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Matrix effects and selectivity of the detector in the determination of butyl- and phenyltins by gas chromatography–flame photometric detection

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Abstract

Two main types of matrix effects were observed during the analysis of environmental samples by ethylation with sodium tetraethylborate–gas chromatography–flame photometric detection: the first one was a disturbance of the GC signal such as baseline discontinuity or decrease of photometric emission and the second one variations of the organotin responses. For the GC signal, organic matter dissolved after acidic extraction was found to be mainly responsible. It was possible to reduce these effects significantly by the removal of organic matter by centrifuging and pH control. The variations of the organotin responses were more difficult to resolve. But it was possible to obtain a reliable quantification using simultaneously standard addition and internal standard methods. The flame photometer appeared sufficiently selective in regard to other selective detectors. However, it was confirmed that sulfur compounds could give a photometric signal at 610 nm. This emission was not a problem for organotin quantification because no coelution of interfering species and analytes was observed. The application of this method to different complex samples such as sediments, biota or sewage sludge has finally confirmed its suitability for pollution control in the environment.

Keywords: Matrix effects; Environmental analysis; Water analysis; Marine sediments; Sewage sludge; Organotin determination

1. Introduction

The environmental impact of some organotin compounds has given particular importance to speciation studies, in order to distinguish the most toxic species from other less toxic ones [1]. Thus, the ecotoxicological effects of tributyltin (TBT) and triphenyltin (TPhT) are today well-known [1,2]. The very varied use of alkylated and arylated tin compounds has induced pollution of many environmental compartments. Both marine [3–5] and freshwater [6–8] media are now recognized as contaminated. Organotin pollution has been also found in urban sewage sludge [9–13], underground waters [8] or rivers without fluvial traffic [14]. Butyl- and phenyltins are mainly detected, but octyltins are also determined in waste waters [15].

In order to control this pollution, many analytical procedures have been developed. They are often based on gas chromatographic (GC) separation, needing a derivatization step in order to obtain organotins in suitable forms for GC analysis. Recently, the direct aqueous-phase ethylation by sodium tetraethylborate ($NaBEt_4$) has been mainly used.

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After derivatization and GC, different specific detection methods can be employed, such as atomic absorption spectrometry (AAS) [16–18], atomic emission spectrometry (AES) [19,20] or flame photometric detection (FPD) [21,22].

Recently, $NaBEt_4$ ethylation–GC–FPD has been developed for the simultaneous determination of butyl- and phenyltins [14] and applied to the analysis of various environmental samples [23–25]. Nevertheless, the determination of these compounds in such complex matrices has led to several problems: disturbances and appearance of unknown peaks during the GC, difficulties in the quantitative analysis. These problems questioned the reliability and accuracy of the method.

So, the aim of the present work was the understanding of these matrix effects in order to resolve analytical problems as much as possible. Several environmental samples chosen as representative were therefore studied: waters, sediments, biota and sewage sludge. Their analysis by $NaBEt_4$ ethylation–GC–FPD according to defined operating conditions was finally carried out in order to verify this method is convenient for the organotin pollution control.

2. Experimental

All organotin concentrations reported in this paper are expressed as the mass of tin (Sn) per mass or volume unit.

2.1. Apparatus

A Varian 3300 gas chromatograph equipped with a FPD system and a 610 nm optical filter (MTO Optique Instrumentale, Massy, France) was used for this study.

Analytical parameters were optimized and precisely described elsewhere [14]. A split/splitless injection was employed using the splitless mode for 1 min and then the split mode (flow-rate of 150 ml min^{-1}). The separation was carried out on a capillary column (30 m×0.25 mm I.D.) coated with methylsilicone (0.25 μm film thickness) (DB-1, Quadrex, New Haven, CT, USA). The column temperature was held at 70°C for the first minute, increased to 190°C at the rate of 30°C min^{-1} and then to 270°C at 15°C min^{-1}. The final temperature was held for 6 min. Nitrogen was used as the carrier gas at a flow-rate of 0.7 ml min^{-1}. The detector was operated at 290°C with an air–hydrogen flame. The flow-rates were respectively, 245 and 185 ml min^{-1}.

