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Identification of organotin compounds in Tunisian surface water by liquid chromatography-electrospray-tandem mass spectrometry

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ABSTRACT

Liquid chromatography coupled to electrospray ionization mass spectrometry (LC-ESI-MS) with positive ion detection was applied for the identification of organotin compounds in water samples. The separation was performed in the gradient mode on reversed phase column with a mobile phase containing 0.05% TFA in acetonitrile–water. Sensitive detection of the selected organotin compounds by ESI-MS was performed on the basis of selected ion monitoring (SIM) mode. Limits of detection (LODs) were ranged between 0.02 and 0.08 μg L^{-1}. Solid phase extraction (SPE) was carried out on C18 cartridges to preconcentrate the analytes from water samples. Under the experimental conditions used, recoveries of organotin compounds obtained for spiked water samples are in the range of 62–98% and the R.S.D.s are 2–11%. Conditions for tandem mass spectrometry (MS–MS) detection of characteristic product ions formed by collision-induced dissociation (CID) of the parent ion are described. A principle of analysis is proposed based on triple quadrupole MS as a method for quantitative determination followed by verification of positive findings by CID-MS–MS. Application of the method for detecting organotin compounds in tap and surface water (river, dam and lagoon) samples is demonstrated.

Keywords: Organotins; Water analysis; Solid phase extraction; LC-ESI-MS; MS/MS

1. Introduction

Organotin compounds (OTs) comprise a group of organometallic moities characterized by a Sn atom covalently bound to one or more organic substituents (e.g., methyl, ethyl, butyl, propyl, and phenyl). Chemically these compounds are represented by the type formulas $RSnX_3$, R_2SnX_2, R_3SnX, R_4Sn, in which R is an alkyl or aryl group and X is an anionic species, for example chloride or hydroxide. Organotins are remarkably various in their physical, chemical and biological properties. Therefore, Sn has a larger number of its organometallic derivatives in commercial use than any other element. This is reflected in their diverse industrial applications (PVC stabilizers, antifouling paints, agrochemicals, wood preservation, glass treatment, materials protection and impregnation of textile) [1].

Tin in its inorganic form is generally accepted as being nontoxic, but the toxicological pattern of

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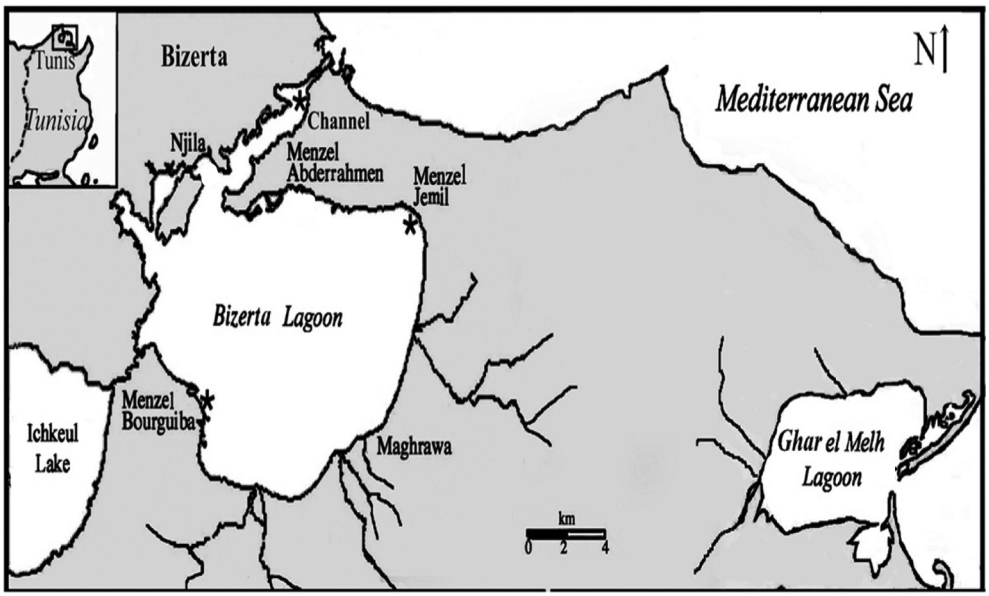

Fig. 1. Map of the lagoon of Bizerte with location of sampling industrial sites (*).

organotins is very complex. The biological effects of the substances depend on both the nature and the number of the organic groups bound to the Sn cation. In general, maximum toxicological activity for organisms is proved for the trisubstituted compounds, but an increase in the n-alkyl chain length produces a sharp drop in biocidic activity and the long-chain species like octyltin derivatives, are essentially nontoxic to all organisms. Tetraorgantins show a delayed toxic activity in organisms. It is suggested that only after their degradation to trisubstituted compounds will symptoms of poisoning be observed [1].

Eight OTs have already been included in the European Community Priority Pollutants List of the protection of the aquatic system (EU, directive 2008/10/EC) [2]. Consequently, reliable analytical methods are required in order to determine OTs in aqueous environmental samples. Various analytical procedures have been implemented for trace analysis of OTs in water. Most of them are based on gas chromatography as a separation technique with different detection mode (mass spectrometry MS, electron capture detection, atomic absorption, atomic emission, flame photometric) [3–8]. However the derivatization [9] required for GC analysis can result in variation in yields between species and in terms of efficiency depending on matrix components. Various HPLC strategies have been developed for a wide variety of tin species. These include micellar HPLC [10], ion exchange [11], and reversed-phase chromatography [12]. Hydrophilic interaction liquid chromatography (HILIC) was also evaluated for the analysis of tributyltin and triphenyltin in water samples [13]. Common HPLC detectors for organotins analysis include fluorescence [14–17], ultraviolet [18] and inductively coupled plasma mass spectrometry (ICP-MS) [19–22]. Mass spectrometry detection coupled to liquid chromatography systems has been scarcely applied for organotin monitoring [20,23,24]. It offers important advantages, since in addition to its sensitivity and the fact that no organotin derivatization is required, it provide as structural information that can be used for confirmatory purposes. Both electrospray (ESI) [25] and atmospheric pressure chemical ionization (APCI) [26] interfaces have been explored for organotin analysis by LC-MS, and a few applications, such as water [24,27,28] have been reported.

