A Manual for the Analysis of Butyltins in Environmental Samples

Prepared for the Virginia Department of Environmental Quality

By
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PREFACE

The Virginia Institute of Marine Science (VIMS) has developed methods for the analysis of tributyltin (TBT) in environmental samples. These methods have been published in the scientific literature where they are freely available to the public. When used by skilled analysts and supported by appropriate quality assurance and quality control procedures (QA/QC), we believe these methods, as well as other published analytical methods for TBT, can provide accurate and precise results. As in any environmental analysis, method performance is a function of the sample type, available instrumentation and skill and care taken by laboratory workers. The suitability of the data produced will only be confirmed by proper QA/QC in the laboratory.

At the request of the Virginia Department of Environmental Quality (DEQ), the Virginia Institute of Marine Science has prepared this laboratory manual as an advisory to those interested in methods for analysis of TBT in environmental samples. This manual is based on the previously published methods developed at VIMS and describes procedures for the analysis of TBT in water, sediment and biota samples. This effort is not intended to endorse these techniques as the only suitable methods for butyltin analysis, but is intended to provide detailed information on procedures which have been developed and successfully used at VIMS for the past ten years. It contains a higher level of detail than previous publications and also incorporates any recent changes in procedures, as well as listing possible sources for reagents and standards. This manual also contains a bibliography which lists published VIMS methods as well as other literature citations in which alternative techniques for the analysis of TBT may be found.

Hopefully, this manual is sufficiently comprehensive so that the analyst can perform these procedures with the information presented. I realize, however, that some questions or difficulties may occur when applying these methodologies at other laboratories, so consultation is available on a case-by-case basis by contacting VIMS. Many individuals contributed to assembling this manual. In particular, I thank: Ellen Travelstead, Tina Minnick, George Vadas, James Greene and Ellen Harvey for their help. I thank Dr. Mory Roberts and Dr. Rob Hale for helpful comments.

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I. INTRODUCTION[1]

To accurately measure tributyltin (TBT) in environmental samples it is important to distinguish between TBT and the degradation products, dibutyltin (DBT) and monobutyltin (MBT) which may also be present. Some early methods attempted to quantify TBT by atomic absorption spectrophotometric analysis (A.A.) of organic extracts of environmental samples. Since such extracts will likely contain some dibutyltin (DBT), monobutyltin (MBT) and other tin/organic complexes, methods without a butyltin speciation technique cannot accurately determine TBT concentrations. This was demonstrated by Dooley and Vafa (1986) while examining organic extracts from bivalve tissue.

Methods that separate TBT from other organotins typically utilize gas chromatography (GC) or a temperature gradient desorption from a purge and trap apparatus. These separation techniques are usually followed by gas chromatography with flame photometric or mass spectrometric detection. One method avoids the use of chromatography completely by utilizing the highly selective technique of mass spectrometry/mass spectrometry (Siu et al., 1989, 1996). This technique is not practical for most environmental laboratories however, because of the cost of such specialized analytical equipment. New specialized ion trap instruments capable of MS-MS detection may make this type of analysis more practical in the future.

Most commonly used methods today, require a derivatization step to form either volatile hydrides or tetraalkyl butyltin derivatives. This manual will concentrate on the advantages and disadvantages of using a hexyl magnesium bromide Grignard reagent to form tetraalkyltin derivatives prior to GC analysis as first described by Unger et al. (1986). Figure 1. shows a flowchart for the general analytical procedure that is followed for the analysis of butyltins in environmental water, tissue or sediment samples.

Derivatization of Butyltin Compounds

A Grignard reagent is an organometallic compound that can be represented by the formula RMgBr, where R can be any alkyl group. These organometallic compounds behave as strong bases and are attracted to electron-deficient centers. Commercial Grignard reagents are usually dissolved in ether and are sealed under an inert atmosphere. Exposure to water or the atmosphere can result in spontaneous reaction. The reaction with water, shown below, is exothermic and typical for these highly reactive compounds.

$$RMgBr + HOH \quad RH + Mg(OH)Br$$

[1]Portions adapted from Unger, M. A., J. Greaves and R. J. Huggett. 1996. Grignard Derivatization and Mass Spectrometry as techniques for the analysis of butyltins in environmental samples. In: Organotins: Environmental Fate and Effects. M. Champ and P. F. Seligman (Eds.). Chapman and Hall, London.

For this reason vessels containing Grignard reagents should be purged with nitrogen whenever open to the atmosphere. Exposure to the atmosphere will reduce the effective concentration of the Grignard reagent in solution, causing low recoveries during derivatization reactions. An apparatus for the safe storage and delivery of Grignard reagents is shown in Figure 2.

When added to organic extracts containing butyltin compounds, Grignard reagents react with the butyltins by adding alkyl groups to form tetraalkyltin derivatives. The following reactions illustrate the derivatization of TBT, DBT and MBT by n-hexylMgBr:

$$(\text{n-butyl})_3\text{Sn} + \text{n-hexylMgBr} \qquad (\text{n-hexyl})(\text{n-butyl})_3\text{Sn}$$

$$(\text{n-butyl})_2\text{Sn}^{2+} + 2(\text{n-hexylMgBr}) \qquad (\text{n-hexyl})_2(\text{n-butyl})_2\text{Sn}$$

$$(\text{n-butyl})\text{Sn}^{3+} + 3(\text{n-hexylMgBr}) \qquad (\text{n-hexyl})_3(\text{n-butyl})\text{Sn}$$

The resulting tetraalkyltins are stable compounds which can be easily separated by gas chromatography. Figure 3 shows a chromatogram containing hexyl derivatives of butyltins. Other tetraalkyltins are present in the chromatogram and illustrate the relative retention times of these compounds. The total number of carbon atoms substituted to the tin is given to illustrate how the elution order of the derivatized compounds is directly correlated.

Unlike hydride derivatives of butyltins which may degrade in hours or days, the tetraalkyl derivatives formed with Grignard reagents are stable for extended periods of time. Huggett et al. (1986) repeatedly analyzed hexyl derivatized sample extracts over a ten week period and found no significant loss of butyltins. We have found that extracts stored for months to years show no noticeable degradation.

Many different Grignard reagents have been used for the derivatization of organotin compounds. Derivatives formed by reaction with methyl and ethyl Grignard reagents are considerably more volatile than those formed with larger alkyl (pentyl or hexyl) groups. Mueller (1984) warned that when concentrating samples containing methyltributyltin, great caution must be used to prevent loss of the analyte through volatization.

The reactions discussed above are applied to organic extracts of samples. Because of the reactive nature and range of Grignard reagents, the choice of extraction solvents and internal standards is important and requires discussion. Variations in extraction procedures, internal standards, Grignard reagents and detection techniques have resulted in many different methods being published for the analysis of TBT and its degradation products. Many of these methods are modifications of those published earlier or are applications of previous methods to new sample matrices. We have

included a listing of currently published techniques in the back of this manual to show the variety of modifications and applications which are available.

A number of different solvents have been shown to be satisfactory for the extraction of TBT from water samples. DBT and MBT are more difficult to extract quantitatively due to their more ionic nature. For this reason, most methods use tropolone added to the solvent as a complexing agent to increase the recoveries. Solid phase extraction (SPE) procedures have also been reported. Mueller (1987) found that tropolone treated C-18 packed columns will successfully remove butyltins from environmental water samples. The butyltins are then eluted from the cartridges with diethyl ether and are ready for derivatization with Grignard reagent. Matthias et al. (1987) also reported on the use of C-18 bonded silica. These authors had good success when butyltins were at high concentrations, but found reduced recoveries at the low ng/L concentrations typically found in environmental samples.

A surrogate standard should be used to reliably quantify low concentrations of butyltins in environmental samples. The surrogate standard should have similar chemical properties to the analyte so that relative recoveries are similar throughout the analytical procedure. When hexyl derivatization is used, tripentyltin chloride has proven to be an excellent surrogate standard and is now commercially available, or can be synthesized through a series of reactions (Unger et al., 1986). Stallard et al. (1989) prepared tripentyltin bromide for use as an internal standard via bromination of tetrapentyltin. Holland (1987) reported on techniques for the direct synthesis of triorganotin compounds. This method may simplify the preparation of tripentyltin or other related compounds.

One of the biggest problems encountered when analyzing environmental samples for low concentrations of TBT (e.g. 1-5 ngL^{-1}) is sample contamination by impure Grignard reagents. Contamination of Grignard reagents may occur when chemical manufacturers use the same inert atmosphere apparatus for synthesizing butyltin compounds and preparing Grignard reagents. This is a common problem with some commercial sources. Therefore, each batch of Grignard reagent should be checked for contamination. To overcome contamination problems, Grignard reagents may be prepared by reaction of magnesium metal with the appropriate alkyl bromide. To assure that the product will be free of organotins, the alkyl bromide should also be checked for butyltin contamination prior to use.

Despite problems encountered with contaminated reagents, methods utilizing Grignard derivatization have proven reliable for a wide variety of sample types. When the longer chain (pentyl or hexyl) Grignard reagents are used, sample extracts can be concentrated to small volumes without significant evaporative losses of the derivatives. The tetraalkyltin compounds produced by these methods are thermally stable, easily separated by gas chromatography and produce characteristic mass spectra.

II. GAS CHROMATOGRAPHY AND MASS SPECTROMETRY OF BUTYLTINS

Gas Chromatography of Butyltins

For the analysis of butyltin compounds, a gas chromatograph equipped with a flame photometric detector (GC-FPD) has proven to be a sensitive and somewhat selective technique. At VIMS, samples are analyzed on a Varian Model 3300 equipped with a dual flame photometric detector using a >600 nm band pass filter installed. This filter reduces the interference from sulphur and phosphorous emissions, present at lower wavelengths. Since this detection relies on the intense emission by SnH, adjusting the flame to a hydrogen rich condition helps to maximize tin response. This is best accomplished by reanalyzing a fixed volume of butyltin standard, while adjusting the gas flows to achieve maximum detector response.

Listed below, are gas chromatography conditions used at VIMS. These should prove to be a good starting point for butyltin analyses:

Carrier gas: helium at 4 ml/min.
Make up: helium at 90 ml/min.
Detector: hydrogen 152 ml/min.; air1: 97 ml/min.; air2: 188 ml/min.
Filter: 600 nm band pass
Column: DB-5; 30m x 0.32 id. x 1.00µm
Injector temperature: 280°C
Detector temperature: 280°C
Initial column oven temperature: 135°C
Final column oven temperature: 300°C
Temperature program rate: 10°C min^{-1}
Final column oven temperature hold time: 5 min.

Chromatograms from environmental samples analyzed by the techniques described in this manual are presented at the end of this manual as a reference. Figure 4 shows a water sample extract from a Hampton Creek Marina. This sample contained 70 ng/L TBT, 36 ng/L DBT and 19 ng/L MBT. The peaks for the internal standard (tetrabutyltin) and the surrogate standard (tripentyltin) are also evident. Hexyl derivatized inorganic tin is also present due to inorganic tin contamination in the Grignard reagent. This will not interfere with butyltin quantification. Figure 5 shows the chromatogram from the analysis of a water sample spiked at 2 ng/L TBT, DBT, MBT. This illustrates the sensitivity of the technique to detect low ng concentrations of TBT in water. Figure 6 is a chromatogram of a clam sample extract from the Elizabeth River, Virginia. This sample contained 130 ug/kg TBT and 10 ug/kg DBT on a wet weight basis. MBT was not detected in this sample. Figure 7 shows a chromatogram from the analysis of a sediment sample from the Navesink River, New Jersey. It contained 26 ug/kg TBT and 7 ug/kg DBT. MBT was not detected (< 2 ug/kg) and is usually difficult to extract quantitatively from sediment samples. Extra peaks in the chromatogram are typical of sediment analyses and are often sulphur containing compounds or organic

contaminants in great enough concentration to still show a FPD response. Passing the extracts over activated copper, as described in the sediment procedure, minimizes these interferences. Some sediment samples heavily contaminated with hydrocarbons, etc., may prove difficult to quantify by GC-FPD due to interfering peaks.

Mass Spectrometry of Butyltins and Related Compounds

Since 1984 there have been numerous techniques published that utilize MS in the analysis of TBT in environmental samples. The mass spectrometer is the only detector that can positively identify, as well as quantify, butyltins in samples. Because of the low detection limit requirements for environmental samples, a variety of sample introduction techniques and ionization methods have been investigated. While not a technique used routinely at VIMS, quantification of butyltins by MS-selective ion monitoring is possible as described by Greaves and Unger (1988). A review of the attributes and disadvantages of various mass spectrometry techniques is given by Unger et al. (1996).

Conformation of TBT at ng/L levels

Analyzing TBT in environmental samples by GC-FPD is a fairly selective technique, but interferences may occur. Thus, it is important to be able to confirm TBT identities in some samples by mass spectrometry. Most modern quadrupole and ion trap mass spectrometers used in the electron ionization (EI) mode can confirm TBT at ng/L concentration levels in environmental samples. Both a Finnigan Incos XL quadrupole and a Varian Saturn 4D ion trap GC/MS have been used at VIMS to confirm TBT identification. Similar results were obtained on both instruments.

To test the utility of a Varian Saturn 4D Ion Trap Mass Spectrometer (equipped with a Varian 3400 GC and 8200cx Autosampler) for tributyltin analysis, a TBT standard and two typical environmental samples were analyzed. The gas chromatograph used a model 1078 style injector operated in the splitless/split mode. It was equipped with a J&W DB-5 MS column (30 m x 0.25mm id x .25 film thickness).

The following gas, column and injector conditions were used:

Carrier gas = helium (typical column flow and split rates)5
Initial injection= splitless for 0.5minutes then split.
Injector temperature = 300 C
Column oven temperature profile: T_i = 75 C , T_{ih} = 1 min, 6 C/min,
T_f = 320 C, T_{fh}= 5 min

The autosampler used hot needle injection and injection delay of 0.2 minutes with a 2 µl sample and a solvent plug.

