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GAS CHROMATOGRAPHIC SPECIATION OF METHYLSTANNANES IN THE CHESAP--ETC(U)
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GAS CHROMATOGRAPHIC SPECIATION OF METHYLSTANNANES IN THE CHESAPEAKE BAY
USING PURGE AND TRAP SAMPLING WITH A TIN-SELECTIVE DETECTOR.

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A method was developed permitting detection and speciation of both volatile and non-volatile organotin compounds in aqueous media. The method employed a commercial gas chromatograph (GC) with a flame photometric detector (FPD) optimized for tin-selective detection. Solvated organotins were volatilized with sodium borohydride during the purge cycle of a commercial automatic purge and trap sampler (P/T). Purged volatiles and species volatilized by hydridization were concentrated on a Tenax-GC filled trap at ambient temperature. Tetramethyltin (Me_4Sn) present in the sample is unaffected by the reduction process. The P/T-GC-FPD method was used to analyze water samples collected from the Chesapeake Bay and Baltimore Harbor. Varying amounts of methyltin compounds, including tetramethyltin and methyltin hydrides, were detected in polluted sites in Baltimore Harbor. In vitro studies using GC-MS confirmed earlier reports of microbial methylation of inorganic Sn(IV) by a strain of Pseudomonas species isolated from the Chesapeake Bay. Consequently, biogenic origins are suspected for the methylstannanes ($\text{Me}_n\text{SnH}_{4-n}$, $n = 2, 3$) found in the Chesapeake Bay.

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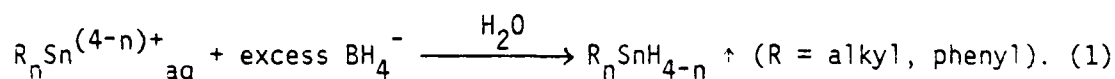
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Studies of Braman and Thompkins (13) and Hodge et al. (14) showed that involatile methyltin species, $\text{Me}_n\text{Sn}^{(4-n)+}_{\text{aq}}$ ($n = 1-3$), are ubiquitous at ng L^{-1} concentrations in natural waters, including both marine and fresh water sources. The latter authors also determined that large quantities of butyltin species also occurred in Lake Michigan where anthropogenic sources are believed to be responsible. These findings underscore the significance of methyltins as intermediate transport species and their availability for further biological or non-biological transformations (15) in aquatic environments. Nonetheless, both of the above reports failed to establish whether tetramethyltin was present in natural waters, because of the inability of the methods used to effectively trap this compound during the combined pre-concentration purge and reductive derivatization steps employed to generate volatile organotin hydrides necessary for tin-specific detection,



In our continuing studies on the environmental degradation of commercial organotin compounds (16) and the involvement of methylstannanes as metabolic intermediates (7,17), we have sought to devise trace speciation methods capable of insuring detection of these tin species along with appropriate pre-concentration and derivatization without loss, decomposition, or alteration of their basic molecular features.

In this paper we describe development of a system employing a purge and trap (P/T) sampler, which collects and concentrates volatile organotins from water samples, coupled automatically to a gas chromatograph (GC) equipped with a commercial flame photometric detector (FPD) modified for tin-specific detection (18). The system was applied to the analysis

Some workers regard biomethylation of heavy metals or metalloids as a substantial pathway for observed (1) transport of certain elements in the environment. Whether by enzymic or by abiotic chemical means, such translocation of heavy elements, exemplified by methylmercury or methylarsines, can present adverse ecological impacts and human health problems if undetected. This concern is similarly expressed for those metals in widespread commercial use which may enter critical biogeochemical cycles (2).

Recent attention has focussed, for example, on reports of biological (3,4) and abiotic (5) formation of volatile tetramethyllead in aquatic media with its apparent large-scale transport into the atmosphere (6). Tin's chemical similarities to lead also imply its widespread environmental formation and gaseous transport as hydrophobic tetramethyltin (Me_4Sn). Biogenesis of this molecule, though not heretofore detected in the aquatic environment, seems reasonable on the basis of recent evidence for in vitro methylation of various inorganic tin and organotin compounds by microbes isolated from the Chesapeake Bay (7,8) and by viable sediments from San Francisco Bay (9) or Canadian fresh water lakes (10). Consequently, just as with the better established biogeochemistry of lead (11), environmental transformations of tin are of current wide interest because of the diverse and significant anthropogenic inputs via commercial materials and effluents (12). Especially important in this connection is development of methods permitting accurate speciation of methylstannanes present in aquatic media, both in field samples and controlled laboratory experiments. Essential to this problem is the requirement that measurements be capable of both rapid non-destructive molecular separation and element-selective detection at environmental trace concentrations.

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of a series of water samples obtained from the Chesapeake Bay at both industrially polluted and relatively pristine sites (8) and examined by the P/T-GC-FPD system. The field findings were compared with a laboratory reexamination by an independent GC-mass spectrometric system of the volatile metabolites of a tin-metabolizing Pseudomonas isolate from Chesapeake Bay previously described by us (7). In addition to evidence for the presence of variable quantities of tetramethyltin in Chesapeake Bay waters, we unexpectedly found other volatile tin species in the form of methylstannanes, $(\text{CH}_3)_n\text{SnH}_{4-n}$, for which presumptive evidence of microbial mediation is presented on the basis of the Pseudomonas study.

Experimental

Materials and Chemical Procedures. Laboratory glassware used for preparation, storage, and dilution of inorganic tin and organotin solutions was cleaned prior to use by leaching with aqueous dilute (5 to 10 percent) nitric acid.

The organic and inorganic tin compounds used for the preparation of standard solutions were obtained from commercial suppliers and used with no further purification. Inorganic tin solutions were prepared at concentrations of 1000 mg L^{-1} in deionized water. Organotin solutions were prepared at concentrations of 200 to 1000 mg L^{-1} , in spectrograde methanol, depending on each compound's solubility. Deionized water of 15 to 18 M Ω -cm resistivity obtained from a Milli-Q Reagent-Grade water system (Millipore, Bedford, MA), was used for dilution of all stock solutions to working strengths of 0.05 to 0.2 mg L^{-1} . Working solutions were prepared just prior to use. Fresh solutions (4 percent w/v) of sodium borohydride in deionized water were prepared from NaBH_4 pellets (Aldrich Chemical Co., Inc., Milwaukee, WI). Occasionally, trace amounts

of stannane were detected in the borohydride solution (13,14), but these were sufficiently small that no further purification of the borohydride was required.

Calibration solutions of gases, such as $(\text{CH}_3)_4\text{Sn}$, $(\text{CH}_3)_2\text{S}_2$, and $(\text{CH}_3)_2\text{S}$, were prepared by direct condensation of measured volumes of each gaseous component into a glass dilution vessel fitted with vacuum-tight glass and teflon valves (J. Young Scientific Glassware, Ltd., London, England), and septa. A measured volume of gas(es) (about 0.03 mmol, 0.65 cm³, STP) was condensed at liquid nitrogen temperatures into a small side arm interconnector between the vacuum line and dilution flask. The dilutor and interconnector sections were valved closed, removed from the vacuum system, and shaken for 30 min. Working solutions of tetramethyltin, with and without combinations of methylsulfides, were freshly prepared by appropriate 1:1000 dilutions in screw-capped septa vials to give typical concentrations of about 0.1 to 0.2 mg L⁻¹ as Sn and of about 0.03 to 0.09 mg L⁻¹ as S. The storage stability of Me_4Sn improved in the mixed solutions with the methylsulfides, possibly by process of complexation, hence mixed solutions were used for calibrations. More stable standard solutions of Me_4Sn used for the purge time optimization experiments were prepared. Ten μL of the 0.1 mg L⁻¹ standard in methanol was added by pipette to 10 mL deionized water for purging in the analysis. Methanol did not cause detection interferences in these amounts.

Biological Procedures. Pure cultures of a tin-resistant *Pseudomonas* species isolated (7a) from the Chesapeake Bay were used as the inoculum in studies of microbiological transformations of inorganic tin(II) and tin(IV). Sterile Nelson's agar medium (7b), stressed with 10 mg L⁻¹ of tin(II) (as SnCl_2) or tin(IV) ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) (added after autoclaving) or

free of tin stress (control), was hardened into slants in sterile 15 mm O-ring, 20 mL borosilicate glass tubes. Immediately after the slants were inoculated, the tubes were capped with sterile 15 to 9 mm O-ring adaptors incorporating a high-vacuum glass and teflon Young valve. Experiments were controlled with sterile and inoculated tubes of tin stressed and unstressed media, respectively. After incubation (23 ± 2 °C) for various intervals the respirant atmosphere above the slants was removed for analysis by gas chromatography-mass spectrometry (GC-MS). On the vacuum line, the atmosphere above the slants was expanded into a glass U-trap chilled with liquid nitrogen and the non-condensable gases were pumped from the sample in the liquid N_2 -cooled trap. After the trap warmed to room temperature, helium carrier gas from the GC was redirected through the trap to carry the contents into the GC-MS system.

• A calibration mixture for the identification of slant atmospheres was generated by the reduction of the di- and trimethyltin chlorides with $NaBH_4$ in the presence of gaseous Me_4Sn in a glass culture tube capped tightly with a Mininert valve. One milliliter gas samples were injected into the GC-MS using a gas-tight syringe.

Chesapeake Bay Sample Collection. Chesapeake Bay and Baltimore Harbor water samples were collected in the early spring and late fall aboard the R/V Ridgely Warfield. Samples were also collected from shore stations in Baltimore Harbor during the spring, summer, and fall months as indicated in Table 1. Surface (5 to 10 cm below the surface) and bottom (~ 40 cm above the bottom) samples were taken from each site. Samples were collected in 3.8 liter amber glass bottles, held upright in a lead-weighted wooden frame. Prior to use, sample collection bottles

were cleaned by dilute nitric acid leaching. No tin impurities from the glass sample bottles were observed over repeated use. After collection, the samples were immediately stored in an ice-cooled container, either in the 3.8 liter sampling bottles or in smaller 1 liter glass bottles. In the laboratory, samples were refrigerated (2 to 4 °C) until 10 to 15 minutes prior to analysis, at which time 10 mL aliquots were transferred into glass sample tubes used as purge vessels, and covered with teflon-lined screw caps. The samples were warmed to room temperature in a 20 °C water bath.