A Varian 3400 gas chromatograph–mass spectrometer Saturn II was used for the identification of peaks observed in GC–FPD analysis of environmental matrices. The capillary column was similar to the one described for GC–FPD. After optimization of the analytical parameters, the injector program was the following: initial temperature: 20°C, final temperature: 250°C with a rate of 300°C min^{-1}. The column program used was: initial temperature: 90°C, increased to 185°C at the rate of 3°C min^{-1} and then to 250°C at 10°C min^{-1}. The final temperature was held for 30 min.

2.2. Reagents

All the mono-, di- and trisubstituted organotins were obtained in the chloride form. Tripropyltin (TPrT, 98%), tripentyltin (TPeT, 95%), tributylphenyltin (TBPhT, 97%), methyltins (mono-: MMT, 97% and tri-: TMT, 97%), butyltins (mono-: MBT, 95%, di-: DBT, 97%, tri-: TBT, 96% and tetra-: TeBT, 93%), tricyclohexyltin (TCHexT, 90%), phenyltins (mono-: MPhT, 98%, di-: DPhT, 96% and tri-: TPhT, 95%) were purchased from Aldrich. Methyltins (di-: DMT, 95% and tetra-: TeMT, >99%) and trioctyltin (TOT, >99%) came from Fluka. The other octyltin compounds (mono-: MOT and di-: DOT) were synthesized in the laboratory. The organotin stock solutions containing 1000 mg l^{-1} as tin were prepared in methanol. When stored in the dark at +4°C, stock solutions were stable for at least one year [26]. They were diluted weekly to 10 mg l^{-1} and daily to 100 μg l^{-1} in water and stored in the dark at +4°C; working standard solutions from 100 to 300 ng l^{-1} were used.

Organosulfur compounds [dimethylsulfide (DMS), dimethyldisulfide (DMDS) and diethyldisulfide (DEDS)] were synthesized in the laboratory. Working standard solutions containing 3 mg l^{-1} were directly prepared in isooctane. Inorganic sulfur (Na_2S, Na_2SO_3 and Na_2SO_4) came from Prolabo. Working standard solutions (10 μg l^{-1}) were prepared in water.

Methanol and sodium ethanoate were purchased from Prolabo. Hydrochloric, nitric and ethanoic acids were obtained from Merck and isooctane from Fluka. The deionized water used was 18 MΩ (Millipore system). Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemical: a working solution was made daily by dissolving 0.02 g in 1 ml of deionized water and stored in the dark at +4°C.

Glassware was rinsed with deionized water, decontaminated overnight in 10% (v/v) nitric acid solution and then rinsed again.

2.3. Environmental samples

Organotins were determined in waters from the Moselle and Meuse Rivers (France). As soon as the samples arrived at the laboratory, they were filtered (0.45 μm), acidified at pH 2 with nitric acid and stored in the dark at +4°C. Analyses were performed within five days, without any other pretreatment.

Suspended matter came from Sarre and Rhine Rivers (France). They were kept directly frozen at −20°C after sampling and transit during few days before their extraction and analysis.

Marine sediment was sampled in Larros Harbour (France). Freshwater sediment came from the Netherlands. For confidential reasons, its precise origin cannot be given. These sediments were both freeze–dried, then sieved and the <63 μm fraction was studied.

A mussel sample was collected in La Spezia Harbor (Italy). It was lyophilized and stored in the dark at −20°C.

The sludge was sampled in an urban treatment plant in the South-West of France. It was mixed and kept frozen at −20°C until studied.

2.4. Analytical procedure

2.4.1. Extraction from the sample

Detailed experimental conditions were precisely described elsewhere [23,24].

A 0.5–2 g sample of freeze–dried sediment or 2 g of wet suspended matter were extracted in glacial ethanoic acid by mechanical stirring for 12 h.

A 0.1–0.3 g sample of freeze–dried mussel sample or 1 g of wet sewage sludge were humidified for 1 (wet sample) or 2 (dried sample) h in methanol and then extracted in a solution of 0.12 mol l^{-1} HCl in methanol by ultrasonic stirring for 1 h.

