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Original Research

Development of an Analytical Method for Determining Tributyltin and Triphenyltin in Seawater, Sediment, and Mussel Samples Using GC-FPD and GC-MS – TOF

Hussein K. Okoro[1]*, Olalekan S. Fatoki[1], Bhekumusa J. Ximba[1], Folahan A. Adekola[2], Reinette G. Snyman[3]

[1]Department of Chemistry, Faculty of Applied Sciences, Cape Peninsula University of Technology, P.O. Box 1906, Cape Town, 7535 South Africa
[2]Department of Chemistry, Faculty of Science, University of Ilorin, P.M.B.1515, Ilorin, Nigeria
[3]Department of Biodiversity and Conservation, Faculty of Applied Sciences, Cape Peninsula University of Technology, P.O. Box 652 Cape Town 8000, South Africa

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Abstract

Analytical methods for speciation of targeted organotin compounds (TBT and TPT) in water samples using SPE cartridge and liquid-liquid extraction has been carried out. Also, sediment analysis using methanol-acid digestion and acid-sonication extraction methods also were developed. Different parameters affecting extraction and peak resolution were optimized. Also, three derivatization procedures were optimized. The accuracy of the extraction procedure also was verified on certified reference material (BCR-462) certified for TBT (54±15 µg/kg) and DBT (68±12 µg/kg). Freeze-dried mussel tissue (ERM-CE 477) was certified for TBT (2.20±0.19 mg/kg), DBT (1.54±0.12 mg/kg), and MBT (1.50±0.28 mg/kg). The two certified reference materials were used for recovery experiments. Good recoveries were obtained with methanol-acid digestion. The result was validated by analyzing the real water and sediment samples collected from Cape Town harbor and the compounds were detected in both water and sediment samples. Extraction of water samples with SPE gave better recovery for TPT than TBT. Performance characteristics such as linearity, detection limit (LOD), quantification limit (LOQ), and recovery were determined. Recoveries of TBT and TPT in spiked water using SPE were 65% and 70%, respectively. Quantitative recoveries also were recorded for the certified reference standards of sediments and mussel materials used.

Keywords: analysis, derivatization methods, organotin compounds, speciation, chromatogram

Introduction

Organotin (OT) compounds have been extensively used in boat paints since 1960 because of their excellent and long-lasting antifouling properties. A considerable number of studies have been conducted on the effects of organotins on aquatic organisms, their concentrations, and their distribution in aquatic environments. Two recently published review works by Okoro and his co-workers have brought to the fore the hazardous effects of organotin compounds on aquatic organisms [1]. Owing to the potential environmental accumulation and harmful biological effects, organotin

*e-mail: okoroowo@yahoo.com; OkoroHK@cput.ac.za

compounds are of growing public concern [2, 3]. Organotin compounds such as tributyltin (TBT) and triphenyltin (TPT) are used mainly in antifouling paints for ship hulls to inhibit growth of algae, barnacles, or mussels, which are killed upon contact with the paint. In addition, butyltins are used as fungicides, biocides, pesticides, wood preservatives, and stabilizing agents in polymers and catalysts [4, 5].

Owing to an increasing awareness of the undesired effects of TBT, efforts have been undertaken to find a global solution to this problem. Countries have passed legislation to control TBT release into the environment. However, the use of TBT in small boats has been prohibited in many countries since the mid-1980s [6, 7]. In spite of the regulation of TBT in various countries, significant concentrations of these compounds and their metabolites are still found in water [2], sediment [8, 9], suspended particles [10], and marine organisms [11]. For many years, organotin speciation has been an important topic in environmental analysis, primarily due to increasing awareness of the toxicological impacts of many organotin compounds [1].

Therefore, it is important to evaluate the status of organotin contamination, the chemistry, and the behavior of these compounds in the coastal environment, especially in Africa, where limited studies have been conducted on organotin speciation in the coastal environment. It is therefore necessary to develop simple, sensitive, selective, rapid, and economical methods for the quantitative determination of organotin compounds in environmental samples.

Different analytical methods have been used for the extraction and analysis of organotin compounds in environmental samples, food, and consumer product matrices. Sample preparation techniques for organotin speciation generally consist of several steps. The necessary steps depend on the physico-chemical properties of the analytes as well as the matrix environment (water, sediment, and biological matrices) [12]. However, the suitability of the sample preparation steps with the chosen analytical technique must also be assured [3]. Each analytical step needed in such determinations (e.g. derivatization, extraction, separation, and detection) can affect the accuracy and precision of the final quantitative speciation results. Therefore, two conflicting issues have to be balanced during extraction, i.e maximizing recovery rates and preventing analyte losses [13]. For GC analysis, a derivatisation step is necessary prior to separation due to the low volatility of the target compounds. Initially, methods were based on extraction with tropolone (a complexing agent) and n-hexane, followed by Grignard derivatization and analysis using gas chromatography (GC) separation and flame photometric detection (FPD).

Recently, insitu ethylation with sodium tetraethylborate ($NaBEt_4$) has largely replaced Grignard derivatization. More recently, new approaches are becoming popular which involve microwave-assisted extraction (MPE), superficial fluid extraction (PLE), solid phase extraction (SPE) [10], and solid phase microextraction (SPME). Thus, SPE and SPME meet modern requirements for analysis after sample preparation. It is therefore imperative that an acceptable extraction method for the determination of organotin compounds must possess sufficient sensitivity and selectivity. Most reported techniques so far involve a separation technique such as gas chromatography (GC) coupled to element-specific detection systems such as atomic absorption spectrophotometry (AAS), flame photometric detection FPD, pulsed flame photometric detection PFPD, or inductively coupled plasma mass spectrophotometry (ICP-MS) [12]. The aim of this study was to develop and optimize a sensitive and selective method for the determination of selected organotin compounds. In this paper we investigated the extraction efficiency of organotin using liquid liquid extraction and solid-phase extraction techniques. The best extraction method for sediment and mussel samples and different derivatization methods was also investigated. The whole analysis was carried out using GC-FPD, while the analytical methods were validated using gas chromatography coupled with time of flight (GC-MS – TOF). The characteristic absorption peaks for the certified organotin reference materials using FTIR techniques were studied.

