



Isotope dilution gas chromatography coupled to electron ionization and tandem mass spectrometry for the determination of butyltin compounds in the Spanish coastal marine sediments

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ABSTRACT

The use of organotin compounds, especially tributyltin (TBT), on ships as anti-fouling agent was banned in 1999 by the International Maritime Organization (IMO) due to their risk for the marine environment. Unfortunately, butylated organotin compounds have remained in the environment due to their high stability, accumulating in marine sediments. Current European legislation requires the continuous monitoring of the levels of organotin compounds in coastal marine sediments. Therefore, the aim of this work was the development and application of a fast and reliable analytical methodology that could be easily implemented for a routine basis to quantify the levels of TBT and its degradation products dibutyltin (DBT) and monobutyltin (MBT) in marine sediments at the low ng/g levels dry weight (d.w.). The technique chosen was Gas Chromatography coupled to electron ionization and tandem Mass Spectrometry after ethylation of the organotin compounds. Extraction of the organotin compounds from the sediment was carried out by 1:3 mixture of methanol and acetic acid. Quantification was carried out by Isotope Dilution Mass Spectrometry (IDMS) using ¹¹⁹Sn-labelled compounds. The detection limits which can be reached for TBT, DBT and MBT were 0.3, 0.3 and 0.1 ng·g⁻¹ d.w. respectively. Validation was carried out with three reference materials (BCR-462, BCR-646 and PACS-2) with satisfactory results. Relative standard deviations were, in all cases, less than 5 % for all compounds. The method was applied to the first monitoring of 87 coastal marine sediments covering the whole Spanish maritime waters. TBT was identified in 13 % of the samples analyzed in the Mediterranean Sea and in 6 % of the samples from the Atlantic Ocean. The implication of the results for coastal monitoring is also discussed.

1. Introduction

Organotin compounds (OTCs), especially tributyltin (TBT), have been widely applied as stabilizers in the PVC industry, material protection, industrial catalysts, wood preservatives and biocides in anti-fouling paints as marine coatings to prevent the growth and attachment of marine fouling organisms since the 1960 s. Due to the high toxicity of TBT in coastal ecosystems, it has been regulated and/or banned in antifouling paints, first in France in 1982 and later in many other countries worldwide, including all Europe. The international Maritime Organization (IMO) demanded a global ban of these paints worldwide

since 2003. The European Union implemented the Convention through the Regulation 782/2003/EC, and the year 2008 was determined as the deadline for the complete removal of TBT coatings from the ship hulls. TBT is also included in the list of priority pollutants in the field of water policy in an EU Water Framework Directive (WFD) and the highest allowed levels in waters according to an annual environmental quality standard (EQS) is 0.2 ng·L⁻¹. According to the WFD, analytical methods applied should have a limit of quantification (LOQ) lower than 30 % of the EQS. Therefore, reference methods with a LOQ lower than 0.06 ng·L⁻¹ are required to monitor these analyses [1].

Despite the implementation of regulations and the relatively fast

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degradation of TBT in seawater, high concentrations of TBT in water [2–6], landfill leachates [7], marine organisms [2–5,8,9] or in bottom sediments [1,3–5,8,10–20] are still detected with high enrichment factors. Half-lives ranged from days to weeks in seawater and from years to decades in sediments due to its hydrophobicity [21]. Being the adsorption on sediment reversible, TBT contaminated sediment could act as a reservoir of this pollutant [17]. Therefore, the problem of TBT pollution is still a subject of concern, especially for the disposal of contaminated dredged sediments [21]. TBT accumulation leads to the decline of reproductive capacity in biological populations and even to their disappearance while in mammals, including humans, OTCs are neurotoxic, hepatotoxic, endocrine disrupters and potential obesogens [22,23].

Analysis of these compounds are usually performed by hyphenated techniques coupling gas chromatography (GC) or high-performance liquid chromatography (HPLC) with spectroscopic techniques [24]. Although the analysis of these compounds by GC requires a previous derivatization step, it is often the preferred separation technique due to the higher resolution achieved and the wide range of atomic and molecular detectors available [1]. Among the detection techniques, ICP-MS in particular monitoring the Sn isotopes [8,25–27] has demonstrated its superiority over other detectors. Molecular mass spectrometry with electron ionization source (EI-MS) or with tandem mass spectrometry (EI-MS/MS) provides reliable measurements of OTC [22,28]. Former derivatization methods for GC analysis based on the extraction with tropolone and n-hexane followed by Grignard derivatization and determination with GC-flame photometric detection have been replaced by the less time consuming ethylation process with sodium tetraethylborate (NaBET_4) in aqueous phase followed by GC and atomic or molecular mass spectrometry [29]. To isolate and pre-concentrate the analytes, different extraction techniques such as liquid–liquid extraction (LLE), supercritical fluid extraction (SFE), solid-phase microextraction (SPME), stir bar sorptive extraction (SBSE), liquid-phase microextraction (LPME), headspace single drop microextraction (HS-SDME) and solid-phase extraction (SPE) has been assayed [1,22,25,29–31]. Also, focused microwave extraction has been used for the quantitative extraction of these pollutants from solid environmental matrices such as sediments or biota [32].

Accurate organotin analysis in different matrices requires the use of appropriate internal standards to alleviate matrix effects and/or recovery problems occurring during sample preparation. Tripropyltin (TPT) and tricyclohexyltin (TCyT) have been used as internal standards for the analysis of organotin compounds in environmental samples. However, it is questionable whether those compounds behave as the analytes during sample preparation and correct for all types of errors throughout the whole procedure. The use of isotope labelled standards for the accurate determination of OTCs by Isotope Dilution Mass Spectrometry (IDMS) has been extensively described in the literature [33–35] using labelled analogues with ^{119}Sn [33,34] or $^2\text{H}_{27}$ [35]. In the latter case [35], a drastic change in the retention time of tributyltin labelled with 27 deuterium atoms was observed. In contrast, isotopic effects were not observed when using ^{119}Sn as labelling isotope [33,34].

