium bromide in diethyl ether were obtained from Ventron (Danvers, MA, U.S.A.); HCl was Aristar grade from BDH, Toronto; 2-hydroxy-2,4,6-cycloheptatrien-1-one (tropolone) was from Aldrich (Milwaukee, WI, U.S.A.), and was recrystallized from diethyl ether before use (m.p. 52°C, uncorr.). All organic solvents were pesticide grade from Caledon Laboratories, Georgetown, Ontario. The water used in these experiments was house distilled water which had been passed through the "Super Q" system (Millipore, Mississauga, Ontario).

Analysis of Butyltins

TBTO (as Bu_3Sn^+ , where Bu = n-butyl), $\text{Bu}_2\text{Sn}^{2+}$, BuSn^{3+} and Sn(IV) were analyzed as n-pentyl derivatives by gas chromatography with a modified flame photometric detector (5 and Appendix).

Adsorption to Glass and Teflon

Preliminary work had indicated adsorption of TBTO from water onto Teflon-coated magnetic stirring bars.

Pyrex centrifuge tubes of 15 mL capacity were filled with aqueous TBTO solutions and a Teflon strip (10 × 1 × 0.02 cm) was added to each tube. The tubes were allowed to stand for 24 hr with occasional shaking. After 24 hr, the Teflon strips were removed and extracted with hexane in new tubes for 48 hr. The water was drained from the original tubes and the tubes were rinsed with fresh water. The combined water aliquots were extracted with hexane. Finally, the original tubes were filled with hexane and allowed to stand for 48 hr to leach any TBTO which had adsorbed to the glass. The three hexane extracts were then analyzed as indicated above. This experiment was done in triplicate at each of three concentrations of TBTO - 0.1, 0.5 and 1 mg L⁻¹.

Aqueous Solubility and Octanol-Water Partition Coefficient

The inside surface of a volumetric flask was coated with about 1 mL of a concentrated solution of TBTO in hexane. The hexane was evaporated under a gentle stream of nitrogen, leaving a thin film of TBTO, and the flask was filled with water. The contents were stirred overnight and then centrifuged at 2000 rpm for 1 hr. A 5 mL aliquot was extracted with hexane and analyzed as indicated above. This experiment was done in triplicate at various pH values between 2 and 10.8 in buffers of ionic strength 0.05.

The octanol-water partition coefficient for TBTO at pH 6 was determined according to the procedure of Platford et al. (6) coupled with the gc-fpd analysis indicated above. The experiment was done in triplicate.

Hydrolysis

Aqueous TBTO solutions in volumetric flasks were incubated in the dark at 20°C for various periods. At each sampling time the

whole volume of water and the inside walls of the volumetric flask were extracted and the extracts were combined and analyzed for Bu_3Sn^+ , $\text{Bu}_2\text{Sn}^{2+}$, BuSn^{3+} and Sn(IV) as indicated above. Samples were taken in triplicate and the experiment was performed at pH 2.9, 6.7, and 10.3.

Vapour Pressure

The vapour pressure of TBTO was estimated by a kinetic comparative method (7) which is described briefly here. Because the volatilization rate is limited by the rate of gaseous diffusion through the essentially stagnant boundary layer, the rate of loss of the compound (v) is closely approximated by:

$$v = cPM^{\frac{1}{2}} \quad (1)$$

where c is a constant determined by the air-flow characteristics of the system and P is the vapour pressure of the compound of molecular weight M . Therefore, for two chemicals, 1 and 2, placed in a constant temperature room with a rate of air change sufficient to ensure that

the vapour-phase concentrations of the chemical are far removed from their saturation values, the vapour pressures of the compounds are related as follows:

$$P_1 = \frac{k_1 P_2 M_2^{\frac{1}{2}}}{k_2 M_1^{\frac{1}{2}}} \quad (2)$$

where the k's are rate constants. This equation can be used to estimate unknown vapour pressures by comparison of the rate of loss of the compound of interest with that of a compound of known vapour pressure.

The rates of loss of TBTO and a reference compound, pentachlorophenol, were measured as follows: 0.5 mL of a hexane solution of each chemical was pipetted onto each of about 40 5-cm diameter watch glasses. After the hexane had evaporated, the watch glasses were placed in a random array in a room at 20°C. The room was not entered except to sample (in triplicate) the watch glasses. At various times, watch glasses were removed and washed thoroughly with hexane. TBTO was analyzed as described above; pentachlorophenol was

methyated with diazomethane and analyzed by gas chromatography with an electron capture detector.

