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Determination of methyltin species in sediments using a pervaporation–gas chromatographic approach†

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A method for speciation of monomethyltin (MMT), dimethyltin (DMT) and trimethyltin (TMT) in sediments based on the coupling between a pervaporation module, a preconcentration system and a gas chromatograph coupled with a pulsed flame photometric detector is reported. All the species are derivatized using sodium tetraethylborate as an appropriate reagent in order to produce volatile compounds. The experimental approach consists of a high-pressure injection valve. In one of the valve positions, the volatile tin species are driven to an appropriate minicolumn as a sorptive trap placed at the valve loop to preconcentrate the analytes. After a fixed time, the current valve position is changed for the injection mode and desorption of the preconcentrated analytes are obtained by heating in a furnace. Estimated detection limits (of tin) for MMT, DMT and TMT using 500 mg of sample are in all cases lower than 21 ng g^{-1}. Excellent recoveries (between 90 and 98%) for tin species were obtained by this extremely simple and easily automated setup. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: organotins; methyltins; pervaporation; gas chromatography; pulsed flame photometric detector; sediments

INTRODUCTION

During the past few decades, worldwide production and use of organotin species in industry and agriculture as heat and light stabilizers, biocides, fungicides and antifoulants has increased markedly.[1] The ecotoxicological impact of most organotin compounds has been demonstrated.[2,3] In general, organometallic species are more toxic than their inorganic salts; the toxicity of organotin compounds increases with the degree of alkylation and decreases when the chain length of the substituents increases.[4] The known pollution and harmful effects caused by organotins, together with the development of sensitive and precise analytical techniques for the quantitative speciation of organotin compounds at trace levels in environmental samples,[5,6] have caused increasing concern about the distribution, fate and impact both of methylated tins produced by biological processes, and of butyltins of anthropogenic origin. Such concern has generated increased studies on biotic/abiotic methylation reactions, degradation rates and the ultimate products of man-made butyltin and phenyltin compounds under natural and simulated environmental conditions. However, only limited data for methyltin species in environmental samples are available in the literature, due to the low levels of methyltins in the environment.[7–9]

It has been shown that the various oxidation states (0, II, IV) of tin and, in particular, individual organotin compounds can be methylated by both abiotic and biotic pathways to yield a variety of methyltin compounds, depending on the redox potential of the environment studied.[10–15]

Several techniques have been developed for the determination of organotin compounds. The current methods usually involve a separation technique, such as high-performance liquid chromatography (HPLC)[16,17] or gas chromatography (GC),[18,19] coupled to a tin detection method, such as atomic absorption spectrometry

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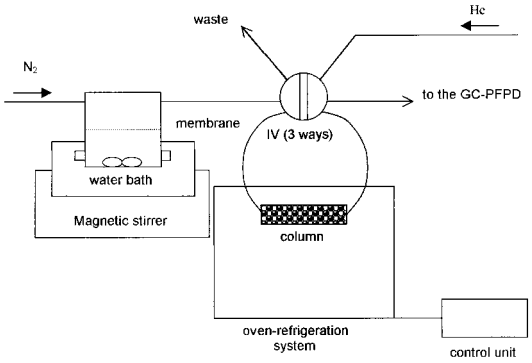

Figure 1. Scheme of instrumental coupling with preconcentration approach for the organotin analysis.

(AAS),[20,21] atomic emission spectrometry (AES),[22] mass spectrometry (MS)[23] or pulsed flame photometric detection (PFPD).[24] Hydride generation with sodium tetrahydroborate[25] or sodium tetraethylborate[26] and alkylation by Grignard reagents[27,28] are used to derivatize the ionic organotin compounds to stable and volatile species.

In the present research, we proposed the use of pervaporation coupled with capillary GC and PFPD. The tin species in the sediment pervaporate through a membrane, where they are collected in a stream of nitrogen and taken to a minicolumn containing a suitable sorbent, in order to preconcentrate the species. Once the species are desorbed from the minicolumn with a helium stream, an optimized GC method is used to separate and detect the methylated species.

EXPERIMENTAL

Instrumentation

The approach for the extraction of the organic tin species from sediments is shown in Fig. 1. It consists of a high-pressure injection valve with a purge and trap system for preconcentration (Análisis Vínicos, Ciudad Real, Spain), the pervaporation unit (home-made device) and the GC–PFPD system (Varian Ibérica, Barcelona, Spain).