The aim of this work was to develop, validate and apply an analytical methodology to quantify ultratrace levels (ng/g) of tributyltin (TBT), dibutyltin (DBT) and monobutyltin (MBT) in coastal sediments using Gas Chromatography coupled to tandem Mass Spectrometry. The combination of IDMS with GC–MS/MS for the determination of organotin compounds in sediments has not been described in the literature thus far and can be easier implemented for a routine basis compared to GC-ICPMS. The method developed was applied to the quantification of OTCs in 87 coastal sediment samples covering for the first time the whole maritime waters around Spain. The resulting TBT concentrations are compared here with the OSPAR environmental quality standard (EQS) value of 0.8 ng/g [36].

2. Materials and methods

2.1. Reagents and materials

Certified reference materials analyzed in this work included PACS-2 (marine sediment), purchased from NRC-CNRC (Ottawa, Canada), BCR-462 (coastal sediment) and BCR-646 (freshwater sediment) purchased to the Institute for Reference Materials and Measurements (Geel, Belgium). For quantification by IDMS a mixture of butyltins enriched in the ^{119}Sn isotope containing both TBT, DBT and MBT was obtained from ISC-Science (Gijón, Spain). This mixture was diluted by weight (1:10 w/w) with a mixture (1:3 v/v) of methanol (>99.9 %, Fisher Scientific, Waltham, Massachusetts, USA) and acetic acid (>99.8 %, Fluka, Morristown, New Jersey, USA). Ethylation of the butyltin species was performed using sodium tetraethylborate (97 %, Sigma–Aldrich, Burlington, Massachusetts, USA). Sodium acetate (≥ 99 %, Sigma–Aldrich) and acetic acid were used to prepare the buffer solution 0.1 M (pH 5.4). Hexane (≥ 97 %, Sigma–Aldrich) was used as organic phase to extract the derivatized organotin compounds. All vials used were glass vials with PTFE plastic stoppers. For microwave extraction, 10 mL glass tubes with silicone caps (CEM corporation, Matthews, North Carolina, USA) and 3 mm magnetic stirring bars were used.

2.2. Instrumentation

Chromatographic analyses were performed with a gas chromatography model 7890A (Agilent Technologies, Santa Clara, California, USA) coupled to an Agilent 7000C Triple Quadrupole mass spectrometer. The GC system was fitted with a multimode inlet and a DB-5MS UI capillary column (30 m \times 0.25 mm i.d., 0.25 μm coating). A deactivated fused silica tubing (1.2 m \times 0.18 mm i.d.) was coupled to the chromatographic column and connected to the MS allowing the instrument to operate in the back-flush mode without disturbing the vacuum of the MS instrument. An analytical balance model AB204-S (Mettler Toledo, Zurich, Switzerland) was used for the gravimetric preparation of all samples and standards. Ultra-pure water was obtained from a Purelab flex 3 (Elga, High Wycombe, United Kingdom). A Heraeus oven (Thermo Scientific, Waltham, Massachusetts, USA) was used to dehydrate the sediments. The extraction of OTCs from sediments was carried out using a focused microwave Explorer Hybrid from CEM Corporation (Matthews, NC). Total organic carbon content was determined using an elemental analyzer (model 2400 series II, CHNS/O, Perkin Elmer, Inc. Shelton, USA). The granulometric fraction of the Mediterranean samples was determined by wet sieving. In the Atlantic samples the granulometry was determined using a Malvern Mastersizer 2000 laser particle size analyzer (Malvern Instruments Ltd., Worcestershire, UK). Underivatized butyltin compounds are stable in mixtures of acetic acid and methanol. We usually store them at -18 °C prior use. In contrast derivatized butyltin compounds can be stored at -18 °C for two days until GC–MS injection but for longer storage times it is recommended to store them at -80 °C.

2.3. Sediment samples

The sampling points both in the Atlantic Ocean (32 samples) and in the Mediterranean Sea (55 samples) are shown in Fig. 1, labelled as A and M respectively. In the Mediterranean Sea sediment sampling campaigns were conducted from 2013 to 2016 along the continental shelf on board the oceanographic vessel Francisco de Paula Navarro (Instituto Español de Oceanografía-CSIC). Atlantic seabed sediment samples were collected during four cruises from 2016 to 2023 on board the oceanographic vessels Ramón Margalef (Instituto Español de Oceanografía-CSIC) and Miguel Oliver (Secretaría General de Pesca). Sampling locations were chosen considering mainly depositional areas covering the whole Spanish Coast comprising a variety of coastal environments affected by different types and degrees of anthropogenic pressure.