The mass spectrometer was tuned and calibrated with FC-43. Mass spectrometer conditions were as follows:

Manifold temperature = 290 C
Transfer line temperature = 290 C
Full scan: EI mode, low mass = 100 m/z, high mass = 500 m/z, scan rate = 870 milliseconds, peak threshold = 0 counts, mass defect = 0 mu/100u, background

Axial Modulation (A/M) Amplitude = 3.0 volts
Emission current = 10 microamps
Automatic gain control (AGC) = on
AGC prescan ionization time = 100 microseconds
AGC Target set high 53300 counts
EI maximum ionization time = 25000 microseconds

Analytical Scan Segments

	1	2	3	4
Time factor %	25	140	140	25
RF level	40.0	40.0	40.0	40.0
Low mass (m/z)	10	100	301	501
High mass (m/z)	99	300	500	650

Spectra from the analysis of standard solutions and environmental samples are presented at the end of this manual for reference. Two uL of a hexyl derivatized butyltin standard solution containing 2.2 ng/µL tetrabutyltin, 2.6 ng/µL TBT, 2.6 ng/µL DBT, 0.91 ng/µL tetrapentyltin and 0.29 ng/µL MBT were analyzed. Elution order on a standard DB-5 column is tetrabutlytin, hexyltributyltin (TBT), dihexyldibutyltin (DBT), hexyltripentyltin (TPT), trihexylbutyltin (MBT) and tetrahexyltin. Figures 8-12 are EI spectra of these compounds. Tetrahexyltin will appear in most samples from the hexylation of inorganic tin but was not present in this standard. It should be noted that generally a molecular ion will not form for any of the TBT analytes. The lack of molecular ion formation is mainly due the weak tin carbon bond in organotins, which breaks more readily than carbon-carbon bonds of substituent groups. Examples of TBT, DBT and MBT spectra from a low concentration environmental sample are presented in Figures 13-15. All mass spectra containing tin have a very distinctive isotope pattern (10 stable isotopes) that is maintained throughout the molecule's fragmentation. As distinctive as this pattern appears, the analyst should be aware that it is similar enough to a tetra-chlorine isotope pattern that it might lead to some false positive identifications.

III. RECOMMENDED QUALITY ASSURANCE QUALITY CONTROL PROCEDURES (QA/QC) FOR TRIBUTYLTIN ANALYSES

As in any environmental analysis, method performance is a function of sample type, available instrumentation and the skill and care taken by laboratory workers. Suitability of the data produced will only be confirmed by proper laboratory quality assurance and quality control procedures. QA/QC requirements may change with the goal of the analysis (ie: required detection limits) and importance of the resulting dataset. These data requirements should be identified prior to analyzing samples.

When extracting samples, laboratory blanks should be analyzed with each batch of environmental samples. Replicate analyses are generally recommended on at least 10% of the samples to document precision. Analysis of matrix spiked samples and/or Certified Reference Materials (CRM) should also be conducted to confirm detection limits and document accuracy for the analyses. At VIMS, butyltin standards and blank samples are analyzed daily to assure gas chromatograph performance. This is accomplished by monitoring peak retention time, response ratios and peak shape.

TBT Recoveries from spiked water samples should be about 90% with the coefficient of variation of less than 15% for most environmental samples (Unger et al, 1986; Greaves and Unger, 1988, Hall et al, 1992). Similar results can be obtained for tissue samples (Rice et al, 1987). A recent analysis of clam homogenate samples from the Elizabeth River, by Roberts et al. (1996) illustrates the low variance possible for the analysis of TBT in replicate biota samples (Figure 16).

Analysis of TBT in environmental sediment samples can be problematic. Natural sediments may contain high concentrations of organic matter and elemental sulfur, as well as various anthropogenic contaminants. TBT may be associated with this organic matter or can be present as a component of paint chips incorporated within the sediments near boat maintenance facilities. Quantitative extraction of these chips, as well as tightly bound TBT molecules associated with organic matter, is difficult to accomplish or verify. The method described here has produced adequate results for the analysis of CRM, PACS-1, giving 90% recovery for TBT and 60% recovery for DBT, but less than quantitative MBT recovery. Results from replicate samples are typically within 10-15%, but may vary considerably depending on sample homogeneity and the presence of paint chips. Additional work to examine the effectiveness of new extraction techniques (i.e. accelerated solvent extraction, ASE) is ongoing. When analyzing sediment samples, frequent replication and quantification of spiked samples are advisable.

IV. PROCEDURE FOR WATER ANALYSIS

Glassware required:	Glass separatory funnels (4 liters) Griffon Beakers (2 liters) Glass powder funnels 500 ml round bottom boiling flasks, cork rings 1 liter Erlenmeyer flask (for hexane/tropolone) 50 ml graduated cylinder Stainless steel spoonula 50 ml graduated centrifuge tubes Chromatographic columns - 22 mm i.d. x 300 mm with stopcock closure 250 ml flask and adaptor for Grignard storage 250 ml flasks (for hexane waste) 500 ml flasks (to hold hexane) 500 ml round bottom flasks saved from earlier Pipettes (9 inch transfer) Volumetric flasks and pipettes
Reagents required:	Grignard reagent (n-hexyl magnesium bromide) Hydrochloric acid Acetone Hexane Tropolone Tripentyltin chloride in ethanol Tetrabutyltin in hexane
Equipment:	Vacuum rotary evaporator Nitrogen blowdown apparatus Ultrasonicator Vortex tube mixer GC-FPD, GC-MS

Extraction:

 All samples should be brought to room temperature prior to extraction. Samples may be warmed in a sink or tub of warm water. Surrogate standard (tripentyltin chloride in ethanol) solution should also be removed from the refrigerator to warm up to room temperature before use.

 Set up and rinse all glassware to be used with hexane. Label glassware with sample names and dates. Volume of sample used (and size of sep. funnels and beakers) is dependent on expected TBT concentration. For environmental samples at stations with known or suspected low concentrations, use 2 liters of water. For higher concentration samples, smaller volumes and glassware may be used.

 Prepare a QA/QC Blank of deionized water (same volume as samples). Adjust the pH of all samples to 2 with HCl. Prepare any other required QA/QC samples at this time (replicates, spiked samples, etc.) at the same volume as other samples being extracted. Shake the warmed water samples until well mixed. Measure the appropriate sample volume into the beaker (or graduated cylinder, if small volume used). Pour the sample into the separatory funnel, using the powder funnel as a guide. Spike all samples and the blank with the TPT internal standard at a concentration similar to the anticipated TBT concentration. Swirl.

 Prepare Hexane/Tropolone mixture: 0.2% tropolone in n-hexane, using enough hexane to extract three times with 40 ml aliquots for each 2 L sample. Ultrasonicate and swirl to dissolve tropolone.

 Add 40 ml hexane/tropolone to each sample and to the blank. Shake vigorously for 3 minutes(make sure to vent separatory funnels several times). Wait for 10 minutes for the phases to separate. Drain the aqueous phase into the beaker. Drain the hexane extract into the 500 ml flask. Pour the aqueous phase from the beaker back into the separatory funnel. Repeat the extraction two more times, using 40 ml hexane/tropolone each time, combining all three extracts in the 500 ml flask.

 Reduce the volume of the extracts to approximately 2 ml of hexane using the rotory evaporator. There will be some water or emulsion in the extract. Make sure there are 2 ml of hexane in addition to this. Quantitatively transfer flask contents to a hexane pre-rinsed 50 ml centrifuge tube, using a Pasteur transfer pipette. Rinse the sides of the flask approximately 10 times with about 2 ml of Hexane. Transfer this to the tube. Repeat twice. Remove the aqueous (bottom) layer from the centrifuge tube, using the pipette and discard. Freeze the sample extracts for one hour to help break up any emulsion that may have formed. Rinse the flasks with acetone two times and with hexane two times. Discard rinses. Put aside labeled flasks for collecting column eluents.

Derivatization:

Hexylmagnesium bromide is used as the Grignard reagent. Some companies (eg. Aldrich) produce this compound dissolved in ether while others (eg. TCI America) produce Grignard reagents in tetrahydrofuran (THF). Ether solutions should be stored in the refrigerator when not in use, but our experience with hexyl magnesium bromide in THF solvent has shown that it will form precipitates at reduced temperatures and therefore should be stored in the dark at room temperature. Grignard reagents will react exothermically with atmospheric moisture, so it is helpful to transfer the solution to a suitable apparatus for storage and delivery. Using dry nitrogen, pressurize the reagent bottle and transfer the reagent through Teflon tubing to a 250 ml flat bottom flask with a connecting adapter and a ground glass stopper (Kontes, P.O. Box 729, Vineland, NJ 08360, 1-609-692-8500, cat. # K211200-2440, Figure 3). A stream of nitrogen can now be passed through the flask via the side arm, so that Grignard reagent can be removed through the top neck of the flask by transfer pipette, without exposing the reagent to atmospheric moisture.

 Warm the Grignard reagent to room temperature. Take the sample extracts, one at a time, from the freezer. Pour the Hexane portion into a Hexane pre-rinsed 50 ml centrifuge tube. Frozen water and emulsion will stay behind in the original tube. Put this tube into a warm (40 C) waterbath until thawed. Using a transfer Pasteur pipette, remove the aqueous (bottom) layer and discard. Pour the Hexane liberated from the emulsion into the tube with the sample extract, rolling the tube as you pour to separate the phases. There should be 10-15 ml of Hexane in the tube. If there is more than 15 ml, reduce the volume with a nitrogen blowdown in a 40 C bath.

 When all of the samples are ready for derivatization, pump nitrogen through the Grignard reagent containing apparatus. Approximately 0.5 ml of Grignard reagent is used to derivatize each sample. Premarked transfer Pasteur pipettes can be used to deliver 0.5 ml volume. Using a pipette pump, transfer 0.5 ml of the Grignard reagent into the tube containing the sample extract. Make sure the Grignard reagent is not exposed to air. Expel it into the tube below the surface of the hexane. Discard the pipette. Agitate the tube with a vortex mixer for 5-10 seconds and vent. Repeat for all samples. Return the sealed Grignard reagent to the refrigerator. Vortex the samples every 5 minutes for 30 minutes.

 Neutralize excess Grignard reagent with concentrated HCl. Add 2 ml HCl to each sample. Shake vigorously and vent. Shake and vent two more times. Any precipitate should be dissolved. Let the samples sit for 30 minutes to separate the phases. Using a Pasteur transfer pipette, remove the lower (aqueous acid) layer and discard.

Sample clean-up:

 Sample extracts should be blown down to approximately 1.5 ml with dry Nitrogen in a 40 C bath before transferring to columns for cleanup. Rinse assembled columns with hexane and allow to air dry. Insert a small glass wool plug in the bottom of each column. Fill each column with 20 grams of activated (110°C) Florisil. Tap the column to pack it down. Add 2 grams of anhydrous Na_2SO_4 on top of the Florisil. Pack. Pour 75 ml of hexane through the column as a rinse into the 250 ml flasks. Discard rinse. Place the 500 ml round bottom flasks, saved from earlier extraction step, under the columns.

 Transfer the samples to the columns, rinsing the tubes three times with hexane onto the columns. Rinse the sides of the columns. Pour 300 ml of hexane through each column. Rinse the centrifuge tubes twice each with acetone and hexane and put the tubes aside to be used later. Reduce the volume of the samples in the 500 ml flasks to approximately 2 ml with the rotory evaporator and transfer back to centrifuge tubes, rinsing three times.

- Spike samples with tetrabutyltin (in hexane) internal standard at a concentration similar to surrogate standard concentrations. Reduce volume under nitrogen prior to injection onto the gas chromatograph. For ultra-trace analyses this is usually about 0.1mL.

V. PROCEDURE FOR TISSUE ANALYSIS

Glassware/supplies required:

- Pint mason jars
- Aluminum weigh pans
- Glass powder funnels
- Soxhlet apparatus (VWR 27613-260)
- Condensers (Friedrichs-Corning, 55/50)
- Soxhlet thimble with a coarse frit (VWR 27743-061)
- 500 ml round bottom flasks, cork rings
- 50 ml graduated cylinder
- Stainless steel spoonula
- 50 ml centrifuge tubes
- Chromatographic columns - 22 mm i.d. x 300 mm with stopcock closure
- 250 ml flask and adaptor for Grignard storage
- 250 ml flasks for hexane waste
- 500 ml flasks to hold hexane
- 500 ml round bottom flasks saved from earlier
- Teflon boiling chips
- Pasteur transfer pipettes (9 in)
- Volumetric flasks and pipettes

Reagents required:

- Grignard reagent (n-hexyl magnesium bromide)
- Sodium sulfate
- QUSO® (precipitated silica)
- Hydrochloric acid
- Acetone
- Hexane
- Tripentyltin chloride in hexane
- Tetrabutyltin in hexane

Equipment:

- Virtis® tissue homogenizer with sample jars
- Vacuum rotary evaporator
- Nitrogen blowdown apparatus
- Ultrasonicator
- GC-FPD, GC-MS
- Vortex tube mixer
- Heating mantle or equiv. (VWR 33787-141)
- Drying oven

The following procedure has been used successfully for the analysis of TBT in shellfish and finfish samples.

Sample preparation:

 Bivalves should be thoroughly rinsed to remove any loose sediment that might interfere with the tissue analysis. Following the cleaning process, they are removed from the shell using a shucking knife. The tissue is placed into flasks and ground using a Virtis® tissue homogenizer to obtain a fluid homogenate. Individual specimens (greater than 10 g) may be analyzed, or individuals combined to form composite samples. Once homogenized, samples should be stored frozen in precleaned glass jars. Finfish are filleted and the skin removed. Muscle tissue should be finely minced or ground and stored frozen if not desiccated immediately.

Chemical desiccation:

 Thaw samples if frozen. Warm the surrogate standard (tripentyltin chloride in hexane) to room temperature. Thoroughly mix the sample using a Spoonula. Place 10 g of the tissue homogenate into a pint glass jar. Spread the tissue over the bottom of the jar.