The P/T-GC-FPD System. A Hewlett-Packard (Avondale, PA) (HP) Model 5730 Gas Chromatograph (GC) equipped with an HP flame photometric detector (FPD) and an HP Model 7675A Purge and Trap Sampler (P/T) was used for this study. A block diagram of the P/T-GC-FPD system is shown in Figure 1. Zero grade gases (certified for total hydrocarbon as $\text{CH}_4 < 0.5$ ppm) are recommended by the manufacturer for use as the carrier and purge gas. Aqueous samples, usually 10 mL, were analyzed in 15 mL, 16 x 125 mm borosilicate glass purge vessels. A typical cycle of the automatic (microprocessor controlled) P/T involved: 5 min pre-purge with zero grade N_2 flow to equilibrate the sorbent trap at room temperature and 10 min sample purge [gas stripping (19,20)] with zero grade N_2 at 20 mL min^{-1} flow rate (total purge volume = 200 mL). Volatile trace components purged from the samples were collected in the P/T on a 60/80 mesh Tenax-GC (Alltech Associates, Arlington Heights, IL) (21,22) filled trap at ambient temperatures. The desorb cycle, which automatically followed the purge cycle, rapidly heated the trap to 250 °C for 5 min while the carrier gas was directed by a 6-port valve through the trap

and into the GC column. Column temperature programming began automatically with the desorb cycle in the P/T. The Tenax trap was heated an additional 50 °C for 3 min to vent any residue not removed by the desorb heating.

Chromatographic separations were made on 2 mm ID x 6 ft glass columns co-packed with 3 percent SP-2401 and 10 percent SP-2100 on 80/100 mesh Supelcoport (Supelco, Inc., Bellefonte, PA). The column oven was generally maintained isothermally at 30 °C for separating the methylstannanes. Temperature programming ($T_1 = 30$ °C for 4 min to $T_2 = 100$ °C at a rate of 16 °C min^{-1}) was used for organostannanes less volatile than butyltin trihydride or the methylstannanes. Zero grade N_2 was used as the carrier gas with a flow rate of 20 mL min^{-1} .

The HP flame photometric detector was modified to permit tin-selective detection of SnH emission in a hydrogen-rich flame (18). The flame was supported by a mixture of H_2 at 110 mL min^{-1} , air at 70 mL min^{-1} , and N_2 (carrier) at 20 mL min^{-1} . The detector temperature was 200 °C. A 600 nm cut-on interference filter (bandpass 600 nm to 2000 nm), (Ditric Optics, Inc., Hudson, MA) was used to transmit the SnH emission lines (19) and bands in the red region with maximum signal. GC-FPD tin selectivity (13) to sulfur, determined from calibrations of Me_4Sn and CS_2 , were 46,700 and 101,200 (molar basis) from a non-linear two-step regression. Water samples were also analyzed in the sulfur mode of the FPD with the flame conditions as recommended by the manufacturer, i.e., 50 mL min^{-1} for H_2 , 50 mL min^{-1} for air and 10 mL min^{-1} for O_2 , and with the 394 nm interference filter supplied by the manufacturer for sulfur-selective detection as S_2 . Deposits from combustion products which collected in the detector seriously reduced the detector sensitivity. Repeated

injections of a fluorine-containing organic compound, in this case, $\text{m-C}_6\text{H}_4\text{F}_2$, generally restored the detector sensitivity. The output signal from the FPD was recorded simultaneously on a strip chart recorder (1 mV full scale) as well as on a Shimadzu Model C-R1A Chromatopac (Columbia, MD) digital integrator-plotter.

GC-MS System. Electron impact (70 eV) mass spectral data were obtained with an Extranuclear (Pittsburgh, PA) SpectrEL quadrupole mass spectrometer interfaced with a Fisher series 4400 Victoreen gas chromatograph. Samples were introduced into the GC-MS system by syringe injection or by the vacuum line injection method. The background pressure in the mass spectrometer with helium carrier flow was 10^{-6} Torr. The GC column, 1/8" OD x 6 ft glass-lined stainless steel, was co-packed with 3 percent SP-2401 and 10 percent SP-2100 on 80/100 mesh Supelcoport. A helium carrier flow rate of 20 mL min^{-1} was used. The GC oven was operated isothermally at 30 °C or 70 °C.

The GC-MS system is interfaced with an on-line Computer Automation, Inc. computer and software from Teknivent, Inc. (St. Louis, MO). This system provided two modes for data acquisition: mass spectrum mode and selected ion monitoring or multiple ion detection (ion chromatogram) mode. Major representative peaks in isotope multiplets of tin were selected from fragmentation patterns (Figure 2A) of mass spectra of tetramethyltin ($m/e = 120, 135, 150, 165$) for use in the selected ion monitoring mode.

Minimum detectable amounts of tetramethyltin in the mass spectrum ($m/e = 100$ to 180) scanning mode were 35 ng (as Sn) in pentane and 50 to 100 ng (as Sn) in a water matrix, the difference being attributed not only to the varying solubility of Me_4Sn in the matrices, but also to the

interference of detector response by the solvent. At these concentrations dissimilarity indices of 0.100 to 0.300 (0.000 is a perfect fit, 50.00 is not a fit) were obtained upon comparison with MS data for tetramethyltin stored in the user NIH/EPA Chemical Information System (24). One or two data points per second were collected in the multiple ion detection mode to visualize the ion chromatograms. Hard copies of the data stored on floppy diskettes were plotted with a Complot Model DP-1 digital plotter (Houston Instruments, Bellaire, TX).

Volatilization of Organotins in the P/T Cycle. Non-volatile organotin species (cations) were volatilized by a modified hydride reduction process (13,14) using an excess of 4 percent aqueous sodium borohydride solution. Analyses for volatile organotins in water did not require additions of borohydride. The purge vessel, containing water samples to be analyzed for volatile species, was attached to the P/T just prior to the 5 min pre-purge. For hydride reduction of the non-volatile species, 100 to 500 μL of 4 percent NaBH_4 were added to the purge vessel containing the sample within the last minute of the Tenax trap pre-purge, and immediately before initiating the 10 min N_2 sample purge. This procedure kept the reaction time for the reduction process to a minimum of 10 minutes. It also served to minimize the loss of volatile hydrides possibly formed in the purge vessel on the initial addition of the borohydride. Simultaneous analysis for volatile and non-volatile organotin species was accomplished by using the procedure for the reduction process. No pre-treatment of the water sample is necessary for use with the P/T-GC-FPD system.

Solution Calibrations and Quantitation of Field Samples.

Calibrations were made for organostannanes with borohydride reduction of the corresponding organotin chlorides in deionized water and in Bay

water. In general, unfiltered Bay water was purged with zero grade N_2 and refrigerated (2 to 4 °C) prior to use with the standards. Nanogram quantities of the tin compounds were pipetted in microliter amounts to the purge vessel containing 10 mL of Bay or deionized water. The plots in Figure 3 illustrate typical calibration curves made with Me_2SnCl_2 , $n-Bu_2SnCl_2$, and $PhSnCl_3$ in Bay water with BH_4^- reduction employing GC column temperature programming. Typical calibrations for tetramethyltin in Bay water and deionized water are shown in Figure 4. Concentrations of Me_4Sn in Bay water samples were also determined using the method of standard additions with extrapolation to the negative intercept of the X-coordinate ($ng\ 10\ mL^{-1}$) as in Figure 5.

Results and Discussion

Analysis of Volatile and Non-volatile Aqueous Organotins.

In environmental studies, it is important to know if the chromatographically speciated volatile organotin hydrides were present in the environment as hydrides or were generated only during the hydride reduction process. The relatively short analysis time, the absence of sample preparation and the small sample sizes used in this study facilitated duplicate analyses of water samples for differentiation of organotins as volatile or non-volatile species. Although both volatile and non-volatile species were trapped simultaneously, we analyzed the Bay water samples in duplicate to distinguish between the methylstannanes present in the Bay water and those generated by hydride reduction in the laboratory. Figure 6 shows the chromatogram of duplicate samples of standards in deionized water with the method used for Bay water analysis. Without the addition of $NaBH_4$, the tetramethyltin standard was purged from the sample while the dimethyltin cation remained in solution. When $NaBH_4$

was added, both volatile species were observed, there being no apparent loss of Me_4Sn as a result of hydride formation. The chromatographic separation of the methylstannanes ($\text{Me}_n\text{SnH}_{4-n}$, $n = 1-4$) mixture is shown in Figure 7. The hydrides ($n = 1-3$) were formed by BH_4^- reduction of the corresponding chlorides in the presence of Me_4Sn .

Calibration Results. Regression analyses are given in Table 2 for various calibration curves of species used in this study. The detection limits of the P/T-GC-FPD system at 95 percent confidence level (25) are given for various species reduced in sparged Bay water as well as for non-reduced species. A comparison of the slopes indicates a trend not only for the detectability of the various species, but also a trend in the relative rates of hydridization. While all hydride reduction reactions were limited to 10 minutes, it is expected that the more Lewis acidic methyltin cations would undergo a biomolecular electrophilic substitution ($\text{S}_{\text{E}}2$) reaction more completely in the given time than the butyl or phenyl analogs. Comparison of the slopes for the methyltins with the butyl- and phenyltins gives evidence to support this. Figure 8 also shows the difference in completeness of reduction for $\text{Me}_2\text{Sn}^{2+}$ and $\text{Et}_2\text{Sn}^{2+}$ with different purge times. Within a given series, increased alkyl-substitution produced larger slopes indicating more efficient H^- additions in the same reaction time.

Although Me_4Sn was not affected by the purge time as with organotin hydride formation, it is evident from Figure 4 that the detection limits are lower than for the methyltin hydrides. The tetramethyltin standards in water (see experimental) were not stable due to the hydrophobicity of Me_4Sn . Consequently, the values for Me_4Sn in Bay water samples may be overestimated.

Consideration of Parameters for Optimizing the P/T-GC-FPD Method.