Experimental

Instrumentation

Analyses were performed on a Shimatzu GC-2010 plus series gas chromatography (GC) instrument with a flame photometric detector (FPD). The GC was equipped with a phenomerex ZB5MSi capillary column (30 m × 0.25 mm I.D × 0.25 μm) coated with 5% phenylpolysiloxane. Automated injection was carried out with an auto sampler (AOC-20S). Optimized conditions of analysis are shown in Table 1.

Confirmation of GC-FPD results were carried out using GC-MS – TOF detection (optimized conditions of analysis for GC-MS – TOF are shown in Table 2).

Other Equipment

pH was measured using a pH meter with glass electrode from Beckman (Fullerton, USA). Lichrolit florisil SPE Cartridges (1000 mg, 6 ml, 125-150 m) were obtained from Sigma-Aldrich. A vortex mixer made by Scientific Industries Vortex Genie 2 was supplied by Lasec, South Africa, and a shaker (Orbishake) supplied by Labotech, Magnetic instrument (FMH instrument) was used.

Water Samples

MilliQ water and sea water samples collected from Cape Town harbor were used for recovery and validation experiments, respectively. Sea water samples were collected at coordinates S33 54.367 E1825.370 in triplicate with the aid of sample Boat Waveride DTC 787C (6.3 m stringray cat hull) supplied by Stringray Marine powered by Suzuki 90 hp 4-stroke engines and equipped with a Van Veen Grab sampler. Garmin GPS was used to locate the sampling coordinates. Samples were collected during low tide. The samples were collected from the Synchrolift and

Table 1. Instrumental Parameters for GC-FPD.

Parameter	Setting
Injection port	Split/Splitless mode: Splitless
Injection volume	1 µl
Injection port temperature	280ºC
Detector temperature	300ºC
Carrier gas – helium flow	1.69 ml/min
Column (Capillary column)	ZB-5MSi (5% phenyl, 95% Phenylpolysiloxane, diameters: 30 m × 0.32 mm × 0.1 µm film thickness
Oven temperature	50ºC for 1 min then 10ºC to 250ºC for 4 mins
Detector type	FPD

Table 2. Instrumental Parameters for GC-MS – TOF.

Instrumentation	Experimental conditions
Chromatographic system	Waters GCT equipped with CTC CombiPAL Auto sampler
Column	DB_XLB (30 m, 0.25 mm ID, 0.1 µm film thickness)
Injector temperature	280ºC
Column flow rate	1 ml/min
Injection volume	1 µl
Injection mode	Splitless
Purge flow	50 ml/min
Purge time	1 min
Carrier gas	Helium
MS mode	EI+
Scanning mass range	35 to 650 m/z
Scan time	0.15 min
Inter-scan delay	0.15 min
Oven temperature	50ºC for 1 min, then 10ºC to 300ºC for 4 mins
Detector type	MS coupled with Time of Flight

Robinson dry dock sites. A harbor map is shown in Fig. 1. The samples were stored in plastic bags in an ice chest and transported to the laboratory.

Standards and Reagents

N-Hexane, methanol, isooctane, dichloromethane, and tripropyltin chloride (98%) used as internal standard, was obtained from Merck (Germany). All organic solvents were of analytical chromatographic grade. They were doubly distilled prior to use. Tributyltinchloride (95%), dibutyltindichloride (96%), triphenyltin trichloride (95%), sodium tetraethyl borate ($NaBEt_4$, Tropolone 92 and hydroxyl- 2, 4, 6-cycloheptatrienone, glacial acetic acid (98%), sodium acetate, toluene (99%), hydrochloric acid (32%), silica gel (60-200 mm), and anhydrous sodium sulphate were purchased from Sigma-Aldrich South Africa. High-purity gases (helium, hydrogen, and medical air (99.999%) were purchased from Afrox (Pty) Ltd. (South Africa). All glassware used was soaked overnight in 1M HNO_3 to remove sorbed organotin compounds, and rinsed with milliQ water and acetone immediately before use.

Solutions

Stock organotin solutions (1000 mg/l) were prepared in methanol and stored at +4ºC in amber bottles in the refrigerator. Working standards of 100 mg/l in methanol were prepared weekly. Solutions containing 10 mg/l were prepared daily by dilution in methanol. The sodium acetate buffer (CH_3COOH /CH_3COONa) was prepared by adding an appropriate amount of sodium acetate in MiliQ followed by pH adjustment with acetic acid to pH (5.4). The working solution of sodiumtetraethylborate was freshly prepared in methanol and stored at +4ºC. Purified water was obtained from a MilliQ water system purchased from Millipore (USA).

Samples

Freeze-dried coastal sediment (BCR-462) certified for TBT (54±15 µg/kg) and DBT (68±12 µg/kg) was obtained from the Institute for Reference Material and Measurement (IRMM), Geel, Belgium. Freeze-dried mussel tissue (ERM-CE 477) certified for TBT (2.20±0.19 mg/kg), DBT (1.54±0.12 mg/kg), and MBT (1.50±0.28 mg/kg) was also obtained from IRMM, Geel, Belgium. These certified reference material were used for recovery experiments.

Optimization of Extraction Method

Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) were tested for extracting the target OTC from water samples as follows:

Liquid-Liquid Extraction

This was carried out according to Ikonomu et al. [14], but with modifications. Three aliquots of 100 mL water samples were transferred into volumetric flasks and acidified to pH 2. The mixture was spiked with a known concentration of standard solution. The spiked samples were shaken manually and left to equilibrate for 15 mins prior to derivatization. 10 ml of 1M sodium acetate buffer at pH 5.4, 1ml of sodium-tetraethyl borate (STEB) in methanol (1% v/v) and 3 ml of isooctane were added for ethylation. This was followed by extraction with 50 ml hexane by shaking for 2 mins. The 50 ml hexane extraction was repeated. The organic layer was dried over anhydrous sodium sulphate to remove water. Purification on activated silica was followed by concentrating the solution to 1 ml under a gentle stream of nitrogen gas. Volumes of 1 µL were injected into the GC-FPD instrument for analysis.