A Varian Star 3400 gas chromatograph fitted with a split/splitless injector and a pulsed flame photometric detector was used for the separation/detection of the organotin compounds. Table 1 shows the chromatographic operating conditions. The detector was operated at 300 °C with a 610 nm optical filter and an air–hydrogen flame. A 30 m × 0.32 mm i.d. fused silica capillary column (SPB1, Supelco, Bellefonte, PA, USA) coated with a 0.25 μm film thickness of polydimethylsiloxane was used to separate the compounds. The injector temperature was maintained at 250 °C. The temperature of the chromatographic oven was programmed at 40 °C (1 min), 10 °C min^{-1} to 150 °C and held at 150 °C for 2 min. Helium (He-2, Air liquide, Barcelona, Spain) at 4 ml min^{-1} was used as carrier gas. A computer

Table 1. Chromatographic conditions for the determination of methyltin species

Parameters	Value
Injection temperature (°C)	250
Relay	
initial relay	+1
relay time (min)	1
final relay	−1
split ratio	4
GC parameters	
Carrier gas Helium flow rate (ml min^{-1})	4
Oven program	
initial temperature (°C)	40
initial time (min)	1
rate (°C min^{-1})	10
final temperature (°C)	150
final time (min)	2
PFPD parameters	
Detector temperature (°C)	300
Flame (air–hydrogen)	
hydrogen flow rate (ml min^{-1})	30
air center flow rate (ml min^{-1})	30
air wall flow rate (ml min^{-1})	22

with Varian Star Chromatography Workstation software for data collection and treatment and an oven/refrigeration system were also used.

To separate the analytes from the solid matrix, a home-made pervaporation unit[29,30] consisting of a lower compartment where the sample was placed, an upper compartment in which the carrier gas collected the volatile analytes, and both were separated by a hydrophobic membrane (PTFE membranes, 40 mm diameter and 1.5 mm thick; Trace Biotech AG, Braunschweig, Germany) placed on a support. The volume of the chambers could be selected by putting spacers between the membrane support and the corresponding compartment. Both chambers were aligned with the membrane support using two metallic bars. The whole module was placed between two aluminium supports and four long screws closed the system tightly.

Standard solutions and reagents

The solvents used in the experiments were analytical grade or Suprapur quality and obtained from Merck (Darmstadt, Germany), Panreac (Barcelona, Spain) and Romil (Barcelona, Spain). Water was double-distilled and deionized, giving blank readings in all the analyses.

Organotin stock solutions were prepared at concentrations (as tin) of 0.2124 mg l^{-1}, 0.2350 mg l^{-1}, 0.2770 mg l^{-1} in methanol for monomethyltin (MMT), dimethyltin (DMT) and trimethyltin (TMT) chlorides (Strem Chemical, Bis-

chheim, France) respectively. Intermediate solutions were prepared by dissolving appropriate volumes of stock solutions in 25 ml of methanol. Working solutions were prepared daily by dilutions of the intermediate solutions with methanol.

Ethanoate buffer (pH 5.0, 0.1 M) was prepared by dissolving 13.6 g of sodium ethanoate in 1 l of deionized water followed by pH adjustment with ethanoic acid. Sodium tetraethylborate ($NaBEt_4$) was obtained from Strem Chemical (Bischheim, France). Working solutions were made up daily by dissolving 0.01 g $NaBEt_4$ in 1 ml of deionized water and stored in the dark at 4 °C.

Type A (100% Tenax), Type C (34% Tenax, 33% silicagel and 33% charcoal), Type I (33.3% Carbopack C, 39.2% Carbopack B, 23.5% Carboxem 1000 and 4% Carboxem 1001), and Type K (58.8% Carbopack B, 35.3% Carboxem 1000 and 5.9% Carboxem 1001) sorbents from Supelco (Bellefonte, PA, USA) were assayed to retain the analytes. Glassware was rinsed in deionized water, decontaminated overnight in 10% (v/v) nitric acid solution and then rinsed again.