Volatilization from Water

Fifty mL aliquots of an aqueous TBTO solution were placed in 30 50 mL Erlenmeyer flasks which were kept in the dark at 20°C in a cupboard which was only opened to take samples. Sampling was done in triplicate. At each sampling time the whole volume of water in each flask was extracted with hexane, and the inside of the Erlenmeyer flask was washed thoroughly with hexane to remove any TBTO adhering to the glass surface. The two extracts were combined and analyzed as indicated above.

In addition to this direct method for measuring the volatilization rate of TBTO from water in a specific system, two other methods, which are in principle capable of predicting the volatilization rate for general situations, were attempted. The first method was the direct determination of the air-water Henry's law constant

(8). This method failed because TBTO was rapidly adsorbed to the inner glass walls of the Henry's law apparatus. The second method involved the determination of the ratio of volatilization rate constant to oxygen re-aeration rate constant for systems of identical turbulence (9-11). Over a wide range of turbulence and temperature, such ratios are constant, hence one may write:

$$\frac{k_{\text{lab}}^{\text{TBTO}}}{k_{\text{lab}}^{\text{O}_2}} = \frac{k_{\text{env}}^{\text{TBTO}}}{k_{\text{env}}^{\text{O}_2}} \quad (3)$$

The value of k^{TBTO} can be calculated since k^{O_2} is known for water bodies such as ponds, lakes and rivers, and the ratio on the left hand side of equation 3 is in principle known from experiments done in the laboratory. This method failed, however, partly because TBTO is fairly involatile and partly because it became adsorbed to the Teflon or glass-coated magnetic stirring bars and to the inner walls of the glass vessels used in the laboratory work. This observation of adsorption of TBTO from water onto glass or Teflon prompted the adsorption experiments described earlier. TBTO will not adsorb onto

glass or Teflon from organic solvents such as methanol, n-octanol, hexane or benzene.

RESULTS AND DISCUSSION

Adsorption to Glass and Teflon

Table 1 summarizes the adsorption results. At 1.11 mg L^{-1} most of the TBTO is dissolved in water, but below this concentration more TBTO is bound to the Teflon and the glass. These results will, of course, vary from vessel to vessel depending on the condition of the glass (or Teflon), but the general conclusion is that glass and Teflon can adsorb trace quantities of TBTO from pure water, and that care must be taken to rinse with organic solvents all glass and Teflon surfaces with which TBTO has come into contact to ensure maximum recovery.

Aqueous Solubility and Octanol-Water Partition Coefficient

Figure 1 shows that the solubility of TBTO in water is about 0.5 to 5.0 mg L⁻¹ at pH 6 to 8 and increases with both decreasing and increasing pH. The abrupt increase at pH 8 is puzzling, but is apparently real since many determinations were done at this pH with overlapping buffer systems to rule out anomalous buffer effects. We presume that these results are unaffected by adsorption of TBTO from water to glass since concentrated TBTO solutions in hexane were initially used to coat the insides of the flasks, and the solubilities were in most cases greater than 1 mg L⁻¹ anyway.

The logarithm of the octanol-water partition coefficient was determined to be 3.19 ± 0.05 at pH 6, but this value may be slightly affected by adsorption to glass since the aqueous solubility of TBTO at pH 6 is less than 1 mg L⁻¹. A value for log K_{ow} of 3.2 suggests moderate potential for bioaccumulation.

Hydrolysis

The constant recoveries of Bu_3Sn^+ over the course of the experiment, shown in Table 2, indicate that there is no hydrolysis (defined here as cleavage of butyl groups) of TBTO over 63 days between pH 2.9 and 10.3. Since the flasks were rinsed with hexane, these results are not affected by adsorption of TBTO to glass.

Vapour Pressure

The rate of loss curves for both TBTO and pentachlorophenol were exponential within experimental error, and using a value of 5×10^{-6} mm for the vapour pressure of pentachlorophenol (7), a value of $(6.4 \pm 1.2) \times 10^{-7}$ mm was estimated for the vapour pressure of TBTO at 20°C.