The direct analysis of OTs in water is not possible since they are present at trace level and that a stage of preconcentration or enrichment is necessary. The preconcentration is classically realized by liquid–liquid extraction which requires high levels of often toxic organic solvent [28]. Recent sample preparation improvements call for the solid phase extraction (SPE). Compaño and co-workers [15,29] developed this technique in 1990s. It was shown that SPE with C18 cartridges is suitable for triphenyltin and tributyltin preconcentration from water sample. Another SPE method using C18 disks was reviewed by Jones-Lepp et al. [24]. The extraction recoveries of tri, di-butyltin, tri and diphenyltin, from water are respectively 86%, 82%, 78% and 56%. Solid phase microextraction (SPME) was developed too for the extraction of phenyltin compounds [30–36].

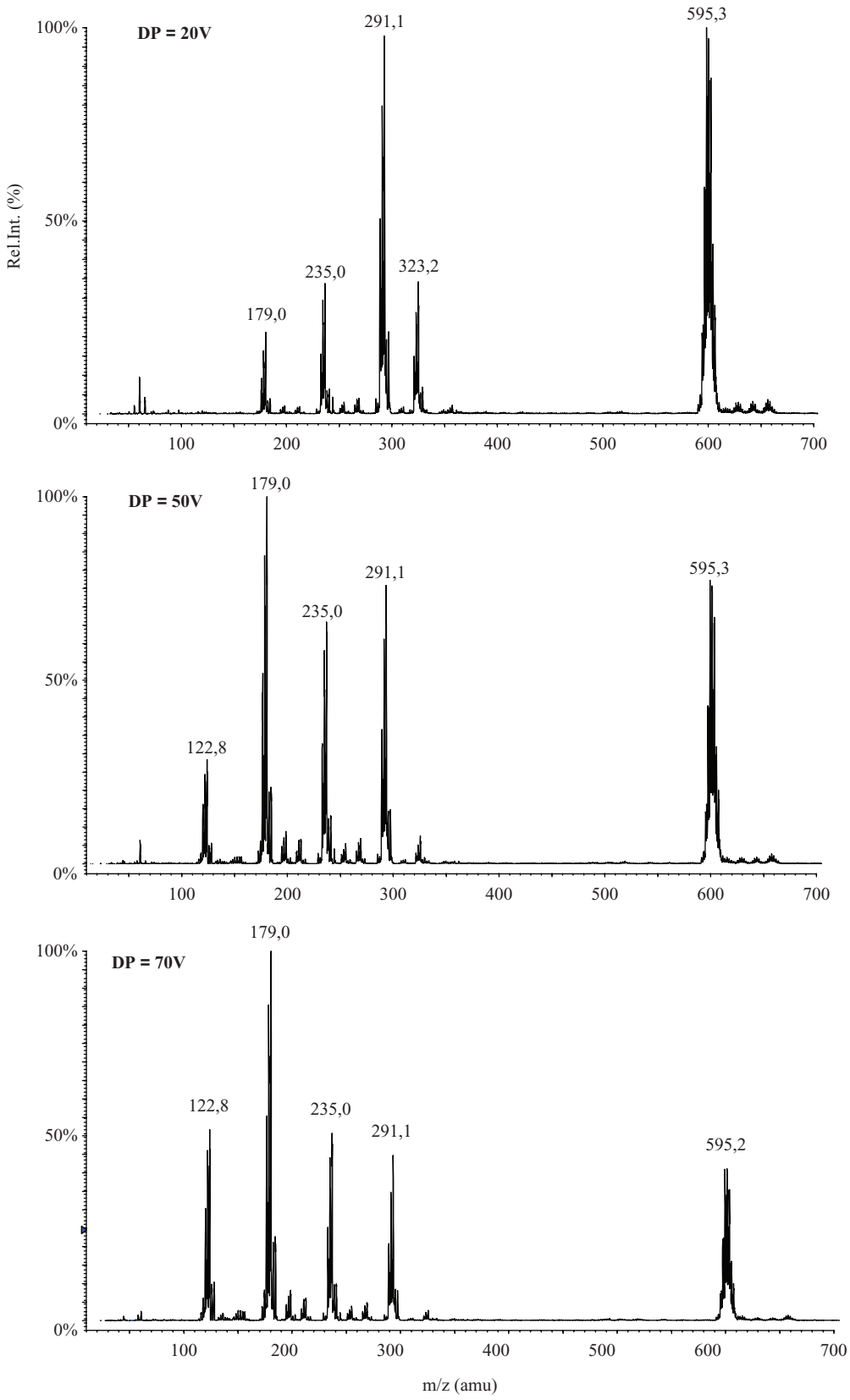

Fig. 2. Variation of the abundance (%) for some fragment ions of TBT vs. the extraction voltage.

The aim of this work was to investigate the use of LC-ESI-MS for the identification of eight organotins belonging to three different classes (di-, tri- and tetra organotins). The separation of each class of compounds on a C18 column with a suitable mobile phase was investigated and the mass spectra were studied, optimizing all the parameters influencing the ion formation. Suitable conditions for performing MS–MS analysis using CID of molecular ion were established. Furthermore, the proposed method was successfully applied to the analysis of OTs in surface waters.