Procedure

An amount of freeze-dried sample (0.5 g spiked diatomaceous earth as sediment) was weighed in the lower chamber of the pervaporation module and 1 ml of ethanoate buffer was added. Organotin compounds were ethylated with 0.1 ml of $NaBEt_4$ solution and a spacer was placed between this compartment and the membrane support in order to leave an empty volume between the sample surface and the membrane. The module was closed after emplacing the membrane and the upper chamber. The mixture was stirred by a magnetic stirrer. Finally, the pervaporation module was placed in a water bath at 70 °C and the mixture was allowed to react for 15 min. Then, a nitrogen stream through the upper chamber drove the analytes to the sorptive column placed in an ice–water bath (0 °C). After 2 min, the preconcentration column was heated electrically to 185 °C and the valve was switched on to allow the analytes to be back desorbed and driven to the gas chromatograph by a helium stream for the chromatographic analysis.

RESULTS AND DISCUSSION

Optimization

For all the experiments, portions of 0.5 g of diatomaceous earth as a general solid matrix were introduced in the lower chamber and spiked with 42 ng of MMT (as tin), 47 ng of DMT (as tin) and 55 ng of TMT (as tin) in distilled water.

The variables of the system that had to be optimized were split into four areas: first, those involved in the chromatographic separation; second, those involved in detection; third the retention/desorption variables; and fourth those involved in the pervaporation step. The variables were all studied using the univariate method.

All the variables studied concerning the chromatographic separation and detection of the organic tin species are shown in Table 1. As the *helium flow rate* was increased from 2 to 6 ml min^{-1} there was a better peak area and definition for all three species, along with greater sampling frequencies; however, above 4 ml min^{-1} there was no significant improvement observed (*t*-test, $p < 0.01$). Thus, 4 ml min^{-1} was chosen as optimum. Similarly, for the *temperature ramp rate*, increased peak area and reduced retention times were found upon increasing the ramp rate from 5 to 20 °C min^{-1}. Above 10 °C min^{-1} there was no improvement observed, and so this value was used for further experiments.

The effect of both the *hydrogen and the air center flow rates* was studied, and a greater peak area was shown for all three species at 30 ml min^{-1}. An *air wall flow rate* of 22 ml min^{-1} was chosen, as this provided the best peak area reproducibility.

Several types of sorbent were investigated as appropriate candidates for the *retention of organotin species* (Types A, C, I and K) in a preliminary study (Table 2). Type I was chosen, as it was the only that provided quantitative sorption and subsequent desorption of the analytes with no peak tailing. The minicolumn was prepared in stainless steel tubing and placed in the loop of the injection valve in such a way that, in the 'load' position, the stream of nitrogen from the acceptor chamber of the pervaporation cell passed through the sorbent and then to waste in a clockwise direction, and the helium carrier stream went directly to the chromatographic column. The flow control was performed with a needle valve placed in the tubing system, which regulated the gas flow from the nitrogen cylinder. An optimum value of 160 ml min^{-1} was selected. Lower flows did not completely carry the analytes to the minicolumn, and higher flows did not allow them to be sorbed. During the desorption step, the flow of nitrogen through the sorbent was stopped by closing off both the entrance and exit to the loop of the injection valve, thus preventing any loss of desorbed analytes prior to injection. Then the valve was diverted through the preconcentration minicolumn in a counterclockwise direction before continuing to the chromatographic column, thus allowing retention and desorption to be carried out in opposite directions. In order to optimize the *retention temperature*, three different alternatives were assayed. The preconcentration column was submerged in either a CO_2(s)–ethanol bath (about −50 °C), an ice–water bath (about 0 °C) or was left at room temperature (about 25 °C). It could be noticed that the same peak areas were obtained in the two first cases, whereas the area was lower in the third case; therefore, the cheapest option, the second one, was chosen as optimal. Thus, 0 °C was chosen as optimum. A home-made heat source was used to study the effect of the *desorption temperature*. The minicolumn, placed in the oven–refrigeration system, was subjected for a preset time at temperatures between 160 and 200 °C prior to switching the injection valve to inject the desorbed species onto the chromatographic

Table 2. Comparison between the recoveries obtained for the assayed sorbents

Sorbent	Recovery (%)		
	TMT	DMT	MMT
Type A	30.3	56.4	<DL[a]
Type C	64.5	75.5	<DL
Type I	98.1	101.7	97.6
Type K	91.3	89.2	96.6

[a] DL: detection limit.

column. As the temperature was increased, better recoveries were observed for all three species; 100% recoveries were obtained at 185 °C for all species, which was confirmed by repeating the desorption process to make sure that the second run provided a blank signal. A *desorption/injection time* of 5 s was sufficient to desorb all analytes quantitatively and allow all the desorbed species to be flushed from the loop to the chromatographic column with a helium flow of 140 ml min^{-1}.

