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Speciation of Underivatized Organotin Compounds in Sediments by Gas Chromatography-triple Quadrupole Mass Spectrometry

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Tributyltin is well recognized as an environmental endocrine disruptor and is listed as a priority substance that requires extended monitoring by the European Water Framework Directive (2000/60/EC). At the same time, due to their high pathogenicity, producing hormonal, immune, metabolic, and reproductive dysfunctions, other butyltin species (*e.g.* monobutyltin, dibutyltin, and tetrabutyltin) are consistently monitored in marine and freshwater aquatic ecosystems; the European Chemicals Agency classified these butyltin species as potential carcinogens and toxic substances for the human reproduction. Several analytical techniques, including gas chromatography and high-performance liquid chromatography, have been used to determine organotin species in aquatic ecosystems. Because of their chemical properties, organotin compounds are poorly stable upon temperature and are thus unsuited for direct analysis through capillary gas chromatography, which is usually performed after a derivatization step. The procedure described in this paper allowed the detection of underivatized chlorinated organotin compounds through gas chromatography-triple quadrupole mass spectrometry. Importantly, the obtained spectra of chlorinated monobutyltin and dibutyltin are herein presented and the fragmentation patterns are identified for the first time. The method was successfully applied to evaluate organotin compounds in sediments, providing the speciation of organotin species. Taking advantage of a simplified procedure of sample treatment, this study provided an innovative protocol for the gas chromatography/mass spectrometry of phenyl and butyl-substituted organotin compounds in contaminated sediments, capable of improving the efficiency of the conventional analysis of organotin compounds.

Keywords: GC-MS/MS, Organometallic pollution, Organotin compounds, Sediment contamination, Tributyltin, Triphenyltin

INTRODUCTION

Organotin compounds belong to a well-distinguished class in organometallic chemistry that has been widely exploited over the last Century to meet the emerging needs of modern society in a variety of applications. Mono-substituted (MBT) and di-substituted (DBT) organotin compounds are employed for home heating, in the production of light-stabilize poly(vinyl chloride) plastics and polyurethane foam, as vulcanizing agents for silicone rubbers and are present in glass coatings [1]. Tri-substituted organotin compounds (TBT) are involved in the production of industrial biocides, preservatives, surface disinfectants, and antifoulant paint additives [1,2], while tetra-substituted organotins (TeBT) are mainly employed as intermediates for the preparation of other organotin substances [1]. The triphenyltin (TPT) derivatives have been widely used since the 1960s for their biocidal action as algaecides and molluscicides in antifouling

products and as pesticides in agriculture due to their high and selective antiparasitic capacity. Despite TPT derivatives being very effective pesticides, to date, their use has been significantly reduced and controlled due to the numerous and evident toxicity tests on insects and aquatic organisms, while many studies on birds and mammals are still in progress.

Great concern has been expressed regarding the environmental impact of this class of organometallic compounds in marine and freshwater aquatic ecosystems, especially for the -butyl-substituted species. Environmental risks of butyl-substituted organotins include persistence in soil and waters and bioaccumulation in the exposed biota [3]. As a result of their low water solubility, these substances can be easily adsorbed by the particulate matter in the aquatic environment [4] or incorporated into the sediment, representing a secondary source of organotins substances. Overall, organotins show high toxicity to non-target organisms even at low concentration levels (< 1 ng l^{-1} in water) [3] and their lipophilic properties can favor bioaccumulation phenomena through the food chain (biomagnification) [5,6].

Toxic effects of butyl-substituted organotins include teratogenic activity, neurotoxicity, hepatotoxicity, and immunotoxicity [4-8], and they are listed in the Environmental Protection Agency's (EPA) Endocrine Disruptor Screening Program (EDSP) [7]. For these reasons, the use of organotin compounds as biocides in anti-fouling products banned in Europe by the European Union Regulation 782/2003/EC [9], and afterward the prohibition was extended in 2008 in more than 70 countries worldwide by the International Convention on the Control of Harmful Anti-fouling Systems on Ships (AFS Convention) [10]. The ECHA (European Chemicals Agency) classified these butyltin species as potential carcinogens and toxic substances for human reproduction [11,12]; at the same time, genotoxicity studies are also being carried out due to their potential ability to form chromosomal mutations [13].