 Spike the surrogate standard solution onto the tissue surface, avoiding any contact with the walls of the jar. If possible, spike surrogate standard at a concentration similar to the expected TBT level. Let sit until the hexane has evaporated.

 Determine the water content of the samples for dry weight concentrations. Place 10 g of the tissue into a pre-weighed aluminum weigh pan. Oven dry overnight at 100 C. Weigh the sample after the tissue cools (~20 min). Reweigh and record weight when constant. Calculate the percent total solids.

 Tissue samples should be dried with three parts desiccant to one part tissue. The desiccant consists of 1:9 (w/w) precipitated silica (QUSO®), and anhydrous granulated sodium sulfate. To each 10 gram sample, add 3 g QUSO® and then 27 g sodium sulfate. Stir with a Spoonula to a uniform consistancy. Freeze overnight.

Extraction:

 Using a Spoonula, transfer the sample into a glass soxhlet thimble with a coarse frit . Place glass wool plugs above and below the sample. Place the thimble in a soxhlet, and set up on a 500 ml round bottom flask containing approximately 400 ml hexane and 3-6 Teflon boiling chips. Place the soxhlet and flask on a heating mantle and under a condenser. Extract for 24 hours. Prepare a Blank with each set using the QUSO®, sodium sulfate and glass wool. Do not add the surrogate standard until after extraction because it cannot be quantitatively recovered if spiked directly onto the QUSO®.

 Reduce volume of the extract down to 2 ml with the rotary evaporator. Transfer, using a Pasteur transfer pipette, to a 50 ml centrifuge tube. Rinse the sides of the flask 10 times with 2 ml hexane. Transfer this to the tube. Repeat twice. Remove any lower

aqueous layer, if present, and discard. If the sample is not between 10 and 15 ml, reduce volume under a gentle stream of nitrogen.

The following steps are identical to those used in water analysis

Derivatization:

Hexylmagnesium bromide is used as the Grignard reagent. Some companies (eg. Aldrich) produce this compound dissolved in ether while others (eg. TCI America) produce Grignard reagents in tetrahydrofuran (THF). Ether solutions should be stored in the refrigerator when not in use, but our experience with hexyl magnesium bromide in THF solvent has shown that it will form precipitates at reduced temperatures and therefore should be stored in the dark at room temperature. Grignard reagents will react exothermically with atmospheric moisture, so it is helpful to transfer the solution to a suitable apparatus for storage and delivery. Using dry nitrogen, pressurize the reagent bottle and transfer the reagent through Teflon tubing to a 250 ml flat bottom flask with a connecting adapter and a ground glass stopper (Kontes, P.O. Box 729, Vineland, NJ 08360, 1-609-692-8500, cat. # K211200-2440, Figure 3). A stream of nitrogen can now be passed through the flask via the side arm, so that Grignard reagent can be removed through the top neck of the flask by transfer pipette, without exposing the reagent to atmospheric moisture.

 Warm the Grignard reagent to room temperature. When all of the samples are ready for derivatization, pump nitrogen through the Grignard reagent containing apparatus. Approximately 0.5 ml of Grignard reagent is used to derivatize each sample. Premarked transfer Pasteur pipettes can be used to deliver 0.5 ml volume. Using a pipette pump, transfer 0.5 ml of the Grignard reagent into the tube containing the sample extract. Make sure the Grignard reagent is not exposed to air. Expel it into the tube below the surface of the hexane. Discard the pipette. Agitate the tube with a vortex mixer for 5-10 seconds and vent. Repeat for all samples. Return the sealed Grignard reagent to the refrigerator. Vortex the samples every 5 minutes for 30 minutes.

 Neutralize excess Grignard reagent with concentrated HCl. Add 2 ml HCl to each sample. Shake vigorously and vent. Shake and vent two more times. Any precipitate should be dissolved. Let the samples sit for 30 minutes to separate the phases. Using a Pasteur transfer pipette, remove the lower (aqueous acid) layer and discard.

Sample clean-up:

 Sample extracts should be blown down to approximately 1.5 ml with dry Nitrogen in a 40 C bath before transferring to columns for cleanup. Rinse assembled columns with hexane and allow to air dry. Insert a small glass wool plug in the bottom of each column. Fill each column with 20 grams of activated (110°C) Florisil. Tap the column to pack it down. Add 2 grams of anhydrous Na_2SO_4 on top of the Florisil. Pack. Pour 75 ml of

hexane through the column as a rinse into the 250 ml flasks. Discard rinse. Place the 500 ml round bottom flasks, saved from earlier extraction step, under the columns.

 Transfer the samples to the columns, rinsing the tubes three times with hexane onto the columns. Rinse the sides of the columns. Pour 300 ml of hexane through each column. Rinse the centrifuge tubes twice each with acetone and hexane and put the tubes aside to be used later. Reduce the volume of the samples in the 500 ml flasks to approximately 2 ml with the rotory evaporator and transfer back to centrifuge tubes, rinsing three times.

 Spike samples with tetrabutyltin (in hexane) internal standard at a concentration similar to surrogate standard concentrations. Reduce volume under nitrogen proir to injection onto the gas chromatograph. For ultra-trace analyses this is usually about 0.1mL.

VI. PROCEDURE FOR SEDIMENT ANALYSIS

Glassware/supplies required:

Pint mason jars
Aluminum weigh pans
500 ml round bottom flasks, cork rings
1 liter Erlenmeyer flask (hexane/tropolone)
50 ml graduated cylinder
Stainless steel spoonulas
50 ml centrifuge tubes
Chromatographic columns - 22 mm i.d. x 300 mm with stopcock closure
250 ml flask and adaptor for Grignard storage
250 ml flasks for hexane waste
500 ml flasks to hold hexane
500 ml round bottom flasks saved from earlier
Pipettes, small and widebore pasteur
Teflon© centrifuge bottle (VWR 21020-403)

Reagents required:

Grignard reagent (n-hexyl magnesium bromide)
Hydrochloric acid
Acetone
Hexane
Tropolone
Tripentyltin chloride in hexane
Tetrabutyltin in hexane
Granulated copper

Equipment:

Wrist action shaker
Vacuum rotary evaporator
Nitrogen blowdown apparatus
Ultrasonicator
Gas chromatograph/flame photometric detector
Vortex tube mixer
Drying oven

Extraction:

 Thaw frozen sediment samples to be extracted. Warm the surrogate standard (tripentyltin chloride in hexane) to room temperature. Homogenize each sample with a spoonula. Weigh out 10 g of each sediment sample into a tared 250 ml Teflon© centrifuge bottle.

 To determine the water content of the samples for calculating dry weight concentrations, weigh approximately 10 g of an additional aliquot of the sediment

sample into a preweighed aluminum weigh pan. Dry overnight in a 100 C oven. Let cool (~20 min), and weigh. Reweigh and record weight when constant. Calculate the percent total solids.

 Weigh 10 grams of pre-extracted sand into a 250 ml Teflon centrifuge bottle to be used as a Blank.

 Spike the Blank and the samples with the surrogate standard at a concentration similar to the anticipated sample concentration. Add spike onto the sediment only avoiding the container walls. Air dry until all the hexane has evaporated.

 Add 20 ml deionized water with the pH adjusted to 2 to each sample and the blank. Prepare a Hexane/Tropolone mixture of 0.2% Tropolone in n-hexane, using enough hexane to extract two times with 100 ml each time. Ultrasonicate and swirl to dissolve Tropolone.

 Add 100 ml Hexane/Tropolone to each sample. Shake vigorously. Vent. Securely attach the bottles to a Wrist Action Shaker and adjust the shaker to high shaking power. Shake for one hour. Allow the layers to separate and pour and pipette the hexane layer into a 500 ml round bottom flask. Swirl to break up any emulsion. Add another 100 ml Hexane/Tropolone to each sample and repeat. Add the additional hexane layer to the 500 ml flask.

 Reduce the volume to about 2 ml with the rotary evaporator. Transfer to a 50 ml centrifuge tube, using a Pasteur transfer pipette. Rinse the sides of the flask 10 times with 2 ml hexane. Transfer this to the tube. Repeat twice. Reduce the sample volume to approximately 2 ml under a stream of dry nitrogen.

Copper Columns:

Most estuarine sediment samples contain high concentrations of sulfur that must be removed prior to concentrating the samples. Sulfur can be removed by passing each sample extract through a small column packed with activated copper.

 Use fine granular copper, which should be activated in an Erlenmeyer flask with 50/50 HCl until it is bright. Drain off the acid. Rinse twice with deionized water. Drain off each time. Rinse and drain three times with acetone and hexane. This should be done immediately prior to use, and the activated copper should be kept under hexane and not exposed to the atmosphere.

 Add the copper (3-5 cm depending on the amount of sulfur to be removed) to a small pipette column which has been rinsed with hexane and plugged with glass wool. Pass more hexane through the column as a rinse.

 Place a 50 ml centrifuge tube under the column and transfer the sample onto the copper. Rinse the tube three times, adding the rinses to the column. Flush the column with additional hexane to bring the level in the tube catching the sample up to 20-40 ml. Reduce the volume of the samples to 10-15 ml under dry nitrogen.

The following steps are identical to those used in water analysis

Derivatization:

Hexylmagnesium bromide is used as the Grignard reagent. Some companies (eg. Aldrich) produce this compound dissolved in ether while others (eg. TCI America) produce Grignard reagents in tetrahydrofuran (THF). Ether solutions should be stored in the refrigerator when not in use, but our experience with hexyl magnesium bromide in THF solvent has shown that it will form precipitates at reduced temperatures and therefore should be stored in the dark at room temperature. Grignard reagents will react exothermically with atmospheric moisture, so it is helpful to transfer the solution to a suitable apparatus for storage and delivery. Using dry nitrogen, pressurize the reagent bottle and transfer the reagent through Teflon tubing to a 250 ml flat bottom flask with a connecting adapter and a ground glass stopper (Kontes, P.O. Box 729, Vineland, NJ 08360, 1-609-692-8500, cat. # K211200-2440, Figure 3). A stream of nitrogen can now be passed through the flask via the side arm, so that Grignard reagent can be removed through the top neck of the flask by transfer pipette, without exposing the reagent to atmospheric moisture.

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 Neutralize excess Grignard reagent with concentrated HCl. Add 2 ml HCl to each sample. Shake vigorously and vent. Shake and vent two more times. Any precipitate should be dissolved. Let the samples sit for 30 minutes to separate the phases. Using a Pasteur transfer pipette, remove the lower (aqueous acid) layer and discard.

Sample clean-up:

 Sample extracts should be blown down to approximately 1.5 ml with dry Nitrogen in a 40 C bath before transferring to columns for cleanup. Rinse assembled columns with hexane and allow to air dry. Insert a small glass wool plug in the bottom of each column. Fill each column with 20 grams of activated (110°C) Florisil. Tap the column to pack it down. Add 2 grams of anhydrous Na_2SO_4 on top of the Florisil. Pack. Pour 75 ml of hexane through the column as a rinse into the 250 ml flasks. Discard rinse. Place the 500 ml round bottom flasks, saved from earlier extraction step, under the columns.

 Transfer the samples to the columns. Rinse the tubes three times with hexane and transfer rinses to the columns. Rinse the sides of the columns. Pour 300 ml of hexane through each column. Rinse the centrifuge tubes twice each with acetone and hexane and put the tubes aside to be used later. Reduce the volume of the samples in the 500 ml flasks to approximately 2 ml with the rotory evaporator and transfer back to centrifuge tubes, rinsing three times.

 Spike samples with tetrabutyltin (in hexane) internal standard at a concentration similar to surrogate standard concentrations. Reduce volume under nitrogen proir to injection onto the gas chromatograph. For ultra-trace analyses this is usually about 0.1mL.

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VIII. Testing Grignard Reagent and Tropolone for Butyltin Contamination

Companies that manufacture Grignard reagents often also produce butyltin compounds and tropolone. Since butyltins and Grignard reagents are both synthesized under an inert atmosphere, the same glassware may be utilized during production and a significant possibility exists for cross contamination. The vendors are usually unconcerned about low level (sub ppm) contamination problems and do not test Grignard reagents for the presence of butyltins. For this reason, before using any new lot of Grignard reagent or tropolone, the analyst should determine it's purity.

To test hexylmagnesium bromide:

Fill two 50 ml centrifuge tubes with 10 ml hexane. Spike each tube with the surrogate standard, tripentyltin chloride, at a concentration that would be equivalent to that encountered when analyzing environmental samples (approximately 50 ng TPT). Add Grignard reagent to the tubes, 0.5 ml reagent to one, and 1.0 ml to the other. After derivatization, pass the samples through Florisil columns and analyze by GC/FPD. If butyltins are present in the Grignard reagent, they will show up in both samples but concentrations should vary by a factor of two due to the varied amounts of Grignard reagent used.

To test tropolone:

Tropolone should be tested by analyzing deionized water samples. Following the procedure for water analysis, use one liter of water for a blank and one liter of water to test the recovery of butyltin spikes. Spike both samples with the surrogate standard, tripentyltin chloride (TPT). The blank should be spiked with TPT at a concentration suitable for 1 ng/L TBT detection limit (approximately 50 ng TPT). To test for the recovery of butyltins, spike the second sample with about 50 ng/l TBT, DBT, MBT and TPT. Analyze samples by GC-FPD according to the procedure for water analysis to note the presence of any TBT in the blank sample or poor recoveries of butyltin standards.

IX. GLASSWARE WASHING PROCEDURE

All glassware, stainless steel or any other surface in contact with samples or sample extracts must be thoroughly cleaned before using. The following procedure has proven adequate over the years on glassware used at VIMS for TBT analyses.