2. Experimental

2.1. Chemicals

Triphenyltin chloride (TPhTCl) and tributyltin chloride (TBTCl) were purchased from Supelco, trioctyltin chloride (TOcTCl) and dibutyltin dichloride (DBTCl) were purchased from Fluka purity ≥96%, diphenyltin dichloride (DPhTCl) and tetrabutyltin (TeBT) were purchased from Aldrich purity ≥93%, dimethyltin dichloride (DMTCl) and trimethyltin chloride (TMTCl) were purchased from Riedel de Haen.

Standard stock solutions of 1,000 μg mL^{-1} were prepared by weighing and dissolving 10 mg of each compound in 10 mL of methanol. These solutions were stored in the dark at 4°C, and were stable for at least 1 year [6]. Standard mixtures were prepared daily by appropriate dilution of a mixed stock solution with methanol ranging from 0.005 to 1 μg mL^{-1}.

Methanol and acetonitrile HPLC grade (Merck) and ultrapure water MilliQ-plus were used throughout. Trifluoroacetic acid (TFA) was also obtained from Merck.

Disposable SPE cartridges containing 100 mg of C18 bonded silica (Bond Elut; Varian) were used for water analysis.

2.2. Apparatus

The LC-MS analyses were performed using a Perkin Elmer LC system consisting of a 200 quaternary pump; a Rheodyne injection valve (model 7125) of 20 μL and PE Sciex API 2000 triple quadrupole mass spectrometer equipped with ESI ionization source.

The HPLC column was Xterra RP18, 250 × 4.6 mm i.d., 5 μm particulate size.

The LC-MS system was connected to analyst station for recording chromatograms.

2.3. Chromatographic conditions

The separation was carried out by class of compounds.

Table 1
Important mass spectral fragments and their relative abundances (R%) obtained by LC-ES-MS at fragmentor voltage of 50 V

Compound	M_w	Ions (m/z)	Relative abundance * (R %)
DPhT	344	197 $[SnPh]^+$	39.36
		275 $[SnPh_2 + H]^+$	98.05
		309 $[SnPh_2Cl]^+$	100
DMT	220	135 $[SnMe]^+$	26.47
		151 $[SnMe_2+H]^+$	54.77
		185 $[SnMe_2Cl]^+$	100
DBT	304	179 $[SnBuH_2]^+$	32.94
		214 $[SnBuH_2Cl]^+$	28.77
		269 $[SnBu_2Cl]^+$	100
TPhT	386	197 $[SnPh]^+$	2.99
		351 $[SnPh_3]^+$	100
		717 $[(Ph_3Sn)_2OH]^+$	48.56
TMT	200	135 $[SnMe]^+$	28.3
		165 $[SnMe_3]^+$	100
		345 $[(SnMe_3)_2OH]^+$	15.73
TBT	326	179 $[SnBuH_2]^+$	100
		235 $[SnBu_2H]^+$	65.87
		291 $[SnBu_3]^+$	65.00
TOcT	494	459 $[SnOc_3]^+$	100
		235 $[SnOcH_2]^+$	35.65
		345 $[SnOc_2H]^+$	21.23
TeBT	348	179 $[SnBuH_2]^+$	100
		235 $[SnBu_2H]^+$	43.07
		291 $[SnBu_3{}^+]$	43.51

Note: * The m/z ratios refer to the ^{120}Sn isotope.

*Triorganotins, diorganotins

Optimal separation was performed in gradient mode with a mobile phase containing 0.05% TFA in acetonitrile-water. The gradient was 45% acetonitrile, which was increased to 100% over 40 min and hold at 100 for 10 min. The flow rate of the mobile phase was 1 mL min^{-1}; the column effluent was split, allowing only 100 μL min^{-1} to enter to the mass spectrometer.

* Tetrabutyltin

An acetontrile-water, containing 0.05% TFA, binary gradient of 50–80% acetonitrile in 40 min was used.

2.4. Mass spectrometer analysis

The ESI-MS interface was operated in positive mode under the conditions of 150°C gas temperature, 40 psi drying gas pressure, 40 psi nebuliser gas, 60 psi additional gas pressure and 5,000 V of capillary voltage. Full scan LC-MS chromatograms were obtained by scanning from m/z 50 to 800. Time scheduled SIM of the most abundant ion of each compound was used for quantification. All MS-MS experiments were