Although our results are reported in concentrations of $\mu\text{g L}^{-1}$, only 10 mL samples were used in present analyses. Larger samples presumably yielding lower detection limits for the system require much longer purge times or faster purge flow rates. This is necessary in order to provide adequate purge volume relative to the size of the sample as defined by equation 3 derived here for 95 percent trapping efficiency in dynamic gas stripping from a liquid (21):

$$t_{0.05} = 3 (V_G + K_i \cdot V_L) / F. \quad (3)$$

Here $t_{0.05}$ is the time required for 95 percent analyte recovery, V_G is the headspace volume, K_i is the partition coefficient of the organotin solute, V_L is the volume of the liquid sample, and F is the purge flow rate. Increasing the purge flow rate for larger samples leads to undesirable breakthrough of the more volatile analyte species (20,21,23) and less trapping uniformity on the Tenax-GC trap. Increasing the purge time not only makes the analysis tedious, but also increases the likelihood of eventual breakthrough of the most volatile species in mixtures, as shown in Figure 3.

Mixtures of Me_2SnCl_2 , Me_4Sn , and Et_2SnCl_2 in 10 mL deionized water (1 ng as Sn for each compound) were subjected to borohydride reduction during the purge cycle. The purge times were varied to determine the optimal purge time required for a fixed purge flow rate of 20 mL min^{-1} . The relative extent of hydride reduction for $\text{Me}_2\text{Sn}^{2+}$ and $\text{Et}_2\text{Sn}^{2+}$ is also reflected in this series. After a 10 min purge (200 mL purge volume), found to be optimal, quantities of all trapped species appear to decrease as a result of breakthrough of the more volatile species.

Another consideration in our trapping procedure and purge time was the resulting retention times of the components on the GC column. During the trapping process, the purged volatiles flow upward onto the trap and move further into the trap during the purge time. The flow of the gas through the trap is reversed during desorption into the GC. Consequently, the longer the sample is purged, the longer will be the resulting retention time on the GC column as would be expected due to the longer travel path in the trap.

Figure 8 also demonstrates the relationship between uniform trapping and the (ideal) Gaussian distribution of the analyte peak shape on the GC column. We found the 10 minute purge again optimal in this test.

If larger samples are needed for an analysis, sequential purge and trapping offers a possibility. Curve (C) in Figure 4 is a calibration of Me_4Sn using a collection of one, two, and three 10 mL samples with sequential 10 min purge cycles finally followed by desorption. Compared to curve (B) where a single 10 minute purge is used for the same total quantity of Sn, sequential purging gives adequate results up to perhaps three consecutive 10 minute purges. Deviations between curves (B) and (C) then begin to increase due to loss of sample from breakthrough on the trap.

Speciation of Organotins in Bay Water Samples. Results from analyses of samples collected during the spring month from an urban run-off in Baltimore Harbor (Jones Falls) gave evidence of the presence of tetramethyltin as well as tin-containing species more volatile than Me_4Sn (Figure 9). These water samples were also analyzed with the P/T-GC-FPD system in the sulfur mode thus showing that these additional peaks were not sulfur-containing. A calibration mixture of the methylstannanes

($\text{Me}_n\text{SnH}_{4-n}$, $n = 1-3$) volatilized by hydride reduction in the presence of Me_4Sn was later analyzed by the P/T-GC-FPD method. Comparison of the calibration chromatogram with the results from Jones Falls in Figure 9 indicated that there were methylstannanes ($n = 2,3,4$) present in the Bay water. Borohydride was not added to the Bay sample for this analysis. A chromatogram of the calibration mixture analyzed without the addition of NaBH_4 is shown in Figure 9B. This resulted in the sparging and detection of only the volatile Me_4Sn . The amounts of methylstannanes present in this sample were estimated from calibration data to be (in $\mu\text{g L}^{-1}$): Me_2SnH_2 (0.2), Me_3SnH (0.4), and Me_4Sn (0.48). These were the highest estimates of methylstannanes speciated at this site in Baltimore Harbor.

Tetramethyltin was also detected at another site in Baltimore Harbor, Colgate Creek, during the spring months. The method of standard additions (Figure 5) was used to determine the concentration of Me_4Sn in the sample. As much as $0.93 \mu\text{g L}^{-1}$ of Me_4Sn were present in the Bay water sample within a 95 percent confidence interval as indicated by the broken lines.

Baltimore Harbor sites were sampled during a consecutive three week period to assess possible trends in the water composition over a shorter range than experienced with most of the water sampling. These results are given in Table 3. The volatile species shown in the table under Mode I were determined by the P/T-GC-FPD method without the hydride reduction step. Non-volatile species (Mode II) were volatilized, trapped, and detected with the volatile species present in the samples. Generally, no changes in the concentration of the volatile species were observed with the hydride reduction step. An increase in

the amount detected, as with Me_2SnH_2 and BuSnH_3 , indicated that the solvated cations were also present in the water samples along with the respective free stannane. The prevailing GC peak at 1.75 ± 0.04 min has not been completely resolved or identified. The retention time is within the range of both dimethylsulfide (Me_2S) and Me_2SnH_2 . Dimethylsulfide is known to be a microbial metabolite present in environmental water (26); therefore this is a possible interference. However, we find that the concentration of Me_2S would have to be extremely high because the selectivity of our FPD detector to tin over sulfur in the red region of the spectrum (> 600 nm) is several orders of magnitude. Identification of the peak as Me_2SnH_2 would be consistent with our results from the spring sample collection. Inorganic tin (volatilized to SnH_4) was detected in as much as 10 to 20 $\mu\text{g L}^{-1}$ quantities at the urban run-off, Jones Falls. None was detected in Colgate Creek in Baltimore Harbor.

The samples collected in the Chesapeake Bay at Tolly Point, Bloody Point, and Eastern Bay (see Table 1) showed minimal amounts of methyltin species. A peak corresponding to MeSnH_3 was observed in the water samples collected from these three sites with the least amount detected in Eastern Bay, a relatively non-polluted area (8). Trace amounts of Me_2SnH_2 were also detected at the same retention times as those observed in the Baltimore Harbor samples. As much as 0.2 $\mu\text{g L}^{-1}$ was detected in the samples collected at Tolly Point and Bloody Point.

At trace levels, as those observed in Bay water, decomposition of organotin hydrides may be in equilibrium with the production of the stannanes (steady state) which would give the appearance of water stabilized hydrides. The question that subsequently arises is in regard to the formation of the various organotin hydrides (methylstannanes in this case) in aquatic environments.

If methylstannanes were present in the environmental samples analyzed by Braman (13) and Hodge (14), they would not have been detected for the same reason that tetramethyltin was not observed, i.e., removal of the volatile methylstannanes during pre-hydride degassing.

In Vitro Methylation of Inorganic Sn(IV) by Ps 244. We have re-examined previous work from this laboratory (7) to determine the extent of methylation of inorganic tin by an aerobic strain of Pseudomonas 244 isolated from the Chesapeake Bay. The respirant atmosphere above 10 ppm tin-stressed, Sn(IV) and Sn(II), inoculated agar slants and sterile controls were observed using GC-MS after incubation for two weeks. Results of representative ion chromatograms are shown in Figure 10. These were obtained with the selected ion monitoring mode of the GC-MS data system for all major fragment ions, including m/e 120 and 165 corresponding to the major isotopes of Sn^+ and Me_3Sn^+ fragments, respectively. A calibration ion chromatogram showing Me_2SnH_2 , Me_3SnH , and Me_4Sn is also given (Fig. 10E) to identify the peaks from the respirant atmosphere above the Ps sp. slants.

The ion chromatogram of the tin(IV)-stressed Ps sp. inoculated slant showed a methyltin compound at ~ 0.95 min which corresponded to Me_4Sn in the calibration, as well as a very broad methyltin peak obviously more volatile than Me_4Sn . The broadness of the peak is indicative of a decomposition reaction of methyltin species on the GC column during elution. Comparison with the ion chromatogram shows an overlap of the broadened peak with the elution of Me_2SnH_2 and Me_3SnH in the calibration chromatogram. However, the mass spectra of Me_3SnH and Me_2SnH_2 , as in figure 2B and 2C, show that the abundance of m/e 165 is small (Me_3SnH) or nonexistent (Me_2SnH_2).

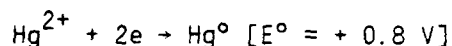
Generally, organotin hydrides are considered to be unstable in aqueous or aerobic environments. In oxidant-free environments, however, their lifetimes are expected to be considerably longer. For example, organotin monohydrides can be stored for a practically unlimited time without decomposition, while the dihydrides are stable for several weeks and the trihydrides only for several days. Upon decomposition, however, the organotin hydrides tend to form R_4Sn , Sn , and H_2 in stoichiometric amounts (27). The appearance of the broadened peak in the ion chromatogram for the $Sn(IV)$ -stressed inoculated slant at $m/e = 165$ would therefore indicate decomposition yielding Me_4Sn since this fragment ion is not a major fragment of Me_3SnH or Me_2SnH_2 .

While a small amount of a volatile methyltin compound corresponding closely to Me_3SnH was also observed above the inoculated slant stressed with tin(II), none was detected in the atmosphere above sterile controls stressed with either tin(IV) or tin(II). These experiments demonstrating methylation of tin by the Ps microorganisms not only confirm the previous work from this laboratory regarding the biomethylation of tin(IV) (7) and the more recent reports of others (8-10), but they also support the idea that methylstannanes present in the Chesapeake Bay may arise in a microbially mediated pathway.

Repeated experiments using the Ps sp. slants stressed with inorganic tin gave irreproducible production of methylstannanes. Because the solidified agar slants are inoculated on the surface, methylation of the tin in the medium depends on the bioavailability of the tin, i.e., the proximity and molecular form of the tin at the surface of the agar slant. Recent studies (8) have indicated a non-uniform bacterial response to $Sn(IV)$ in agar media.

Bioreduction by Ps 244. Reduction processes are defined as (1) the addition of hydrogen, (2) the addition of electrons, and (3) the removal of oxygen.

Bioreduction of metals and metalloids is considered commonplace in the environment. The Pseudomonas strain 244 has been observed to have the capability to reduce mercuric ions to elemental mercury gas under aerobic conditions (7):



Bioreductions have also been known to generate methylmetals as with the production of trimethylarsine (28) involving from 2 to 4 electron steps. Chen and Focht (29) reported bioreduction plus biomethylation by Ps sp. of As(V) and As(III) in sediments to form arsine and methylarsines and pure cultures (figure 11). We can therefore presume that the Ps organism has the potential to further reduce methylated tin cations (figure 11) to the corresponding hydrides since it seems well within the physiological redox range for the couple $\text{Sn(IV)} \rightarrow \text{Sn(II)}$ [$E^\circ = + 0.15 \text{ V}$]. The reported instability and decomposition of organotin hydrides (methylstannanes) may well account for the presence of tetramethyltin in Bay water samples as well as in the in vitro experiments performed for this study. Kinetic information on decomposition (protolysis or oxidation) rates of $\text{Me}_n\text{SnH}_{4-n}$ in sea water are now required to evaluate their flux.