When the *pervaporation temperature* was studied, it was not surprising to find that as the temperature was increased so was the efficiency of the pervaporation.[29,31,32] The pervaporation cell was placed in a water bath, which was filled with water to the level of the lower donor chamber, and the temperature was studied from 60 to 90 °C. Here, 70 °C was chosen as optimum, as higher temperatures did not increase the signal and, moreover, the precision decreased, probably due to the poorer stabilization of the bath temperature. Another variable studied was *the reaction time* to derivatize the analytes. Values ranging from 5 to 20 min were assayed and, on finding that for 15–20 min there was no significant improvement observed, 15 min was selected as optimum. The final variable to be studied was the *time of the pervaporation* process. Again, not surprisingly, longer times were found to yield better results, due to the dynamic character of the acceptor gas, which means that analyte-free gas is continually being placed in contact with the membrane, permitting an efficient and continuous displacement of the analytes from the air gap above the sample and diffusion through the membrane. The nitrogen was allowed to pass through the acceptor chamber continuously before passing to the preconcentration minicolumn for times ranging from 0.5 to 5 min, while the pervaporation cell was placed in the water bath at 70 °C. As the times were increased from 0.5 to 5 min, the recoveries improved dramatically; however, for 2–5 min there was no significant improvement observed, and so 2 min was chosen as optimum in terms of recovery and analysis time. A summary of the optimization process, showing all the variables, ranges studied, and the optimum values found, is shown in Table 3.

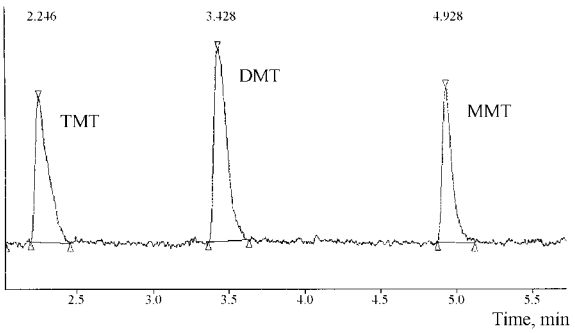

Figure 2. Chromatogram obtained for sediment 6.

Table 3. Optimization of retention/desorption and pervaporation variables for the organotin analysis

Parameter	Range studied	Optimum value
Temperature of pervaporation (°C)	60–90	70
Reaction time (min)	5–20	15
Time of pervaporation (min)	0.5–5	2
Retention temperature (°C)	−50–25	0
Desorption temperature (°C)	160–200	185
He flow (ml min^{-1})	50–150	140
N_2 flow (ml min^{-1})	100–200	160

Figure 2 shows the chromatogram obtained for sediment 6 spiked with 50 ng of MMT (as tin). The retention times were 2.2 min, 3.4 min and 4.9 min for TMT, DMT and MMT respectively.

Features of the method

In order to check the effectivity of the pervaporation, the preconcentration and the desorption systems, calibration curves corresponding to each species studied were performed by direct injection on the chromatograph. These were compared with those obtained by injecting the standards in the pervaporation module (Table 4).

The detection limits were computed as

$$3 \times \text{standard deviation of mean} + \text{value of mean standard blank}$$

for $n = 7$ standard blanks runs.

Aliquots of 1 µl were injected into the chromatograph and analyzed by GC–PFPD (Table 4). The calibration curves were linear for organotin (as tin) amounts of less than 169 ng (correlation coefficient, $r^2 = 0.992$) for MMT, 188 ng ($r^2 = 0.990$) for DMT and 221 ng ($r^2 = 0.997$) for TMT. The detection limits were estimated to be 24.8 ng, 32.4 ng and 16.5 ng for MMT, DMT and TMT respectively. The sensitivities (slope of the calibration curve) were $20.2 \pm 2.8\ \mu g^{-1}$, $39.0 \pm 3.5\ \mu g^{-1}$ and $62.9 \pm 2.1\ \mu g^{-1}$ of tin for MMT, DMT and TMT respectively. The solutions were analyzed at least five