In addition, the U.S. Environmental Protection Agency and the European Union established water quality criteria for several priority hazardous substances, including TBT [2,14, 15,16]. Overall, the guidelines highlight the significant role of accumulation phenomena in each ecosystem compartment, requiring the monitoring of sediment and biota to evaluate the actual contamination level and long-term impact on the aquatic environment. In this regard, Italian laws transposed the regulations from the European Water Framework Directive [14] by establishing annual average environmental quality standards (AA-EQS), which for tributyltin in sediment was set at 5 µg/kg [17].

In this scenario, a variety of analytical methods have been developed for the detection of organotin species in sediments. The conventional protocols require firstly the extraction of organotins from the sediments, then gas chromatography (GC) and high-performance liquid chromatography (HPLC) techniques are typically employed in combination with selective detectors (FPD, PFPD, MIP-AES, MS, ICP-MS), as reported in several papers [6,18-24]. The most common methods for the analysis of butyltin compounds in sediments rely on gas chromatography-mass spectrometry (GC-MS), which ensures high sensitivity and resolution power and allows for a cost-effective and fast analysis in comparison with other techniques. Nevertheless, the application of GC-MS requires the derivatization of organotin compounds to obtain more volatile and thermally stable species, which is necessary to ensure correct analytical performance in terms of analytical precision and recoveries [25]. The necessity of a derivatization step represents an analytical limitation, resulting in a complex and time-consuming approach and contributing to hindering the in-depth analysis of the environmental contaminants. For instance, the possible occurrence of debutilization reactions from TBT to DBT and MBT [26] can require the speciation of the butyltin compounds to provide a thorough evaluation of the toxicity of the contaminated soil. Table 1 provides a summary of the reactions involved, the reagents employed, and the main characteristics highlighted in the literature along with their respective advantages and disadvantages.

In this regard, the present work aimed to develop a sensitive and selective method for the detection and quantification of PTP and butyltin compounds in sediments at trace level, based on capillary gas chromatography-triple quadrupole mass spectrometry without the need for derivatization. In detail, the use of an innovative solvent mixture was studied to allow for the separation and detection of underivatized PTP and TeBT and chlorinated MBT, DBT, and TBT in GC-MS/MS. The proposed procedure was suitable for successfully recording the GC-MS/MS spectra of underivatized TeBT and chlorinated MBT, DBT, TBT, and

TPT. Importantly, the GC-MS/MS spectra of chlorinated MBT and DBT were herein observed for the first time and their fragmentation pattern were identified. The reliability of the method was demonstrated for the measurement of TPT and butyltin compounds in real sediment samples, obtaining results consistent with the Italian national requirements for TPT and TBT levels in sediment. The advantages achieved, especially in terms of the reduced time of analysis, can pave the way for extended monitoring programs in contaminated soil, favoring the speciation of the butyltin compounds and thus a more comprehensive understanding of the long-term environmental effects.

Table 1. Summary of the Reactions Involved, the Reagents Employed, and the Main Characteristics Highlighted in the Literature along with their Respective Advantages and Disadvantages

Derivatization method	Reaction	Pros	Cons
Hydride generation	$R_nSn^{(4-n)+} + NaBH_4 + H^+ \rightarrow R_nSnH_{(4-n)} + H_2$ (R: organic substituent; n: 1-3)	Success in the certification of butyltin compounds in coastal sediment (CRM 462)	Need accurate conditions Influenced by the complexity of the matrix Low yields and poor reproducibility
Grignard reaction	$RX + Mg \rightarrow RMgX$ (R: organic substituent; X: alkyl halide)	Wide applicability for various organotin species (methyltins, butyltins, phenyltins) High reproducibility and derivatization yields Suitable for various environmental matrices (water, sediment, biota) Formation of stable derivatives like mixed tetra-alkyltin compounds ideal for GC separation	Hazardous substances that need careful handling Additional analytical steps increase the risk of contamination, decomposition, and losses Need to destroy the Grignard reagent and re-extract the mixed tetra-alkyltin compounds. Experimental conditions need to be carefully controlled
Ethylation with sodium tetraethyl borate	$NaBH_4$	Suitable for aqueous samples Direct in situ derivatization possible Reduction in analytical steps compared to Grignard reactions	Requirement of careful pH control for optimal yields and recoveries Higher $NaBEt_4$ concentration is needed for sediment and biological samples Influenced by the presence of metals in the matrix