Rinse with hexane.
Wash with Alconox, water and a brush.
Soak overnight in a 5% Contrad© solution (~200 ml concentrated Contrad in ~ 4 l deionized water).
Return Contrad to jugs for reuse. Discard when cloudy or discolored.
Rinse thoroughly with tap water.
Rinse with 3N HCl.
Rinse at least three times with deionized water.
Rinse well with acetone, making sure any tape residue is removed.
Air dry.
Bake overnight at ~ 100 C
(be certain no traces of acetone remain before baking).
Cool; cover with Parafilm or aluminum foil for storage.
Prior to using, rinse well with hexane.

X. COLLECTION AND STORAGE OF ENVIRONMENTAL SAMPLES

Precautions should be followed when collecting environmental samples for TBT analyses. All containers should be pre-cleaned and sampling gear cleaned between stations. When collecting from boats confirm that hulls of sampling vessels are not painted with organotin antifoulant paints. Many aluminum hulled vessels still use TBT-based paints.

Water samples for monitoring purposes should be collected at the same point in the tidal cycle (ie:slack before ebb). Our laboratory uses a sampling apparatus consisting of a 4 liter amber glass solvent bottle held in an aluminum frame, attached to the end of a 4 meter long, 2.5 centimeter diameter aluminum pipe. A Teflon plug which fits into the bottle opening is attached to a 0.5 cm aluminum rod which is guided by screw eyes attached to the pipe. This plug can be inserted or removed from the bottle by raising or lowering the rod. This apparatus allows collection of water samples from elevated docks or piers.

Due to increased contaminant concentrations in the surface microlayer film, care should be used to avoid including the surface film when collecting water samples. Surface water samples are collected approximately 15 cm below the surface. The bottle is lowered with the plug in place. At sampling depth, the plug is removed, allowing the bottle to fill. The plug is replaced and the bottle is retrieved with the water which is discarded as a rinse. The procedure is repeated for collection of the sample.

Previous work has shown that the best sample container material to reduce sorption losses of butyltins from water samples is polycarbonate. Once collected, samples are transferred to clean 2 liter polycarbonate bottles, acidified to pH 2 with HCl and stored in a dark, cool (4° C) location until analyzed. Repeated analyses of acidified samples stored in the dark at 4° C has shown that they are stable for at least 13 weeks (Huggett et al, 1986).

Sediment samples are obtained by standard techniques used for collecting samples for organic analysis (ie. grab samplers and gravity cores). Sampling equipment is cleaned with copious amounts of water and then rinsed with methanol between stations. Samples are homogenized in the field and stored on ice in precleaned quart glass jars with Teflon© lined lids. Sediment samples are then kept frozen until analysis. Biota samples should be rinsed with clean water, wrapped in solvent rinsed aluminum foil and stored frozen prior to analysis.

XI. POTENTIAL SOURCES FOR REAGENTS AND SUPPLIES

The sources listed are presented as a guide only and not as an endorsement. Other companies may also offer similar products suitable for TBT analyses. Regardless of the source, reagents and solvents should be checked for purity by analysis of suitable reagent blanks prior to use.

VWR Scientific Products
8350 Arrowridge Blvd
Charlotte, NC 28217
1-800-932-5000

21835-032 Alconox
hydrochloric Acid: JT9535-3 Baker Hydrochloric Acid 36.5-38.0 %, “Baker Analyzed” Reagent grade
n-hexane: BJ 216-4*DK Hexane UV, Burdick & Jackson
acetone: BJ010-4*DK Acetone, Burdick & Jackson
copper: MK 464904

Aldrich Chemical Co.
P.O. Box 2060
Milwaukee, WI 53201
1-800-558-9160

tripentyltin chloride:	37,135-1
tributyltin chloride:	T5,020-2
dibutyltin dichloride:	20,549-4
monobutyltin trichloride:	20,105-7
tropolone:	T8,970-2
n-hexylmagnesium bromide:	25,502-5 *

* often contaminated with low levels of tributyltin

TCI America
9211 N. Harbor gate Street
Portland, OR 97203
1-800-423-8616

H0821 n-hexylmagnesium bromide in THF**

**Some batches contain inorganic tin, but this does not interfere with analyses

Fisher Scientific Co.
2775 Pacific Drive
P.O. Box 4829
Norcross, GA 30091
1-800-766-7000

Florisil: F101-3 Florisil, 100-200 mesh
Sodium Sulfate: S421-10 Sodium Sulfate, Anhydrous, granular
Contrad 70:04-355-1

GC gases available from various vendors

Nitrogen:1107-300 Nitrogen, prepurified
Air: 1001-300 Air Ultra Zero, size 300
Hydrogen: 1075-300 Hydrogen Ultra High Purity, size 300
Helium: 1069-300 Helium Ultra High Purity

XII. BIBLIOGRAPHY

Tributyltin analysis, like most environmental analytical chemistry, is a rapidly evolving field. The methodologies presented in this manual represent an ongoing evolution of techniques that has occurred at our laboratory. This evolution will continue through our own research and through the adaptation of the developments of others. A recent literature search on analytical methods for the analysis of TBT in environmental samples produced the following bibliography. It is not intended to be all inclusive or an indorsement for listed methodologies but is provided to the reader as a resource. Citations are listed in reverse chronological order.

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Determination of trace amounts of metallorganics in marine ecosystem by high-pressure liquid chromatography followed by inductively coupled plasma atomic emission spectrometric detection.

Mazzucotelli, Ambrogio; Rivaro, Paola
Istituto Chimica Generale, Univ. Genova, Genoa, 16132, Italy
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Gremm, Thomas J.; Frimmel, Fritz H.
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Environ. Sci. Technol. (1982), 16(2), 110-19

1981

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Jewett, K. L.; Brinckman, F. E.
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J. Chromatogr. Sci. (1981), 19(11), 583-93

Determination of butyltin species in water by gas chromatography with flame photometric detection.

Maguire, R. James; Huneault, Henri
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From: Gov. Rep. Announce. Index (U. S.) 1978, 78(25), 105

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Environ. Sci. Technol. (1978), 12(3), 288-93

XIII. LIST OF FIGURES

Figures are placed as a group at the back of this manual for quick reference by the analyst. Chromatograms and mass spectra from standards and environmental samples are provided.

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2 Apparatus for the Storage and Delivery of Grignard Reagent

3 Chromatogram of Alkyltins

4 Chromatogram: Hampton Creek Marina Water Sample

5 Chromatogram: Water Sample Spiked at 2ng/L

6 Chromatogram: Clam Extract

7 Chromatogram: Sediment Extract

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10 Mass Spectra: Dihexyldibutyltin (DBT) Standard

11 Mass Spectra: Hexyltripentyltin (TPT) Surrogate Standard

12 Mass Spectra: Trihexylbutyltin (MBT) Standard

13 Mass Spectra: Confirmation of TBT in an Environmental Water Sample

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15 Mass Spectra: Confirmation of MBT in an Environmental Water Sample

16 Measured TBT Concentrations in Elizabeth River Clam Samples: Mean and Standard Deviations for Replicate Samples

Figure 1. General Analytical Methodology for TBT Analysis

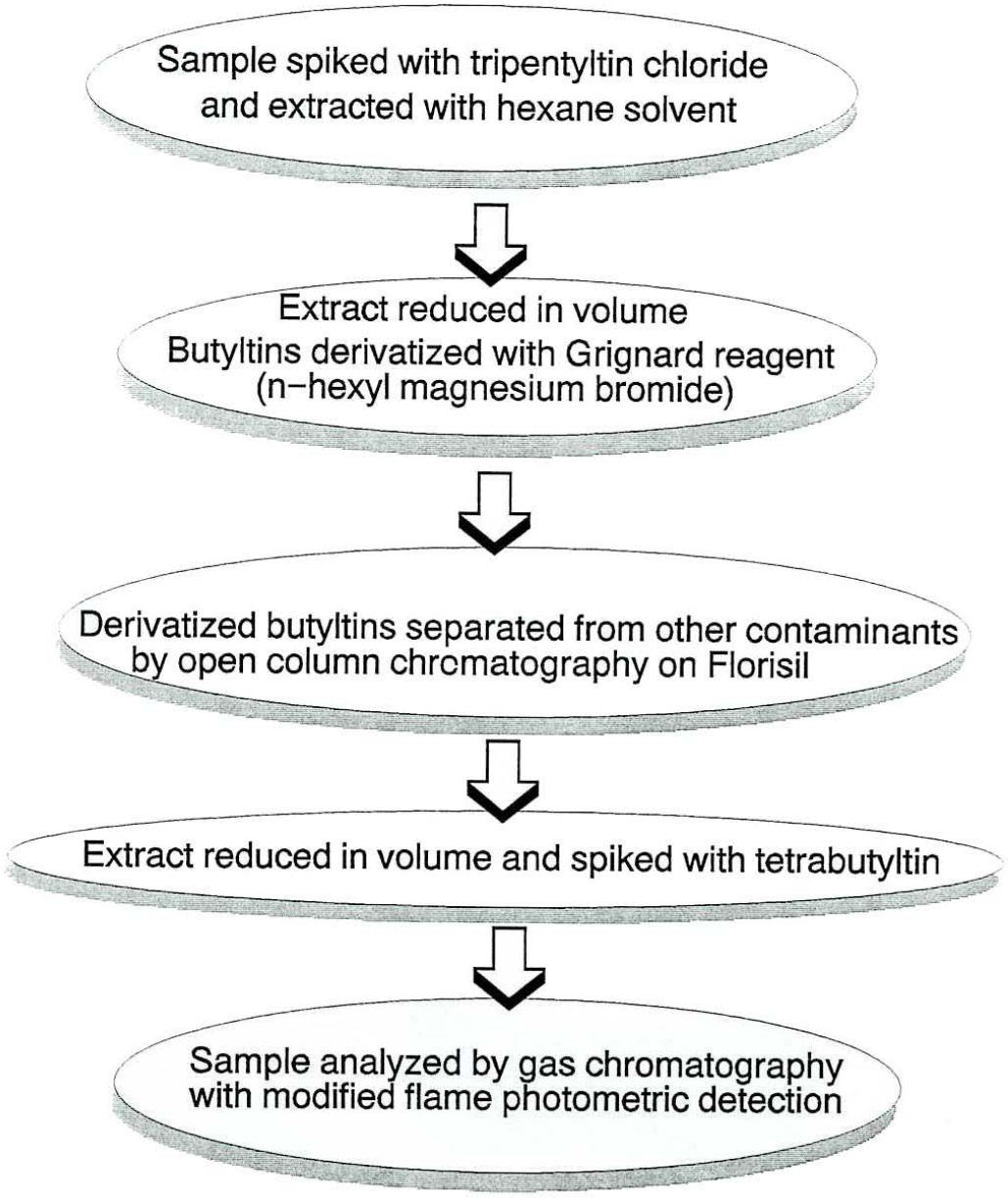
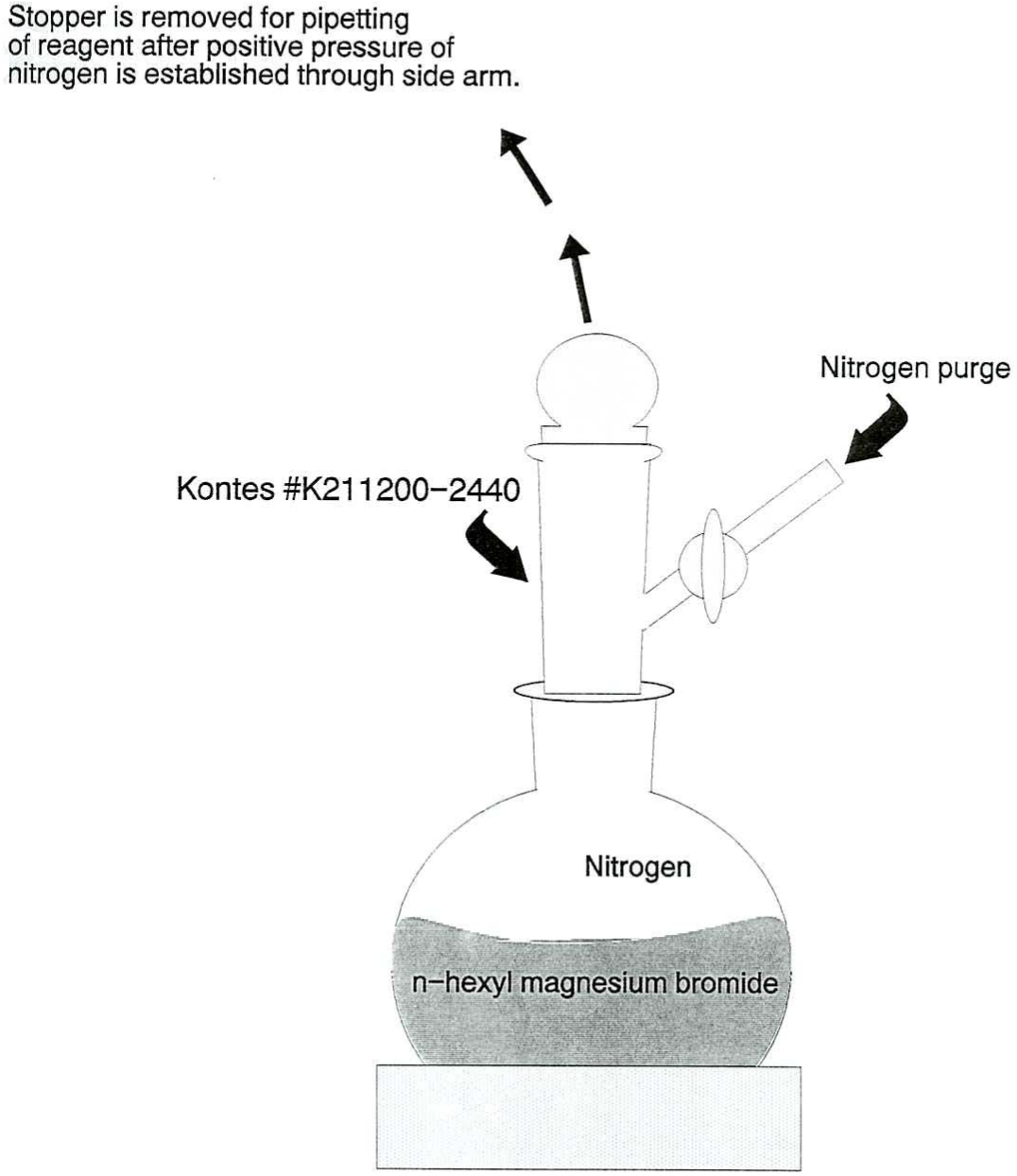