Volatilization from Water

The constant recoveries of Bu_3Sn^+ shown in Table 3 indicate that there was no volatilization of TBTO from water over a period of

62 days. Since the flasks were rinsed with hexane, these results are not affected by adsorption of TBTO to glass. It might be argued that TBTO did not volatilize from water since it was adsorbed to the glass, but the results of Table 1 show that at 1 mg L^{-1} , most of the TBTO is dissolved in the water; in any event, in natural waters the presence of dissolved and particulate matter will probably serve to slow the volatilization even more.

The original purpose in attempting to determine the Henry's law constant (H) directly was to be able to make general predictions about the rate of volatilization of TBTO from water, and to compare the results with those shown above for a specific system.

The volatilization rate of a chemical C from water is:

$$-\frac{d[C]}{dt} = k_v[C] \quad (4)$$

where k_v is the volatilization rate constant. By application of the classical Whitman two-film mass transfer model (12), k_v is expressed

in terms of the mass transfer rates of the substance across liquid- and gas-phase boundary layers. The general expression for k_v is:

$$k_v = \frac{1}{L} \left(\frac{1}{k_1} + \frac{RT}{Hk_g} \right)^{-1} \quad (5)$$

where k_v has units of hr^{-1} , L is the depth (cm), k_1 is the liquid-film mass transfer coefficient (cm hr^{-1}), R is the gas constant ($8.2 \times 10^{-5} \text{ L torr } ^\circ\text{K}^{-1} \text{ mole}^{-1}$), T is the temperature ($^\circ\text{K}$), H has units of torr L mole^{-1} , and k_g is the gas-film mass transfer coefficient (cm hr^{-1}).

To use equation 5 it is necessary to estimate k_g , k_1 and H . Liss and Slater have estimated k_1 for CO_2 to be 20 cm hr^{-1} and k_g for water to be $3 \times 10^3 \text{ cm hr}^{-1}$ and assume that for other substances the values could be calculated as follows (13):

$$k_1^{\text{TBTO}} = \left(\frac{\text{MW}_{\text{CO}_2}}{\text{MW}_{\text{TBTO}}} \right)^{\frac{1}{2}} \times k_1 = 5.43 \times 10^{-2} \text{ m hr}^{-1} \quad (6)$$

$$k_g^{\text{TBTO}} = \left(\frac{\text{MW}_{\text{H}_2\text{O}}}{\text{MW}_{\text{TBTO}}} \right)^{\frac{1}{2}} \times k_g = 5.21 \text{ m hr}^{-1} \quad (7)$$

Although we were unable to measure H directly, it can be calculated from the vapour pressure and the aqueous solubility (14):

$$H = \frac{P}{S} \quad (8)$$

At 20° and pH 6 to 7 (where $S \sim 1 \text{ mg L}^{-1}$), $H = 0.38 \text{ torr L mole}^{-1}$, and k_v from equation 5 is $1.08 \times 10^{-4} \text{ hr}^{-1}$ for a depth of 1 m. For a first-order process, the corresponding half-life is 267 days, which is at least consistent with observations made in the laboratory, although this calculation does not take into account the probable slowing of volatilization of TBTO through binding to dissolved and particulate organic matter.

CONCLUSIONS

The solubility of TBTO at pH 5 to 8 is 1 to 10 mg L⁻¹, its octanol-water partition coefficient ($\log K_{ow} = 3.2$) suggests the potential for a moderate degree of bioaccumulation, and in water it is both chemically stable and not subject to volatilization over a period of two months. Further experiments are planned on (i) sunlight photolysis, (ii) adsorption to sediment, (iii) bacterial transformation, and (iv) uptake by algae and fish.

ACKNOWLEDGEMENT

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TABLE 1. Recovery of TBTO from Water, Teflon and Glass at Three Concentrations

[TBTO] initial mg L ⁻¹	Percent Recovery*		
	Water	Teflon	Glass
1.11	85.7 ± 6.5	7.7 ± 1.9	6.6 ± 2.3
0.55	73.4 ± 17.8	20.5 ± 5.2	6.1 ± 2.5
0.12	38.0 ± 3.2	14.9 ± 1.8	47.0 ± 12.4

* Normalized to 100% total recovery.