Optimization for Derivatization Procedure

Three derivatisation methods were employed for organotin ethylation. The one with the best yield was employed for the experiment.

Derivatisation Method I

1 ml of organotin standard, 1 ml of acetate buffer (82 g/l) sodium acetate in water, adjusted to pH 4.5 with acetic acid), and 50 µl of a derivatizing reagent were added. The derivatizing agent was prepared by dissolving 2 g $NaBEt_4$ in 10 ml methanol (20%). This solution was freshly prepared. The sample mixture was shaken and allowed to react for 30 mins. After the addition of 5 ml water, the derivatized compounds were extracted in 1 ml hexane. The mixture was centrifuged for 10 secs and the two phases were allowed to separate. The clear upper layer was transferred to an auto sampler vial for analysis. The resulting organotin compounds are ethyl derivatives.

Derivatization Method II

1ml of acetate buffer was added to 1 ml of organotin standard. 1 ml of 1 % STEB in methanol followed by 3 ml of isooctane were added to this mixture. The mixture was shaken for 30 mins and dried over anhydrous sodium sulphate and later concentrated to 1ml under gentle stream of nitrogen and then reconstituted by adding 1 ml of n-hexane.

Derivatization Method III

The same reagents were added as described in method II, but the difference was that after drying over anhydrous sodium sulphate, the extract was then blown to dryness over a hot plate and reconstituted with 1 ml of isooctane. The three mentioned derivatization methods gave a satisfactory yield and good resolution. Method I was preferred due to its excellent resolution, highest yield, and sharp peaks (Fig. 2).

Solid Phase Extraction Procedure

The sample was first pre-treated by filtering through a 90 mm filter paper to remove suspended particles. A 1 M solution (2 ml) of hydrochloric acid was added to the sample as a preservative. The mixture were stored in a 1-L acid-washed amber glass bottles and kept refrigerated at 4ºC for later use. The extraction was carried out according to Vidal et al. [15] with some modifications. 500 ml of water sample was adjusted to pH 2 with HCl. 15 g of NaCl was added

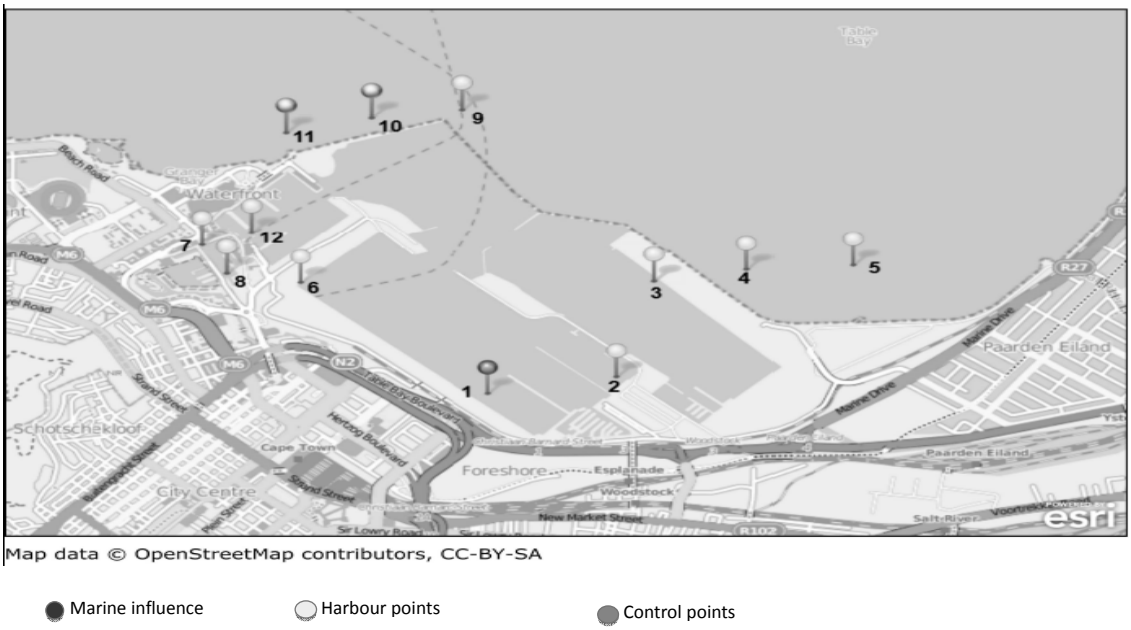

Fig. 1. Map of the twelve sampling sites at Cape Town harbor.

in order to simulate seawater samples. Each water sample was aspirated through Strata C18 SPE cartridges previously conditioned with a sequence of 5 ml of toluene, 5 ml of methanol, and 5 ml of milliQ water. Each cartridge was dried for 45 minutes before use. The cartridges were not allowed to dry completely during the extraction process, and air contact with the column was avoided during the extraction process. A vacuum pump connected to PTFE tubing was used to pump the water sample through the column. The sample flow rate was controlled at 8 to 10 ml/min. The analytes were eluted from the SPE cartridge with 10 ml of toluene under gravity and concentrated to 2 ml by bubbling nitrogen gas in the sample. The samples were then ready for GC-FPD analysis.