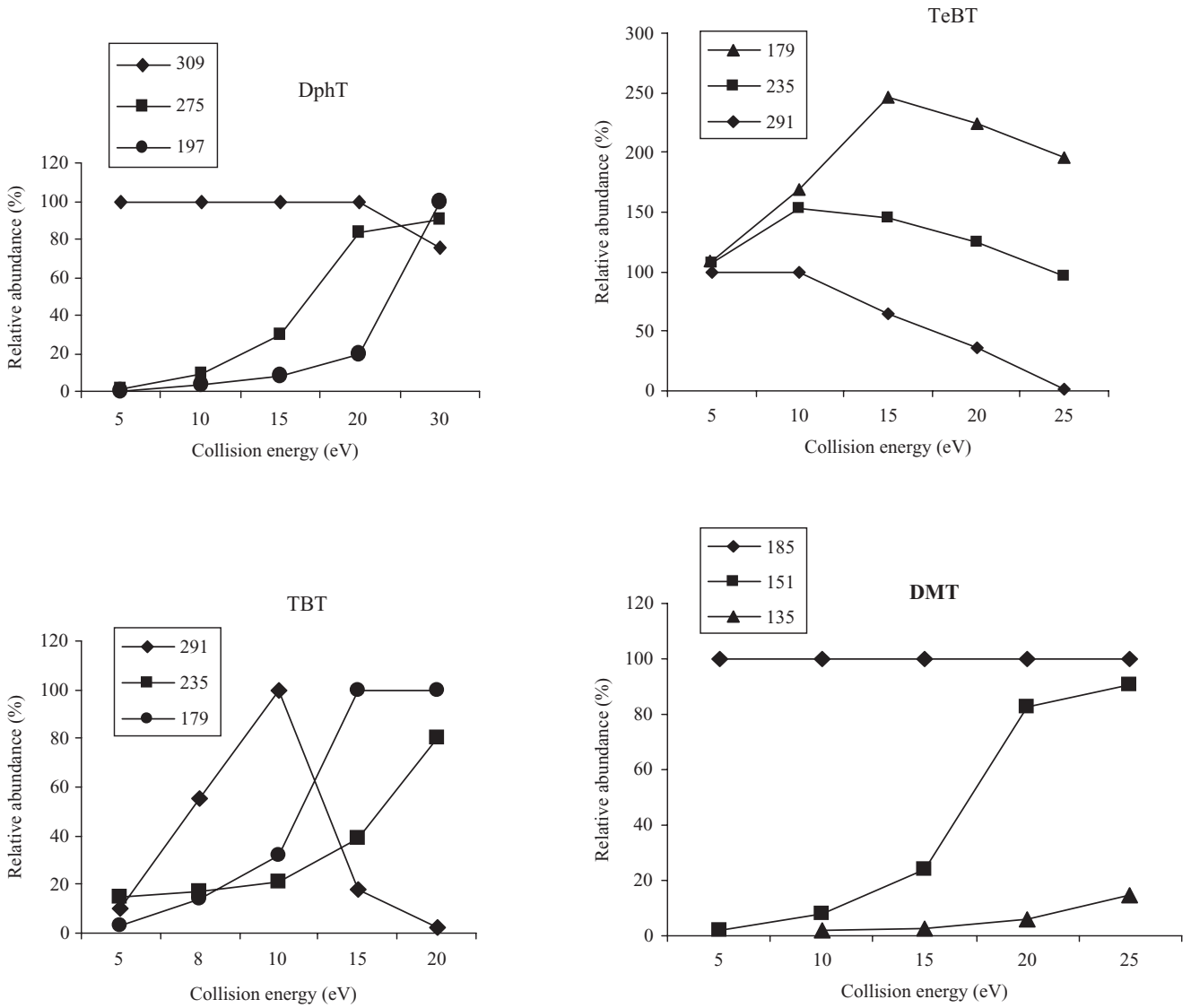

Fig. 3. Variation of the relative abundance (%) of the fragments ions vs. collision energies for (a) DPhT (b) TBT (c) TeBT (d) DMT (e) TOcT.

performed using N_2 as the collision gas at a collision cell pressure of 2 mTorr and with collision energy ranging between 5 and 40 eV.

2.5. Sampling

We led three sampling campaigns of samples: the first one in March 2009, the second in September 2009 and the third in December 2009. Sampling points are Medjerda river and Sidi Salem dam. In addition other samples of drinking water have been made in our laboratory. We also collected samples from the lagoon of Bizerte. The site selection was made taking into account the influence of continental waters, but also the position of potential sources of pollution. The different sampling sites are shown in Fig. 1.

2.6. Sample preparation

Water samples were collected in glass amber bottles, filtered through a 0.45 μm glass microfiber filter (whatman, maidstone, UK), stored at 4°C.

The disposable C18 cartridge was conditioned by rinsing with 5 mL of methanol, followed by 10 mL of 10^{-2} M aqueous hydrochloric acid solution. Afterwards, a 500 mL aliquot of water sample was passed through the cartridge at a flow rate of 5 mL min^{-1}. After retention, the cartridge was washed with 10 mL