TABLE 2. Stability of TBTO in Aqueous Solution as a Function of Time at Various pH Values*

Time, days	[Bu ₃ Sn ⁺], mg L ⁻¹		
	pH 2.9	pH 6.7	pH 10.3
0	2.1 ± 0.3	1.3 ± 0.4	5.8 ± 0.9
1	2.4 ± 0.2	1.1 ± 0.1	6.3 ± 0.2
2	2.1 ± 0.4	1.0 ± 0.2	5.9 ± 0.4
4	1.9 ± 0.3	1.4 ± 0.5	5.9 ± 0.3
8	2.3 ± 0.1	1.2 ± 0.2	5.8 ± 0.2
15	2.2 ± 0.4	1.0 ± 0.1	5.9 ± 0.8
31	2.1 ± 0.2	1.2 ± 0.3	6.0 ± 0.1
63	2.2 ± 0.3	1.4 ± 0.2	5.9 ± 0.4

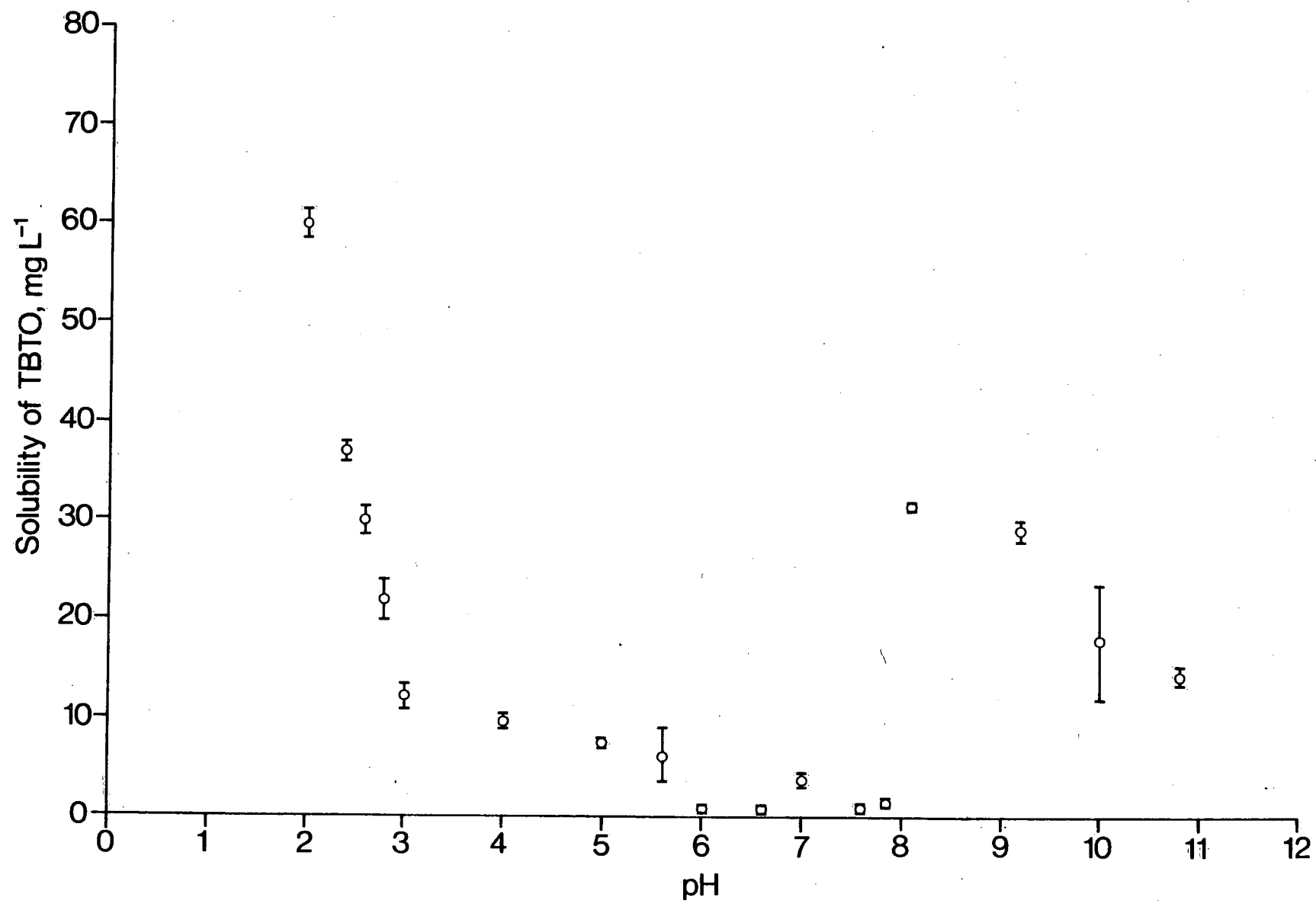
* Solutions stored in the dark at 20°C.