EXPERIMENTAL

Chemicals

All chemicals used in this study were of the highest analytical purity grade. Hydrochloric acid, methanol, and toluene were obtained from Sigma-Aldrich (Milan, Italy). PCB No. 209 (decachlorobiphenyl) 100 ng μl^{-1} in isooctane was purchased from Dr Ehrenstorfer (Sesto San Giovanni, Milan, Italy). Triphenyltin chloride 99% pure powder synthesis compound from Sigma Aldrich). Organotin Cal Std Mix (composed of monobutyltin, di-n-butyltin, tetrabutyltin, and tributyltin 1000 µg ml^{-1}) was supplied by Sigma-Aldrich (Milan, Italy). Tributyltin D27 10 µg ml^{-1} was obtained from A2S (Bordeaux, France). N,O-bis (trimethylsilyl)trifluoroacetamide with trimethylchlorosilane (BSTFA+TMCS; 99:1) was purchased from Sigma-Aldrich (Milan, Italy). Helium 5.5 and Nitrogen 5.5 were supplied by Sol (Monza, Italy). Purified water was obtained from a Milli-Q water system purchased from Millipore (USA).

Standard Solutions and Sediment Samples

Stock TeBT and chlorinated MBT, DBT, and TBT solutions (0.1 mg l^{-1}) were prepared in methanol and stored at +4 °C. Working surrogate mix Tributyltin D27 standard solution (0.1 mg l^{-1}) was prepared in methanol weekly. The injection standard PCB 209 was prepared at a concentration of 1 mg l^{-1}. Triphenyltin solution 10 mg l^{-1} was obtained by diluting the powder in 10 ml of methanol.

Blank samples (not contaminated sediments) were employed for the recovery studies and validation experiments. Real sediment samples were gathered in the Tyrrhenian Sea, along the coast of Rome (western Italy), from 3 to 12 nautical miles from the shoreline. Real soils were collected in the Lazio region. After collection, the sediments and soils were stored at -20 °C until analysis because frozen storage has been shown to be effective in preserving sample stability with respect to organotin concentrations for at least 100 days.

Sample Preparation

A 4-g aliquot of sediment sample was spiked with 200 µl of deuterated TBT standard solution 0.1 mg l^{-1}. The sediment was extracted by adding 10 ml of a 50:50 v/v toluene-methanol mixture and 100 µl of HCl (35%) in an ultrasound bath for 60 min; the resulting concentration of surrogate standard is 2 µg l^{-1} in the extract solution. Centrifugation at 5000 rpm for 10 min was applied to remove the eventual emulsion occurring during the extraction, using a Thermo Scientific IEC CL31R Multispeed.

500 µl of the extract was added together with 50 µl of PCB 209 injection standard solution (1 mg l^{-1}) to obtain the final concentration of 91 µg l^{-1} of PCB 209. Afterward, 100 µl of the resulting solution was transferred into micro-vials with micro-volume conical insert together with 15 µl of BSTFA (with 1% TMCS). This mixture containing MeOH and trimethylsilyl derivatives of methanol (MeOTMS) resulted to be suitable for the GC analysis of underivatized TBT in seawater: indeed, the mixture was shown to act as a lubricant and allow for carrying out a clean injection as well as for achieving good chromatographic resolution of chlorinated MBT, DBT and TBT, and TeBT, as reported in a previous work [27] (Table 2). Finally, the micro-vials were stored at +4 °C, ready to be analyzed.

Table 2. Summary of the Silanizing Agent's Behavior and its Effects on the Sample and Chromatographic Performance

Silanizing agent	BSTFA/TMCS (99:1)
Reaction	The addition of BSTFA/TMCS (99:1) to methanolic extract reacts with excess methanol to form trimethylsilyl derivatives. HCl produced in the reaction ensures organotin compounds remain unchanged and underivatized
Advantages	Prevents organotin compounds from adhering to glass liner walls, enabling clean injection and good chromatographic resolution
Memory effects	The method prevents sorption and memory effects, even at trace levels
Sample composition	No alteration

Creation of the Calibration Curve

The preparation of the analytical standards and the white sample (medium without the analyte of interest) was performed using the same sediment sample containing 1.2 mg/Kg of inorganic tin; this pre-analytical method is not able to extract the inorganic tin present in the sediment sample. The preparation was performed by using the same procedure described above: 4 g of the sediment sample was spiked with TeBT, MBT, DBT, and TBT solutions at 0.1 mg l^{-1}. Standard solutions of TeBT, MBT, DBT, TBT (ranging between 0.5 µg l^{-1} and 60 µg l^{-1}), and TPT (ranging between 40 and 120 µg l^{-1}) were used for obtaining the calibration curve for each butyltin compound and the triphenyltin.