2.4.2. Derivatization and analysis

A 100-ml aliquot of water sample or 0.1 to 0.5 ml of centrifuged extract was directly introduced into the derivatization reactor. Ethylation was carried out using $NaBEt_4$ (0.1 to 0.3 ml) in sodium ethanoate–ethanoic acid buffer (100 ml, pH 4.8) and 0.3 ml of isooctane. The mixture was shaken at 420 rpm for 30 min. Afterwards, 1 to 4 μl of isooctane extract was directly injected into the GC–FPD system.

2.4.3. Quantitation

The internal standard (I.S.) relative chromatographic responses of butyl- and phenyltin compounds were calculated at once from standard solutions prepared in deionized water and samples. All these responses were evaluated using the standard addition procedure (made two to five times). The responses in deionized water were considered as reference in comparison with those evaluated from the samples.

The quantification was made using I.S. procedure: it was applied to three to five aliquots of 100-ml river water and to three portions of acidic extract for each of the other solid material samples (five extractions per sample).

3. Results and discussion

3.1. Matrix effects

3.1.1. Disturbances of the GC signal

3.1.1.1. Description

The most spectacular effects appearing during the GC were the distortion of the baseline and appearance of a large band as shown in Fig. 1a. This band was always located at the end of the chromatogram, for a retention time over 10 min. These effects appeared for the only solid matrices, when raw acidic extracts were directly ethylated and extracted in isooctane. No problem was noted for water analyses.

Another effect was the decrease or the disappearance of some peaks, as the comparison between Fig. 1a Fig. 1b shows. This phenomenon was not sys-

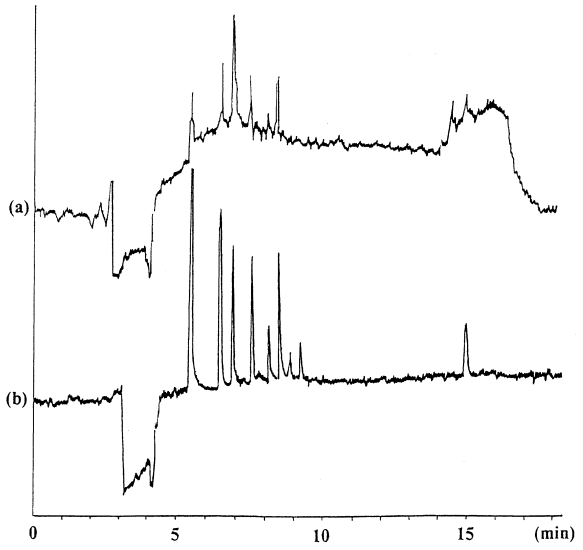

Fig. 1. Typical chromatograms of the mussel analysis (a) with and (b) without matrix effects.

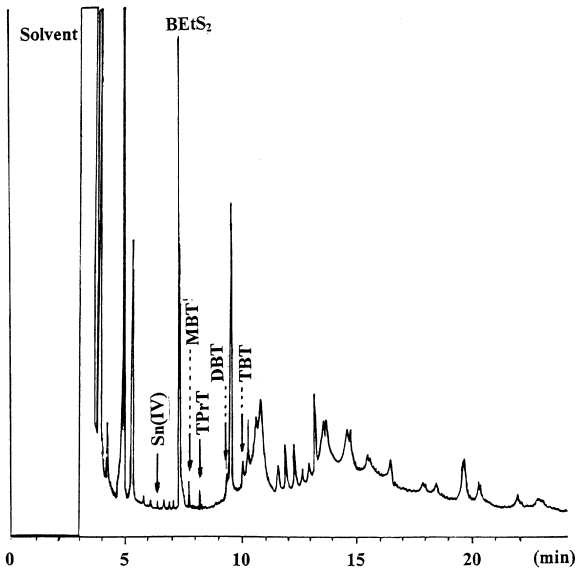

Fig. 2. GC–MS chromatogram for the marine sediment.

tematically observed and so, induced poor repeatability.