TABLE 3. Volatilization of TBTO from Water

Time, days	[Bu ₃ Sn ⁺]* mg L ⁻¹
0	1.0 ± 0.2
1	1.0 ± 0.1
2	1.1 ± 0.1
4	0.8 ± 0.4
8	0.9 ± 0.1
16	1.0 ± 0.3
30	1.1 ± 0.1
62	1.0 ± 0.1

* Corrected to original solution volume of 50 mL; 20% of the water evaporated over 62 days.

FIGURE 1. Solubility of TBTO as a Function of pH.



APPENDIX

Tributyltin, dibutyltin, butyltin and Sn(IV) are not volatile enough to be analyzed by gas chromatography so a series of volatile derivatives was prepared. A summary of the results appears elsewhere (5) and the details are given in this appendix. Table A-1 shows the derivatives whose synthesis was attempted.

Hydride derivatives of other organotins have been prepared successfully under "in situ generation conditions", i.e., when they were prepared in a trap and immediately swept into the appropriate analytical instrument (15-18), and they have been prepared under "batch conditions" which involved no subsequent concentration of the solution of the derivative (19,20) but we found that tributyltin hydride (Bu_3HSn) suffered evaporative and decomposition losses with subsequent handling or even upon standing in hexane or benzene for a few days.

Attempts to prepare derivatives of tributyltin with electron capturing properties were unsuccessful.

Alkylation of the butyltins and Sn(IV) with Grignard reagents proved, in general, to be a successful method of preparing volatile derivatives. All solutions of the butyltins in hexane or benzene were refluxed with excess Grignard reagent for one hour; Sn(IV) was brought into benzene solution with the use of tropolone as a complexing agent (5). Organotinins were detected qualitatively by the thin-layer chromatographic technique of Meinema et al. (21) which employed detection of dithizone complexes, and Sn(IV) was detected qualitatively by the pyrocatechol violet method (22). Standards were purified by elution in hexane from an activated Florisil column, and detected quantitatively by the GC-FPD method (5). Phenyl- and cyclohexylmagnesium bromide gave low yields of products, but the methyl, ethyl, propyl and pentyl Grignard reagents all gave the appropriate derivatives in quantitative yield, with no "scrambling" of alkyl groups.

The mass spectra of some of the derivatives in Table A-1 are given in Figures A-1 to A-5; the mass spectra of the butylpentyltins are given in reference (5).

Table A-1 shows that in general, the methyl, ethyl and propyl series of derivatives are not suitable for all four species Bu_3Sn^+ , $\text{Bu}_2\text{Sn}^{2+}$, BuSn^{3+} and Sn(IV) since some of the derivatives suffer evaporative losses when their hexane or benzene solutions are stripped of solvent in the "rotovap" or "vortex evaporator". In this regard, the pentyl series of derivatives is suitable and so, in general, pentylation was the method of choice when preparing derivatives of all four species in a single mixture. However, we have occasionally used methylation of TBTO in situations in which we were only interested in the parent compound, and in which we were sure there were no degradation products of TBTO. The advantage in this is that TBTO can be methylated by CH_3MgBr at room temperature, while pentylation in general requires refluxing.