Conclusions

We have described a method which combines readily available commercial instrumentation (appropriately modified for tin-selective detection) with classical volatilization processes. This extended method permits non-destructive speciation and detection of trace organotins, including

hydrophobic species, in aqueous systems. We have also demonstrated that volatile organotin compounds (including hydrides presumably unstable in water) can be stored for periods of time on Tenax-GC at ambient temperatures and desorbed for GC analysis without decomposition. The P/T-GC-FPD system detection limits determined from linear calibrations for organotins in water at the 95 percent CI were .013 to .052 $\mu\text{g L}^{-1}$, depending on the individual organotin species. However, methyltin species ($n = 2,3,4$) were detected on concentrations as low as 0.005 $\mu\text{g L}^{-1}$. Greater selectivity of speciation can be achieved by using capillary GC separations.

Water samples collected from the Chesapeake Bay and Baltimore Harbor were analyzed by the P/T-GC-FPD method. We detected varying amounts of methyltin species, including not only hydrophobic Me_4Sn , but also, quite unexpectedly, methylstannanes ($\text{Me}_n\text{SnH}_{4-n}$, $n = 1-3$). Although biogenic origins are suspected, there is an apparent relationship between the concentration gradients observed for the methylstannanes in the sampling locations and tidal fluxes, run-off, and anthropogenic activity as indicated by Hallas (8).

Re-examination of previous work from this laboratory by GC-MS has confirmed the biomethylation, possibly coupled with bioreduction, of Sn(IV) by a Pseudomonas sp. (isolated from the Chesapeake Bay) to form methylstannanes ($n = 2,3,4$). The production of Me_4Sn in these experiments may result from decomposition of the methyltin hydrides under aerobic conditions.

The results from this work open new areas of study for determining biological pathways and fluxes of organotins in the service environments.

Acknowledgments

We gratefully acknowledge the generous support of the Chesapeake Bay Institute and the Johns Hopkins University for making shiptime available on the R/V Ridgely Warfield. We are indebted to Professor R. Colwell and her associates for assistance in field sampling. We also wish to acknowledge the experimental assistance of Mr. Craig Freden and Miss Patricia John.

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TABLE 1

Chesapeake Bay and Baltimore Harbor Collection Sites and Water Parameters

Sample Site	Collection Method	Location	Collection Dates	Station Depth,m	Salinity, S ₀ /‰ ^{a,b}	pH ^a
Jones Falls (Baltimore Harbor)	ship	76°36'14"W	03/25/80	6.0	8.29	7.20
		39°16'58"N	12/08/80	3.3	13.2	8.07
	land	76°36'19"W	04/22/80	2.0		
		39°17'14"N	07/09/80	0.7		
			08/08/80	1.0		
			09/09/80	1.0		
			09/30/80	1.3		
			10/07/80	1.0		
			10/15/80	1.2		
			12/15/80	3.3		
Colgate Creek (Baltimore Harbor)	ship	76°32'15"W	03/25/80	8.3	7.78	7.42
		39°15'20"N				
	land	76°32'8" W	04/22/80	1.3		
		39°15'28"N	07/09/80	1.5		
			08/08/80	1.1		
			09/09/80	1.3		
			09/30/80	1.7		
			10/07/80	1.0		
			10/15/80	1.2		
			12/15/80	1.0		
Tolly Point (Chesapeake Bay)	ship	76°25'75"W 38°55'80"N	12/09/80	9.6	16.2	8.27
Bloody Point (Chesapeake Bay)	ship	76°23'90"W 38°49'80"N	12/09/80	30.5	16.6	8.43
Eastern Bay (Chesapeake Bay)	ship	76°17'0.5"W 38°51'0.7"N	12/09/80	10.1	17.2	8.14

^a at 1 m depth^b S₀/‰ = parts per thousand

TABLE 2
Regression Analysis of Calibrations in Bay Water

Species	Mean $t_r \pm$ S.E. ^a	Detection Limit ^b		Regression		N	R	Relative sensitivity of regression slopes
		$\mu\text{g L}^{-1}$	$\mu\text{g L}^{-1}$	Slope $\pm$ S.E.	Slope $\pm$ S.E.			
SnH_4	0.88 ± 0.07	0.030	0.030	21.6 ± 2.8	21.6	10	0.937	0.012
MeSnH_3	1.24 ± 0.04	0.053	0.053	604 ± 126	604	6	0.923	0.33
BuSnH_3	3.98 ± 0.08	0.018	0.018	329 ± 24	329	7	0.987	0.18
Me_2SnH_2	1.57 ± 0.04	0.013	0.013	6683 ± 367	6683	7	0.993	3.76
$\text{Bu}_2\text{SnH}_2^c$	11.12 ± 0.06	0.037	0.037	726 ± 110	726	7	0.947	0.40
PhSnH_3^c	8.27 ± 0.04	0.023	0.023	265 ± 24	265	7	0.979	0.14
Me_4Sn	2.86 ± 0.11	0.023	0.023	1777 ± 186	1777	11	0.954	1.00
Me_2S	1.71 ± 0.03	--	--	--	--	--	--	--

^aDetermined with column oven $T = 30^\circ\text{C}$

^bP/T-GC-FPD System detection limits based on 10 mL sample solutions

^cDetermined with oven-temperature programming

TABLE 3

Three-Week Baltimore Harbor Sampling

Site ^c	Collection Date	SnH ₄ (0.88 ± 0.07) ^d			Me ₂ SnH ₂ (1.57 ± 0.04) ^d			Me ₃ SnH (2.16 ± 0.03) ^d			Me ₄ Sn (2.86 ± 0.11) ^d			BuSnH ₃ (3.98 ± 0.08) ^d		
		Mode I ^d	Mode II ^{e,f}	Mode I ^{g,f}	Mode II ^{g,f}	Mode I ^{h,f}	Mode II ^{h,f}	Mode I ⁱ	Mode II ⁱ	Mode I ^f	Mode II ^f	Mode I ^f	Mode II ^f	Mode I ^f	Mode II ^f	Mode I ^f
		0.92 ± 0.01 ^b		1.75 ± 0.04 ^b		2.23 ± 0.13 ^b		2.99 ± 0.05 ^b		4.16 ± 0.06 ^b						
JFS	09/30/80	---	10 ⁻²⁰	< 0.01	< 0.01	---	< 0.01	---	< 0.01	---	---	0.05-0.1	0.2-0.3	---	---	---
JFS	10/07/80	---	0.3-0.5	< 0.01	< 0.01	---	---	---	---	0.2-0.3	0.2-0.3	---	---	---	---	---
JFS	10/15/80	---	3-4	---	---	---	---	---	---	---	---	---	---	---	---	---
JFB	09/30/80	---	0.6-0.7	---	< 0.01	---	---	---	---	---	---	0.05-0.1	0.05-0.1	---	---	---
JFB	10/07/80	---	0.2-0.3	0.02-0.05	0.05-0.1	---	0.01-0.02	---	---	0.05-0.1	0.05-0.1	---	---	---	---	---
JFB	10/15/80	---	0.7-0.8	< 0.01	< 0.01	---	---	---	---	---	---	---	---	---	---	---
CCS	09/30/80	---	---	< 0.01	0.5-0.1	---	< 0.01	---	< 0.01	0.01-0.05	0.01-0.05	0.05-0.1	0.05-0.1	---	---	---
CCS	10/07/80	---	---	< 0.02	< 0.02	---	< 0.01	---	< 0.01	---	---	---	---	---	---	---
CCS	10/15/80	---	---	< 0.005	< 0.005	---	< 0.005	---	< 0.005	< 0.01	< 0.01	---	---	---	---	---
CCB	09/30/80	---	---	< 0.02	< 0.02	---	---	---	---	0.15-0.3	0.15-0.3	0.05-0.1	0.05-0.1	---	---	---
CCB	10/07/80	---	---	< 0.02	< 0.02	---	---	---	---	---	---	---	---	---	---	---
CCB	10/15/80	---	---	< 0.005	< 0.005	---	---	---	---	---	---	---	---	---	---	---

^d Identified species with mean $\bar{x}$ ± S.E. as determined with standards^e In $\bar{x}$ ± S.E. determined from samples over three-week period^f Surface samples, B = bottom samples; JF = Jones Falls, and CC = Colgate Creek^g Mode I = samples analyzed for volatile species without addition of NaBH₄ for reduction^h Mode II = samples with NaBH₄ added, gives small mean, mainly is for volatile and non-volatile speciesⁱ Quantities expressed in concentrations of $\mu\text{g l}^{-1}$ ^j Counting species for Me₂SnH₂