3.1.1.2. Identification

In order to resolve these problems, GC–MS analyses of the environmental samples were carried out. Heavy organic fragments were detected, especially after a retention time of 10 min (which corresponds to TBT retention time as presented in Fig. 2).

Thus, the isooctane phase was found to widely contain organic matter (OM) mainly constituted of organic acids such as polycarboxylic acids with many ramifications (C_n–H_{2n+1} or aromatic groups) and high molecular mass (M_r=150 to over 450).

Although these acids have low solubility in organic solvent, they can be present in the isooctane extract due to their important amount in the acidic extract.

After a systematic study of each step of the analytical process, the organic matter was found to mainly interfere according to the three following points: (i) The phenomenon of precipitation in isooctane was usually observed. Separation between aqueous and organic phases was also more difficult, making the isooctane phase non-homogeneous; (ii) The consumption of ethylating reagent was also observed. This problem was easily resolved by adding a more important amount of $NaBEt_4$ solution. Later on, this parameter was carefully checked and 0.3 ml of this solution was always found to be widely sufficient; (iii) The large presence of organic matter decreased the Sn–H photometric emission. This phenomenon previously described in the literature is generally attributed to the coeluted hydrocarbonated products [27]. Few studies studying these effects demonstrated that over 500 nm, quenching effects exist [28]. So, the hypothesis which could be made in the present work was that the presence of C–H bonds in large amounts could contribute to decrease or totally suppress any tin signal.

3.1.1.3. Solutions

In order to decrease these disturbances, the removal of organic matter as much as possible appeared essential. However, because OM was very soluble in acidic extract, the centrifuging step performed before derivatization was not sufficiently efficient. So, it was found that the increasing of the pH to 4.8 using the aqueous ethanoic acid buffer before centrifuging could increase the precipitation of a part of the organic matter.

Nevertheless, OM was still present during the derivatization. The centrifugation of the isooctane

extract appeared impossible due to its very small volume (0.3 ml). An overnight decanting step was found to be efficient. So, the organic matter extracted in isooctane could at once widely precipitate and decant at the water–isooctane interface.

Thus, no noticeable disturbance of the chromatographic signal has been observed and the repeatability has improved.

3.1.2. Variations of organotin responses

The choice of an internal standard allowing a quantification independent at once of the experimental conditions and sample nature is very important for a reliable routine analysis. This choice had to take into consideration two main criteria: that the I.S. does not interfere with the analytes and it is chemically close to the organotins determined. In the literature, several internal standards were previously used for the determination of both butyl- and phenyltins; there were only alkylated compounds due to the difficulty in finding arylated organotins: DMT [29], TeBT [30,31], pentyltins [9,32,33], triethyltin (TET) [34] and TPrT which has been the most usually used [9,14,21,33–36]. Some of them are not appeared suitable to the present analytical method due to their possible presence in the sample (DMT, TeBT) or in the reagents (TET). In these conditions, TPrT seemed to be an appropriate standard and was used in all our previous studies [23–25].

Unfortunately, TPrT-relative organotin responses varied according to the analyzed samples. The relative variations of the three butyltins were in the same order of magnitude and generally appeared similar, especially for DBT and TBT. The same observations could be made for the phenyltins. So, Fig. 3 presents the mean variations for butyl- and phenyltins. Considering the precision on the reference results (i.e., the standard deviation calculated for the responses in deionized water), the variations are weak for butyltins, whereas they can reach 80% for the phenyltins in the mussel sample.

From these observations, the TPrT could not appear as the best internal standard, especially in comparison with phenyltin results. For these arylated compounds, it could be supposed that the difference of chemical nature of the I.S. was mainly responsible. So, in order to find an internal standard such that the corresponding relative responses could remain constant whatever the sample was, two other internal standards were tested: TPeT and TBPhT. Unfortunately, it must be noted that TPeT and TBPhT have the same retention times and so, can not be used simultaneously. Moreover, TBPhT, as a tetrasubstituted compound, did not appear adapted to the analytical method because it was not ethylated during the derivatization step, leading to more important variations of responses.