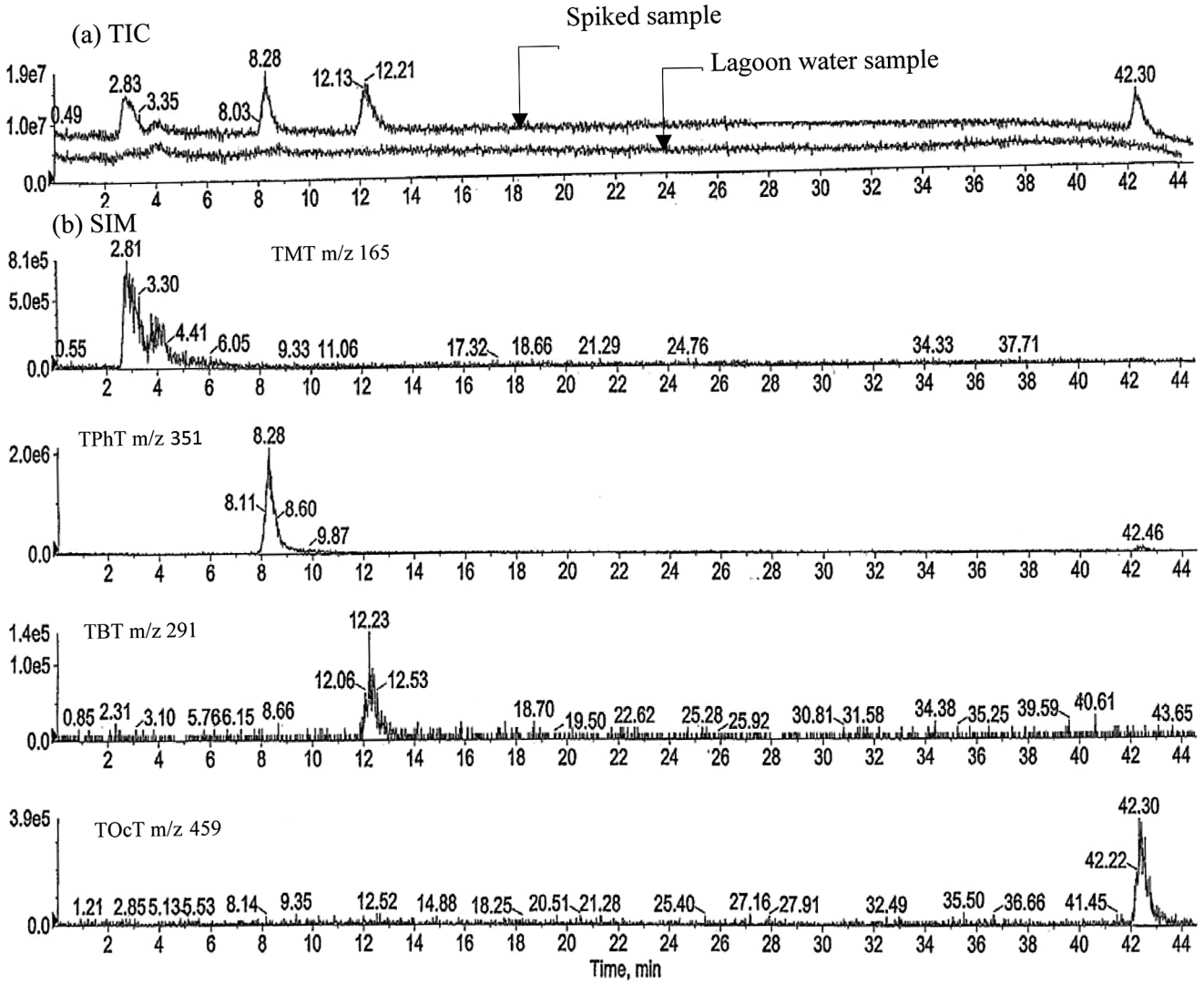

Fig. 4. Chromatograms obtained from the analysis of lagoon water samples by SPE-LC-ESI-MS. (a) Total ion current chromatograms from a lagoon water sample and a spiked lagoon water sample with triorganotins at 10 μg L^{-1} (b) Selected ion monitoring (SIM) chromatograms from the spiked water sample.

of water. Elution was performed with 2 mL of methanol at flow rate of 0.5 mL min^{-1}. The eluent was collected in a graduated tube and concentrated, under stream of nitrogen with Kuderna-Danish evaporator to 1 mL. The eluate was filtered through a 0.22 μm nylon membrane and injected into the chromatographic system.

3. Results

3.1. Optimization of the MS parameters

In order to optimize the ESI-MS parameters under the LC conditions described; flow injection methodology was used to introduce the analytes into the mass spectrometer.

The extraction voltage was the most important parameter, since it greatly affected both the appearance of the spectra and the response intensity. Thus, in order to establish the optimum conditions for the analysis of all the compounds, standard solutions were injected at extraction voltages from 20 to 90 V and the mass spectra were recorded in full scan mode. In positive mode, the fragmentor voltage of 50 V caused little fragmentation and the sensitivity was the highest for all the compounds. Based on the individual mass spectrum, three specific ions per analyte were chosen according to the highest abundances and lowest background levels and monitored by the selected ion monitoring (SIM) mode. The main ions obtained and their tentative assignments are shown in Table 1.