Optimization for Clean-up Procedure

Activated silica was spread on aluminium foil and oven-dried at 180ºC for 24 hrs and at 240ºC for 2 hrs before use. The one baked at 240ºC for 2 hrs gave efficient extract

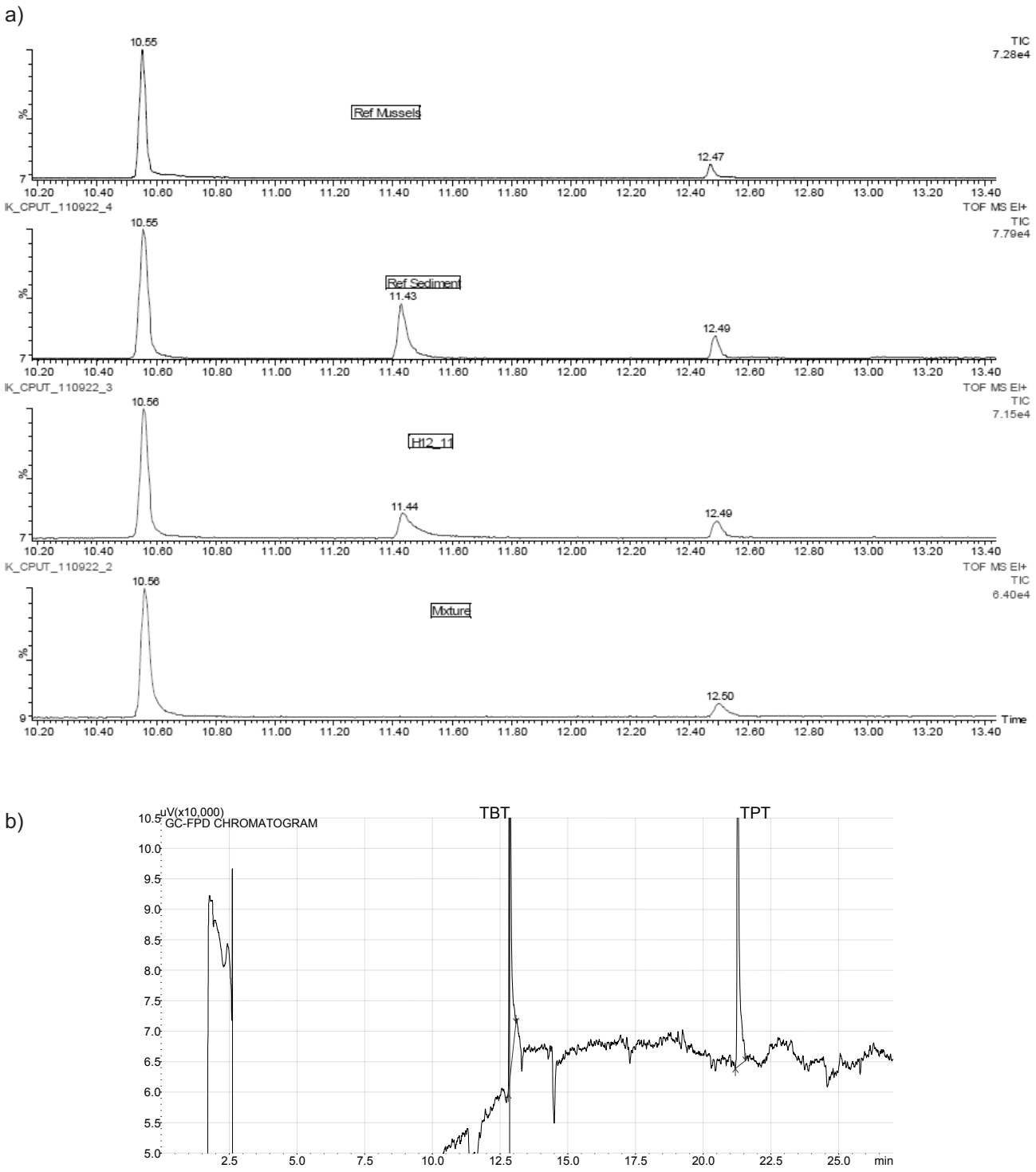

Fig. 2. a) GC-MS TOF chromatograms for the analysis of organotin in reference sediment, sample and mixture TBT: 11.42; b) GC-FPD showing chromatogram of reference standards.

Table 3. Calibration data for the GC-FPD.

Analyte	Retention time	Calibration plot	r^2	R	LOD	LOQ	Mean RF	%RSD
TBT	12.85	Y= 4358x+12619	0.998	0.90	0.01	0.003	97850.81	25,838
TPT	21.286	Y= 10345x-28859	1.00	0.91	0.01	0.003	8, 1714e-^{06}	11,637

Table 4. Comparison of experimental and reference values of the certified reference material.

Organotin compound	Reference material	Certified value	Obtained value	% Recovery
Tributyltins	BCR462 reference material for Coastal sediment	54 ±15 µg/kg	35±15 µg/kg	64.81
	ERM-CE 477 reference material for mussel	2.20±0.19 µ mg/kg	1.5±0.19 µ mg /kg	68.18

Table 5. Experimental data from GC-MS – TOF measurement.

Organotin solute reagent derivatives	Abbreviation	Molecular ions	Molecular formula
Tributyltin	TBT	291, 289, 207, 205	$C_{12}H_{27}Sn$
Tributyltin acetate	TBT-OAC	57, 121, 179, 233, 293	$C_{14}H_{30}O_2Sn$
Tributylpheny	TBPh	41, 78, 197, 311.	$C_{18}H_{32}Sn$
Tributylethy Stannane	TBE	41, 57, 71, 121, 177, 207, 235, 263, 288	$C_{14}H_{32}Sn$
Triphenyltin	TPT	51, 78, 120, 149, 197, 273, 351	$C_{18}H_{15}Sn$

clean-up. The column was prepared by first packing anhydrous sodium sulphate on the bottom, followed by silica gel in the middle, and anhydrous sodium sulphate on top. The main reason for the clean-up step was to purify the extracts as well as to remove the color that might be present. This could affect the injector in the GC. The main purpose for using activated silica was to trap the analyte of interest, and release it during the elution step. Anhydrous sodium sulphate allows free flow of eluent during elution and also removes water that might be in the eluent after extraction. After the optimized procedure, the derivatized extracts were purified on a column containing activated silica gel soaked with a mixture of n-hexane and toluene (1:1 (v/v). The solvents used for conditioning the column and sample elution were toluene and n-hexane. The good percentage recovery reveals that the solvent is good for the clean-up process. Organotin compounds were eluted with the same solution. The eluted samples were then ready for analysis on the GC-FPD.