Figure 2. Apparatus for Storage and Delivery of Grignard Reagents



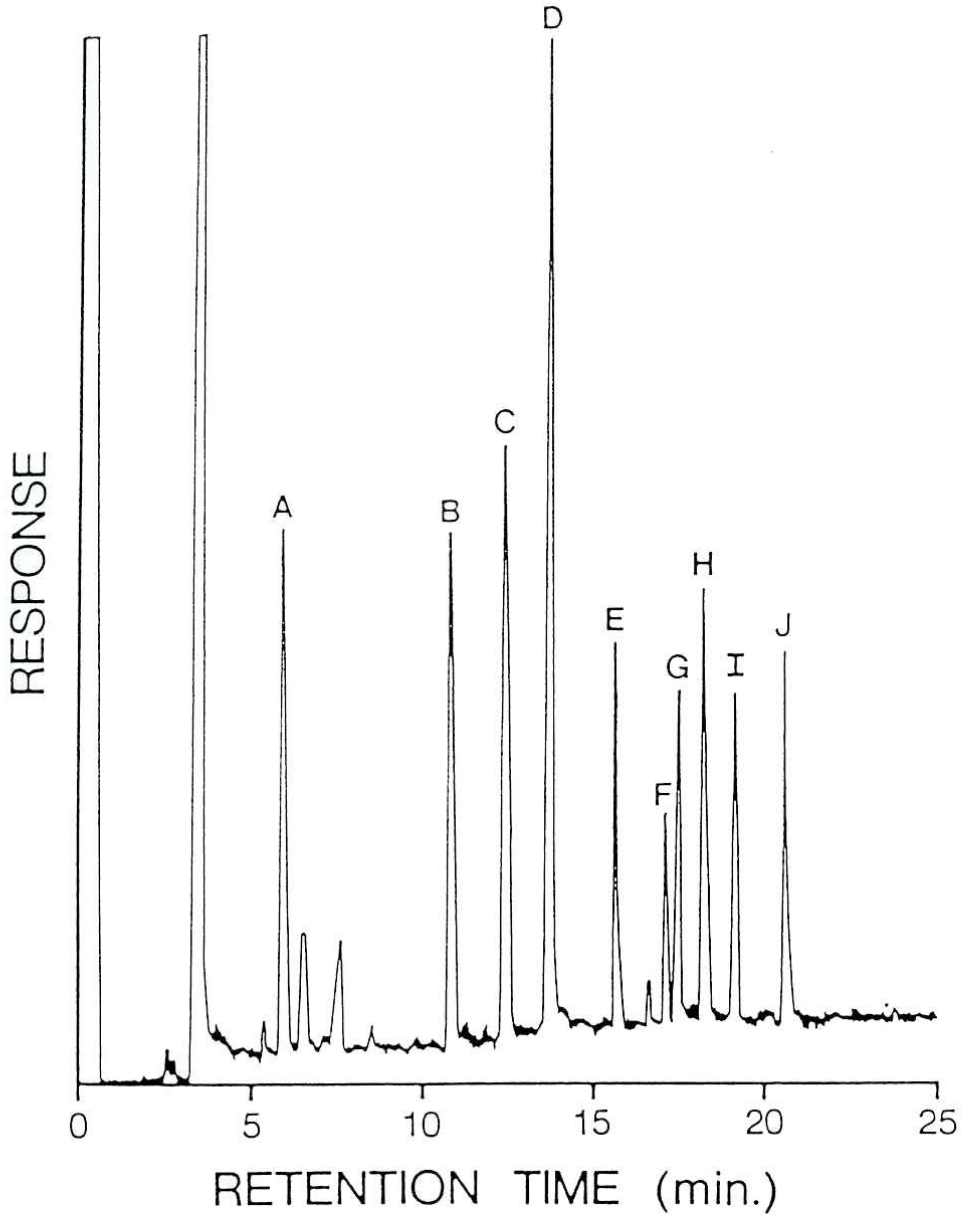


Figure 3. Chromatogram of Alkyltins (adapted from Unger et al, 1986). A. Hexyltrimethyltin (9C), B. Methyltributyltin (13C), C. Dihexyldimethyltin (14C), D. Tetrabutyltin (16C), E. Hexyltributyltin (18C), F. Trihexylmethyltin (19C), G. Dihexyldibutyltin (20C), H. Hexyltripentyltin (21C), I. Trihexylbutyltin (22C), J. Tetrahexyltin (24C).