Instrumentation

The analyses were performed by an Agilent triple quadrupole GC/MS system (7890B/7000C) equipped with a multimode inlet (MMI). The chromatographic separation was performed by an Agilent VF-XMS capillary column (60 m × 0.25 mm i.d. × 0.25 µm). Helium was used as carrier gas at a constant flow rate of 1.5 ml min^{-1}.

Different acquisition programs were used for the analysis of TeBT, MBT, DBT, TBT, and TPT as described in Table 3. The total GC analysis time was 38 min for the TPT, and 43 min for the TeBT, MBT, DBT, and TBT.

The mass spectrometer was employed in electron ionization mode (EI, 70 eV) and MS/MS mode (multiple reaction monitoring, MRM). For the MS/MS experiments, Nitrogen 5.5 was used as collision gas and the collision cell flow was set at 1.5 ml min^{-1}. The temperature of the transfer line and ion source was set at 310 and 300 °C, respectively. The mass spectrometer was calibrated weekly with perfluorotributylamine (PFTBA). The optimized MS/MS acquisition was carried out with the transitions reported in Table 4.

Sn-containing fragments were identified by comparison of their isotopic patterns with those predicted using NIST software (MS Interpreter 2.0).

Method Validation

Besides the calibration curve in the matrix, the method validation was performed, by using the metrological approach as indicated by the UNI CEI EN ISO/IEC 17025, analyzing, with the same method, the recoveries of i) 6 sediment samples spiked with the TPT (100 µg/kg) and butyltin compounds (5 µg/kg for each analytical species) ii) a blank, *i.e.* sediment which does not contain the analyte or contain it in a concentration lower than the lowest point of the curve. The evaluation of the blank is necessary to verify the absence of background pollution, therefore, the comparison between the analysis of the blank and the fraction recovered from the doped samples has to produce values comparable to the background noise of the chromatogram.

Table 3. Different GC Acquisition Programs for the Analysis of TeBT, MBT, DBT, TBT and TPT

	TeBT, MBT, DBT, TBT	TPT
Injection Volume	5 µl	10 µl
Injection Parameters	Initial heater temperature 82 °C held for 0.6 min, 900 °C min^{-1} up to 360 °C, hold time 9 min, 900 °C min^{-1} up to 90 °C	Initial heater temperature 90 °C held for 0.6 min, 900 °C min^{-1} up to 380 °C, hold time 4 min, 900 °C min^{-1} up to 90 °C
Oven Parameters	Initial oven temperature 70 °C*4.8 min, 40 °C min^{-1} up to 155 °C, hold time 1 min, 9 °C min^{-1} up to 240 °C, hold time 10.5 min, 20 °C min^{-1} up to 340 °C, hold time 10 min	Initial oven temperature 90 °C*4.8 min, 40 °C min^{-1} up to 155 °C, hold time 1 min, 10 °C min^{-1} up to 340 °C, hold time 10.5 min
Pressure	26 psi	28 psi

Table 4. A Comprehensive Comparison, Detailing the Key Features of Various Methods Reported in Literature for the Analysis of Organotin Compounds in Environmental Samples Compared to the Method Developed in the Present Study

Matrix	Extraction	Derivatization	Technique	Quantification		Analytes	LOD (organotin compounds)	References
				Method	Surrogate standard			
Sediments and drinking water	Solid phase extraction		LC-ICP-MS	1. external standard calibration		MBT, DBT, TBT, MPT, DPT, TPT	1. 1.5 to 25.6 ng l^{-1}	Bishop *et al*., 2015 [28]
				2. isotopic dilution			2. 0.5-1.2 ng l^{-1}	
Sediments	Toluene/HOAc (10: 4) – sonication + LLE with APDC 0,05%	PeMgBr	GC–PFPD	Internal standard additions with TeBT	TPrTCl + TCyTCl	MBT, DBT, TBT, MPT, DPT, TPT	1.9 to 3.6 µg/kg	Almeida *et al*., 2014 [29]
Sediments	Toluene/Methanol (1:1)		GC-MS/MS	Injection standard PCB209	Tributyltin D27	TeBT, MBT, DBT, TBT and TPT	0.4 to 50 µg/kg	Our method