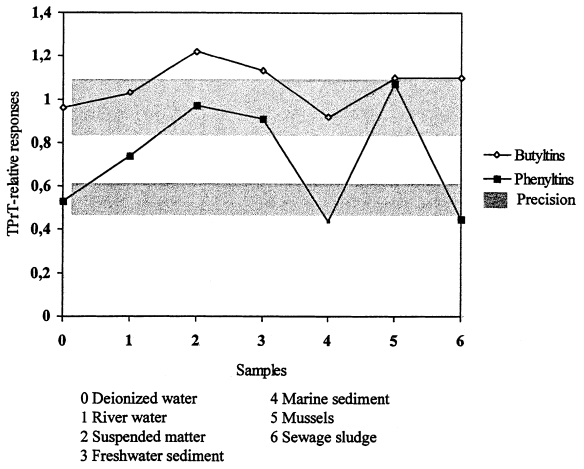

Fig. 3. Variations of the TPrT-relative responses according to the nature of the sample. (Precision is evaluated from the standard deviation of the response in deionized water).

Consequently, only TPrT and TPeT were compared. Fig. 4 shows the relative variations of the responses for these two internal standards, calculated from the freshwater suspended matter and the Moselle water. According to this figure, it is obvious that the TPeT-relative responses vary a lot, whatever the organotin is. The mean absolute variations were therefore about 15% with TPrT and about 50% using TPeT. This fact could not be attributed to the chemical natures of the two internal standards because they were similar (alkylated and trisubstituted). However, the comparison of the retention times appeared important because TPeT was located before DPhT, in a zone where coeluted products are generally widely present and likely to interfere, whereas TPrT was in the start of the chromatogram where no many products appeared, as it is confirmed by Fig. 2. So, it could be concluded that the presence of coeluted compounds with the internal standard could

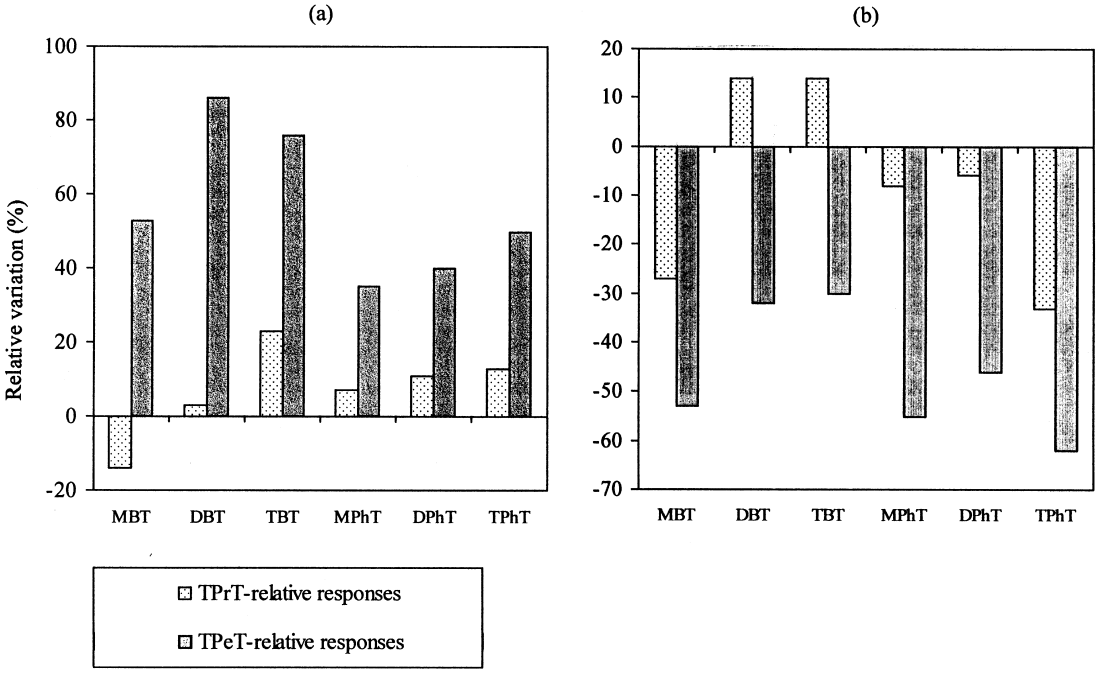

Fig. 4. Variations of the relative responses according to the nature of the internal standard for (a) Rhine suspended matter (b) Moselle river water.

also lead to important variations of the relative organotin responses.