TABLE A-1. Preparation and Characterization of Derivatives of TBTO and Metabolites

Derivative*	Yield, percent	Mass Spectrum**	Rotovap Losses
Bu ₃ HSn	15		
Bu ₃ Sn-HFBA	0		
Bu ₃ Sn-PFBS	0		
Bu ₃ PhSn	20		
Bu ₃ CySn	20		
Bu ₃ MeSn	99 ± 8	Yes	No
Bu ₂ Me ₂ Sn	94 ± 17	Yes	Yes
BuMe ₃ Sn	103 ± 1		Yes
Me ₄ Sn	91 ± 13		Yes
Bu ₃ EtSn	93 ± 4		No
Bu ₂ Et ₂ Sn	109 ± 21	Yes	Yes
BuEt ₃ Sn	100 ± 7		Yes
Et ₄ Sn	83 ± 14		Yes
Bu ₃ PrSn	106 ± 11	Yes	No
Bu ₂ Pr ₂ Sn	94 ± 8	Yes	Yes
BuPr ₃ Sn	94 ± 10		Yes
Pr ₄ Sn	98 ± 7		Yes
Bu ₃ PeSn	100 ± 3	Yes	No
Bu ₂ Pe ₂ Sn	96 ± 6	Yes	No
BuPe ₃ Sn	95 ± 7	Yes	No
Pe ₄ Sn	99 ± 4	Yes	No

* Ph = phenyl; Cy = cyclohexyl; HFBA = heptafluorobutyric anhydride; PFBS = pentafluorobenzenesulfonyl chloride; Me = methyl; Et = ethyl; Pr = n-propyl; Bu = n-butyl, Pe = n-pentyl.

** The mass spectra of some of the methyl, ethyl and propyl derivatives are shown in Figures A-1 to A-5; the mass spectra of the pentyl derivatives are given in reference (5).

APPENDIX - FIGURES

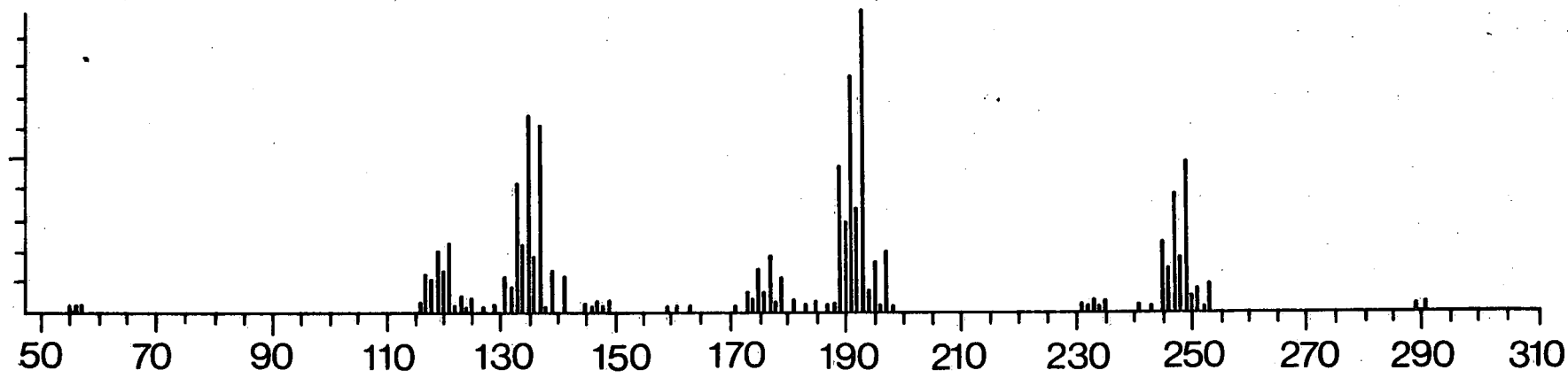
Figure A-1. Mass Spectrum of Bu_3MeSn . Prominent ions are Bu_2MeSn^+ (249), BuMeSnH^+ (193), MeSnH_2^+ (137), BuSnH_2^+ (179).