RESULTS AND DISCUSSION

This study aimed to develop a novel analytical method based on capillary gas chromatography-triple quadrupole mass spectrometry for the analysis of organotin compounds in sediments. The challenge was to avoid the requirement of a derivatization step, which is the main drawback in the conventional chromatographic protocols for butyltin compounds (Table 2). The herein-developed approach, based on the use of an innovative solvent mixture for the sample treatment, was proved to be suitable for the identification and the quantification of chlorinated MBT, DBT, TBT, and TeBT at trace levels, by recording GC-MS/MS spectra of the investigated organotin compounds. The use of the solvent mixture, composed of methanol and trimethylsilyl derivatives of methanol (MeOTMS), was proved to be suitable for organotin speciation in seawater of underivatized organotin compounds (*i.e.* MBT, DBT, TBT, and TeBT) in a previous work [27]. This mixture provided a lubricant effect that allowed for obtaining a clean injection and good resolution of the chromatographic response. The proposed approach can promote the speciation of butyltin compounds in the soil environment. To the best of our knowledge, the GC-MS/MS spectra of MBT and DBT were herein recorded for the first time.

Optimization of GC-MS/MS Parameters

To develop a robust GC analysis method for organotin compounds detection, a series of optimizations were conducted to enhance both the chromatographic efficiency and resolution.

The initial focus was on the solvent mix acting as a "lubricant" to facilitate the analysis. Observations revealed that the silylation step promoted by adding BSTFA (silylating agent) and TMCS (silylation catalyst) to the methanolic extract significantly enhanced the chromatographic efficiency and resolution of organotin compounds when the multimode inlet (MMI) was in solvent vent mode.

Following the solvent mix optimization, the GC and MS/MS instrumental conditions were further fine-tuned. The chromatographic runs were optimized to elute and separate other chlorinated semi-volatile compounds in subsequent runs.

To detect butyltin species using multiple reaction monitoring (MRM) mode, full-scan and product ion spectra were acquired for each compound. Firstly, the mass spectra

were recorded for each compound to select the most abundant mass-to-charge ratio (m/z) for further studies. Figure 1 and 2 show, respectively, the positive EI ionization mass spectra of MBT, DBT, TBT, TeBT, and TPT and the relative chromatograms. Thus, the dissociation conditions were optimized for each compound (Table 5). In detail, the precursor ions were selected as a compromise between selectivity (m/z) and sensitivity (intensity). A stable enriched isotope, namely Tributyltin D27 chlorinated TBT, was added as a surrogate standard, and PCB 209 was employed as an injection standard.

The comprehensive optimization of the solvent mix and instrumental conditions has culminated in the development of a robust GC-MS/MS method for the analysis of organotin compounds. This optimized method ensures accurate and reliable results for environmental samples, setting a new benchmark in analytical chemistry methodologies.

Fragment Identification

The GC-MS/MS spectra of butyltin compounds illustrate m/z fragment peaks from successive losses of the butyl and/or ethyl group, which are characteristic of derivatized butyltin products [30], with a limited number of other fragments ascribable to the loss of chlorine atoms and, in some cases, HCl. Each peak cluster exhibited the overlapping of the isotope patterns characteristic of tin and chlorine.

Sn-containing fragments were identified by comparison of their isotopic patterns with those predicted using NIST software (MS Interpreter 2.0). When a peak cluster was the result of the overlapping of isotopic patterns of two or more fragments, the fragment identification was carried out taking into account first the predicted isotopic distribution for each fragment, followed by the determination of the molar fractions of all the hypothesized fragments best fitting the MS spectrum.

Table 5. Retention Time and Precursor/Product Ions of the Butyltin Compounds Herein Examined and Standard Injection (Panel a); Retention Time and Precursor/Product Ions of the Triphenyltin Herein Examined and Standard Injection (Panel b)

Panel a Compound	Retention time (min)	MW	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)
MBTCl3	9.5	282.2	253	225	10
			251	223	10
			225	155	35
DBTCl2	13.7	303.8	247	57	10
			245	57	10
			212	155	10
TBTClD27	14.4	352.7	287	186	10
			287	155	10
			287	66	10
TBTCl	14.7	325.5	269	155	10
			267	153	10
			213	155	10
TeBT	16.2	347.2	291	179	10
			235	123	10
			179	123	20
PCB209	35.4	498.7	498	428	20

Panel b Compound	Retention time (min)	MW	Precursor ion (m/z)	Product ion (m/z)	Collision energy (eV)
TPTCl	22.8	385.5	309	197	13