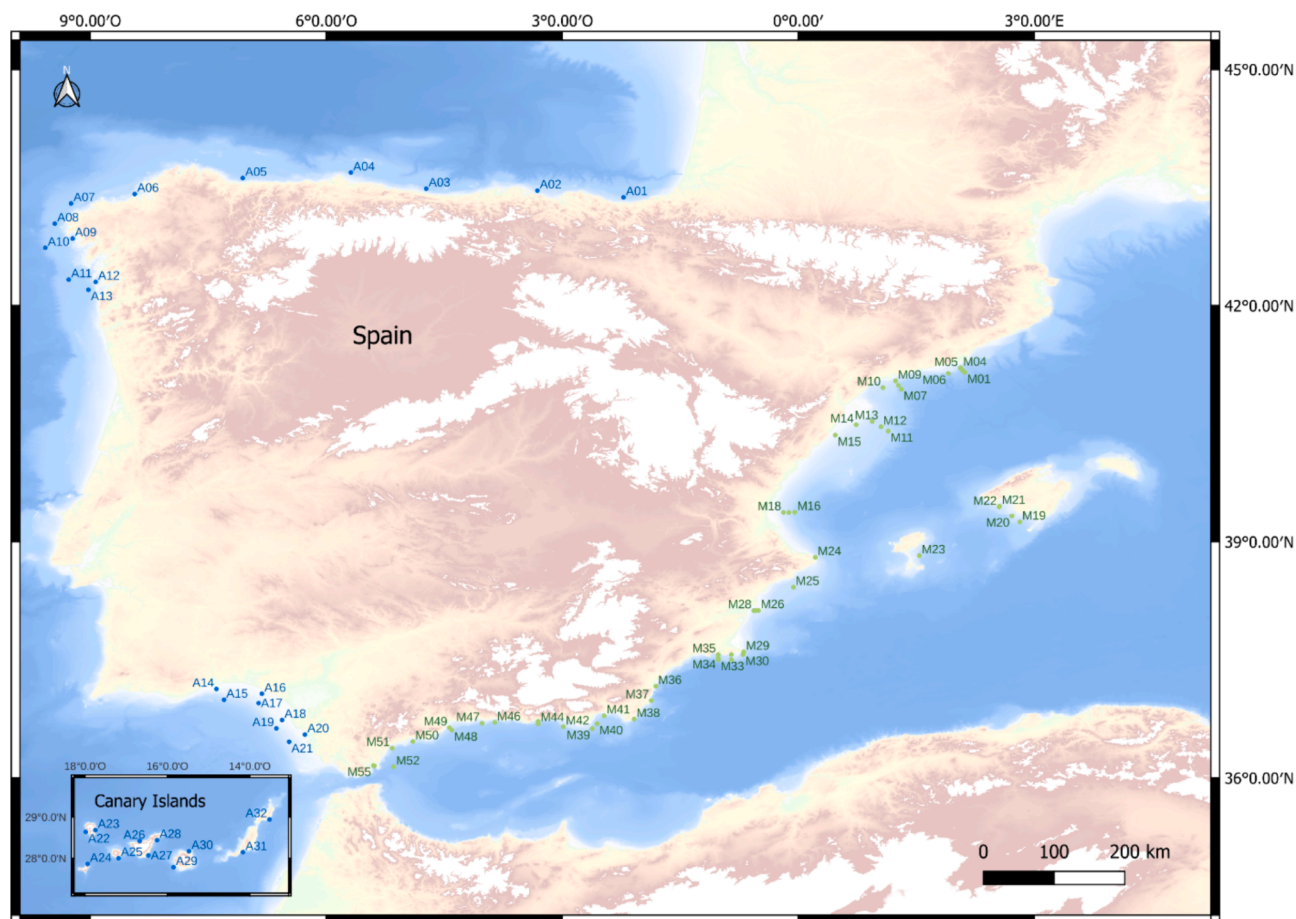


Fig. 1. Sampling points on the Atlantic and Mediterranean coasts. The points on the Atlantic coast are blue colored and named as A whereas those on Mediterranean coast are green colored and named as M. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Surface sediments were collected using a stainless-steel box-corer (17x10 cm), preserved in clean aluminum containers and stored until analysis at $-20\text{ }^{\circ}\text{C}$. The samples were lyophilized and then sieved through a 2 mm mesh to remove large fragments. Total fraction ($<2\text{ mm}$) was used for the analysis of OTCs.

2.4. Procedures

2.4.1. Sample preparation

Gravimetrically controlled amounts of ca. 200 mg of dry sediment samples and ca. 50 mg of the diluted ^{119}Sn -enriched butyltin mixture were introduced in a disposable 10 mL glass vial specifically designed for the focused microwave system. For the analysis of the reference materials only 50 mg of the sediments were taken due to relatively high concentration of organotin compounds in the materials. Then, 4 mL of the methanol:acetic acid (1:3, v/v) mixture and the magnetic stirring bar were added, and the vial was capped. The vial was introduced in the focused microwave unit and exposed to MW irradiation to achieve $80\text{ }^{\circ}\text{C}$ for 4 min in the vial. After digestion, the mixture was allowed to stand for about 20 min until a clear supernatant appeared. A volume of ca. 1.5 mL of the supernatant was transferred with the help of a Pasteur pipette into a glass vial and 4 mL of the acetic acid/acetate buffer solution was added. Then, 200 μL of a 2 % w/v sodium tetraethylborate in Milli-Q water and 1 mL of hexane were added and the glass vial was shaken manually for 5 min. Most of the organic phase (ca. 0.8–0.9 mL) was transferred to a 2 mL vial so that hexane was evaporated with a gentle stream of nitrogen down to ca. 40 μL before being injected into the gas chromatograph. It should be noted that the actual volume of extracts taken (both before and after derivatization) and the final volume of

hexane after preconcentration do not need to be known when applying IDMS.

2.4.2. Separation and measurement of OTCs by GC–MS/MS

The chromatographic separation of the butyltin compounds was based on that employed previously [32] and was performed by using helium as carrier gas with a constant flow of $1\text{ mL}\cdot\text{min}^{-1}$. The inlet was kept at $250\text{ }^{\circ}\text{C}$ and the injection (2 μL) was performed in splitless mode. The column temperature was initially maintained at $60\text{ }^{\circ}\text{C}$ for 1 min, increased at $30\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ to a final temperature of $300\text{ }^{\circ}\text{C}$ and a 3.5 min post-run was carried out at $300\text{ }^{\circ}\text{C}$ in backflush mode. The transfer line and ion source temperatures were $280\text{ }^{\circ}\text{C}$ and $230\text{ }^{\circ}\text{C}$, respectively. Electron ionization (EI) was performed at 70 eV. Fig. 2 shows the retention times of the three ethyl derivatives of the organotin compounds, being 5.27, 6.00 and 6.62 min for MBT, DBT and TBT, respectively. Compounds were identified by their retention time and their mass spectra acquired in scan mode.