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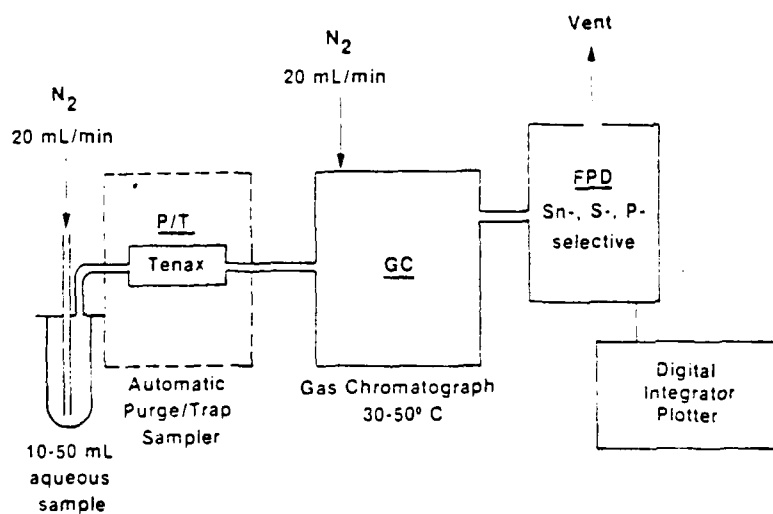
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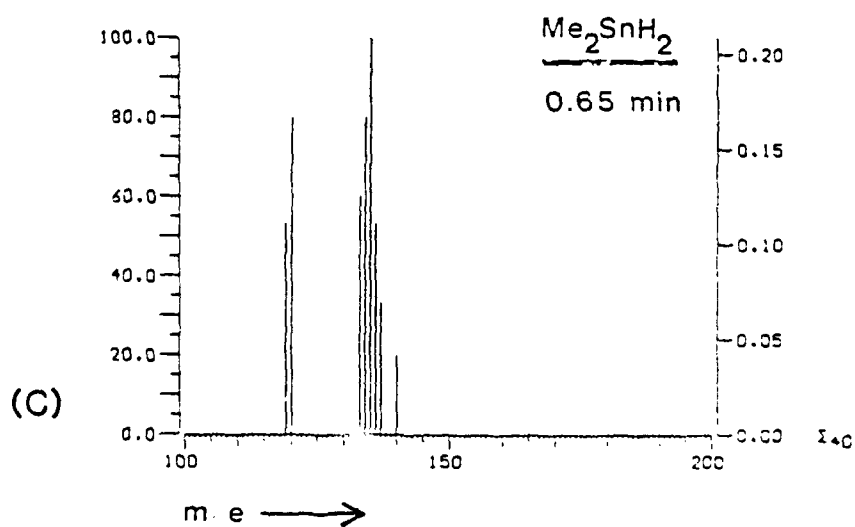
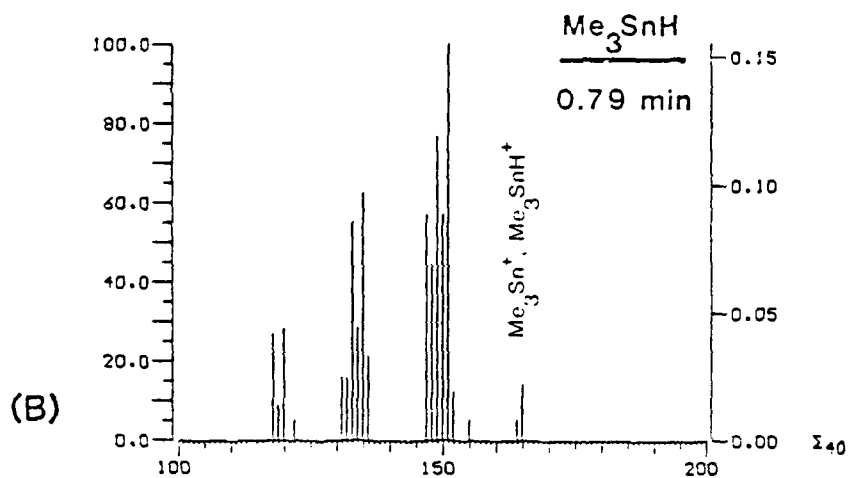
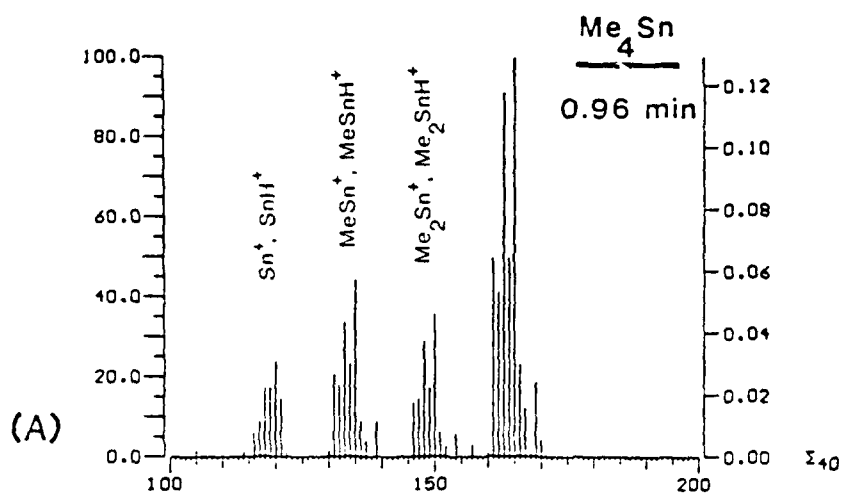
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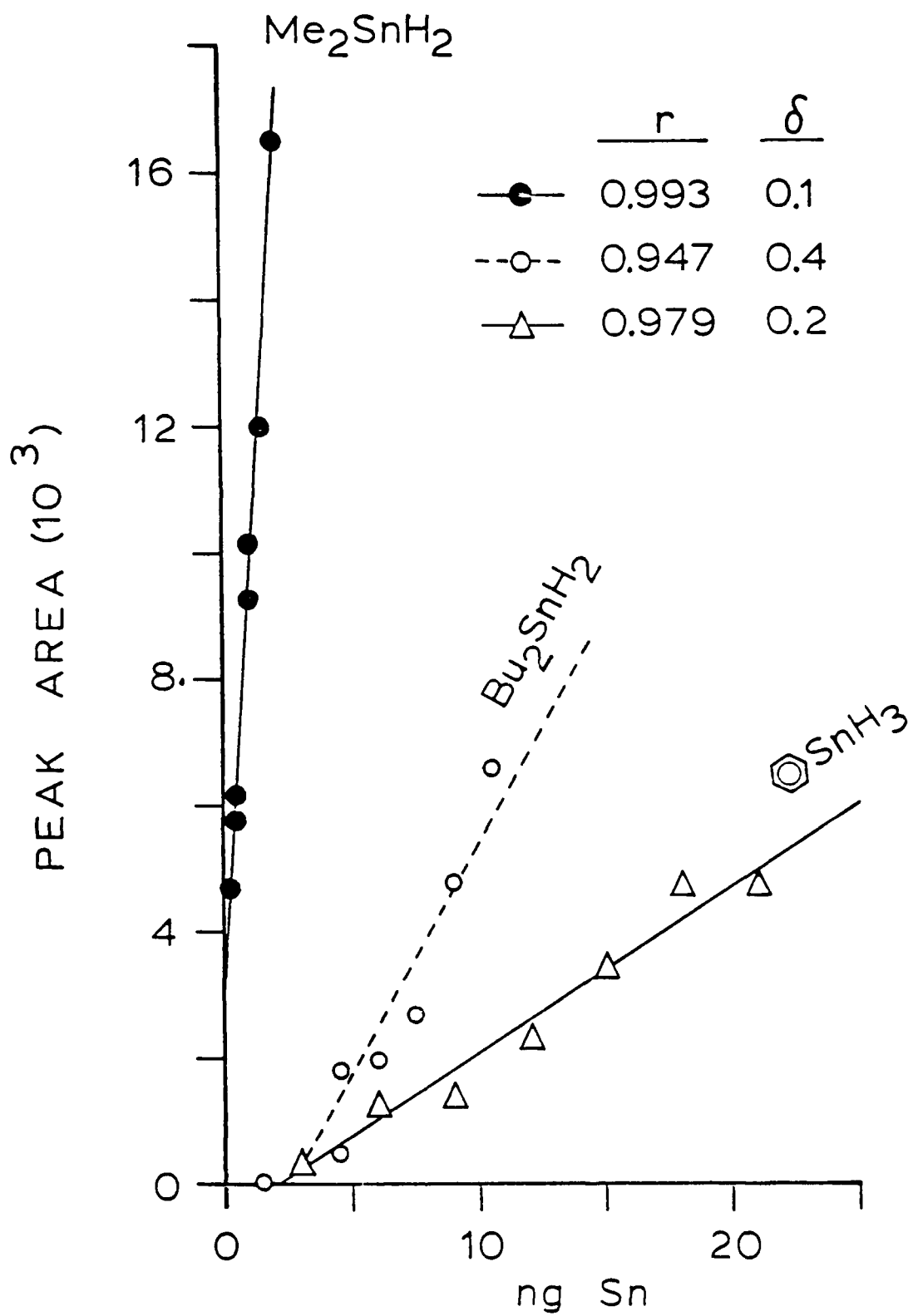
Figure Captions