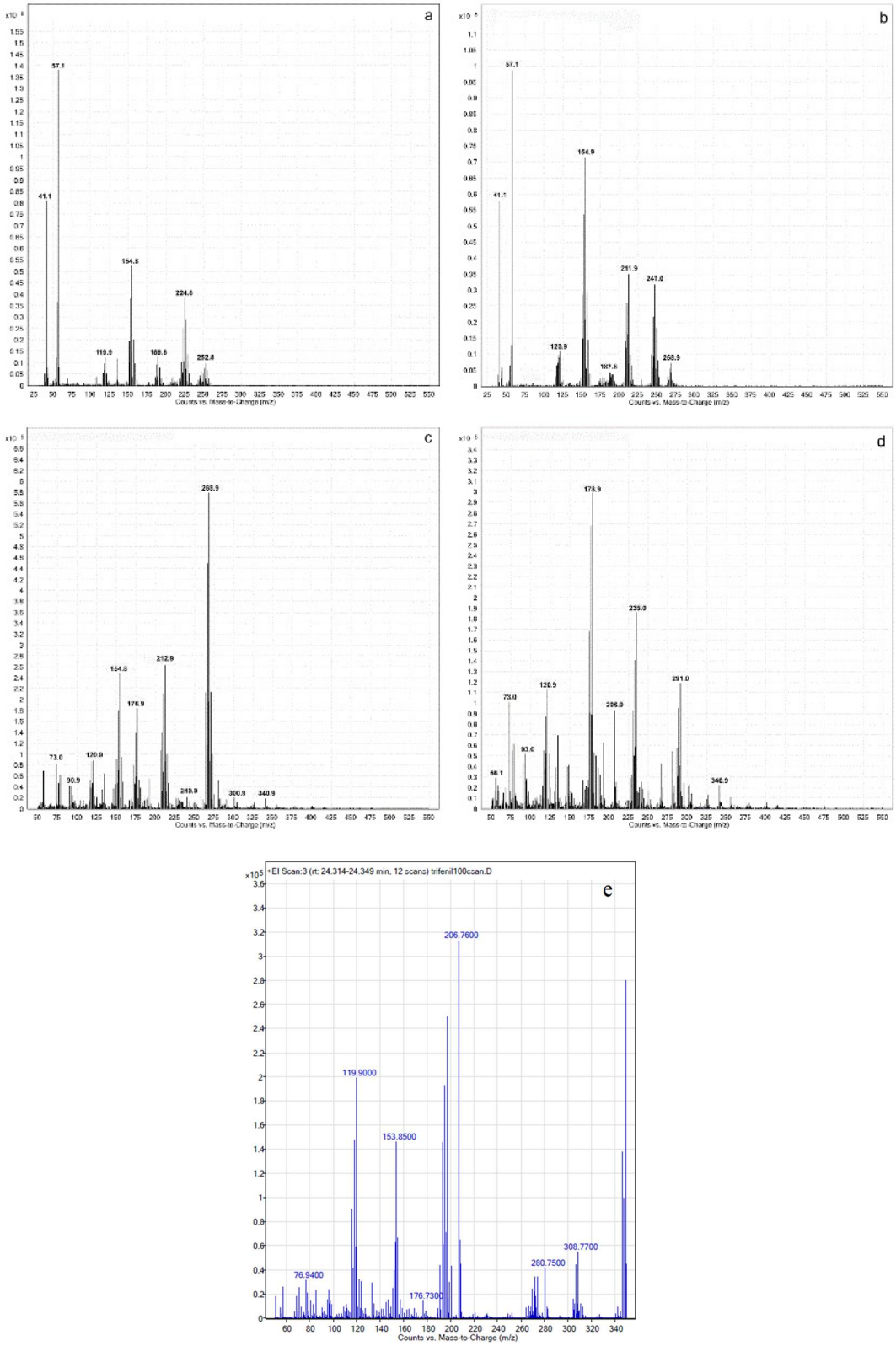

Fig. 1. Positive EI ionization mass spectra of monobutyltin trichloride (a), dibutyltin dichloride (b), tributyltin chloride (c), tetrabutyltin (d) and triphenyltin (e).