Moreover, the variations of the relative responses generally observed as presented in Fig. 3 could have an another explanation. These responses depend on the whole analytical process and in particular on the acidic extraction and derivatization steps. Thus, in order to evaluate the influence of the acidic extraction, the internal standard was introduced before and after this step. In these two cases, the same responses were obtained which indicated that this step was not responsible of the variation of responses. Then, the yields of acidic extraction and ethylation/extraction (derivatization) were evaluated for butyl- and phenyltins and are presented in Table 1. They are compared to the mean relative variations of the responses. It could be noted a correlation between ethylation/extraction yields which are not all quantitative and the variations of responses. This fact could indicate that the derivatization step is disturbed by the presence of coextracted matter. So, the yields of ethylation/extraction could be modified at once according to the nature of the organotin determined and the studied matrix, which could induced variations of the organotin responses.

Finally, in the present knowledge, among the internal standards proposed in the literature and the organotins commercially available, the TPrT seems to be the most satisfactory compound. Nevertheless, in order to determine the organotin concentrations in spite of variations of their responses, the standard addition and internal standard methods have been simultaneously used, allowing the calculation of the organotin responses in the sample before quantification. This process, which allows a good compromise between reliability, accuracy and rapidity of the analysis, has given good results as it will be presented later on. But this solution was not totally satisfactory because it does not permit a real routine analysis.

3.2. Selectivity of FPD

The high selectivity of the Sn–H emission at 610 nm has been previously noted by several authors [37,38]. The only two main interfering elements

Table 1
Extraction and derivatization yields compared with mean relative variations of TPrT-relative responses

Compounds	Mean extraction yields (%) ([23,24])	Ethylation/extraction yields (%)[a]	Mean relative variations of TPrT-relative responses (%)[b]
MBT	n.e.	100±0	8±1
DBT	105±3	97±9	15±2
TBT	106±4	70±7	33±4
Butyl	**100±5**	**89±9**	**19±2**
MPhT	n.e.	45±5	41±4
DPhT	n.e.	62±6	47±5
TPhT	104±4	53±5	53±8
Phenyl	**98±5**	**53±5**	**47±6**

[a] Yields are calculated by comparison of responses evaluated from a standard solution of organotin chlorides in deionized water and responses of ethylated organotin standards synthesized in laboratory.
[b] Mean relative variations of the responses are evaluated from the variations of the responses in samples in comparison with the responses in deionized water.
n.e.=Not evaluated.

reported in the literature are sulfur and phosphorus. According to the authors, the selectivity of tin over S ranged from 10^2 to $\geq 10^3$ and the selectivity of tin over P from 40 to $>10^2$ [39,40]. Considering these selectivity ratios, the possible interferences during GC–FPD analysis seemed to be reduced. Nevertheless, Marr et al. [41] have recently detected elemental sulfur in the analysis of sediment.

The analysis of environmental samples performed in our laboratory has also showed some unknown peaks. However, the corresponding compounds could be other organotin species such as methyl-, octyl- or tricyclohexyltins, due to their use in industrial or domestic products [42]. So, in order to check the selectivity of the detector, firstly two different sorts of solutions were analyzed: (i) a standard solution with 15 organotins, (ii) standard solutions of organic (DMS, DMDS and DEDS) and inorganic (S^{2-}, SO_3^{2-} and SO_4^{2-}) sulfur.