Table 4. Features of the methods for the organotin analysis

Analyte	Linear range (ng Sn)	Sensitivity (calibration line slope)	r^2	Detection limit (ng Sn)
Pervaporation method features				
TMT	<249	65.9	0.996	12.1
DMT	<211	35.8	0.990	23.7
MMT	<191	25.8	0.993	22.5
Direct injection method features				
TMT	<221	62.9	0.997	16.5
DMT	<188	39.0	0.990	32.4
MMT	<169	20.2	0.992	24.8

Table 5. Concentrations (ng g^{-1}) of TMT and DMT (as tin) in the Mar Menor sediments[a]

Sample	TMT[b]	DMT
Sediment 1	62.4	75.2
Sediment 2	34.1	48.8
Sediment 3	27.3	50.2
Sediment 4	40.7	76.6
Sediment 5	62.1	62.5
Sediment 6	<DL	45.1

[a] Concentrations for MMT were in all cases below the detection limit.
[b] DL: detection limit.

times, with the relative standard deviation lower than 7% when peak height was used. The response of the detector using peak area was usually lower than 6%. For this reason, peak area was used throughout.

The calibration curves using the pervaporation approach (Table 4) obtained by using standards at five different concentrations (three replicates for each one) were linear for organotin (as tin) amounts of less than 191 ng ($r^2 = 0.993$) for MMT, 211 ng ($r^2 = 0.990$) for DMT and 249 ng ($r^2 = 0.996$) for TMT. The detection limits were estimated to be 22.5 ng, 23.7 ng and 12.1 ng for MMT, DMT and TMT respectively. The sensitivities (slope of the calibration curve) obtained by this method were $25.8 \pm 1.6\ \mu g^{-1}$, $35.8 \pm 2.8\ \mu g^{-1}$ and $65.9 \pm 3.0\ \mu g^{-1}$ of tin for MMT, DMT and TMT respectively. Reproducibilities of less than 8% were obtained by analysis of five samples spiked with 40 ng of each organotin species on different days.

Therefore, comparative values were obtained for the features of the direct injection and the preconcentration pervaporation methods. Although the detection limits were very similar in both methods, the pervaporation method allowed the direct determination of the analytes in sediments without any preliminary treatment (*e.g.* extraction of the analytes in an appropriate solvent), which avoids the need of preconcentrating the final sample solution to obtain an analyte concentration higher than the respective detection limit.

The sample throughput was of the order of three samples per hour.

Application to natural samples

The proposed method was validated by studying recoveries in spiked samples, since, to our knowledge, reference materials for methyltin species are not available. Six sediments collected from the Mar Menor in Spain were selected as representative environmental samples (Table 5). The presence of two methyltin species (TMT and DMT) was confirmed in all the sediments. These results demonstrate the existence of bioalkylation microorganisms in the sedi-

Table 6. Organotin recoveries for Mar Menor sediments[a]

Sample	TMT		DMT		MMT	
	Found (ng Sn)	Recovery (%)	Found (ng Sn)	Recovery (%)	Found (ng Sn)	Recovery (%)
Sediment 1	97.2	95	107.8	93	47.2	94
Sediment 2	68.2	92	80.2	91	46.3	93
Sediment 3	64.8	96	81.5	90	47.9	95
Sediment 4	78.3	98	110.6	95	46.8	93
Sediment 5	93.5	91	98.8	96	46.3	92
Sediment 6	38.3	95	74.3	91	47.2	94

[a] Results obtained using the pervaporation module with preconcentration in column.

ments. However, MMT levels in all the sediments were below the detection limit. The normally high temperatures in the Spanish summer (higher than 35 °C) may cause volatilization of this species. MMT, DMT and TMT at different concentration levels have also been found in the coastal waters of the Mediterranean, Marmara and Black Seas.[33]

Therefore, recovery experiments were carried out on these samples, which were spiked with 50 ng of MMT, 40 ng of DMT and 40 ng of TMT. Results were obtained by external calibration and are summarized in Table 6. Recoveries were higher than 90% for all the organic tin species.

CONCLUSIONS

A simple and effective method for the separation of organotin species from sediments prior to preconcentration and separation by GC–PFPD has been developed. The continuous removal of the volatilized analytes through the membrane from the air gap above the sample provides displacement of the mass-transfer equilibrium and results in a higher efficiency of the extraction process. In addition, this pervaporation method allowed the direct determination of the analytes in sediments without any preliminary treatment (*e.g.* extraction of the analytes in an appropriate solvent).