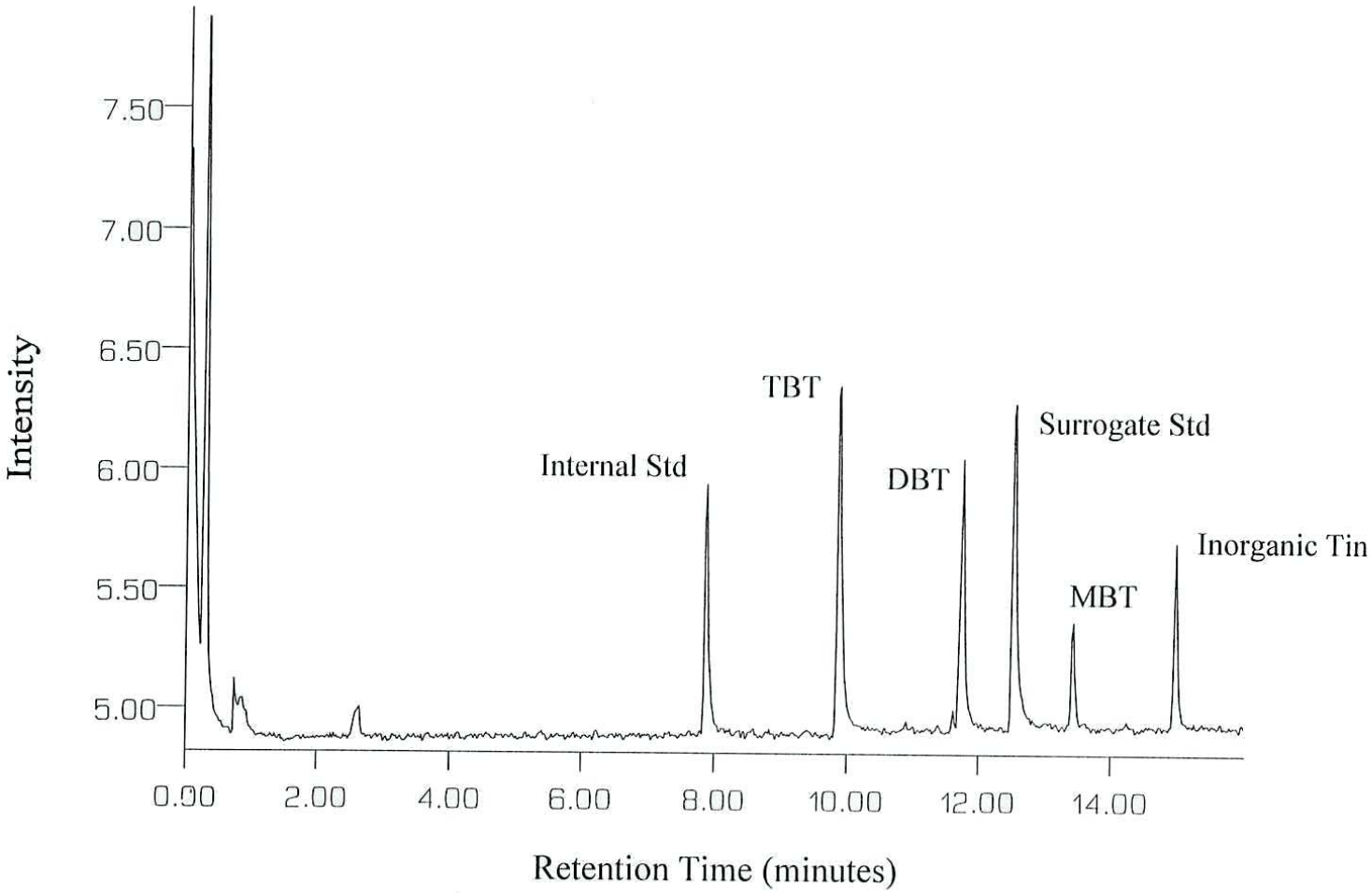


Figure 4. Chromatogram: Hampton Creek Marina Water Sample

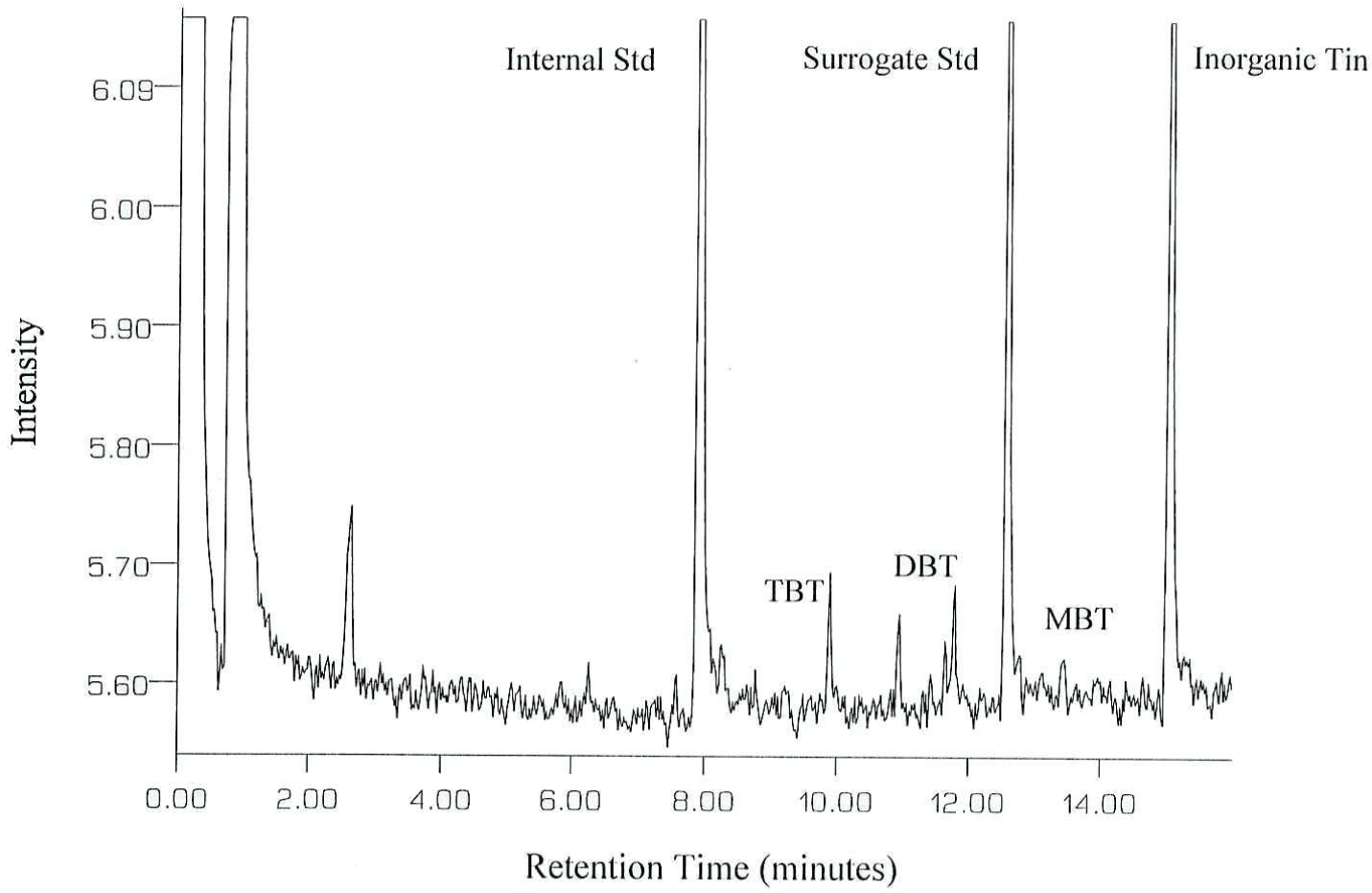


Figure 5. Chromatogram: Water Sample Spiked at 2 ng/L

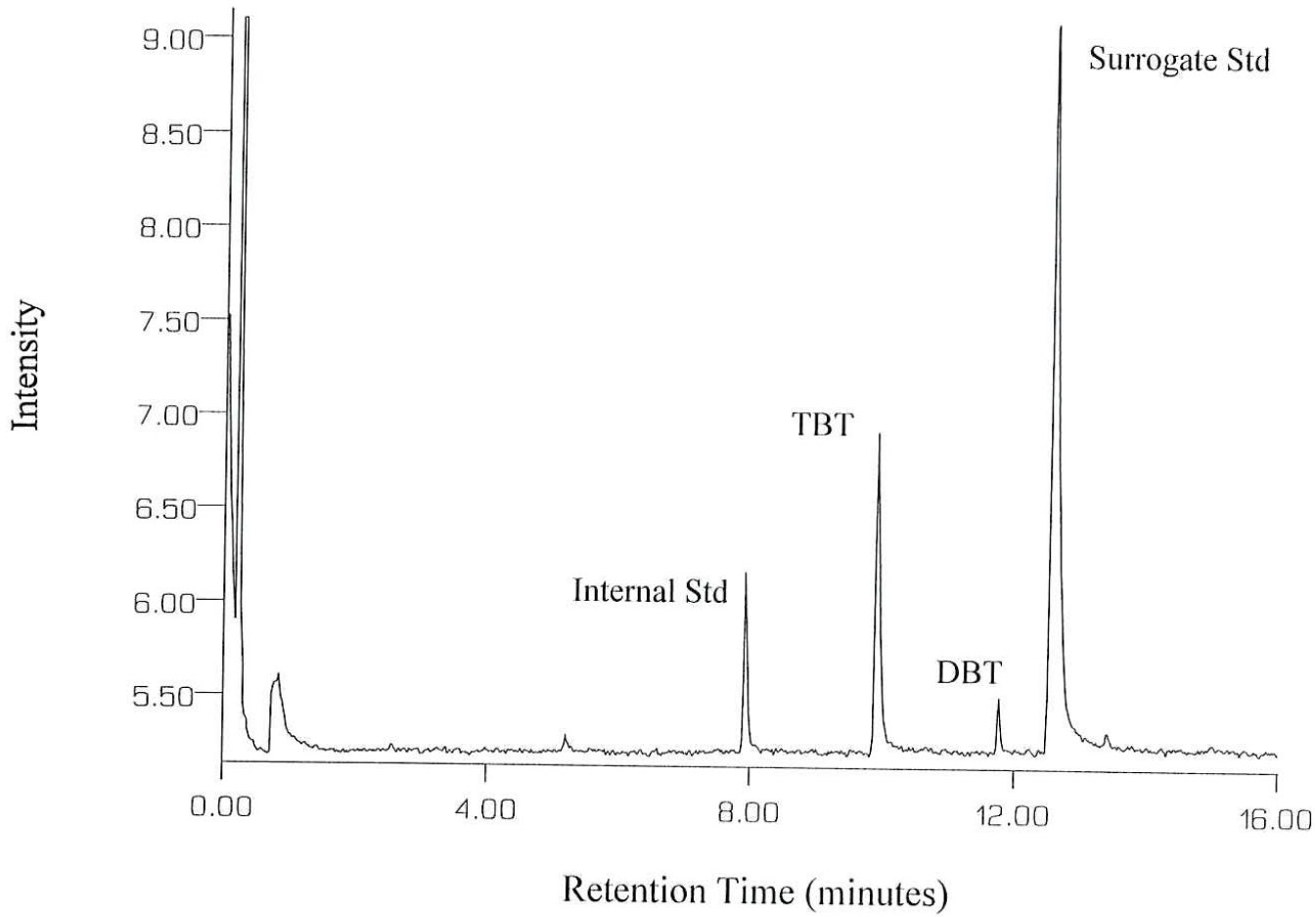


Figure 6. Chromatogram: Clam Extract

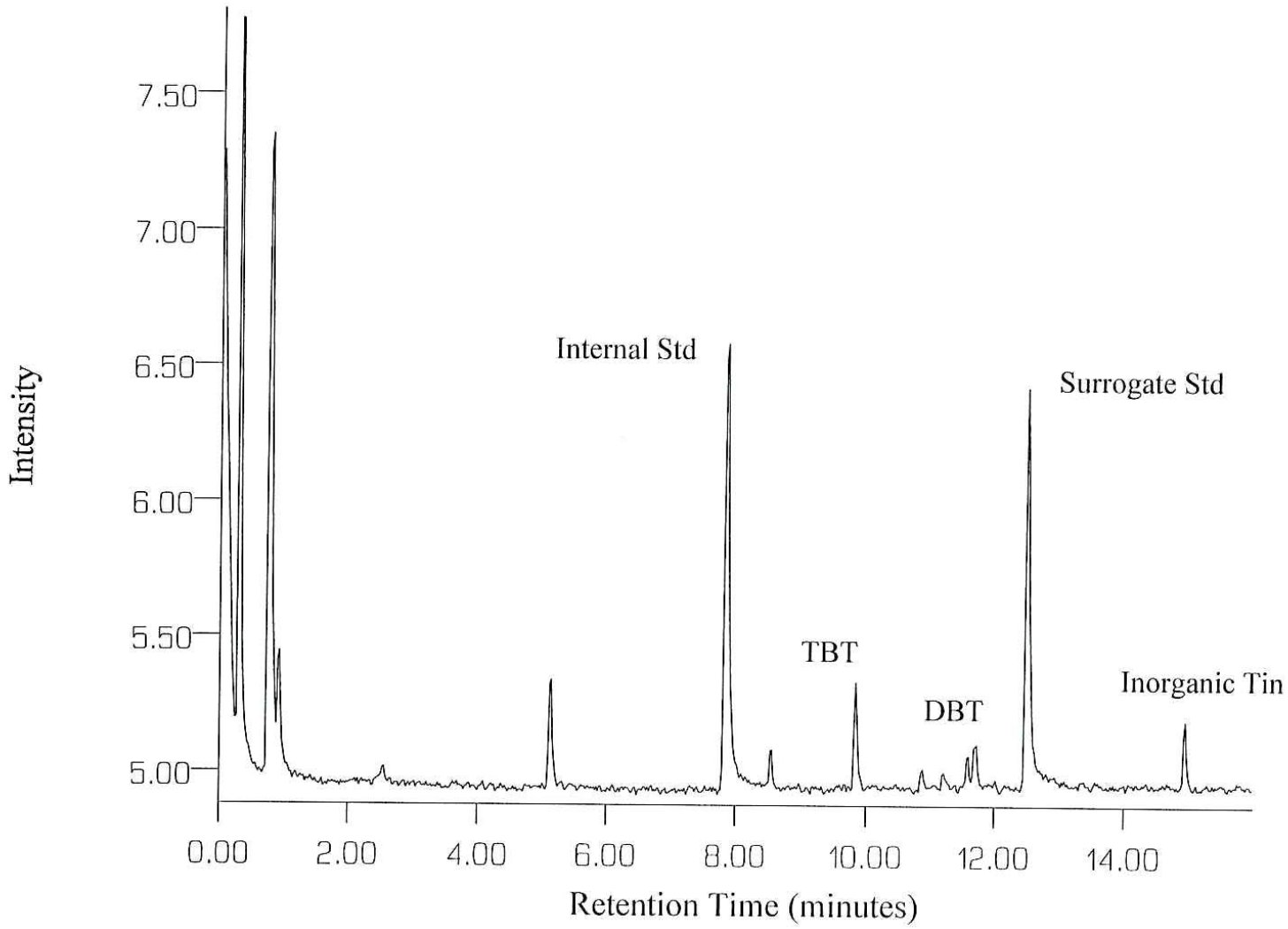


Figure 7. Chromatogram: Sediment Extract

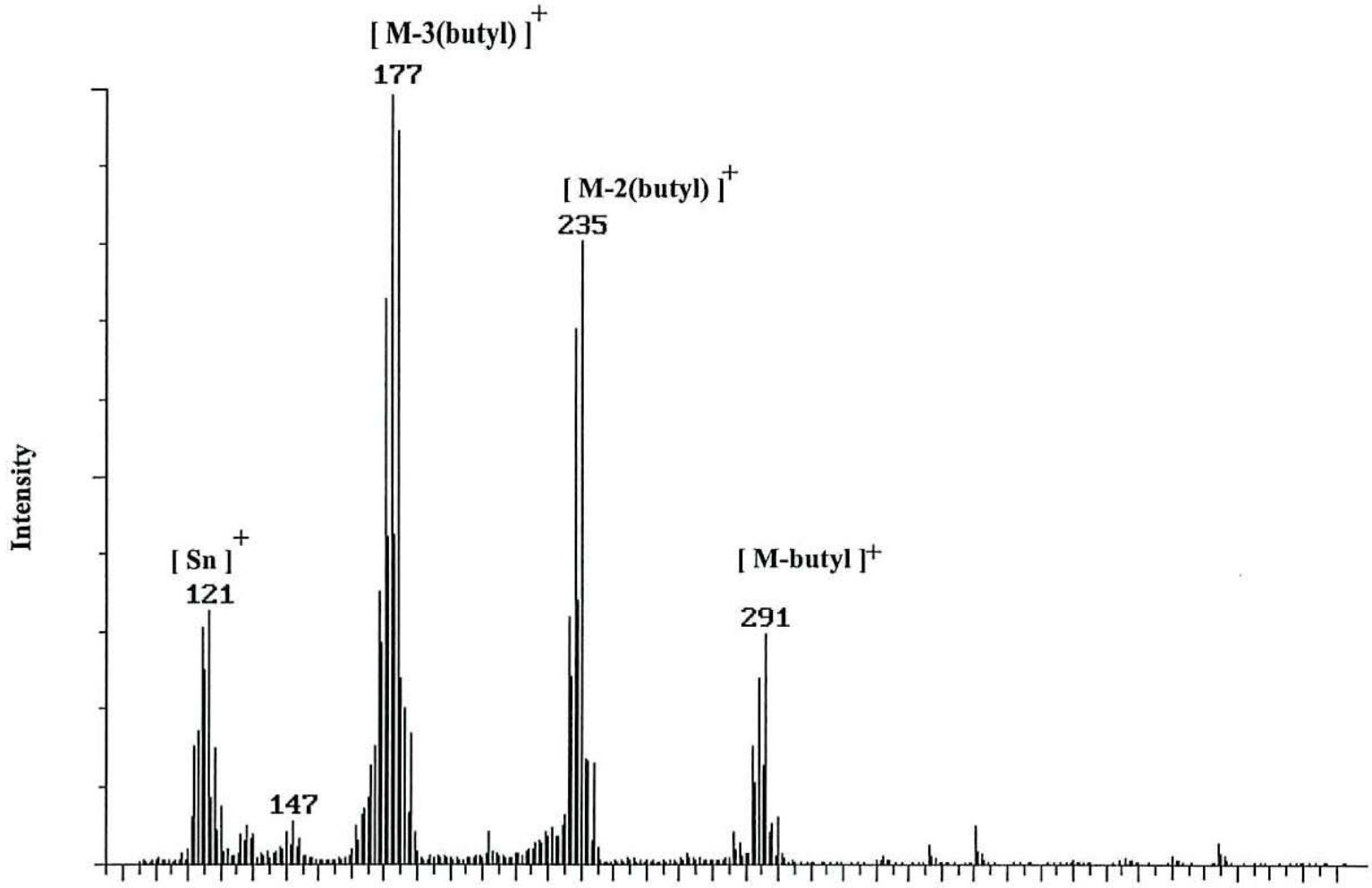


Figure 8. Positive EI spectra of tetrabutyltin - standard