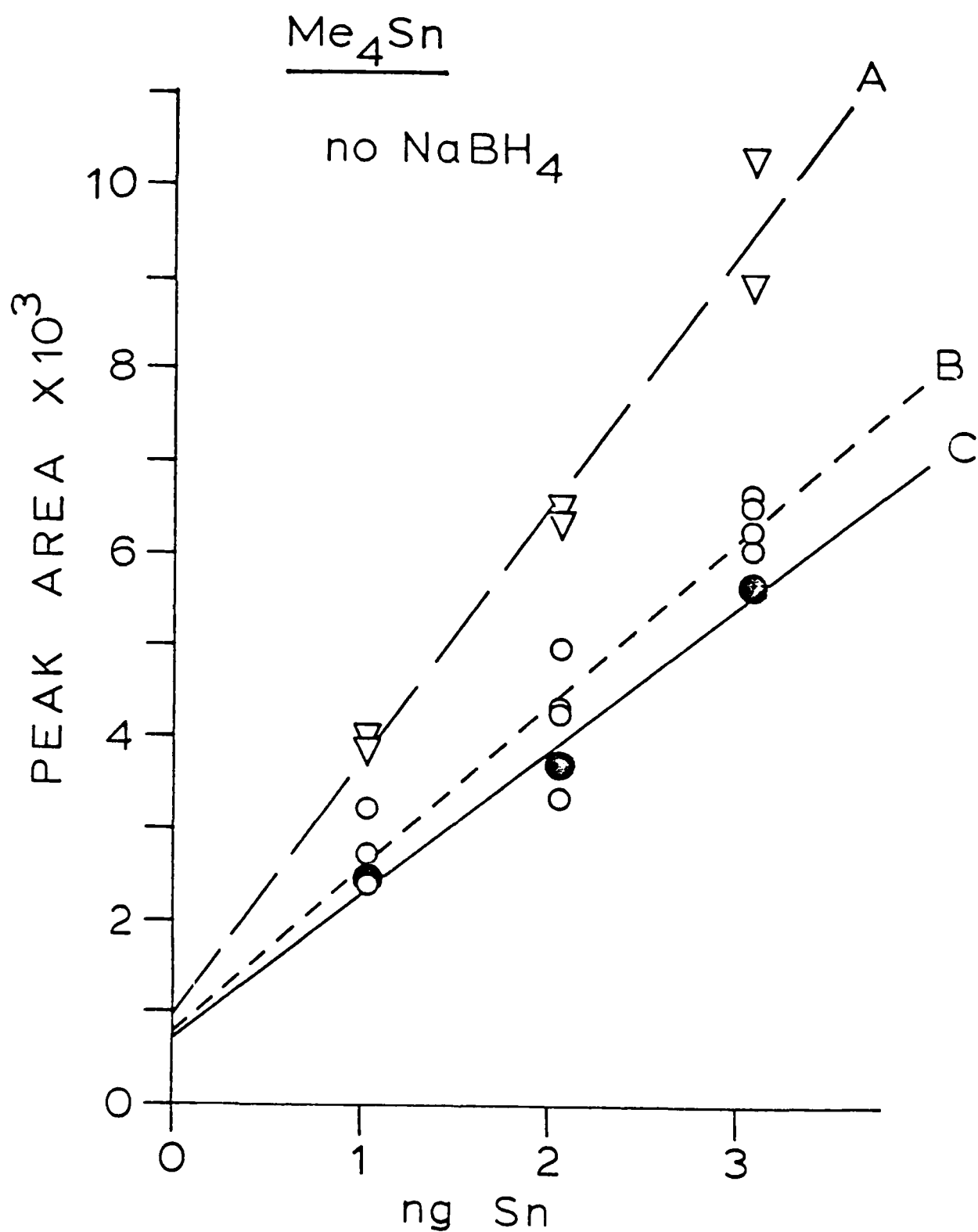
1. Block diagram of the P/T-GC-FPD system indicating typical operating parameters.
2. Mass spectra of (a) tetramethyltin, (b) trimethyltin hydride, and (c) dimethyltin dihydride, obtained by GC-MS at 70 eV, showing principal masses selected within characteristic tin isotope multiplets of the fragments indicated. Spectra were obtained during the GC peak maxima at 0.96 min, 0.79 min and 0.65 min for Me_4Sn , Me_3SnH , and Me_2SnH_2 , respectively, with column temperature at 70 °C.
3. Typical GC calibrations of simultaneously reduced Me_2SnH_2 , Bu_2SnH_2 , and PhSnH_3 using temperature programming with P/T-GC-FPD system. Correlation coefficients (r) and system detection limits in ng (δ) are also indicated.
4. P/T-GC-FPD calibration of Sn response in $\text{Me}_4\text{Sn}/\text{Me}_2\text{S}$ mixture in (a) deionized water and (b) Bay water. Curve (c) shows additive effect of sequential sample purging of Sn as Me_4Sn in Bay water.
5. Extrapolation for concentration determination of Me_4Sn in Bay water from Colgate Creek in Baltimore Harbor using method of standard additions with $\text{Me}_4\text{Sn}/\text{Me}_2\text{S}_2$ standard.
6. Gas chromatograms of duplicate samples of methyltin standards in deionized water (A) with borohydride reduction for simultaneous analysis of volatile and non-volatile methyltins, (B) without borohydride volatilization, and (C) shows deionized water blank.
7. P/T-GC-FPD separation and detection of the four methylstannanes ($\text{Me}_n\text{SnH}_{4-n}$, $n = 1-4$) in deionized water, where $n = 1-3$ are formed by hydride reduction.

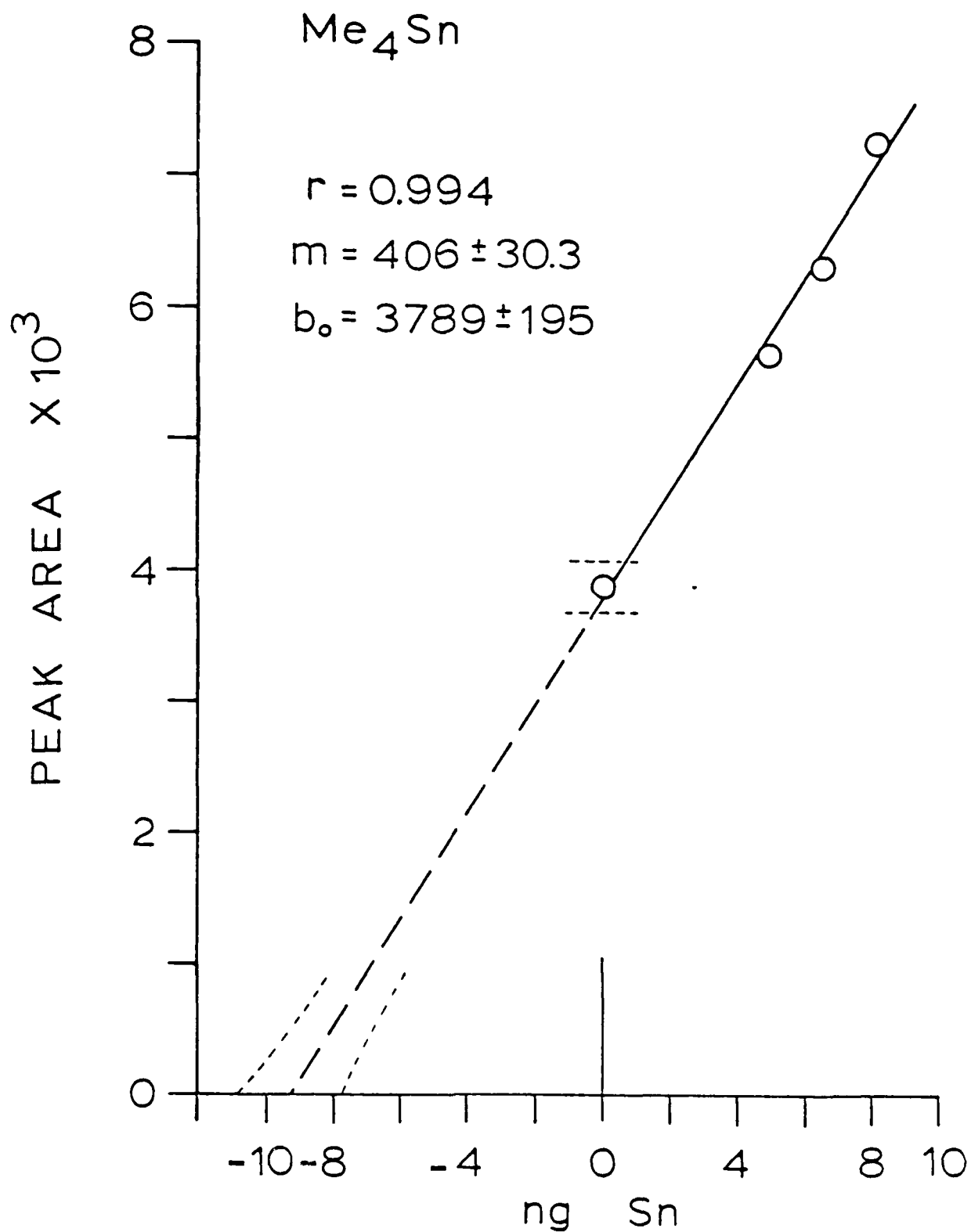
- (8) Optimization of purge time for trapping volatiles on Tenax-GC trap using 1 ng (as Sn) each of Me_2SnCl_2 , Me_4Sn , and Et_2SnCl_2 with 4 percent NaBH_4 added to volatilize $\text{Me}_2\text{Sn}^{2+}$ and $\text{Et}_2\text{Sn}^{2+}$ to the corresponding hydrides. Optimum purge time indicated at 10 min.
- (9) Gas chromatograms of methylstannanes (A) formed in calibration mixture with hydride reduction, (B) in calibration solution without hydride reduction showing Me_4Sn , and (C) found in sample from Jones Falls in Baltimore Harbor without hydride reduction as obtained using P/T-GC-FPD method. Arrow denotes Me_4Sn .
- (10) GC-MS ion chromatograms of respirant atmosphere above agar slants: (A) sterile control with Sn(IV) stress, (B) sterile control with Sn(II) stress, (C) Ps 244 inoculated with Sn(IV) stress, (D) Ps 244 inoculated with Sn(II) stress, and (F) Ps 244 inoculated, no tin stress. (E) shows the ion chromatogram from a gaseous calibration mixture of Me_2SnH_2 , Me_3SnH , and Me_4Sn .
- (11) Scheme of biomethylation and bioreduction of As(V) and As(III) by Pseudomonas sp. to form arsines in sediments (32) is compared with proposed biomethylation and bioreduction by Ps 244 to form methylstannanes in aquatic environments.