The results obtained are presented in Fig. 5. It can be noted that the chromatogram of the organotins gives a satisfactory separation. For the sulfur, only the organic compounds are detected but their peaks do not interfere with those of butyl- and phenyltins. To obtain these peaks, solutions containing high concentrations of sulfur (corresponding to 10 $\mu g\ l^{-1}$ of sulfur in water) were necessary, which confirms the selectivity ratios and the previous experimental observations [41]. So, the 610-nm detector appeared about 100-times less sensitive for these compounds than for the organotins. In the case of the inorganic-sulfur solutions which did not give any peak, these results could indicate either the sensitivity is still weaker or the derivatization step is not efficient for these species. For the phosphorus, the same experiments carried out with inorganic solutions did not allow the observation of any peak and the same conclusions can be made.

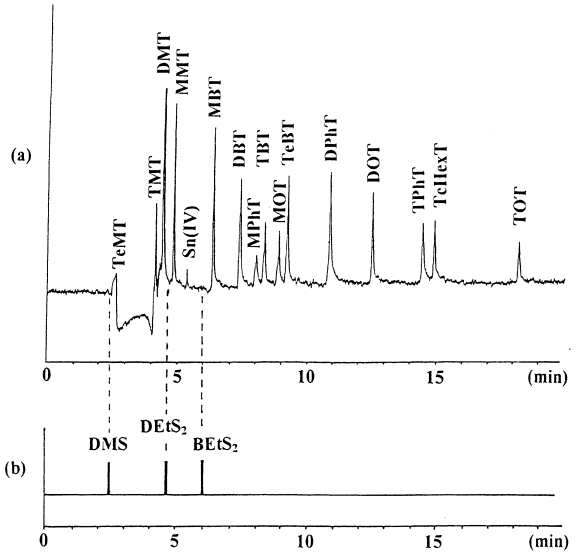

Fig. 5. (a) Chromatogram of a synthetic solution containing 15 organotin compounds at 200 ng (Sn) l^{-1}. (b) Schematic chromatogram of sulfur compounds.

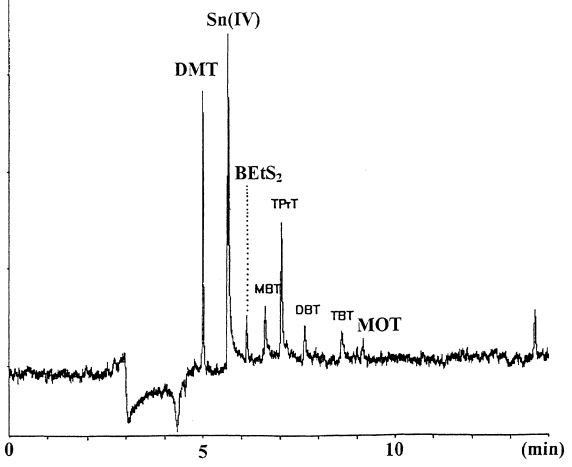

Fig. 6. Chromatogram of the sewage sludge analysis.

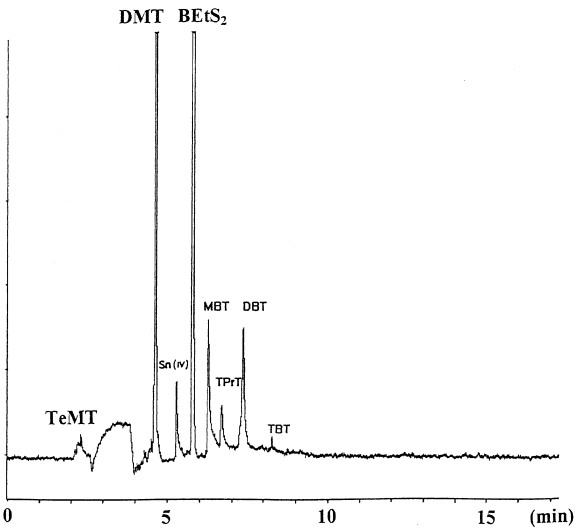

Fig. 7. Chromatogram of the marine sediment analysis.