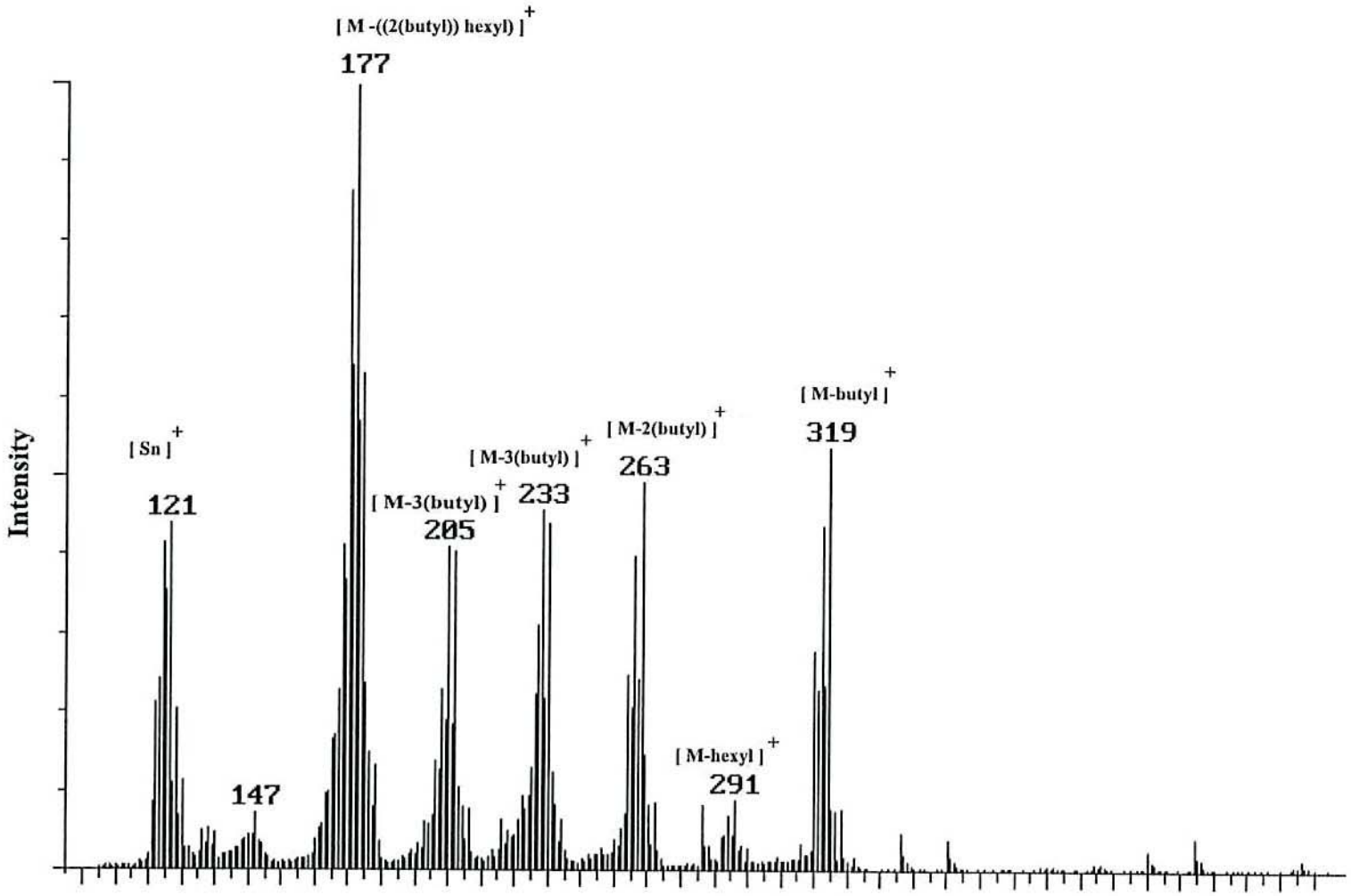


Figure 9. Positive EI spectra of hexyltributyltin (TBT) -standard

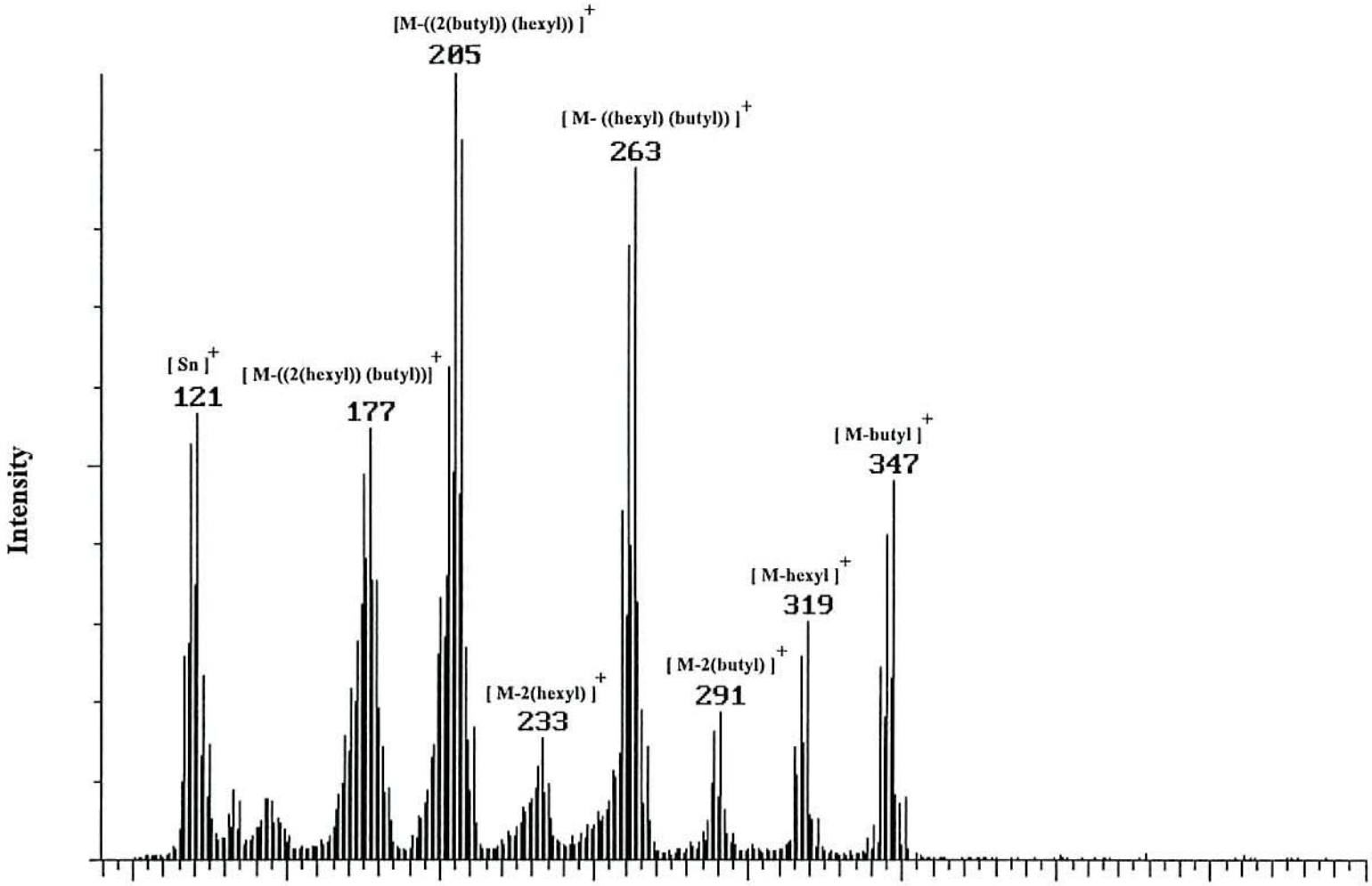


Figure 10. Positive EI spectra of dihexyldibutyltin (DBT) - standard

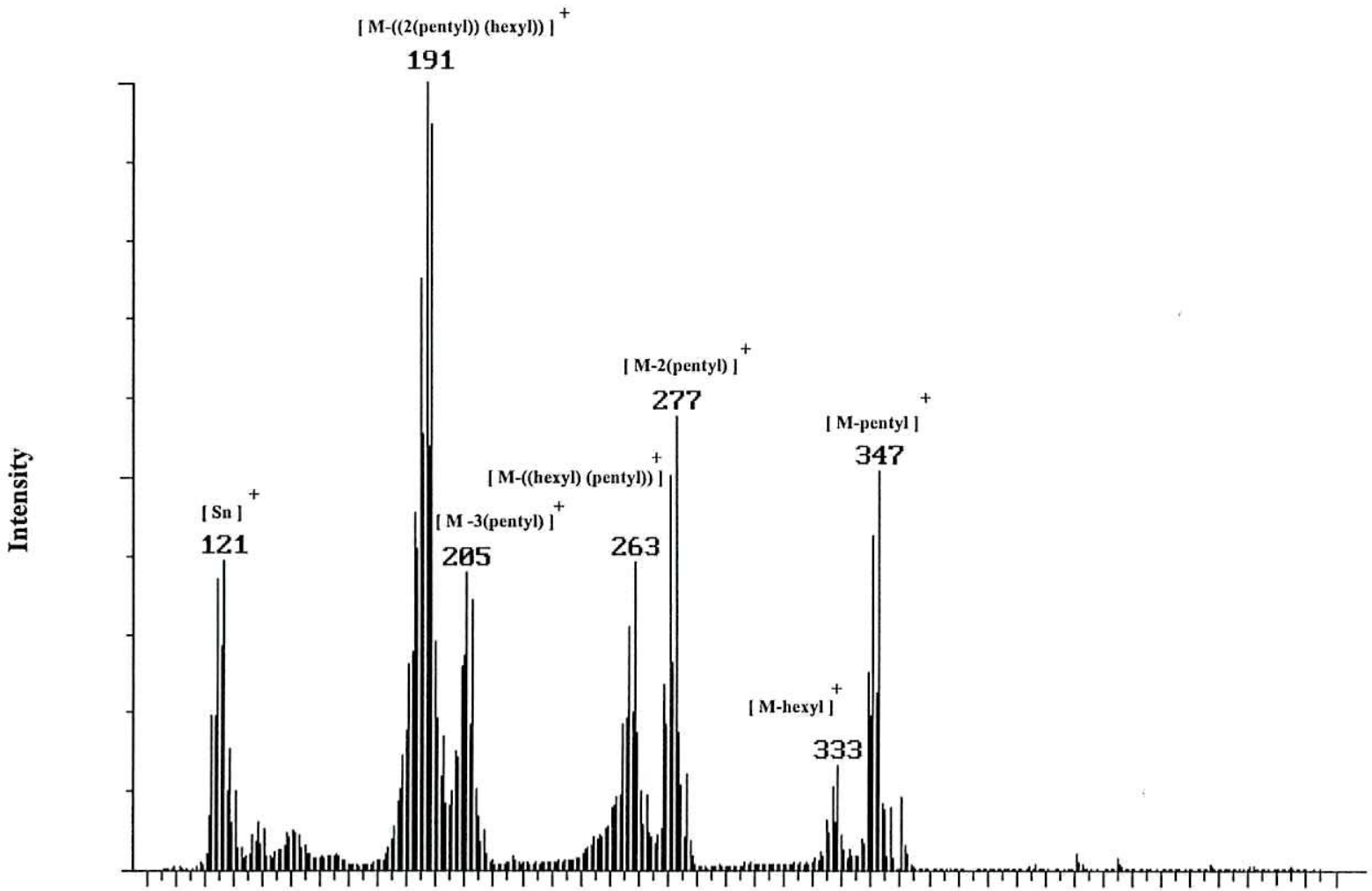


Figure 11. Positive EI specta of hexyltripentyltin - standard

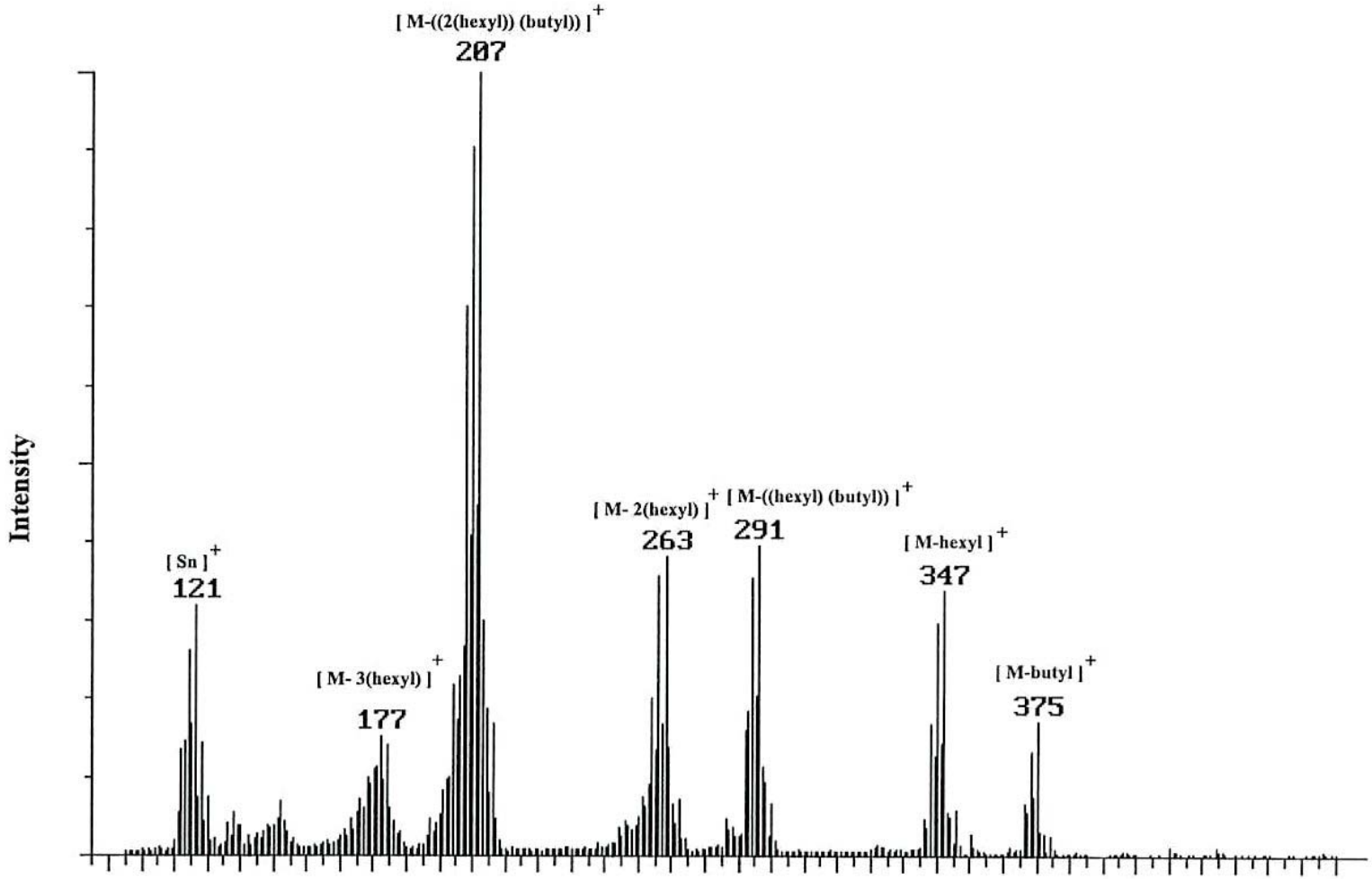


Figure 12. Positive EI spectra of trihexylbutyltin (MBT) -standard

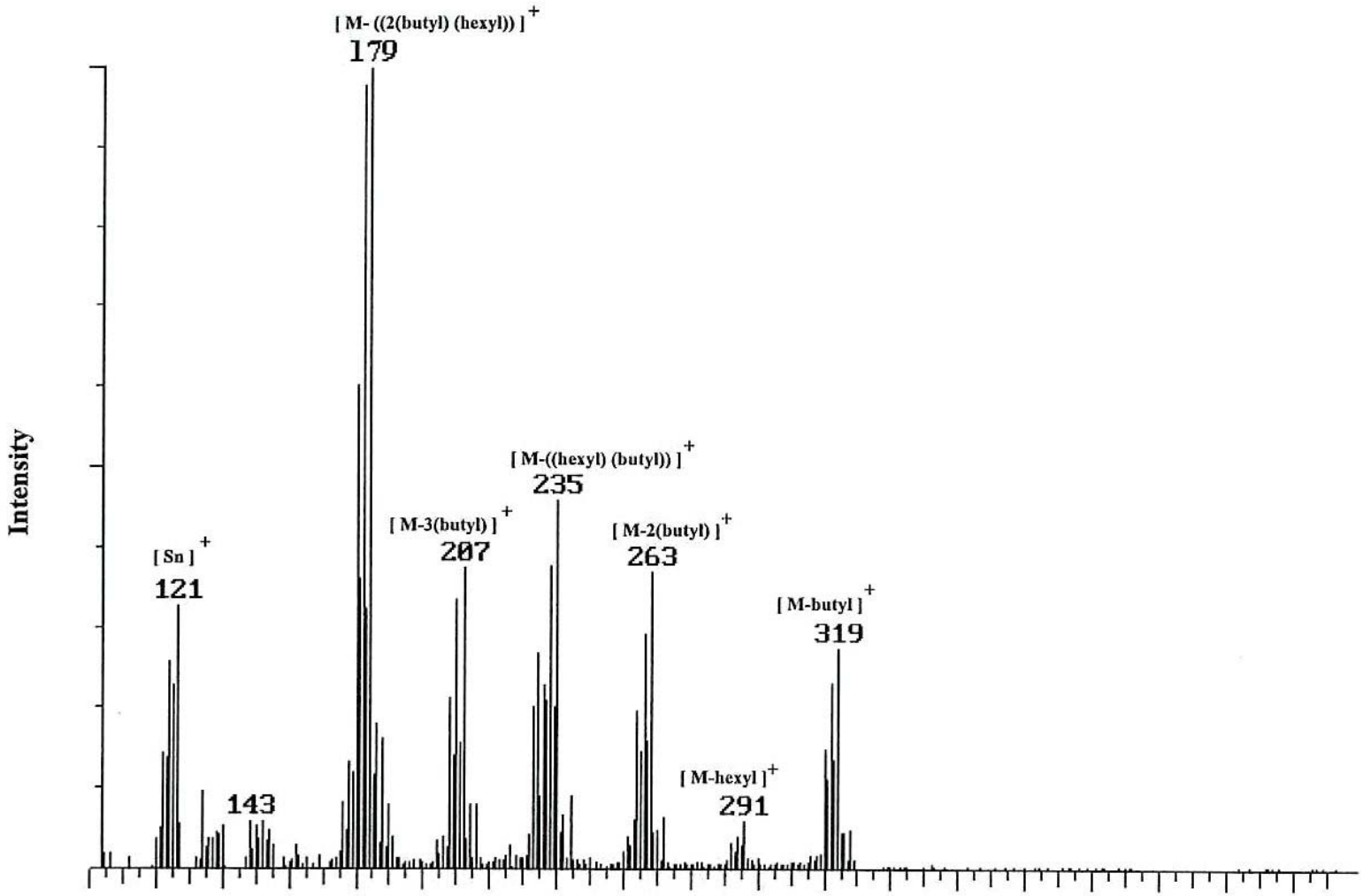