The isotopic distribution of TBT, DBT and MBT was measured by Selected Reaction Monitoring (SRM) using 10 ms of dwell-time and resolution of $\text{FWHM}=0.7\text{ Da}$ in both mass analyzers and a gain factor of 10. The collision cell was pressurized with a Helium flow of $1.0\text{ mL}\cdot\text{min}^{-1}$ to reduce background noise and with a N_2 flow of $1.5\text{ mL}\cdot\text{min}^{-1}$ to perform collision induced dissociation. The fragment ion $\text{C}_4\text{H}_{11}\text{Sn}^+$ was selected for the analysis of TBT and MBT while $\text{C}_6\text{H}_{15}\text{Sn}^+$ was selected for the analysis of DBT. The collision energy employed for TBT, DBT and MBT were 10 eV, 2 eV and 4 eV, respectively. The isotopic distribution of TBT was measured using the SRM transitions $291.1 \rightarrow 179.1$, $290.1 \rightarrow 178.1$ and $289.1 \rightarrow 177.1$. For DBT, the measured SRM transitions were $263.1 \rightarrow 207.1$, $262.1 \rightarrow 206.1$ and $261.1 \rightarrow 205.1$.

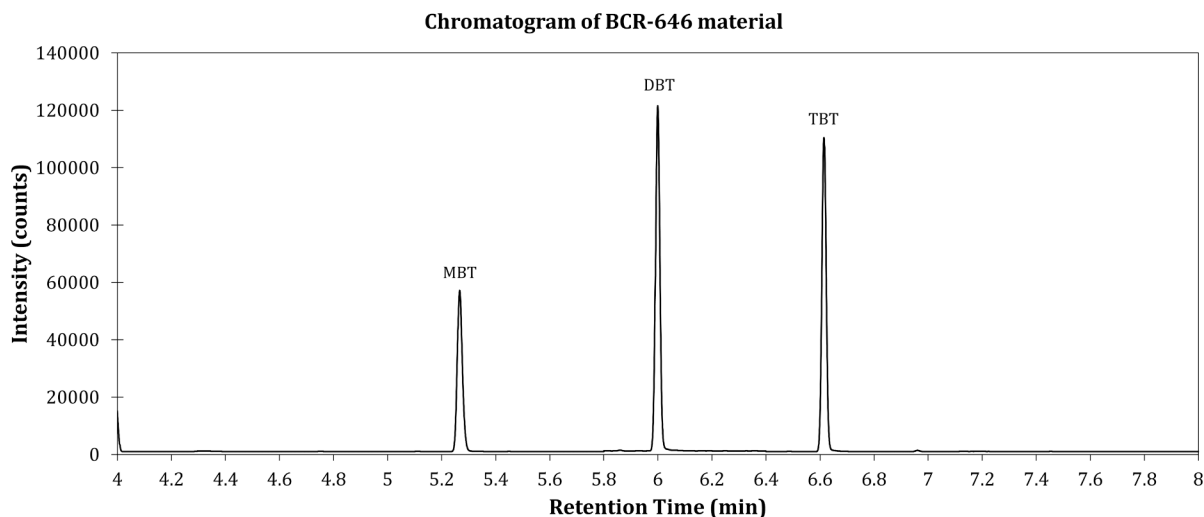


Fig. 2. Total Ion Count GC-MS/MS chromatogram obtained in SRM acquisition mode of BCR-646 material pre-treated according to the sample preparation protocol described above.

Finally, for MBT the SRM transitions were 235.1 → 179.1, 234.1 → 178.1 and 233.1 → 177.1.

2.4.3. Quantification by IDMS

The theoretical isotopic distributions of natural abundance and ^{119}Sn -enriched fragment ions (probability of occurrence of each SRM transition) were computed using the software developed by Ramaley and Cubero Herrera [37]. The experimental isotopic abundances of TBT, DBT and MBT in the mixture (sediment sample spiked with ^{119}Sn -enriched TBT, DBT and MBT) were calculated by integrating the peak areas of the monitored fragment ions. The quantification of natural organotin compounds in the sediment samples was performed by IDMS using three transitions per compound. In this way, the experimental relative abundances of the fragment ions (m/z) in the mixture (m) were expressed as a linear combination of the corresponding theoretical values for both the sample (s) and ^{119}Sn -enriched compounds (t). For instance, the equations for the quantification of TBT when working in SRM mode can be expressed in matrix notation as Eq. (1):

$$\begin{bmatrix} A_m^{291.1>179.1} \\ A_m^{290.1>178.1} \\ A_m^{289.1>177.1} \end{bmatrix} = \begin{bmatrix} A_s^{291.1>179.1} & A_t^{291.1>179.1} \\ A_s^{290.1>178.1} & A_t^{290.1>178.1} \\ A_s^{289.1>177.1} & A_t^{289.1>177.1} \end{bmatrix} \times \begin{bmatrix} x_s \\ x_t \end{bmatrix} + \begin{bmatrix} e^{291.1>179.1} \\ e^{290.1>178.1} \\ e^{289.1>177.1} \end{bmatrix} \quad (1)$$

where A_m is the experimental relative abundance of each fragment ion. A_s and A_t are the theoretical relative abundances of the fragment ions corresponding to natural abundance TBT and ^{119}Sn -enriched TBT, respectively. Similar matrices can be written for DBT and MBT. The molar fractions of the natural compound (x_s) and the tracer (x_t) are calculated by multiple linear regression [38]. Once the molar fractions were calculated, the final concentrations of the compounds in the sample were calculated using Eq. (2):

$$C_s = C_t \times \frac{x_s}{x_t} \times \frac{m_t}{m_s} \times \frac{w_s}{w_t} \quad (2)$$

where C_s is the concentration of the analyte in the sample (unknown, $\text{ng}\cdot\text{g}^{-1}$). C_t is the known concentrations of the tracer, ($\text{ng}\cdot\text{g}^{-1}$); m_s and m_t are the masses (g) taken from sample and the tracer during sample preparation, while w_s and w_t are the molecular weights ($\text{g}\cdot\text{mol}^{-1}$) of the natural abundance and labelled analytes respectively [38].