Secondly, GC–MS analyses of the environmental samples were made. They allowed the identification of some unknown GC–FPD peaks as it can be seen in Fig. 6 Fig. 7 which present the chromatograms obtained respectively, for sewage sludge and marine sediment. These chromatograms have been chosen in order to show that, although the complexity of the matrix is great, generally few unknown peaks appeared. Thus, the only non-organotin compound detected by GC–FPD was a butylethyldisulfide ($BEtS_2$) (added in Fig. 5). It must be noted this compound was often detected during environmental analyses previously performed [23–25] or carried out during the present work. Different organotin compounds such as methyl- or octyltins also appeared. Moreover, from all these environmental analyses, no coelution between several organotins or between organotins and interfering elements (S or P) was observed.

Table 2
Determination of butyl- and phenyltins in the environmental samples

Sample	Analytical method	Concentration [ng (Sn) g^{-1} (dry mass)$\pm\sigma$]					
		MBT	DBT	TBT	MPhT	DPhT	TPhT
River water	**GC–FPD**	**14±5**	**≤10**	<D.L.	<D.L.	**≤15**	**11±3**
(Meuse)	GC–FPD*	10±5	12±2	<D.L.	<D.L.	4±1	10±0
Marine	**GC–FPD**	**105±9**	**44±4**	**20±1**	**10±2**	<D.L.	<D.L.
sediment	HG-QFAAS	77±6	42±4	24±4	n.d.	n.d.	n.d.
Freshwater	**GC–FPD**	**106±31**	**412±15**	**793±113**	**145±29**	**27±5**	<D.L.
sediment	HQ-QFAAS	68±4	384±11	746±39	n.d.	n.d.	n.d.
Mussel sample	**GC–FPD**	**1306±126**	**800±44**	**1155±140**	**926±39**	<D.L	**552±93**
	HG-QFAAS	1737±347	1115±38	1198±43	n.d.	n.d.	n.d.
Sewage sludge	**GC–FPD**	**91±7**	**121±3**	**195±6**	<D.L.	<D.L.	<D.L.
	HG-QFAAS	78±2	143±11	216±19	n.d.	n.d.	n.d.

D.L.=Detection limit; n.d=not detectable.
[a] Other GC–FPD method.
HG-QFAAS=Hydride generation-quartz furnace atomic absorption spectrometry.

Finally, the presence of interfering species such as sulfur compounds did never appear as a problem for butyl- and phenyltins-quantification and the flame photometer can be considered as a highly-selective detector in regard to the presence of many coeluted products.

3.3. Applications

The determination of butyl- and phenyltins in environmental samples was performed using $NaBEt_4$ ethylation–GC–FPD and the results compared with those obtained by an other analytical method previously validated in our laboratory [43,44]. The concentrations presented in Table 2 show that the different values obtained are close to or in the same order of magnitude, which is satisfactory considering: (i) the complexity of the matrices which contain many other potentially-interfering elements coming from industrial and domestic pollution or present in the sample such as organic matter; (ii) the presence of peaks attributed to $BEtS_2$, methyl- or octyltins or the appearance of other unknown peaks (such as the one at the end of the chromatogram in Fig. 6); (iii) the low organotin concentrations [$\leq$100 ng (Sn) g^{-1} or 20 ng (Sn) l^{-1}] found in several samples such as sediments, sewage sludge or river water.

The examination of Table 2 also shows that the precision is satisfactory, generally about 4–12%, which is comparable to the one of the other analytical methods. These results finally confirm the suitability and reliability of the method.

4. Conclusions

The first part of the present study has allowed the understanding of most of the matrix effects observed during the analysis of environmental samples. These effects were widely due to the organic matter. Its removal by means of centrifuging and decanting steps has given good results. The consequence has been a better control of the analytical process. Unfortunately, due to the variations of organotin responses which need the quantification by the both standard addition and internal standard methods, the analyses remained too time-consuming.

In a second part, the flame photometer has been found sufficiently selective in spite of some sulfur interferences which have not been a problem up to now. Moreover, the precise quantification of butyl-, phenyl- and also octyl- or cyclohexyltins appeared possible.

Finally, even if the $NaBEt_4$ ethylation–GC–FPD cannot be considered today as an actual routine technique, the organotin determination in various complex matrices has confirmed the convenience of this method for the pollution control in all the parts of the aquatic environment.

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