Figure 13. Positive EI spectra of tributylhexyltin (TBT) - marina water sample (HRM#2)

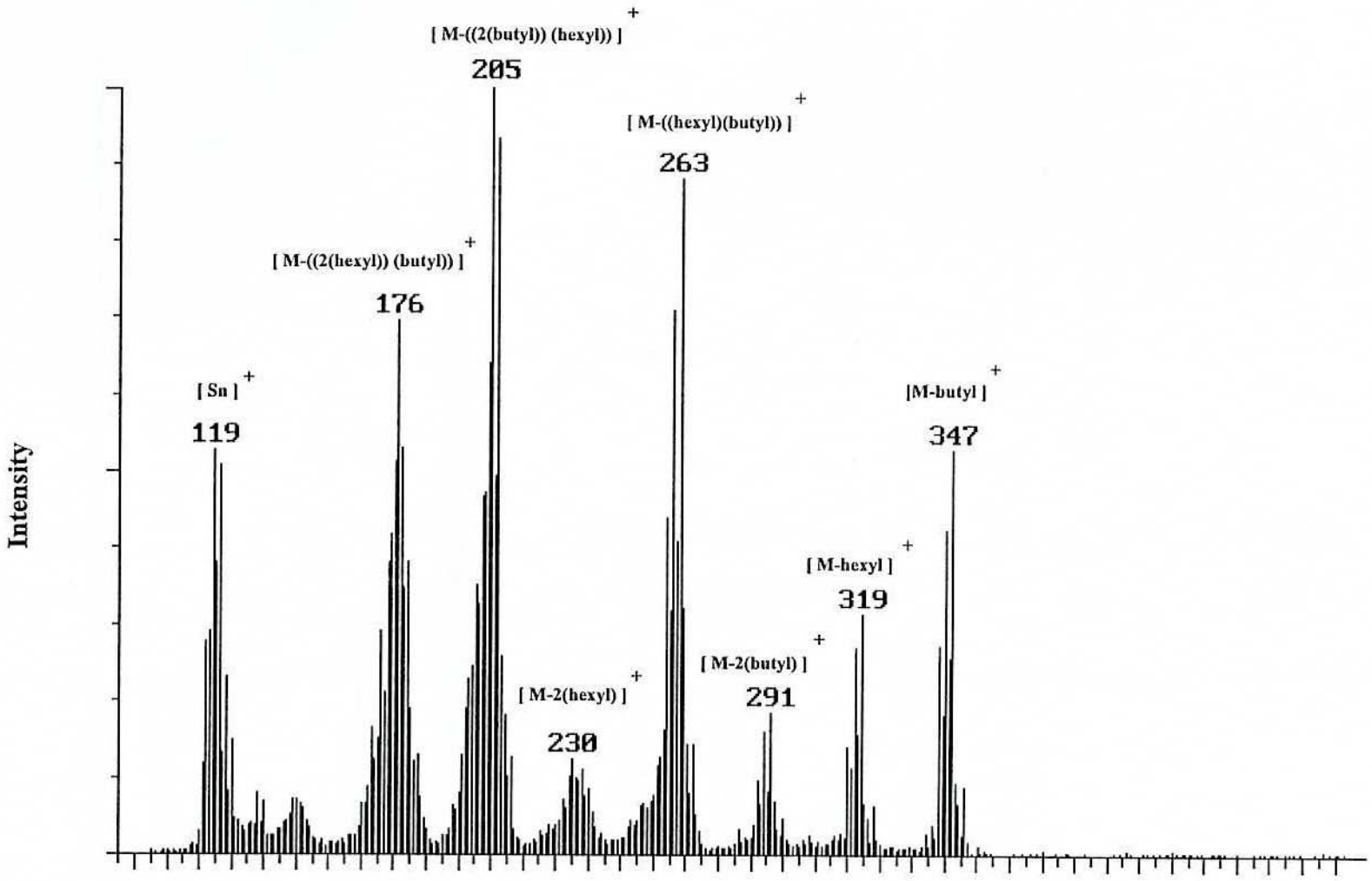


Figure 14. Positive EI spectra of dihexyldibutyltin (DBT) - marina water sample (HRM#2)

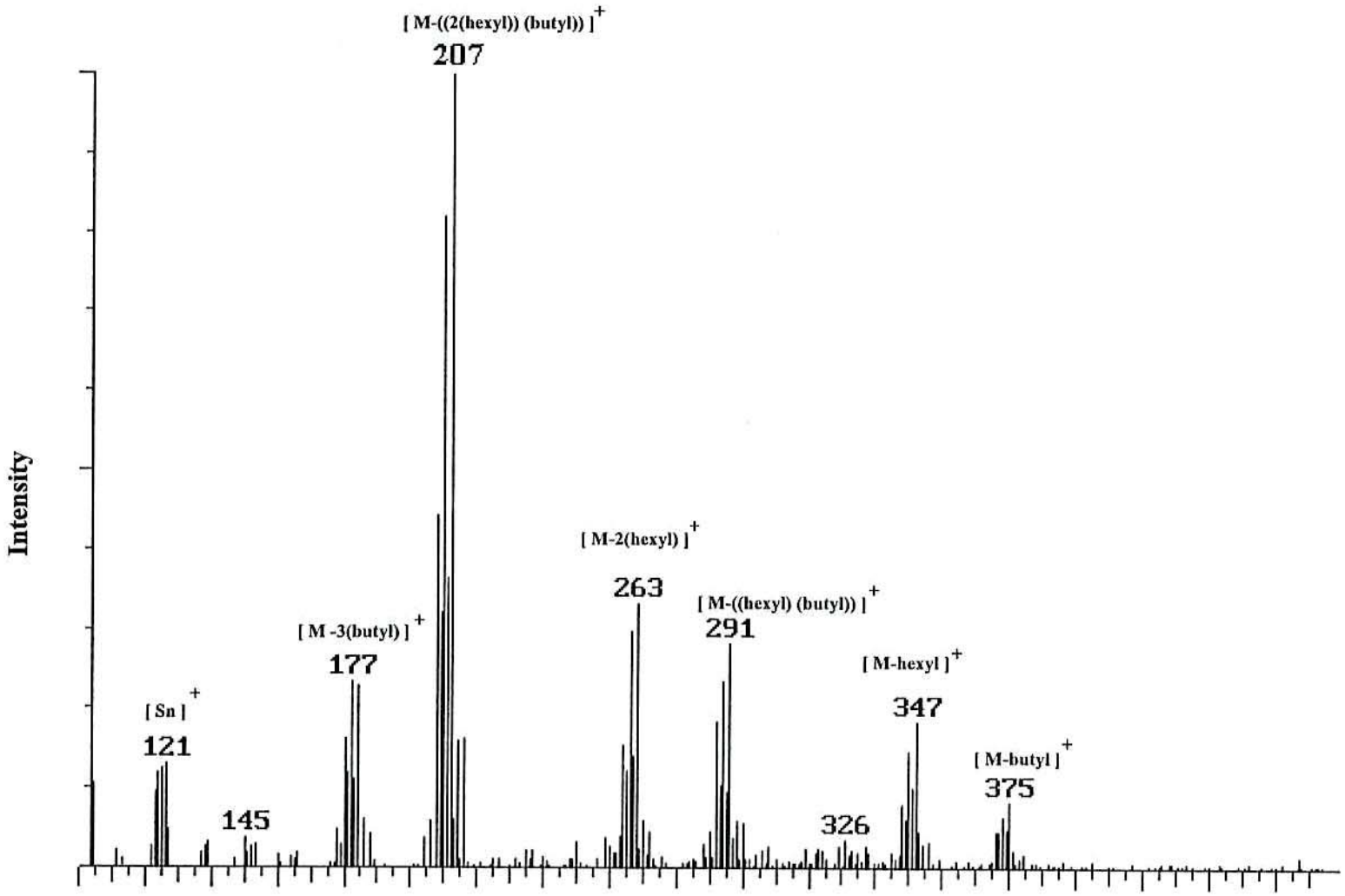


Figure 15. Positive EI spectra of trihexylbutyltin (MBT) - marina water sample (HRM#2)

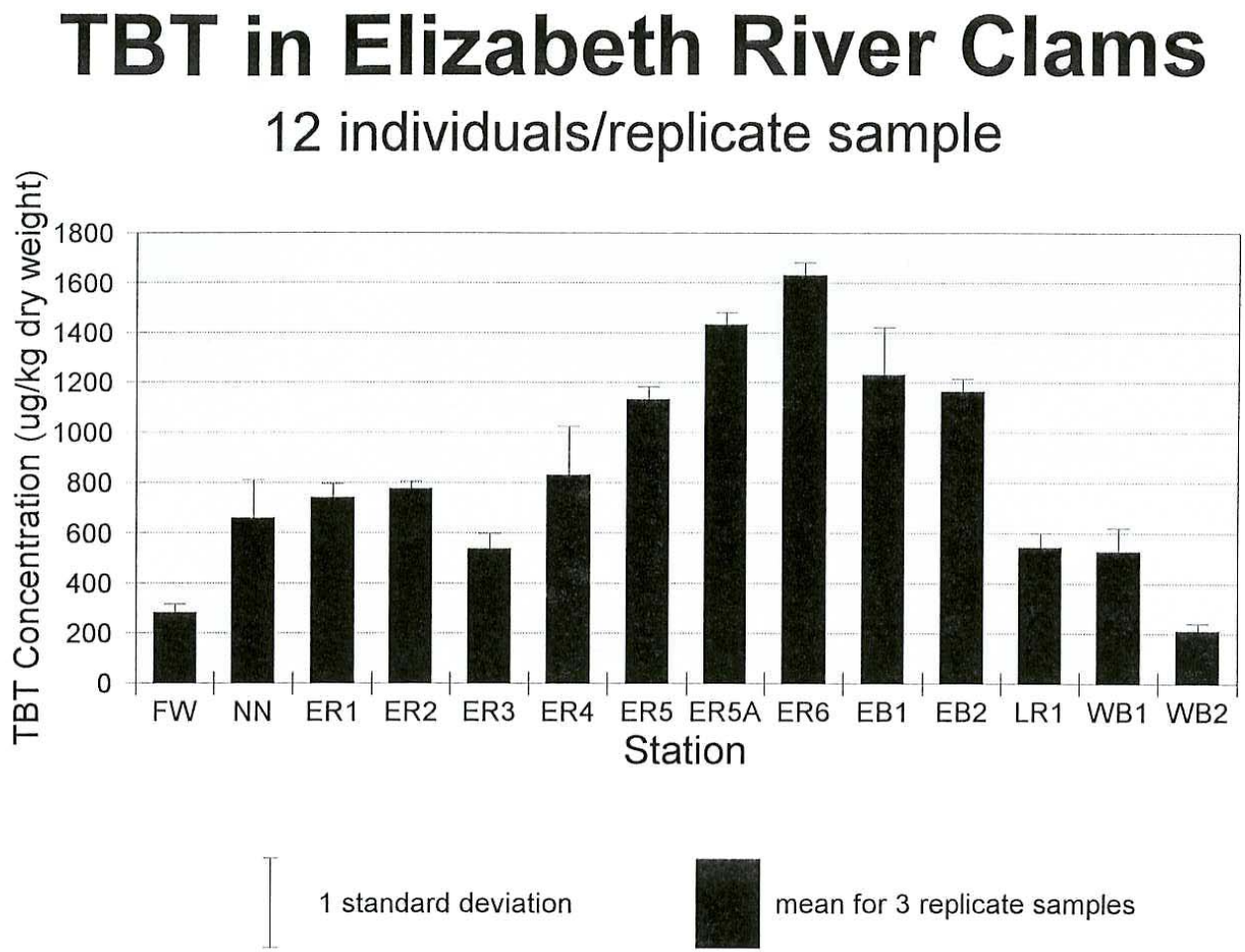


Figure 16. Measured TBT Concentrations in Elizabeth River Clam Samples