For water samples, the clean-up of the extract was accomplished by an SPE method using florisils. The procedure was very simple owing to the fact that cartridges retained the organotin when extracts were passed through without retaining any potential interference that had been co-extracted with the target analytes. The organotins were then eluted with toluene and n-hexane (1:1; v/v). One major advantage of the clean up step is that it increases the stability of the analytes in the extracts. Extracts obtained without proper cleanup steps showed lower stability than those extracts obtained with clean-up.

Extraction of Organotin Compounds from Sediments

Three different methods were employed for the extraction of organotins from sediments

Method I
(Methanol/Acetic Acid Digestion)

0.2 g of air-dried sediment sample was placed in a reaction vessel. 4 ml of a mixture of acetic acid and methanol (3:1), 3 ml of acetic acid and 1ml of methanol were added. The resulting slurry was exposed to ultrasonic sonication (80 W) for 30 mins. A volume of 1ml of the extract was derivatised as described above.

Method II
(Methanol/Hydrochloric Acid Digestion)

0.5 g of air dried sediment was placed in a centrifuge tube. 2 g of NaCl, 12 ml of toluene, 7 ml of 0.03% (w /v) tropolone in methanol and 0.7 ml of 32% HCl were added. The capped tubes were shaken for 60mins. The organic layer was collected and concentrated for further analysis.

Method III
(Mechanical shaking)

10 g of air dried sediment was weighed into a 250-ml round bottom flask. 10 g of sodium chloride, 20 ml of

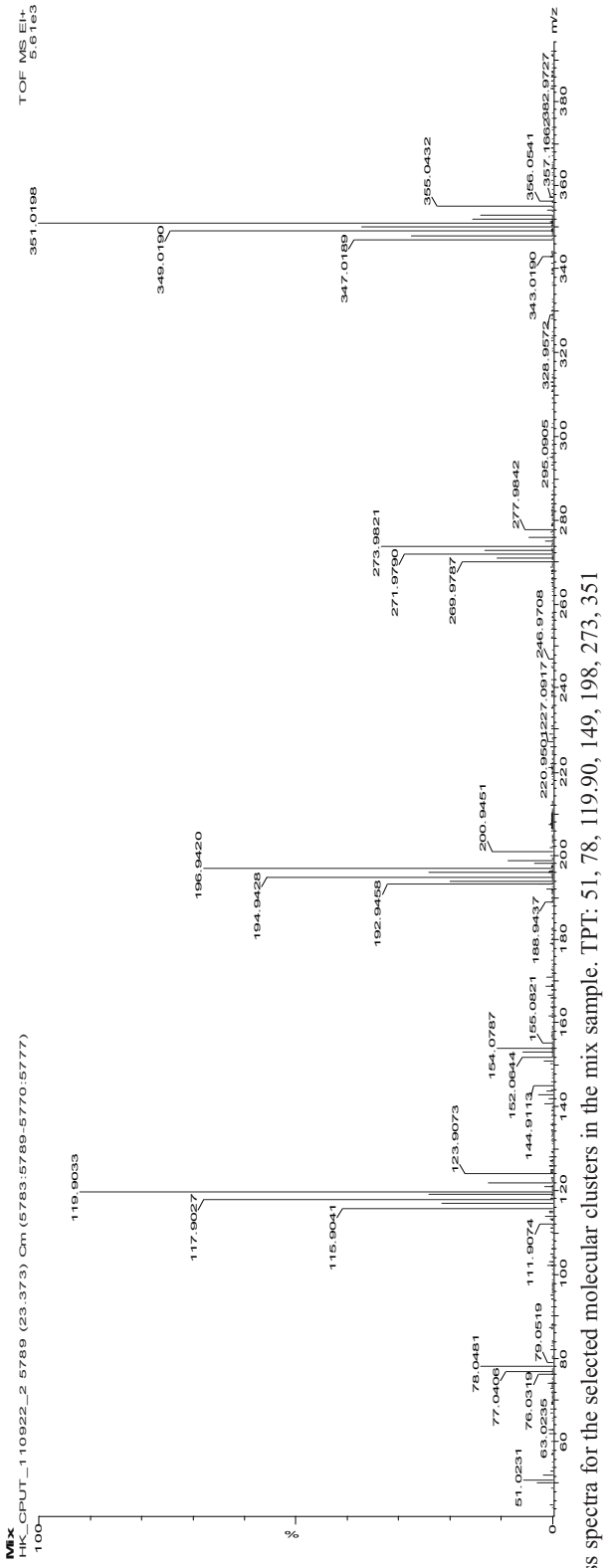

Fig. 3. TPT mass spectra for the selected molecular clusters in the mix sample. TPT: 51, 78, 119.90, 149, 198, 273, 351

deionized water, 2 ml of concentrated HCl, 20 ml of 0.02 % tropolone in methanol and 100 ml of hexane were added in that order. The flask was covered and shaken vigorously for 12 hrs. The resulting slurry was filtered and collected over anhydrous sodium sulphate (drying agent) to remove the water. The extract was then concentrated on a water bath. It was then loaded on silica column for clean up as described above. Ethylation of the extract was done by adding 1 ml of sodium acetate buffer followed by 1 ml of 1% STEB in methanol, and the mixture was shaken for 10 minutes. It was then dried over anhydrous sodium sulphate. The final extract was dried by purging with a gentle stream of nitrogen, and reconstituted with 1 ml of hexane. 1 µl of the final extract was injected into a GC-FPD for analysis. Fig. 9 represent overall extraction procedures for water, sediment and mussel samples.