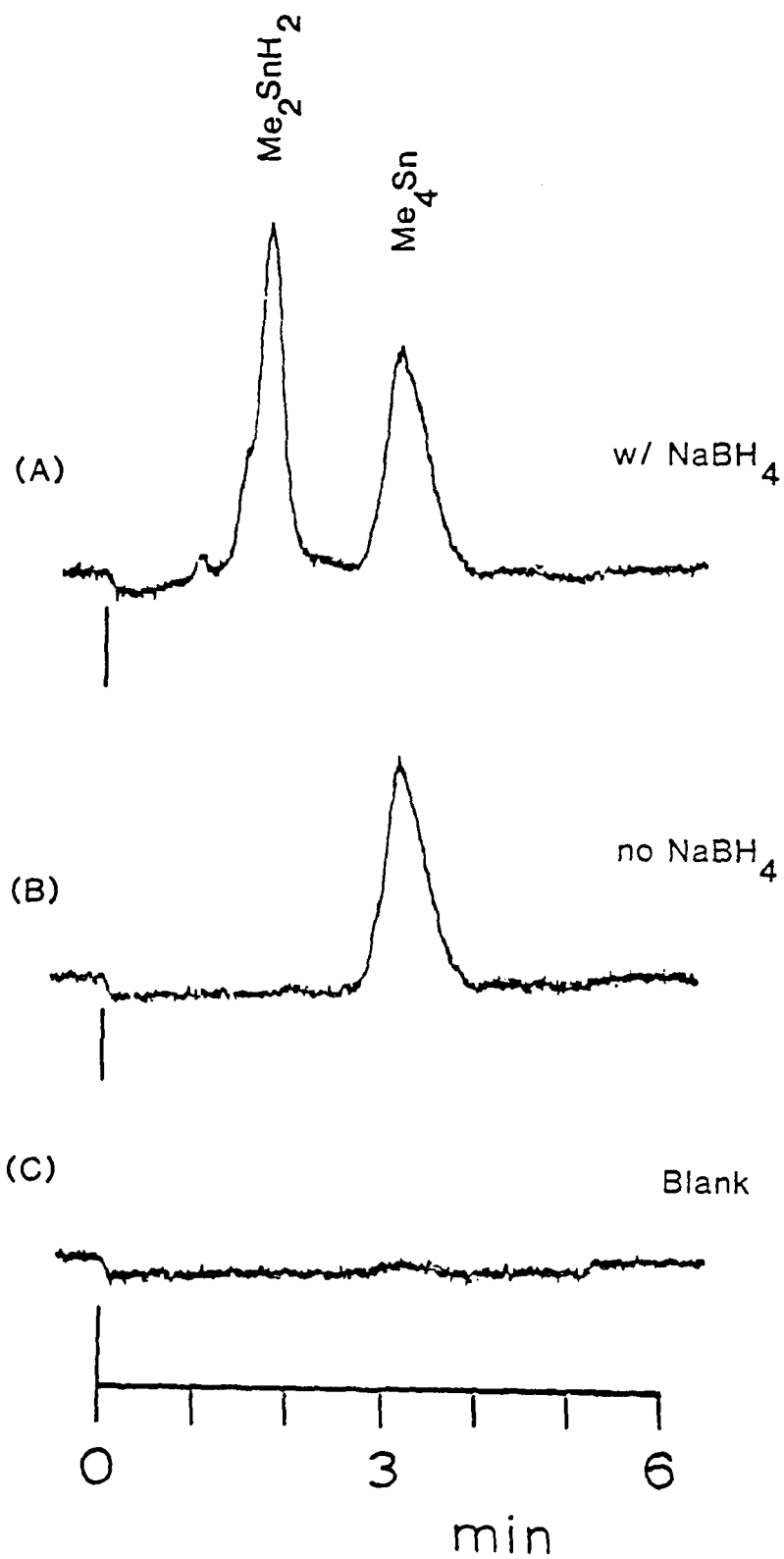


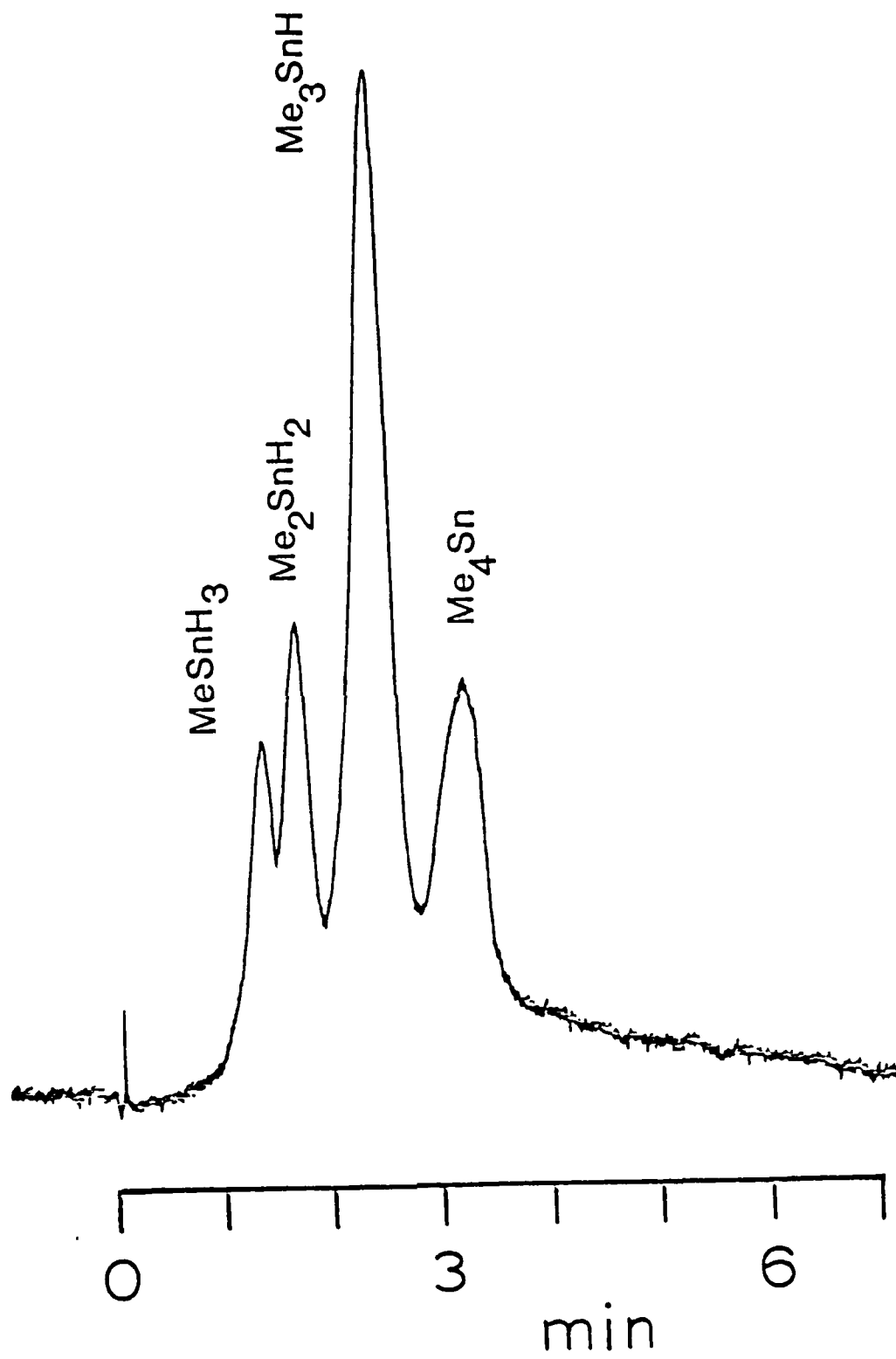


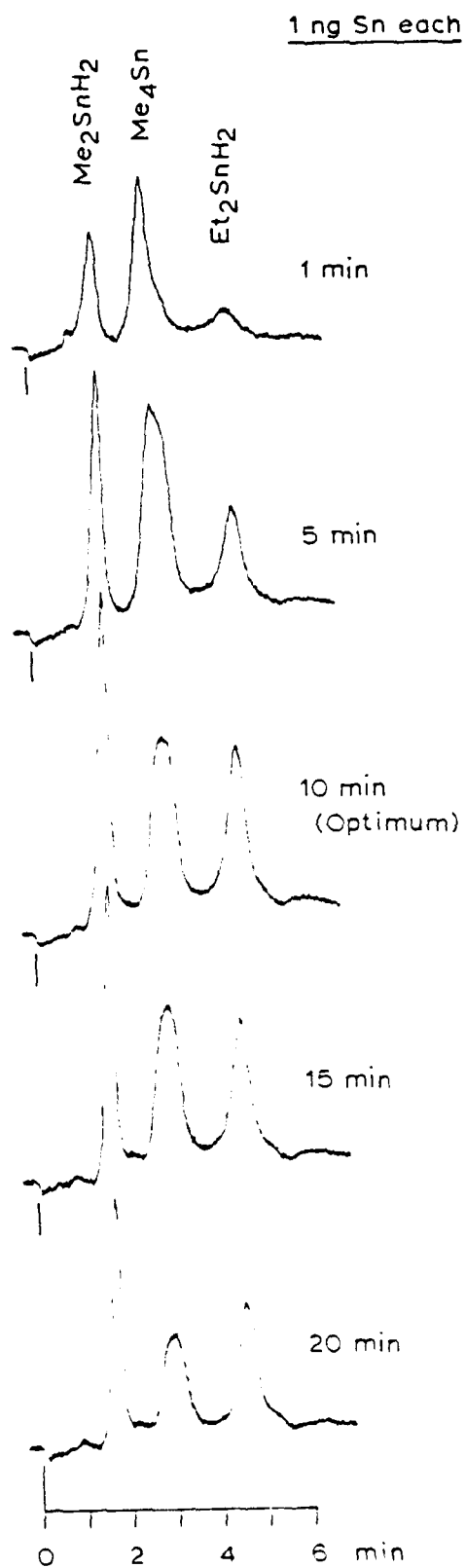


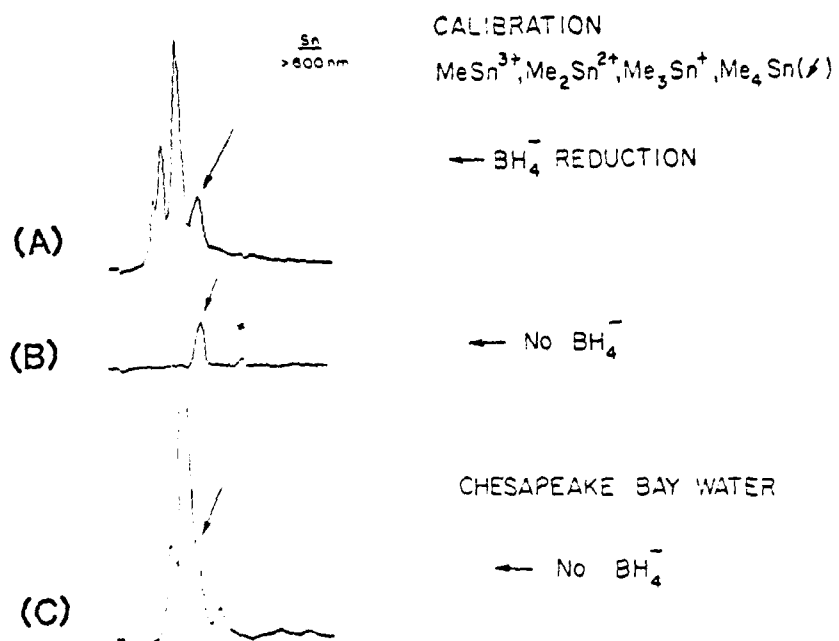


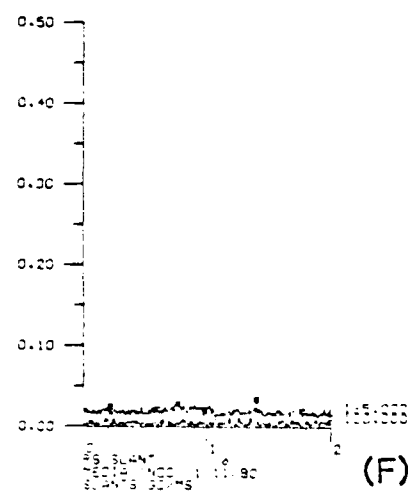
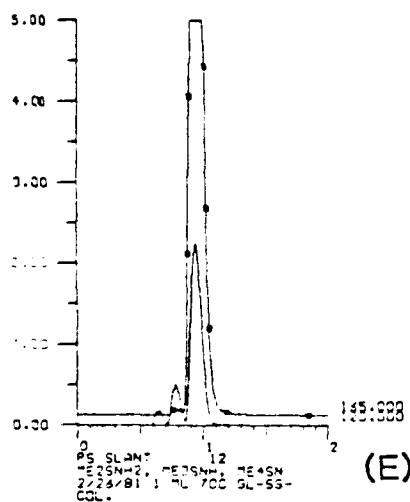
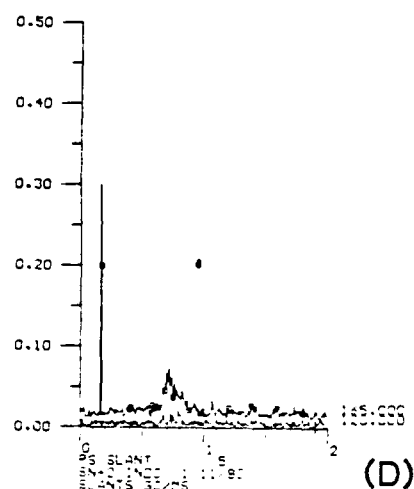
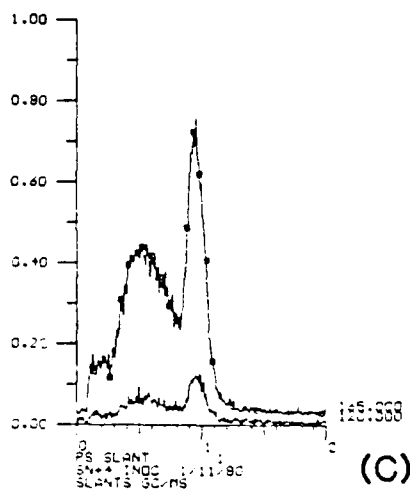
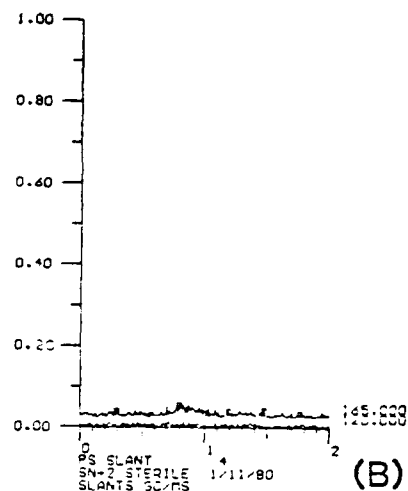
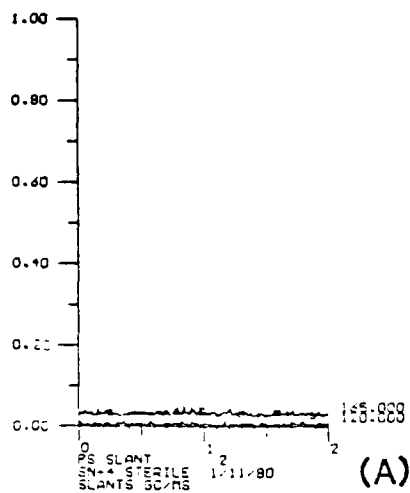


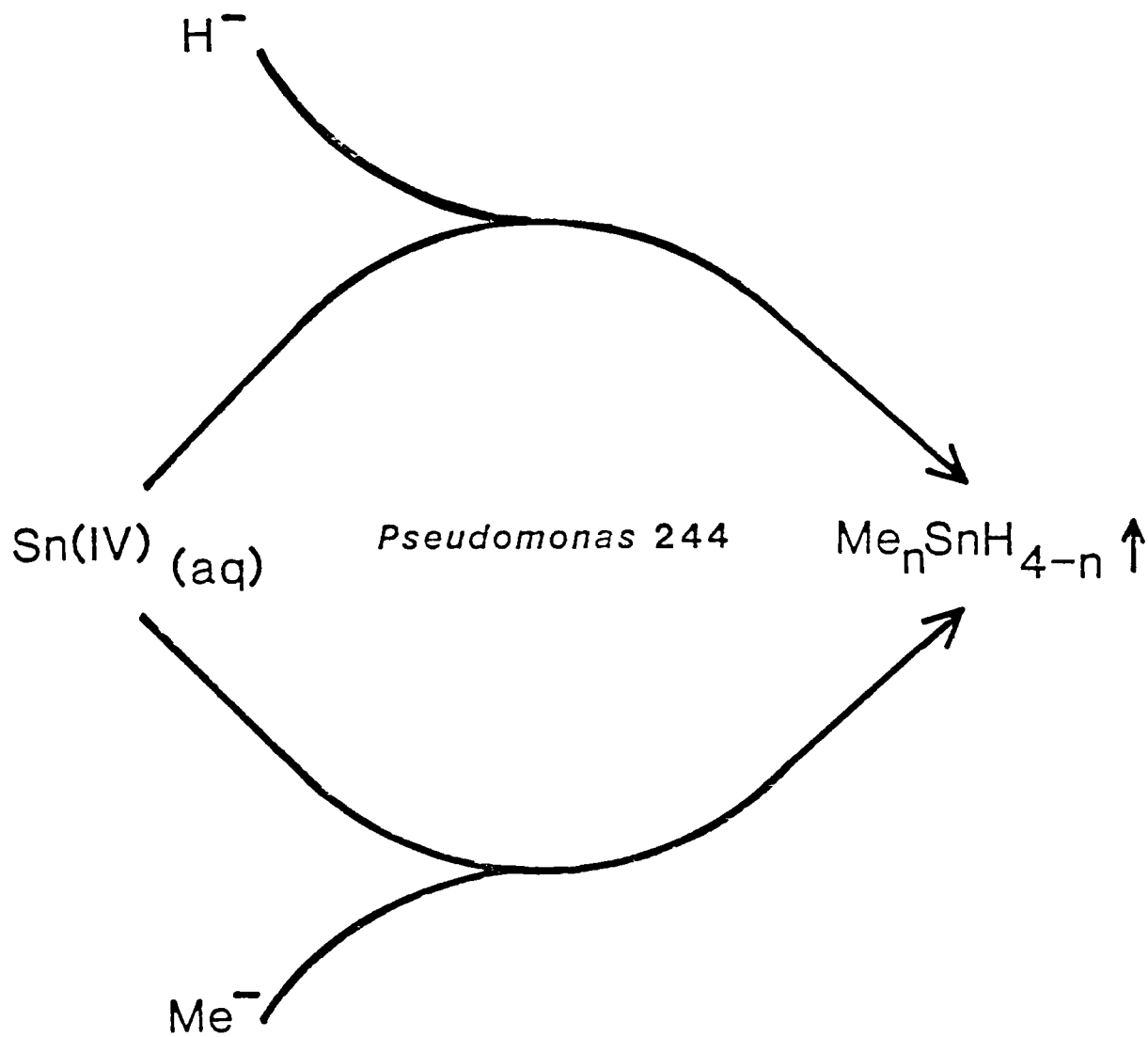
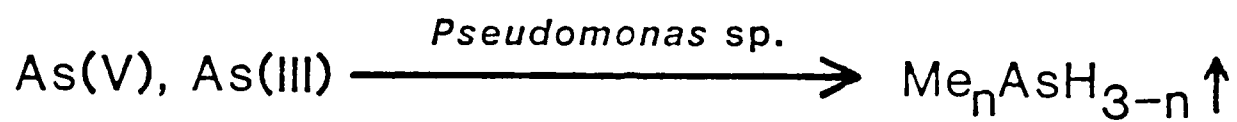












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4. TITLE (and Subtitle) Gas Chromatographic Speciation of Methylstannanes in the Chesapeake Bay Using Purge and Trap Sampling With a Tin-Selective Detector		5. TYPE OF REPORT & PERIOD COVERED Interim Technical Report
7. AUTHOR(s) J. A. Jackson, W. R. Blair, F. E. Brinckman and W. P. Iverson		6. PERFORMING ORG. REPORT NUMBER 5610406
9. PERFORMING ORGANIZATION NAME AND ADDRESS Chemical and Biodegradation Processes Group Chemical Stability and Corrosion Division National Bureau of Standards, Washington, D.C. 20234		8. CONTRACT OR GRANT NUMBER(s) N00014-81-F-0013 NR 083-471
11. CONTROLLING OFFICE NAME AND ADDRESS Department of the Navy Office of Naval Research Arlington, VA 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