3. Results and discussion

3.1. Spectral accuracy of isotope distributions measured by tandem MS

When working with tandem MS the real isotopic distribution of an in-cell molecular fragment of n isotopologues obtained after collision induced dissociation (CID) cannot be directly measured by n SRM transitions as several isotopologues of the precursor molecule may contribute to the same isotopologue of the fragment ion. For this reason, the theoretical isotopic distribution of natural abundance and ^{119}Sn -enriched fragment ions after CID was computed using the polynomial expansion algorithm developed by Ramaley and Cubero Herrera [37]. The theoretical isotope distributions calculated are shown in Table 1. To compare the theoretical distributions with those experimentally measured it is necessary to normalize the theoretical distributions as only three transitions were experimentally measured. The comparison between the normalized theoretical and experimental values obtained for the isotopic distribution of the product ions after CID for each compound is also shown in Table 1. A good agreement between the experimental isotopic distributions of the fragment ions with the normalized theoretical isotopic distributions was obtained indicating the adequate “spectral accuracy” of the triple quadrupole system employed, as described previously [39].

3.2. Measurement of isotope distributions in the spiked samples and IDMS calculations

The unnormalized theoretical values shown in Table 1 were used in the IDMS computation Eq. (1). For the calculation of the molar fractions, x_s and x_t , in the samples spiked with the ^{119}Sn -enriched compounds the peak areas measured for the different transitions could be employed directly in Eq. (1). Table 2 shows an example of the IDMS calculations for the determination of TBT in the BCR-646 reference material. The peak areas measured for the three transitions are transformed into abundances and then Eq. (1) is applied. The excel function LINEST allows the determination of x_s and x_t which are then used in Eq. (2) to calculate the concentration of TBT. The average concentration of the five injections is 432 ng/g TBT (as cation) with a standard deviation of 2 ng/g .

3.3. Validation of the method

Three certified reference materials (BCR-462, BCR-646 and PACS-2)

Table 1

Comparison of the theoretical and experimental isotopic distribution after CID for the product ions selected for both natural and ^{119}Sn enriched TBT, DBT and MBT. Theoretical isotopic distribution was calculated according to the procedure described by Ramaley et al. [37] and then normalized to be compared with the experimental distributions. The standard uncertainty of the results corresponds to the standard deviation of $n = 5$ independent GC-MS/MS injections of the BCR-646 material and the mixture of TBT, DBT and MBT enriched in ^{119}Sn .

Organotin compound	Precursor ion	Product ion	Theoretical [37] isotopic distribution (%)	Normalized theor. isotopic distribution (%)	Experimental isotopic distribution (%)
TBT natural	$\text{C}_{12}\text{H}_{27}\text{Sn} (m/z)$	$\text{C}_4\text{H}_{11}\text{Sn} (m/z)$			
	289.1	177.1	21.53	36.55	36.51 ± 0.05
	290.1	178.1	8.48	14.39	14.36 ± 0.03
	291.1	179.1	28.90	49.06	49.13 ± 0.04
TBT enriched	289.1	177.1	12.30	13.41	13.6 ± 0.02
	290.1	178.1	72.98	79.56	80.31 ± 0.01
	291.1	179.1	6.45	7.03	6.33 ± 0.02
DBT natural	$\text{C}_{10}\text{H}_{23}\text{Sn} (m/z)$	$\text{C}_6\text{H}_{15}\text{Sn} (m/z)$			
	261.1	205.1	22.17	36.31	36.52 ± 0.05
	262.1	206.1	9.15	14.99	14.89 ± 0.03
	263.1	207.1	29.73	48.70	48.59 ± 0.02
DBT enriched	261.1	205.1	12.58	13.25	13.15 ± 0.01
	262.1	206.1	74.88	78.87	78.98 ± 0.04
	263.1	207.1	7.48	7.88	7.87 ± 0.03
MBT natural	$\text{C}_8\text{H}_{19}\text{Sn} (m/z)$	$\text{C}_4\text{H}_{11}\text{Sn} (m/z)$			
	233.1	177.1	22.50	36.55	36.57 ± 0.04
	234.1	178.1	8.86	14.39	14.32 ± 0.04
	235.1	179.1	30.20	49.06	49.11 ± 0.03
MBT enriched	233.1	177.1	12.86	13.52	13.37 ± 0.05
	234.1	178.1	76.26	80.21	80.31 ± 0.04
	235.1	179.1	5.96	6.26	6.33 ± 0.07

Table 2

Process for the determination of TBT in BCR-646 by IDMS using Eqs. (1) and (2). Data for 5 injections of the same extract.

Injection no.	GC-MS/MS		Normalization Abundances	Eq. (1)		Eq. (2)
	Transition	Peak area		x_s	x_t	Concentration TBT ng g^{-1}
1	289 → 177	47,181	0.2778	1.038	0.423	429
	290 → 178	67,325	0.3964			
	291 → 179	55,329	0.3258			
2	289 → 177	48,978	0.2792	1.042	0.420	434
	290 → 178	69,240	0.3947			
	291 → 179	57,221	0.3262			
3	289 → 177	46,490	0.2804	1.042	0.420	433
	290 → 178	65,403	0.3945			
	291 → 179	53,891	0.3251			
4	289 → 177	47,468	0.2754	1.043	0.420	433
	290 → 178	68,160	0.3954			
	291 → 179	56,754	0.3292			
5	289 → 177	45,323	0.2740	1.043	0.421	433
	290 → 178	65,457	0.3958			
	291 → 179	54,607	0.3302			

were analyzed using the protocol indicated in the procedures and then measured by quintuplicate in the GC-MS/MS instrument. The results obtained are given in Table 3, including the experimental uncertainty as 2SD to be compared with the expanded uncertainty U of the reference materials. As it can be observed, the experimental values agree with the certified values for all materials and compounds when considering the

uncertainties. Reproducibility was evaluated with a real sediment sample that contained less than 10 ng/g of each OTC. To assess reproducibility, 5 different digestions were carried out, three of them on the same day and the other two on subsequent consecutive days. The whole set of results are shown in Table 4 with standard deviations lower than 1 ng/g for all three compounds at these very low concentration levels. The

Table 3

Results obtained in the validation of the GC–MS/MS procedure using the three certified reference materials for TBT, DBT and MBT.