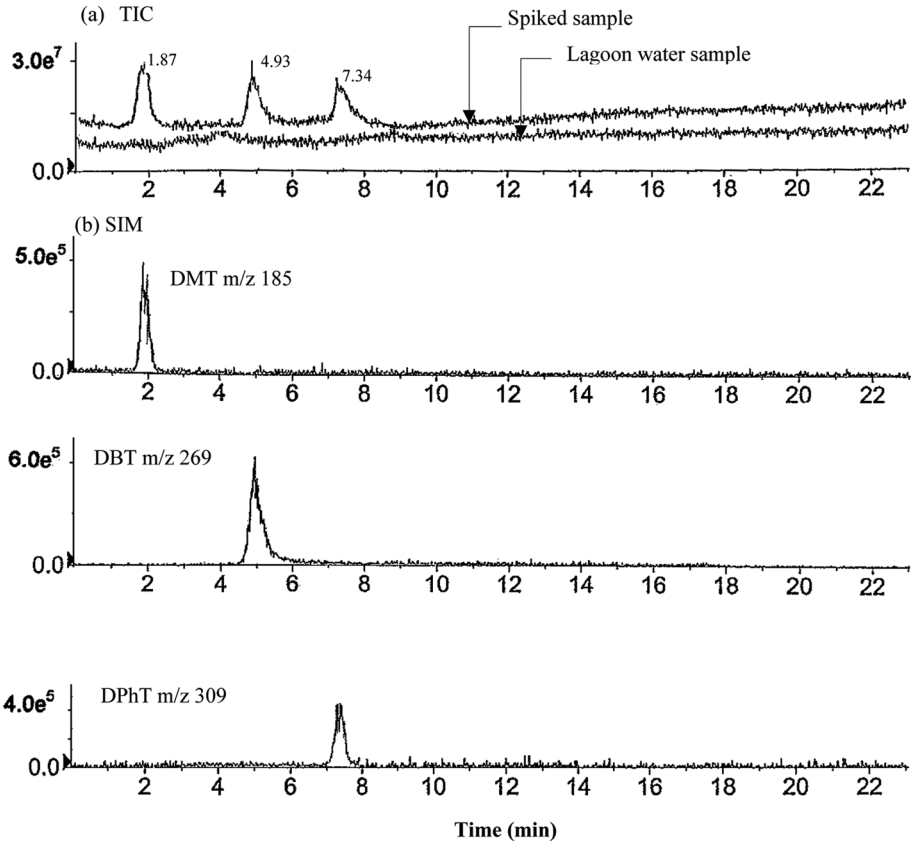

Fig. 5. Chromatograms obtained from the analysis of lagoon water samples by SPE-LC-ESI-MS. (a) Total ion current chromatograms from a lagoon water sample and a of spiked lagoon water sample with diorganotins at 10 μg L^{-1}(b) Selected ion monitoring (SIM) chromatograms from the spiked water sample.

The effect of modifying the fragmentor voltage in the production of diagnostic ions is illustrated in Fig. 2 for TBT in ESI positive. At fragmentor voltage of 20 V, there are three ions corresponding to *m/z* 179, 291 and 235 which are attributed respectively to $BuSnH_2^+$, Bu_3Sn^+ and Bu_2SnH^+. Increasing the voltage to 50 V the fragmentation of Bu_3Sn^+ was more important with *m/z* 179 as the most abundant isotope. At 80 V SnH^+ (*m/z* 121) and SnH_3^+ (*m/z* 123) were detected. All mass spectra found were in good agreement with those found in the literature [27,37–38]. Organotins followed the same fragmentation pattern. The mass spectra of di-organotins compounds consist of the loss of one group (Me, Bu, or Ph). In the case of tri-organotins the loss of one and two groups was noticed. The obtained fragment peaks are characteristic ion fragment masses for organotins.

3.2. LC-ESI-MS

The system sensitivity was fully optimized using SIM. The quantification was carried out using the

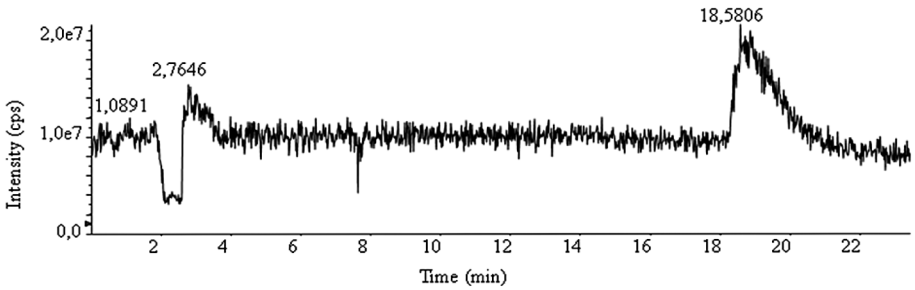

Fig. 6. Chromatogram of spiked lagoon water sample with tetrabutyltin at 10 μg L^{-1}.

Table 2
Recoveries of organotins added at two concentration levels to different water samples

Compound	Recovery (RSD)* (%)					
	Mili-Q water	Drinking water	River water	Dam water	Lagoon water[a]	Lagoon water[b]
DPhT	80 (4)	77 (7)	89 (3)	85 (9)	81 (9)	80 (6)
TPhT	82 (6)	79 (5)	92 (6)	86 (7)	83 (7)	82 (4)
TBT	78 (2)	74 (8)	98 (2)	84 (8)	79 (8)	78 (2)
DBT	68 (3)	62 (3)	88 (3)	65 (4)	68 (4)	63 (3)
TeBT	75 (5)	71 (4)	85 (5)	74 (5)	74 (5)	72 (5)
TMT	77 (7)	72 (5)	97 (6)	91 (10)	83 (10)	81 (3)
DMT	83 (8)	80 (6)	73 (8)	98 (5)	86 (5)	85 (5)
TOcT	84 (7)	79 (11)	94 (7)	85 (6)	85 (6)	79 (8)

Note: *Five replicate.
[a]Spiking level 10 μg/L.
[b]Spiking level 5 μg/L.

proposed SIM program in order to obtain lower detection limits. LC with ESI provided a linear response from amount injected in the range of 5–1,000 μg L^{-1} with a good correlation coefficient (r^2 between 0.994 and 0.999). The limits of detection (LODs, S/N = 3) and the limits of quantification (LOQs, S/N = 10) were estimated from a dilution series of standard mixtures. LODs were between 0.02 and 0.08 μg L^{-1}. The LOQs values ranged of 0.1–0.5 μg L^{-1}. The RSDs of seven replicates were calculated. At the 1 μg mL^{-1}concentration level of eight OTs, the RSDs for determination of OTs were between 3% and 9%.

3.3. Conditions for CID-MS-MS

MS-MS using CID is a means of obtaining structurally related spectral information from the initially formed parent ion. We have investigated the possibilities of using this technique to improve the probability of correct identification of OTs analyzed by ESI-MS. The extent of the fragmentation of the initially formed parent ion depends on the collision energy and the collision gas pressure in the collision cell between the first quadrupole and the collision cell. We have collected product ion spectra of eight solutes at collision energies between 5 and 30 eV. Fig. 3. shows the relationship of relative abundances of the fragment ions of studied OTs and the collision energy values. The effect of the collision energy on the peak distribution in mass spectrum is clearly seen. High collision energy leads to decomposition of the organotin species into elemental tin. The optimum collision energy value for the analysis of the eight organotins was found to be 10 eV.