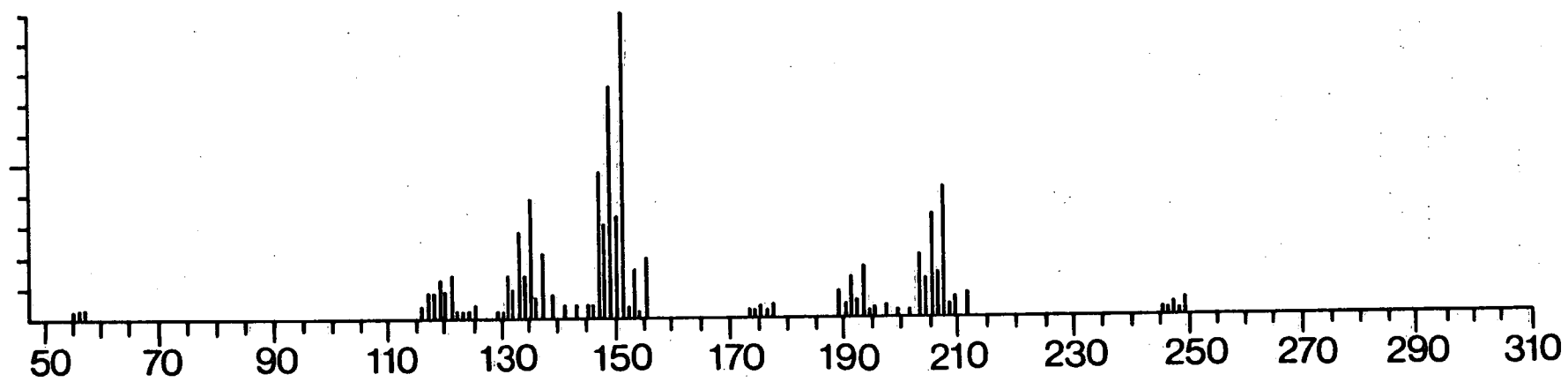
Figure A-2. Mass Spectrum of $\text{Bu}_2\text{Me}_2\text{Sn}$. Prominent ions are BuMe^2Sn^+ (207), BuMeSnH^+ (193), Me_2SnH^+ (151), MeSnH_2^+ (137).

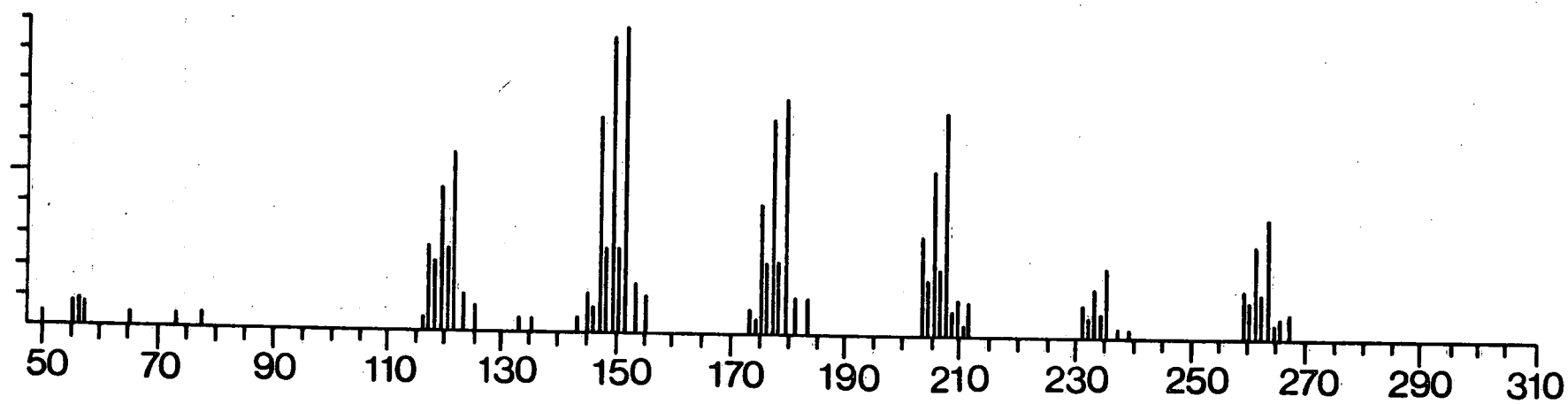
Figure A-3. Mass Spectrum of $\text{Bu}_2\text{Et}_2\text{Sn}$. Prominent ions are Bu_2EtSn^+ (263), Bu_2SnH^+ (235), BuEtSnH^+ (207), BuSnH_2^+ (179), EtSnH_2^+ (151).