		TBT (ng TBT·g ⁻¹)		DBT (ng DBT·g ⁻¹)		MBT (ng MBT·g ⁻¹)	
		Mean	U (2SD)	Mean	U(2SD)	Mean	U(2SD)
BCR-462	Experimental	38	2	60	2	140	6
	Certified	54	15	68	12	–	–
BCR-646	Experimental	432	4	767	22	541	68
	Certified	480	80	770	90	610	120
PACS-2	Experimental	2166	80	1978	32	867	88
	Certified	2174	257	2054	126	889	–

Table 4

Results of the reproducibility assessment by analysis of a real sample at low concentration levels for TBT, DBT and MBT with 5 digestions carried out in three different days.

Replicate	TBT (ng TBT·g ⁻¹)	DBT (ng DBT·g ⁻¹)	MBT (ng MBT·g ⁻¹)
1 (day 1)	2.49	5.77	7.26
2 (day 1)	2.52	6.10	7.16
3 (day 1)	4.22	4.78	8.35
4 (day 2)	2.52	6.04	6.55
5 (day 3)	2.39	5.93	7.26
Mean ± SD	2.8 ± 0.8	5.7 ± 0.5	7.3 ± 0.6

relative standard deviation (RSD%) obtained during the same day (intraday variability) for n = 3 independent replicates was 32 %, 12 % and 9 % for TBT, DBT and MBT, respectively, whereas the interday variability obtained for n = 5 independent replicates analysed in two different measurement sessions was 28 %, 9 % and 9 % for TBT, DBT and MBT, respectively. This values improve significantly when rejecting sample replicate three of Table 4 obtaining 1 %, 4% and 1 % (intraday) and 2 %, 2 %, 5 % (interday) for TBT, DBT and MBT.

The limits of detection (LOD) were calculated by preparing 6 blanks and 6 extractions of a real sample with concentration levels close to the expected detection limits. Samples and blanks were spiked with the ¹¹⁹Sn-enriched mixture of TBT, DBT and MBT at two different concentration levels: samples were spiked at the levels indicated in the procedure while blanks were spiked at a 10 times lower level. The spiked samples and blanks were quantified by the IDMS method described above (assuming a sample weight of 0.2 g for the blanks) and the limits of detection were calculated as 3 times the standard deviation of the measured concentrations (n = 6 for each type). The results are shown in Table 5.

As it can be observed, for the blanks LODs are below 0.3 ng g⁻¹ for all compounds. The LODs degrade when the amount of spike added is higher and equal that employed for the analysis of the samples. This is a well-known fact for IDMS as error propagation increases for non-optimum spike-to-analyte ratios [38]. It is important to understand that the LODs are not limited by instrumental sensitivity but only by the precision in which the isotopic composition of the spiked samples can be measured. For very low-level samples the amount of spike added can be reduced and the blank LODs could be achieved for the real samples. In this work the expected concentrations were higher, and so the amount of spike was adjusted accordingly. The Limits of quantification (LOQ) were

Table 5

Limits of detection (LOD) and quantification (LOQ) for the GC–MS/MS methodology developed.

	TBT	DBT	MBT
LOD (ng·g ⁻¹), blank	0.3	0.3	0.1
LOD (ng·g ⁻¹), low-level sample	0.7	1.1	0.7
LOQ (ng·g ⁻¹), low-level sample	2.3	4.0	1.7

calculated as 10 times the standard deviation of the blanks and are also shown in Table 5. In our experience, for IDMS quantification, the LOQs calculated using the 10-sigma criterion are too conservative. For real samples we have quantified all samples at or above the detection limits obtained for the low-level sample.

3.4. Analysis of real samples

Marine sediment samples were collected from the Atlantic Ocean and the Mediterranean Sea as shown in Fig. 1. Tables 6 and 7 show the results obtained, most of the samples contained levels of TBT, DBT and MBT below the detection limits established for this analytical methodology.

3.4.1. Quality control during the analysis of real samples

Every time a batch of real samples were extracted the reference material BCR-646 was also employed as quality control for that batch. In total 7 independent extractions of the reference material were performed on 7 different days and the results shown in Table 8. As it can be observed, results in agreement with the reference values were found in all cases. In addition the interday variability (expressed as %RSD) obtained for the analysis of the BCR 646 during 7 measurement session was 3 %, 3 % and 7 % for TBT, DBT and MBT, respectively, in agreement with the values obtained when rejecting one of the replicates of Table 4.

3.4.2. Occurrence and distribution of OTCs in the Mediterranean and Atlantic continental shelf

As previously indicated, most of the samples contained levels of TBT, DBT and MBT below the detection limits established for this analytical methodology. In general, a higher presence was detected in the Mediterranean area where, in 7 out of 55 samples all three OTCs were detected (concentrations > LOD) simultaneously. In the Atlantic area

Table 6

Concentrations in ng/g expressed as cation for marine sediments collected in the Atlantic Ocean.