Quality Assurance and Quality Control (QA/QC)

Solvent blanks and procedural blanks were included in each batch of analyses and they were always analyzed after every sample injection. Procedural and spiked water samples were treated in the same manner. A calibration standard solution of known concentration was injected in duplicate to monitor the instrument sensitivity and reproducibility each time prior to chromatographic analysis. Reference standards used for recovery experiments and to confirm extraction efficiency were freeze-dried coastal sediment (BCR-462) certified for TBT (54±15 µg/kg) and DBT (68±12 µg/kg), and freeze–dried mussel tissue (ERM-CE 477) certified for TBT (2.20±0.19µ mg/kg), DBT (1.54±0.12 mg/kg) and MBT (1.50±0.28 mg/kg). Both standards were obtained from IRMM. Both water and sediment samples collected from Cape Town harbor were used to validate the results.

Extraction of TBT from Mussel Tissues

Two different methods were employed for the extraction of TBT from mussels

Method 1

The first extraction step of the analysis was based on the method described by Liscio et al. [11]. Freeze dried certified reference material (ERM-CE 477) for mussel was weighed (0.5 g) into a 50 ml glass tube. A rehumidication step was carried out by adding 1 ml of methanol followed by 10-minute sonication. The extracts contained in the tubes were stored at -20ºC overnight. The resulting slurry formed was further extracted with 15 ml of methanol containing tropolone (0.005%), sonicated for 20 minutes, and then the suspension was shaken for 10 minutes. The resulting slurry was filtered to remove water and concentrated on a water bath at 80ºC and then cleaned up as described above. The extracts were then derivatised by adding 1 ml of sodium acetate buffer, 1 ml of 1% STEB in methanol and mixture was shaken for 10

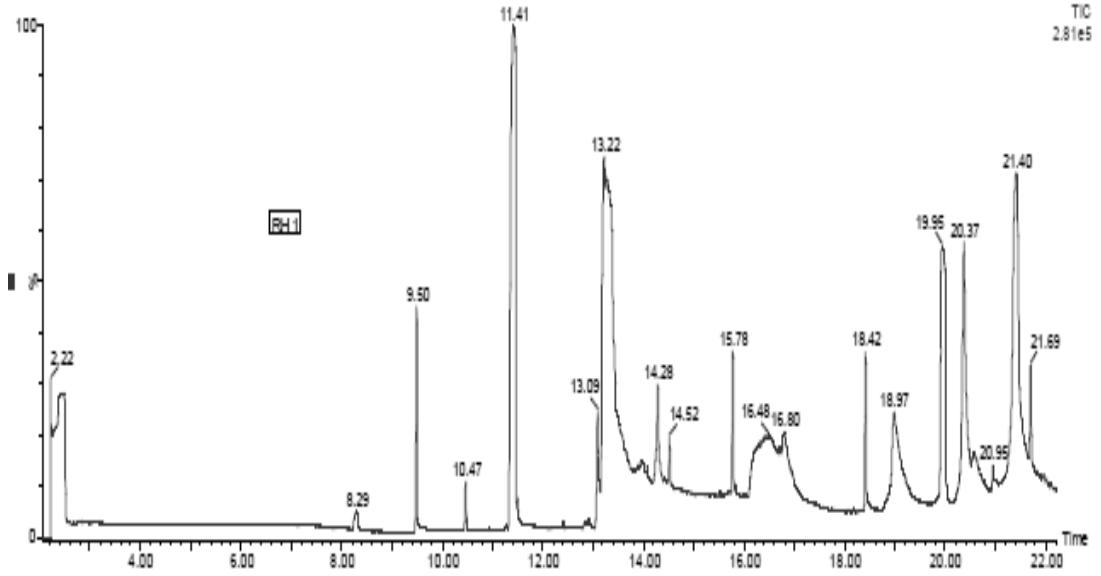

Fig. 4. Chromatogram of organotins in the spiked water sample taken from the laboratory recorded from GC-MS – TOF. TBT: 11, 41; TPT: 21, 40

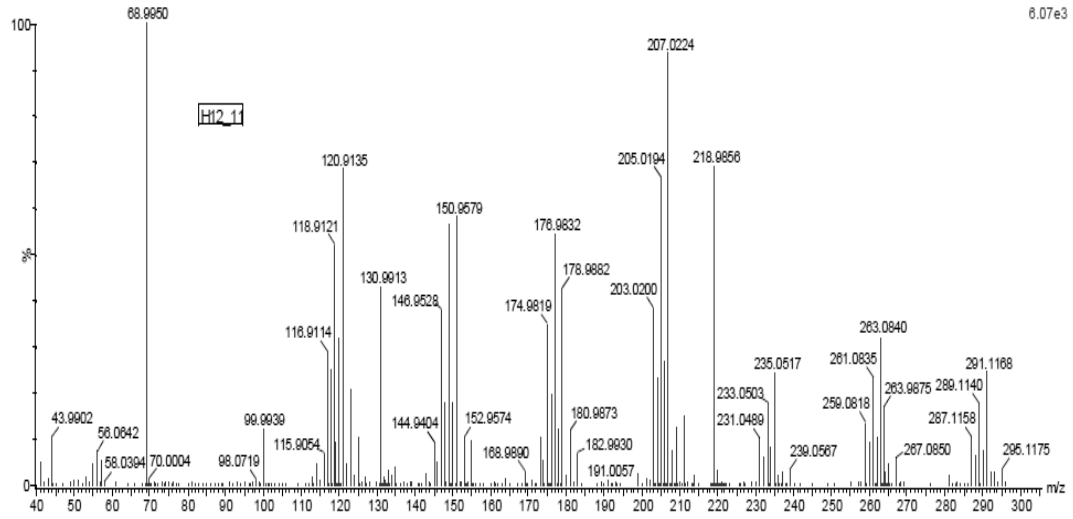

Fig. 5. Mass spectra of organotins in the real water samples from Cape Town harbor. TBT: 207.0224; TPT: 120.9135

minutes. The extracts were dried over anhydrous sodium sulphate. The final extract was purged to dryness using a gentle stream of nitrogen and reconstituted with 1 ml of hexane. 1 µl of the final extract was injected into a GC-FPD for analysis.

Method II

This extraction was achieved by adding 4 ml of a mixture of acetic acid and methanol (3:1 v/v) to 0.2 g of sample, and the resulting slurry was heated in a water bath at 37ºC for 1 hour. The resulting extract (1 mL) was derivatised and cleaned up as described above.