3.4. Applications to real samples

The only data on the concentrations of organotins compounds and their distribution over the time relate specially sediments and mussel tissue from Bizerte lagoon. It was reported that The Bizerte sediments can be generally considered as moderately polluted. The trisubstituted organotin concentrations appear generally significantly higher in winter, remaining however lower than 40 μg (Sn) kg^{-1} [39]. In this work, the applicability of the proposed method was evaluated for determining OTs in surface water samples. The spiked samples were analyzed. Figs. 4, 5 and 6 show chromatograms of eight OTs in the spiked water sample. The extraction recoveries of the eight OTs from spiked water samples are shown in Table 2. It is obvious from the experimental results that good recoveries (62–98%) and R.S.D. (2–11%) were obtained for the spiked water samples.

Unspiked samples were analyzed using LC with ESI-MS detection in SIM mode. As shown in Figs. 4, 5 and 6 no analyte signals were found in the non-spiked sample within the detection range of the method.

4. Conclusion

Eight organotins belonging to three different classes (di-, tri- and tetra organotins) have been successfully separated and quantified with LC-ESI-MS method developed in the course of this work. A SPE method was successful to simultaneously extract organotins compounds from tap and surface water with good recoveries and reproducibility. Furthermore, it has been demonstrated that increase confidence in organotins identification can be obtained by MS-MS based on detection of product ions formed by CID of the initially formed parent ion.

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References

[1] M. Hoch, Organotins compounds in the environment – an overview, Appl. Geochem., 16 (2001) 719–743.
[2] Directive 2008/105/EC, Off. J. Eur. Comm., L 348 (2008) 84–97.
[3] M. Abalos, J-M. Bayona, R. Compaño, M. Granados, C. Leal and M-D. Prat, Analytical procedures for the determination of organotin compounds in sediment and biota: a critical review, J. Chromatogr. A, 788 (1997) 1–49.
[4] K.-M. Attar, Analytical methods for speciation of organotins in the environment, Appl. Organomet. Chem., 10 (1996) 317–337.
[5] J. Szpunar-Lobinska, C. Witte, R. Lobinski and F-C. Adams, Separation techniques in speciation analysis for organometallic species, Fresenius J. Anal. Chem., 351 (1995) 351–377.
[6] C. Carlier-Pinasseau, G. Lespes and M. Astruc, Determination of butyltin and phenyltin by GC-FPD following ethylation by NaBEt4, Appl. Organomet. Chem., 10 (1996) 505–512.
[7] J. Jacobsen, F. Stuer-Lauridsen and G. Pritzl, Organotin speciation in environmental samples by capillary gas chromatography and pulsed flame photometric detection (PFPD), Appl. Organomet. Chem., 11 (1997) 737–741.
[8] C. Arnold, M. Berg, S. Müller, U. Dommann and R. Schwarzenbach, Determination of organotin compounds in water, sediments, and sewage sludge using perdeuterated internal standards, accelerated solvent extraction, and large-volume-injection GC/MS, Anal. Chem., 70 (1998) 3094–3101.
[9] R. Morabito, P. Massanisso and P. Quevauviller, Derivatization methods for the determination of organotin compounds in environmental samples, Trends Anal. Chem., 19 (2000) 113–119.
[10] Y. Ionue, K. Kawabata and Y. Suzaki, Speciation of organotin compounds using inductively coupled plasma mass spectrometry with micellar liquid chromatography, J. Anal. At. Spectrom., l0 (1995) 363–366.
[11] R. Compaño, M. Granados, C. Leal and M-D. Prat, Determination of triphenyltin in sea water samples by liquid chromatography with fluorimetric detection, Anal. Chim. Acta, 302 (1994) 185–191.
[12] H.-J. Yang, S.-J. Jiang, Y.-J. Yang and C.-J. Hwang, Speciation of tin by reversed phase liquid chromatography with inductively coupled plasma mass spectrometric detection,Anal, Chim. Acta, 312 (1995) 141–148.
[13] T. Sano, H. Takagi, K. Nagano and M. Nishikawa, Analysis of triorganotin compounds in water samples by hydrophilic interaction liquid chromatography–electrospray ionization-mass spectrometry, J. Chromatogr. A, 1217 (2010) 4344–4346.
[14] C. Leal, M. Granados, R. Compaño and M-D. Prat, Liquid chromatography with fluorimetric detection of triorganotin compounds in marine biological materials, J. Chromatogr. A, 809 (1998) 39–46.
[15] R. Compaño, M. Granados, C. Leal and M-D. Prat, Liquid chromatographic determination of triphenyltin and tributyltin using fluorimetric detection, Anal. Chim. Acta, 314 (1995) 175–182.
[16] E. Graupera, C. Leal, M. Granados, M-D. Prat and R. Compaño, Determination of tributyltin and triphenyltin in sediments by liquid chromatography with fluorimetric detection: Assessment of spiking procedures, J. Chromatogr. A, 846 (1999) 413–423.
[17] E. Gonzàlez-Toledo, R. Compaño, M. Granados and M-D. Prat, Determination of butyltin and phenyltin species by reversed-phase liquid chromatography and fluorimetric detection, J. Chromatogr. A, 878 (2000) 69–76.
[18] A. Praet, C. Dewaele, L. Verdonck and G-P. Van der Kelen, Liquid chromatography of organotin compounds in cyanopropyl silica gel, J. Chromatogr. A, 507 (1990) 427–437.
[19] B. Fairman, T. Catterick, B. Wheals and E. Polinina, Reversed-phase ion-pair chromatography with inductively coupled plasma-mass spectrometry detection for the determination of organo-tin compounds in waters, J. Chromatogr. A, 758 (1997) 85–92.
[20] S. White, T. Catterik, B. Fairman and K. Webb, Speciation of organo-tin compounds using liquid chromatography–atmospheric pressure ionisation mass spectrometry and liquid chromatography–inductively coupled plasma mass spectrometry as complementary techniques, J. Chromatogr. A, 794 (1998) 211–218.
[21] C. Rivas, L. Ebdon, E-H. Evans and S-J. Hill, An evaluation of reversed-phase and ion-exchange chromatography for use with inductively coupled plasma-mass spectrometry for the determination of organotin compounds, Appl. Organomet. Chem., 10 (1996) 61–68.
[22] S. Chiron, S. Roy, R. Cottier and R. Jeannot, Speciation of butyl- and phenyltin compounds in sediments using pressurized liquid extraction and liquid chromatography–inductively coupled plasma mass spectrometry, J. Chromatogr. A, 879 (2000) 137–145.
[23] E. Rosenberg, V. Kmetov and M .Grasserbauer, Investigating the potential of high-performance liquid chromatography with atmospheric pressure chemical ionization-mass spectrometry as an alternative method for the speciation analysis of organotin compounds, Fresenius J. Anal. Chem., 366 (2000) 400–889.
[24] T-L. Jones-Lepp, K-E. Varner, M. Mc-Daniel and L. Riddick, Determination of organotins in water by micro liquid chromatography-electrospray/ion trap mass spectrometry, Appl. Organomet. Chem., 13 (1999) 881–889.
[25] J. Wu, Z. Mester and J. Pawliszyn, Determination of tributyltin by automated in-tube solid-phase microextraction coupled with HPLC-ES-MS, J. Anal. At. Spectrom., 16 (2001) 159–165.
[26] G. O' Connor, R. Wahlen, B. Fairman and K-S. Webb, Comparison of GC–ICP–MS and HPLC–ICP–MS for species-specific isotope dilution analysis of tributyltin in sediment after accelerated solvent extraction, in: E. Gelpi (Ed.), Advances in Mass Spectrometry Wiley, New Work, 2001.
[27] E. Gonzàlez-Toledo, R. Compaño, M-D. Prat and M. Granados, Determination of triorganotin species in water samples by liquid chromatography–electrospray-mass spectrometry, J. Chromatogr. A, 946 (2002) 1–8.
[28] K. Békri, R. Saint-Louis and E. Pelletier, Determination of tributyltin and 4-hydroxybutyldibutyltin chlorides in seawater by liquid chromatography with atmospheric pressure chemical ionization-mass spectrometry, Anal. Chim. Acta, 578 (2006) 203–212.
[29] R. Compaño, M. Granados, C. Leal and M-D. Prat, Determination of triphenyltin in sea water samples by liquid chromatography with fluorimetric detection, Anal. Chim. Acta, 302 (1994)1 85–191.
[30] G. Lespes, V. Desauziers, C. Montigny and M. Potin–Gautier, Optimization of solid-phase microextraction for the speciation of butyl- and phenyltins using experimental designs, J. Chromatogr. A, 826 (1998) 67–76.
[31] S. Aguerre, C. Bancon-Montigny, G. Lespes and M. Potin- Gautier, Solid phase microextraction (SPME): a new procedure for the control of butyl- and phenyltin pollution in the environment by GC-FPD, Analyst, 125 (2000) 263–268.
[32] S. Aguerre, G. Lespes, V. Desauziers and M. Potin–Gautier., Speciation of organotins in environmental samples by SPME-GC: comparison of four specific detectors: FPD, PFPD, MIP-AES and ICP-MS, J. Anal. At. Spectrom., 16 (2001) 263–269.
[33] S. Aguerre, C. Pécheyran, G. Lespes, E. Krupp, O-F-X. Donard and M. Potin–Gautier, Optimisation of the hyphenation between solid-phase microextraction, capillary gas chromatography and inductively coupled plasma atomic emission spectrometry for the routine speciation of organotin compounds in the environment, J. Anal. At. Spectrom., 16 (2001) 1429–1433.
[34] M. LeGac, G. Lespes and M. Potin-Gautier, Rapid determination of organotin compounds by headspace solid-phase microextraction, J. Chromatogr. A, 999 (2003) 123–134.