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19. KEY WORDS (Continue on reverse side if necessary and identify by block number) biomethylation; Chesapeake Bay; flame photometric detector; gas chromatography; mass spectrometry; methylstannanes; organotin hydrides; Pseudomonas; purge and trap sampling; speciation; tetra methyltin; tin-selective detection.		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A method was developed permitting detection and speciation of both volatile and non-volatile organotin compounds in aqueous media. The method employed a commercial gas chromatograph (GC) with a flame photometric detector (FPD) optimized for tin-selective detection. Solvated organotins were volatilized with sodium borohydride during the purge cycle of a commercial automatic purge and trap sampler (P/T). Purged volatiles and species volatilized by hydridization were concentrated on a Tenax-GC filled trap at ambient temperature. Tetramethyltin (Me ₄ Sn) present in the sample is unaffected by the reduction process. The P/T-GC-FPD		

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Number 20 (continued) Abstract

method was used to analyze water samples collected from the Chesapeake Bay and Baltimore Harbor. Varying amounts of methyltin compounds, including tetramethyltin and methyltin hydrides, were detected in polluted sites in Baltimore Harbor. In vitro studies using GC-MS confirmed earlier reports of microbial methylation of inorganic Sn(IV) by a strain of *Pseudomonas* species isolated from the Chesapeake Bay. Consequently, biogenic origins are suspected for the methylstannanes ($\text{Me}_n\text{SnH}_{4-n}$, $n = 2,3$) found in the Chesapeake Bay.

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