Result and Discussion

All the OTs studied required a derivatization step prior to GC analysis. The major aim of derivatization was to transform the analyte into compounds with higher volatility. STEB has been developed to minimize analysis time. The STEB procedure allows a simultaneous extraction- derivatization in a buffered medium and produces more thermally stable derivatives [12]. In order to achieve high yield, a large amount of STEB was used for the direct ethylation of organotins in sediment and biological samples. This is very important to compensate for the consumption of reagents by side reactions with metals and other compounds in the

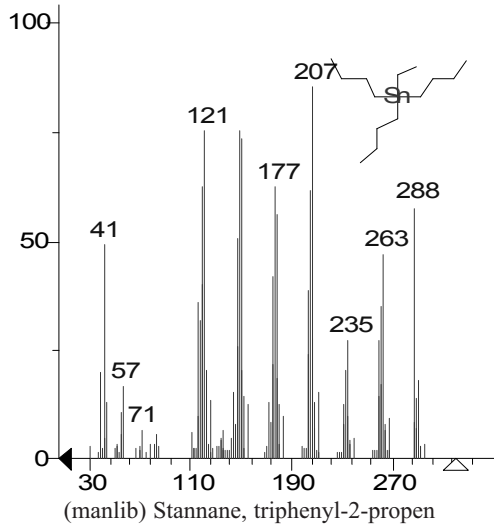

Fig. 6. Mass spectra of TBT derivatives TBT: 207.

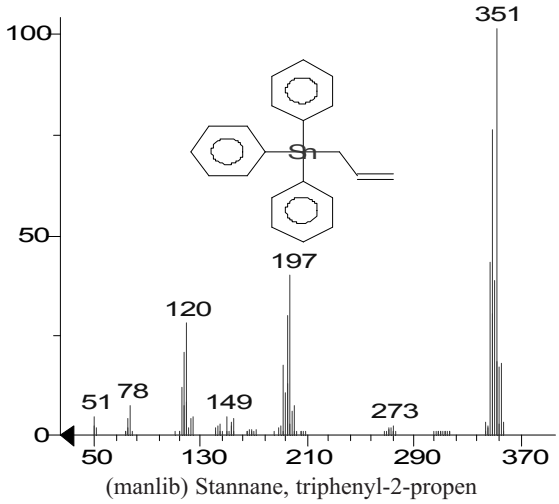

Fig. 7. Mass spectra of TPT derivatives. TPT: 351

matrix. A typical chromatogram for organotin reference sample for sediment, mussel, and organotin standards derivatized using derivatization method II mentioned above (ethyl-derivative with $NaBEt_4$) is shown in Fig. 2. The compounds elute according to their boiling points. The mass spectra obtained for TPT in a mix sample is shown in Fig. 3, while Figs. 6 and 7 represent the spectra of TBT and TPT derivatives.

Analytical Characteristics of the Methods

The analytical characteristics of the methods are listed in Table 3. There were no traces of organotin compounds found in the procedural blanks and the blank samples. The instrument detection limit (IDL) for both TBT and TPT was determined. The individual standards for TBT and TPT were prepared in concentrations ranging from 0.01-1 ppm for each analyte. The derivatized organotin standards were run. The instrument was able to detect the compounds up to 10 ppb levels for both TPT and TBT. The precision of the method was based on measurement of repeatability. This was determined by replicate injection of standard mixtures prepared in the laboratory. The standard deviation expressed as the coefficient of variation was recorded. From the literature, various methods for determining the LOD and LOQ were reported. For this study, the LOD (0.01ppm) was calculated as three times the standard deviation, while the LOQ (0.003 ppm) was calculated as three times the LOD.

Linearity and Precision

For the organotin compounds investigated, the calibration standard was prepared at concentrations ranging from 0.01 to 2 ppm. in order to get better regression (R) value of the linear graph. Calibration data was obtained from peak area measurement. Regression parameters are

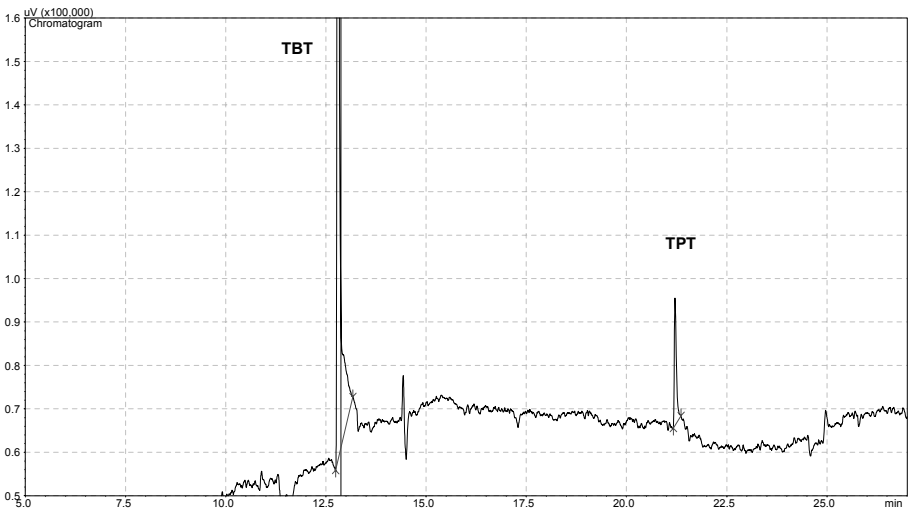

Fig. 8. GC-FPD chromatogram for organotin compounds in real sediment samples from Cape Town harbor.

recorded in Table 3 together with the correlation coefficient (r^2). The TPT recorded the highest regression parameter while the TBT recorded the lowest regression value. The slope also varied from 2.122 to 3.268 for TBT and TPT, respectively.