[35] M. Crnoja, C. Haberhauer-Troyer, E. Rosenberg and M. Grasserbauer, Determination of Sn- and Pb-organic compounds by solid-phase microextraction-gas chromatography-atomic emission detection (SPME-GC-AED) after *in situ* propylation with sodium tetrapropylborate, J. Anal. At. Spectrom., 16 (2001) 1160–1166.

[36] J. Vercauteren, A. De Meester, T. De Smaele, F. Vanhaecke, L. Moens, R. Dams and P. Sandra, Headspace solid-phase microextraction-capillary gas chromatography-ICP mass spectrometry for the determination of the organotin pesticide fentin in environmental samples, J. Anal. At. Spectrom., 15 (2000) 651–656.

[37] S.D. Papaspyrou, N.S. Thomaidis, E.N. Lampi and A. Lioupis, Determination of migration of n-butyltins and n-octyltins to food simulants by gas chromatography–mass spectrometry, Appl. Organomet. Chem., 21 (2007) 412–424.

[38] C. Devos, M. Vliegen, B. Willaert, F. David, L. Moens, P. Sandra, Automated headspace-solid-phase micro extraction–retention time locked-isotope dilution gas chromatography–mass spectrometry for the analysis of organotin compounds in water and sediment samples, J. Chromatogr. A, 1079 (2005) 408–418.

[39] N. Mzoughi, G. Lespes,T. M. Bravo, M. Dachraoui and M. Potin-Gautier, Organotin speciation in Bizerte lagoon (Tunisia), Science of the total environment, 349 (2005) 211–222.