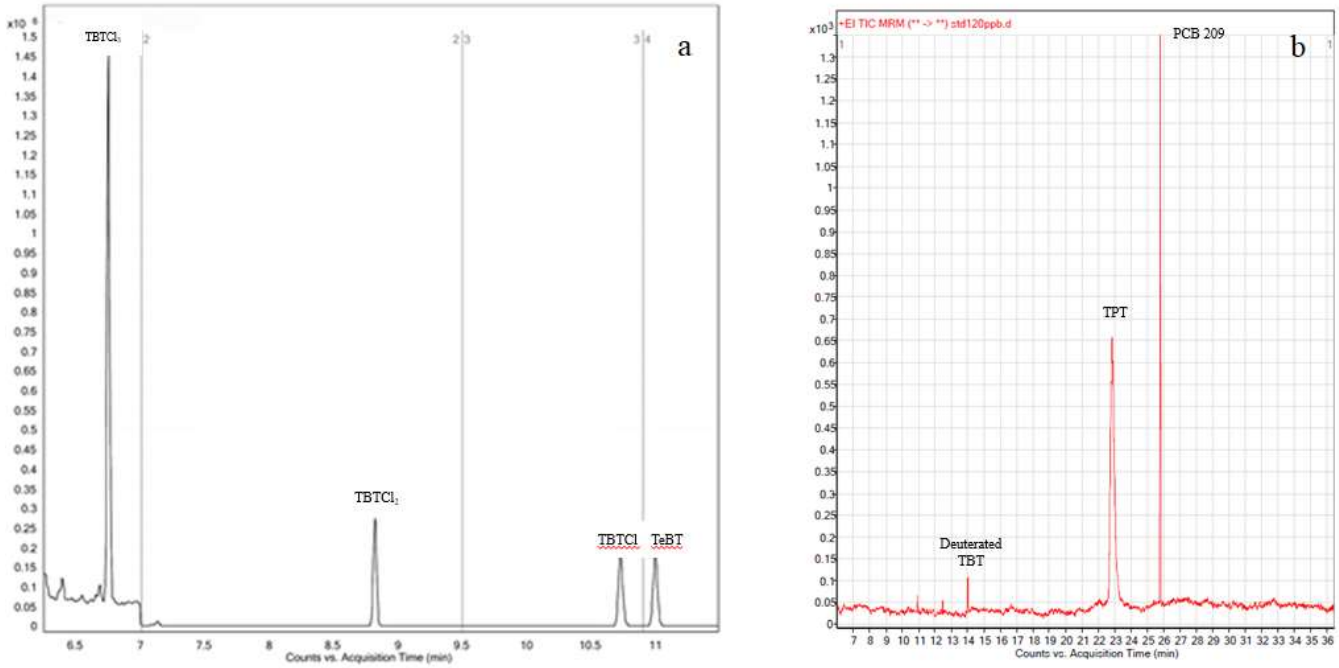

Fig. 2. Chromatogram of monobutyltin trichloride, dibutyltin dichloride, tributyltin chloride, and tetrabutyltin (Panel a). Chromatogram of triphenyltin (Panel b).

Once the molar fractions for all the hypothesized fragments were determined, the whole pattern was simulated and compared with that obtained in the EI-MS acquisition. More in detail, the most abundant peak for each hypothesized fragment was chosen for the mathematical treatment and, among them, the most abundant one obtained in the real spectrum was used as reference. Then, the abundance ratios of those peaks compared to that of the reference peak (obtained from the EI-MS analysis) were expressed in terms of the contribution of each fragment (obtained by the NIST prediction software) corrected by its unknown fraction. The solution of the n-1 equation system thus obtained (where n is the number of the fragments hypothesized to be present) gave the molar fraction of all the fragments in terms of 1:x:y:z: where 1 is referred to as the reference peak.

Sediment Analysis

To check the suitability of the proposed method for environmental monitoring, the analytical procedure was applied to the analysis of sediments for the speciation of MBT, DBT, and TBT compounds; TeBT and TPT were not required from the project and the results are shown in the Table 6. Sediment samples were collected in the Tyrrhenian Sea (as described in paragraph 2.2) and prepared for the analysis without the need for any derivatization procedure (as described in paragraph 2.3) The obtained results showed that this method is adequate for determining butyltin compounds in sediments, with recoveries higher than 60% and limits of detection of 0.1 ng/g for “DBTCl2”, “TBTCl” and “TeBT” and “TPT” and 0.5 ng/g for “MBTCl3”.

In compliance with Directive 2009/90/EC (“Directive 2009/90/EC” 2009), the limits of detection (LOD) were estimated as three times the standard deviations at the lowest (injected) spiked concentrations of organotin compounds; the limits of quantification (LOQ) were estimated as ten times the standard deviations at the lowest (injected) spiked concentrations of butyltin compounds. LOD values below 0.1 ng/g and LOQ values below 1.5 ng/g were obtained for TBTCl.