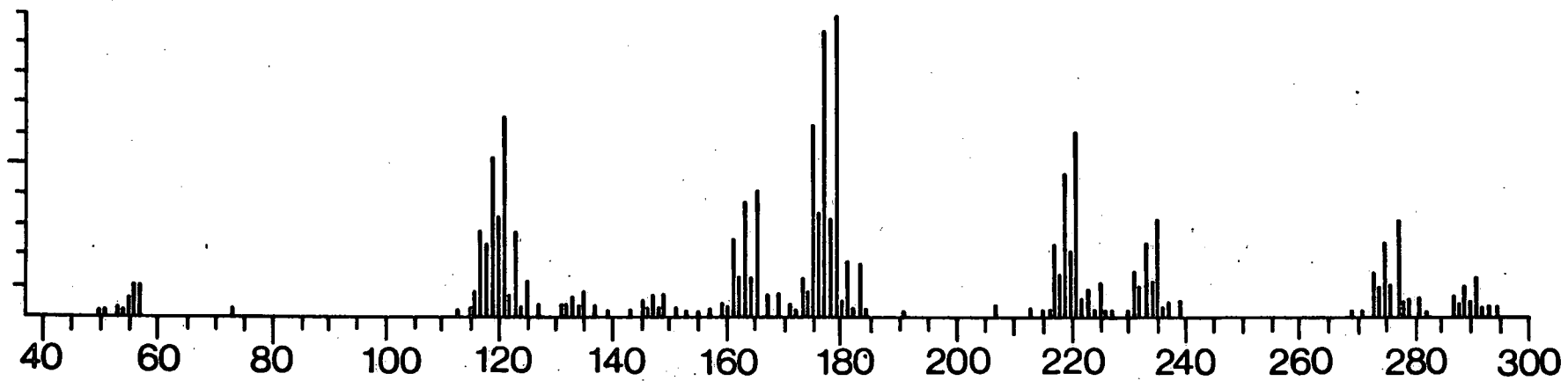
Figure A-4. Mass Spectrum of Bu_3PrSn . Prominent ions are Bu_2PrSn^+ (277), Bu_3Sn^+ (291), BuPrSnH^+ (221), Bu_2SnH^+ (235), BuSnH_2^+ (179), PrSnH_2^+ (165).

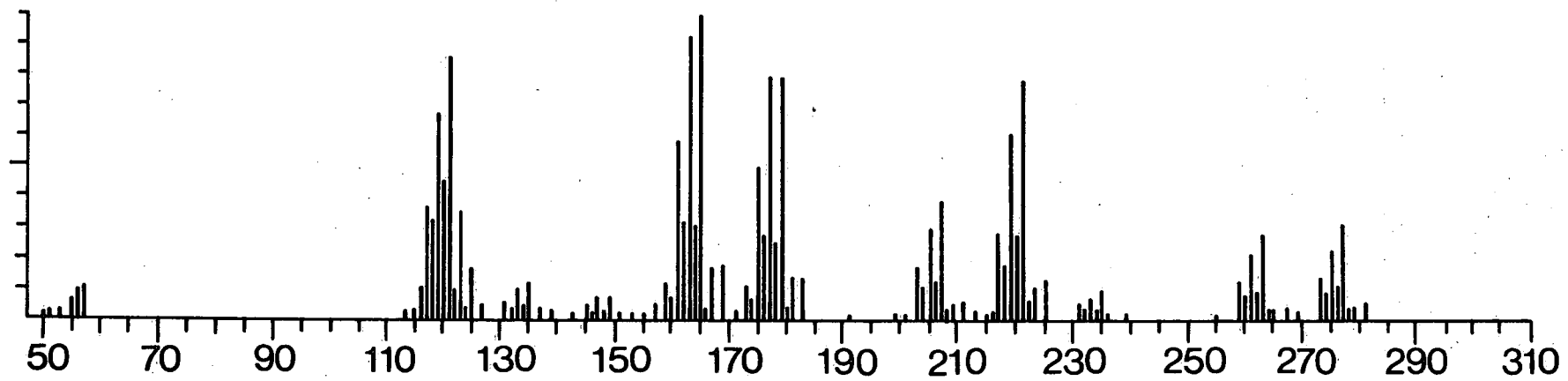
Figure A-5. Mass Spectrum of $\text{Bu}_2\text{Pr}_2\text{Sn}$. Prominent ions are BuPr_2Sn^+ (263), Bu_2PrSn^+ (277), Pr_2SnH^+ (207), BuPrSnH^+ (221), Bu_2SnH^+ (235), PrSnH_2^+ (165), BuSnH_2^+ (179).











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