Sample name	[TBT]	[DBT]	[MBT]	Sample name	[TBT]	[DBT]	[MBT]
A01	<LOD	<LOD	1.4	A17	<LOD	<LOD	0.8
A02	<LOD	<LOD	0.8	A18	<LOD	<LOD	1.8
A03	<LOD	<LOD	<LOD	A19	<LOD	<LOD	0.7
A04	<LOD	1.1	0.8	A20	2.4	1.5	2.4
A05	<LOD	<LOD	<LOD	A21	<LOD	<LOD	0.8
A06	<LOD	1.1	1.1	A22	<LOD	<LOD	0.7
A07	<LOD	<LOD	<LOD	A23	<LOD	<LOD	<LOD
A08	<LOD	<LOD	<LOD	A24	<LOD	<LOD	<LOD
A09	<LOD	<LOD	1	A25	<LOD	<LOD	<LOD
A10	<LOD	<LOD	<LOD	A26	<LOD	<LOD	<LOD
A11	<LOD	<LOD	<LOD	A27	<LOD	<LOD	0.7
A12	<LOD	<LOD	<LOD	A28	1.3	2.7	2.4
A13	<LOD	1.7	1.5	A29	<LOD	<LOD	<LOD
A14	<LOD	<LOD	0.7	A30	<LOD	<LOD	<LOD
A15	<LOD	<LOD	0.7	A31	<LOD	<LOD	<LOD
A16	<LOD	10.3	6.9	A32	<LOD	3.8	<LOD

Table 7

Concentrations in ng/g expressed as cation for marine sediments collected in the Mediterranean Sea.

Sample name	[TBT]	[DBT]	[MBT]	Sample name	[TBT]	[DBT]	[MBT]
M01	<LOD	5.6	3.6	M29	<LOD	2.8	0.9
M02	<LOD	8.5	4.2	M30	<LOD	<LOD	0.8
M03	<LOD	6.2	4.2	M31	<LOD	<LOD	0.8
M04	<LOD	2.7	1.6	M32	1.2	3.3	4.4
M05	<LOD	<LOD	0.8	M33	<LOD	2.6	1.8
M06	<LOD	<LOD	0.7	M34	<LOD	<LOD	1.3
M07	<LOD	1.5	1.5	M35	<LOD	<LOD	0.9
M08	<LOD	1.1	2	M36	<LOD	<LOD	<LOD
M09	<LOD	<LOD	0.8	M37	<LOD	<LOD	<LOD
M10	<LOD	<LOD	1	M38	<LOD	<LOD	<LOD
M11	<LOD	<LOD	<LOD	M39	<LOD	<LOD	<LOD
M12	<LOD	<LOD	0.7	M40	<LOD	1.7	<LOD
M13	<LOD	<LOD	0.8	M41	<LOD	<LOD	0.7
M14	<LOD	<LOD	<LOD	M42	<LOD	<LOD	<LOD
M15	<LOD	<LOD	0.8	M43	<LOD	<LOD	<LOD
M16	<LOD	<LOD	1.4	M44	<LOD	<LOD	<LOD
M17	<LOD	<LOD	<LOD	M45	<LOD	<LOD	<LOD
M18	<LOD	<LOD	<LOD	M46	<LOD	<LOD	<LOD
M19	<LOD	<LOD	0.9	M47	<LOD	<LOD	0.8
M20	<LOD	<LOD	<LOD	M48	<LOD	<LOD	<LOD
M21	<LOD	<LOD	<LOD	M49	<LOD	<LOD	<LOD
M22	<LOD	<LOD	<LOD	M50	<LOD	<LOD	<LOD
M23	<LOD	<LOD	<LOD	M51	<LOD	<LOD	1.1
M24	<LOD	<LOD	1.1	M52	24.8	11.5	5.7
M25	<LOD	<LOD	0.7	M53	87.8	27.1	17
M26	9.9	5.3	4.1	M54	12.9	5	3
M27	<LOD	2.7	5.8	M55	17.9	3.3	2.4
M28	0.9	2	2.6				

Table 8

Quality control for the analysis of real samples using BCR-646. Concentrations in ng/g expressed as cation.

Measurement	TBT	DBT	MBT
1	434	790	563
2	426	787	543
3	438	809	566
4	434	771	496
5	428	801	567
6	442	792	556
7	464	846	619
Average	437.8	799.3	558.5
Standard deviation	12.6	23.5	36.5
RSD (%)	2.9	2.9	6.5
Certified value ± Uncertainty	480 ± 80	770 ± 90	610 ± 120

only 2 of the sampled stations reflected this situation. In both areas the most present OTC was MBT, detected in 62 % of the samples analyzed in the Mediterranean Sea and in 53 % of the samples from the Atlantic Ocean, followed by DBT in 31 % and in 22 % and TBT in 13 % and 6 %, respectively. The fact the LOD of MBT is slightly lower than DBT and TBT also contributes to its higher frequency of detection. The highest levels of OTCs (MBT, DBT, TBT) were simultaneously found in the same sample (M53, Algeciras Bay) in the Mediterranean; in the Atlantic the highest levels of MBT, DBT was found in sample A16 (Huelva) and for TBT the highest level corresponded to sample A20 (Gulf of Cadiz).

The concentration of MBT ranged from <LOD to 17 ng/g in M53. These monobutyltin levels are higher than those reported for the same locations in the Mediterranean coast in 2011–2012 [40]. On the contrary values from Atlantic coast (Portugal and Gulf of Cádiz) are lower than those reported in previous studies [10,41]. Similarly, the values reported for the Spanish North Coast (Cantabria and Basque Country) were also higher than the present observations [42,43].

DBT levels found were similar to those of monobutyltin: <LOD to 27.1 ng/g in M53. These concentrations are higher than those reported in recent previous studies in the Mediterranean coast [40]. In general, in

those locations with the same TOC content or far from marinas and ports, the levels of MBT and DBT were like those found along the years through the Mediterranean coast [18,44–46]. Regarding to subregions, sample M53 in Algeciras Bay in Strait-Alborán and sample M26 in Santa Pola in Levantine-Balearic showed the highest DBT concentrations. The concentrations reported here for the Atlantic Coasts are lower than those reported previously for similar areas. The highest value found for the Gulf of Biscay area in this study (1.7 ng/g) is similar to the lowest values reported in previous studies in the same area [43].