Thanks to the treatment of these analytes with a selected solvent mixture, the herein proposed GC-MS/MS analysis was shown to be able to directly analyze butyl-substituted organotin compounds after extraction from sediments, maintaining high selectivity and sensitivity in the

Table 6. Two Groups of Sand Samples Analyzed with the Method Here Described; in the First Group, we Obtained Positive Results while in the Second One Negative Results

Sediment samples in a port area to be reclaimed: 2020	MBT µg/kg	DBT µg/kg	TBT µg/kg	Sands sample for coastal nourishment: 2022	MBT µg/kg	DBT µg/kg	TBT µg/kg
18603	< 1.2	< 1.5	20	5931	< 1.2	< 1.5	< 1
18605	< 1.2	< 1.5	18	5934	< 1.2	< 1.5	< 1
18606	< 1.2	< 1.5	33	5947	< 1.2	< 1.5	< 1
18607	< 1.2	< 1.5	50	5949	< 1.2	< 1.5	< 1
18608	< 1.2	< 1.5	6746	5950	< 1.2	< 1.5	< 1
18609	< 1.2	< 1.5	1168	5951	< 1.2	< 1.5	< 1
18610	< 1.2	< 1.5	43	5952	< 1.2	< 1.5	< 1
18611	< 1.2	< 1.5	18	5953	< 1.2	< 1.5	< 1
18612	< 1.2	< 1.5	25				
18614	< 1.2	< 1.5	35				
18615	< 1.2	< 1.5	362				
18616	< 1.2	< 1.5	15				
18617	< 1.2	< 1.5	8				
18618	< 1.2	< 1.5	10				
18619	< 1.2	< 1.5	18				
18620	< 1.2	< 1.5	1208				
18622	< 1.2	< 1.5	642				
18623	< 1.2	< 1.5	10				
18624	< 1.2	< 1.5	10				
18625	< 1.2	< 1.5	8				
18629	< 1.2	< 1.5	5				
18630	< 1.2	< 1.5	10				
18631	< 1.2	< 1.5	8				
18632	< 1.2	< 1.5	10				
18633	< 1.2	< 1.5	10				
18635	< 1.2	< 1.5	10				
18636	< 1.2	< 1.5	18				
18637	< 1.2	< 1.5	8				
18639	< 1.2	< 1.5	8				
18640	< 1.2	< 1.5	8				

determination. The solvent mixture, based on methanol and trimethylsilyl derivatives of methanol, was hence proved to be effective in the simplification of the treatment of samples from butyltin-contaminated sediments, avoiding the need for their derivatization. At the same time, the procedure results are less affected by contamination and errors. The analytical method validation highlighted the values in Table 7.

Furthermore, despite some samples being positive, the real samples analysis revealed that the concentrations of triphenyltin chlorides are well below the maximum permissible limits, confirming the excellent effectiveness of our analytical method.

Table 7. Parameters of the Analytical Method Validation

Analytical species	Recovery (%)	LOQ (µg/kg)	Uncertainty (%)	Concentration in the spiked sediment samples (µg/kg)
MBT	109	1.2	25	5
DBT	62	1.5	27	5
TBT	107	1	32	5
TeBT	60	1	30	5
TPT	86	50	22	100

CONCLUSIONS

In the present work, a novel procedure for the analysis of butyl (and phenyl)-substituted organotin compounds was presented. The separation of these compounds, containing from one to four butyl groups (or phenyl group), was accomplished through the GC technique without the need for a derivatization step, which is typically employed for conferring thermal stability to these analytes. GC separation method was then coupled with mass spectrometry, allowing for the sensitive detection of each butyltin compound as well as their speciation in real sediment samples. Thanks to the treatment of these analytes with a selected solvent mixture, the herein proposed GC-MS/MS analysis was shown to be able to directly analyze butyl-substituted organotin compounds after extraction from sediments, maintaining high selectivity and sensitivity in the determination, as well as providing a procedure that reduces the occurrence of sample contamination.

Importantly, GC-MS/MS spectra of monobutyltin trichloride and dibutyltin dichloride are herein presented and interpreted for the first time. The corresponding fragment ions were identified with an isotope pattern reconstruction through the comparison with mathematically predicted patterns. Further studies will be realized to extend the analytical method to other polar chemicals and increase its sensitivity.

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