Recovery studies were carried out by addition of natural standard of TBT and TPT to MilliQ water. The MilliQ water was spiked with known concentrations of TBT and TPT (0.5 and 1 ppm). 100 ml of MilliQ water was spiked with these concentrations of TPT and TBT using solid phase extraction. Quantitative recoveries of 70% were recorded for TPT and 60% for TBT (Fig. 4).

Analysis of Reference Materials

Tributyltin was determined in BCR 462 and ERM-CE 477 reference materials. The value found for the TBT was close to the certified values. The GC-MS chromatogram is shown in Fig. 2a while the GC-FPD chromatogram of the reference organotin standards is shown in Fig 2b. Results for BCR 462 and ERM-CE 477 showed a good agreement between the certified value and the one found values from the experimental method. Sonication method I used for the ERM-CE 477 showed good recovery than method II. The mechanical shaking procedure (method III) used for BCR-

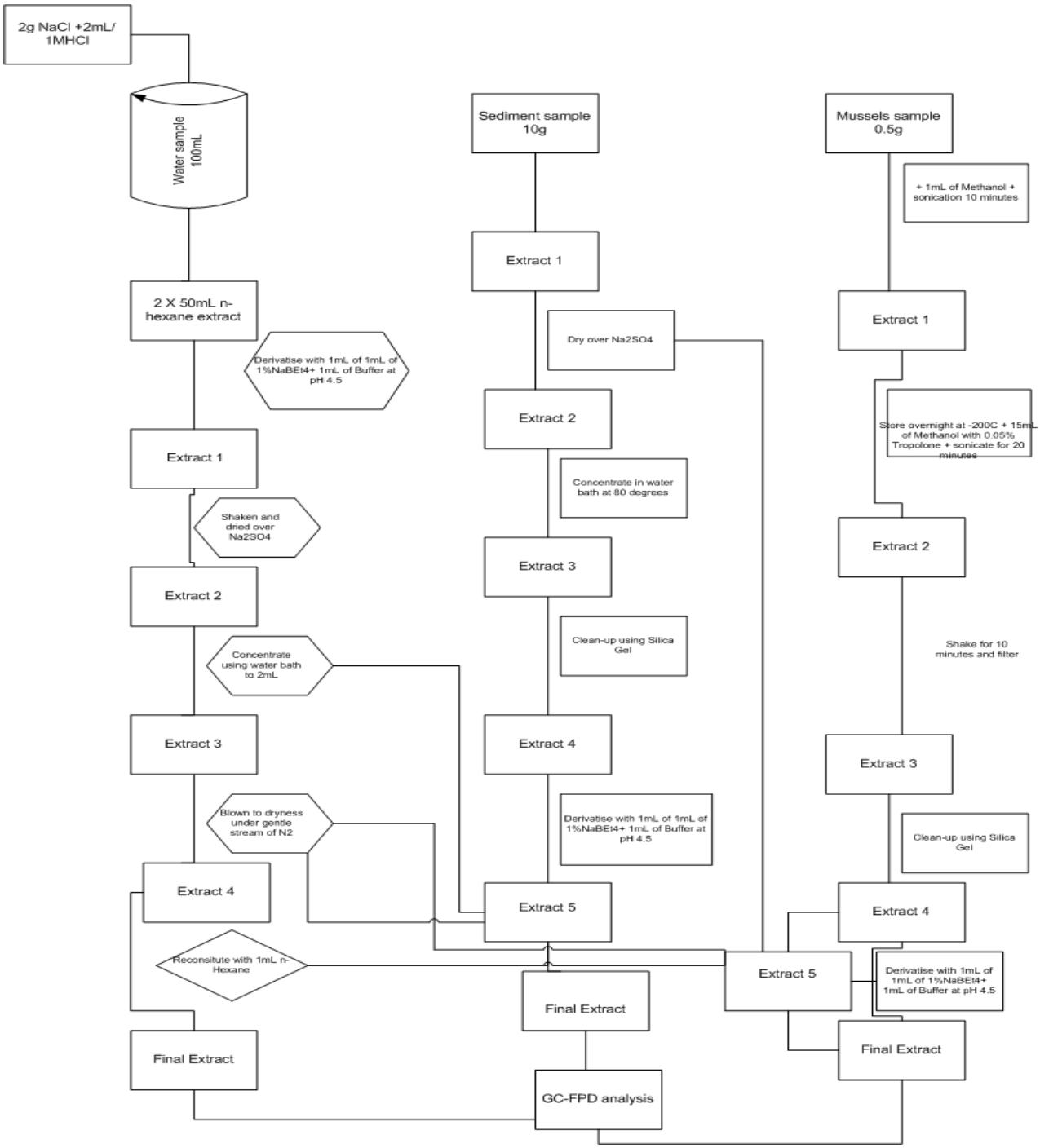

Fig. 9. A schematic diagram of overall extraction procedures for water, sediment, and mussel samples.

462 (reference sediment) showed good recoveries than method 1 and II respectively. The same analytical procedure was applied to the real water and sediment samples collected from the Robinson dry dock site of the Cape Town harbour. Replicate samples were analyzed and both TBTs and TPTs were detected. This means that it is imperative to monitor OT compounds at the Cape Town harbour. The GC-MS mass spectra for the organotins in real water samples are shown Fig. 5. The GC-FPD chromatogram of TBT in real sediment sample is shown in Fig. 8.

Conclusion

A simple, fast, precise, and accurate method has been developed for the simultaneous determination of organotin compounds in water extracts, sediment, and mussel samples. Three different derivatization procedures have been described. GC-MS – TOF confirmed the presence of the organotins in both real and standard samples and their characteristic ions were established. The mechanical shaking method for extraction of target organotin compounds in sediments was optimized, which gave a better recovery than the sonication method. The cleanup of the extracts was carried out on a glass column packed with activated silica and anhydrous sodium sulphate. From all the solvent tested, toluene and N-hexane were found to give a better recovery. The idea of blowing the final extract to dryness and reconstituting to 1 ml gives a proper account of the actual volume of the final extract used for GC analysis. The developed method was applicable to real samples.

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