The low sample amount required and the acceptable sample throughput make the method suitable for routine analysis of environmental samples, thereby offering sufficient selectivity and detection limits. In addition, the sensitivity can be improved by increasing the sample amount placed into the pervaporation cell. Further, the method developed can be used for the analysis of samples from biomethylation studies, in order to provide data that may contribute to a better understanding of natural alkylation processes of tin.

Finally, the process, which is easily automated and simple to use, has versatility as an important characteristic, since it can be applied to the separation and speciation of any volatile analyte or reaction product.

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REFERENCES

1. Piver WT. *Environ. Health Perspect.* 1973; **4**: 61.
2. Fent K. *Environ. Pollut.* 1992; **76**: 187.
3. Fent K and Meier W. *Arch. Environ. Contam. Toxicol.* 1992; **22**: 428.
4. Vela NP and Caruso JA. *J. Anal. At. Spectrom.* 1992; **7**: 971.
5. Braman FE and Tompkins MA. *Anal. Chem.* 1979; **51**: 12.
6. Hodge VF, Seidel SL and Goldberg ED. *Anal. Chem.* 1979; **51**: 1256.
7. Sanz-Asencio J, Martínez-Soria MT, Plaza-Medina M and Pérez-Clavijo M. *Anal. Chim. Acta* 2000; **409**: 171.
8. Ceulemans M and Adams FC. *J. Anal. At. Spectrom.* 1996; **11**: 201.
9. Yemeniciogu S, Tugrul S, Kubilay N and Salihoglu I. *Mar. Pollut. Bull.* 1997; **34**: 739.
10. Ridley WP, Dizikis LJ and Wood JM. *Science* 1977; **197**: 329.
11. Guard HE, Cobet AB and Coleman WM. *Science* 1981; **213**: 770.
12. Hallas LE, Means JC and Cooney JJ. *Science* 1982; **215**: 1505.
13. Craig PJ and Rapsomanikis S. *Environm. Sci. Technol.* 1985; **19**: 726.
14. Rapsomanikis S and Weber JH. *Environm. Sci. Technol.* 1985; **19**: 352.
15. Donard OFX and Weber JH. *Nature* 1988; **332**: 339.
16. Rivaro P, Zaratin L, Frache R and Mazucotelli A. *Analyst* 1995; **120**: 1937.
17. White S, Catterick T, Fairman B and Webb K. *J. Chromatogr. A* 1998; **794**: 211.
18. Fernández-Escobar I and Bayona JM. *Anal. Chim. Acta* 1993; **355**: 269.
19. Rodríguez I, Schmitt VO and Lobinski R. *Anal. Chem.* 1997; **69**: 4799.
20. Schulze G and Lehmann C. *Anal. Chim. Acta* 1994; **288**: 215.
21. Sarradin PM, Leguille F, Astuc A, Pinel R and Astruc M. *Analyst* 1995; **120**: 79.
22. López-Avila V, Liu Y and Beckert WF. *J. Chromatogr. A* 1997; **785**: 279.
23. Prange A and Jantzen E. *J. Anal. At. Spectrom.* 1994; **10**: 105.
24. Gómez-Ariza JL, Giráldez I and Morales E. *J. Environ. Monit.* 1999; **1**: 197.
25. Segovia-García E, García-Alonso JI and Sanz-Medel A. *J. Mass Spectrom.* 1997; **32**: 542.
26. Martin FM and Donard OFX. *Fresenius' J. Anal. Chem.* 1995; **351**: 230.
27. Forsyth DS and Jay B. *Appl. Organomet. Chem.* 1997; **11**: 551.
28. Gómez-Ariza JL, Giráldez I and Morales E. *Appl. Organomet. Chem.* 1995; **9**: 51.
29. Papaefstathoiu I, Luque de Castro MD and Valcárcel M. *Fresenius' J. Anal. Chem.* 1996; **354**: 442.
30. Gómez-Ariza JL, Velasco A, Giráldez I, Sánchez D and Morales E. *Int. J. Environ. Anal. Chem.* 2000; **78**: 427.
31. Mattos IL and Luque de Castro MD. *Anal. Chim. Acta* 1994; **298**: 159.
32. Papaefstathoiu I, Tena MT and Luque de Castro MD. *Anal. Chim. Acta* 1995; **308**: 246.
33. Yemenicioglu S, Tugrul S, Kubilay N and Salihoglu I. *Mar. Pollut. Bull.* 1997; **34**: 739.