Finally, TBT showed the highest concentration (87.8 ng/g in M53) of the three OTCs and all samples studied. This concentration was the highest detected in the Strait-Alborán subregion. Also, this concentration was higher than the levels measured at same location in Algeciras Bay (10.6 ng/g) in 2011 [40]. Tributyltin also showed the highest concentration (9.9 ng/g in M26) in the Levantine-Balearic subregion and was higher than the value measured at the same location in Santa Pola (5.04 ng/g) in 2012 [40]. Values previously reported for the Atlantic Coasts were higher than those reported here for the same area [10,42,43]. The decrease noted in the Atlantic area has been reported previously [47] for other areas because of increased precautionary protective measure implemented. Otherwise, an increase of OTCs has also been recorded associated with ship channels, ports, harbors, and marinas as it happens in some studied Mediterranean points.

Sediment properties (granulometry and total organic carbon, TOC) could influence contaminant distribution, especially if there is variability between the samples collected in the different locations. In the samples analyzed here, the fine fraction (fraction lower than 63 µm) ranged between 9.3 % and 99.7 % and the TOC content between 0.2 % and 2.0%. Using a Spearman correlation factor, no clear correlation was established between fine fraction content and C_{org} , although the highest concentrations of OTCs were found in sediments with the lowest percentage of fines (grain size less than 63 µm). The same statistics was applied identifying correlations between TBT and MBT in both areas and between TBT and DBT in the Mediterranean area but not for the Atlantic region.

3.4.3. Evaluation of the potential ecological toxicity of TBT in marine sediments

The Swedish Agency of Marine and Water Management (SwAM) has established a national EQS of 0.8 ng/g for TBT in sediment from a $Q_{S_{sediment}}$ that is based on ecotoxicity studies on benthic organisms. The EQS is normalized to 2.5 % organic carbon and is applied in all subregions [48]. However, the Iberian Sea and Gulf of Cadiz sediment concentrations are assessed using non-normalised concentrations because of the granulometry of the sediment in this area according to its regional variability. According to this and keeping in mind that the LOD of TBT is 0.7 ng/g, concentrations encountered in most samples from the Atlantic areas were below the established threshold. On the other hand, concentrations found in M32 (Cartagena; 1.2 ng/g), M52–M55 (Algeciras Bay; 24.8, 87.8, 12.9, 17.9 ng/g) and M28, M26 (Santa Pola; 0.9, 9.9 ng/g) could be causing toxic effects to marine benthic biota.

The butyltin degradation index (BDI) has been used to evaluate the fate and degradation of TBT in the environment, which is defined as $BDI = (MBT+DBT)/TBT$. A BDI value of <1 indicates a recent TBT contamination, assuming that the decomposition of TBT is the only source of DBT and MBT [18] or a low TBT degradation rate that may be found under certain conditions (e.g., hypoxia, darkness, low temperature, low microbial activity, and high levels of TBT) [10]. Different BDI values may represent different sources of BTs or different degradation rates caused by different environmental conditions [49]. To calculate the BDIs, the concentrations given in Tables 6 and 7 were employed. The value of LOD/2 was used for the same calculations when the compounds were below of LOD. The butyltin degradation index (BDI) was calculated for the samples in which at least one of the three OTCs was detected. In our study, the BDI values were lower than 1 only in five samples (M52–M55 and M26) which corresponds to Algeciras Bay and Santa Pola in the

Mediterranean Sea. These $BDI < 1$ values found in this study, added to the factor that no correlation found with TOC, suggests contemporary TBT inputs and/or low TBT degradation rate. On the other hand, most samples produced BDI values higher than 1 (90 % of the samples in the Mediterranean area and 100 % of the Atlantic ones) indicating that there were no recent inputs of butyltins to the studied sediments.

4. Conclusions

A fast, reliable, and sensitive procedure has been developed for the determination of MBT, DBT and TBT in marine sediments using GC-MS/MS in combination with Isotope Dilution. The accuracy of the method was demonstrated by the analysis of several reference materials both before and during sample analysis for quality control purposes. The detection limit obtained for TBT under the standard operating conditions ($0.7 \text{ ng} \cdot \text{g}^{-1}$) was lower than the EQS of $0.8 \text{ ng} \cdot \text{g}^{-1}$ for TBT in sediments established by the Swedish Agency of Marine and Water Management. The method was used to evaluate sediments from the Spanish coast, TBT was identified in 13 % of the samples analyzed in the Mediterranean Sea and in 6 % of the samples from the Atlantic Ocean, DBT in 31 % and in 22 % and MBT in 62 % and 53 % of the samples respectively. The highest concentrations were found in the south of the Iberian Peninsula, in Algeciras Bay (M53). The concentrations determined were compared with previous studies finding that Mediterranean areas seem to show higher concentrations than the previous ones while Atlantic seems to be lower. The BDI index confirms this idea suggesting contemporary TBT input in the samples from Algeciras Bay and Santa Pola in the Mediterranean Sea. In terms of ecological toxicity only sediments from the Mediterranean region could be causing toxic effects to the marine benthic biota.

CRedit authorship contribution statement

Helí Potes-Rodríguez: Writing – original draft, Validation, Methodology, Investigation, Data curation, Conceptualization. **Juan Manuel Marchante-Gayón:** Writing – review & editing, Writing – original draft, Supervision, Project administration. **Pablo Rodríguez-González:** Writing – review & editing, Project administration, Methodology, Investigation, Funding acquisition, Conceptualization. **Ana V. Filgueiras:** Writing – review & editing, Resources, Investigation, Formal analysis. **Lucía Viñas:** Resources, Formal analysis, Data curation. **Begoña Pérez-Fernández:** Resources, Formal analysis, Data curation. **Rubén Moreno-González:** Supervision, Resources, Investigation, Data curation. **Cristina López-Galindo:** Writing – review & editing, Resources, Methodology, Investigation. **Juan Antonio Campillo González:** Writing – review & editing, Supervision, Project administration. **J. Ignacio García Alonso:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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