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# Multielemental speciation analysis of organometallic compounds of mercury, lead and tin in natural water samples by headspace-solid phase microextraction followed by gas chromatography–mass spectrometry

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**Abstract**

The development of a simple and rapid multielemental speciation method is described with the ultimate goal to simultaneously determine various organometallic compounds of mercury, lead and tin (inorganic mercury, methylmercury, trimethyllead, triethyllead, monobutyl-, dibutyl- and tributyltin) in natural water samples. The analytical method consists on the ethylation with $NaBEt_4$, simultaneous headspace-solid phase microextraction (HS-SPME) of the derivatives and final gas chromatographic-mass spectrometric (GC–MS) analysis. After optimization of important process parameters, like SPME fiber coating, extraction time and extraction temperature, the analytical characteristics were evaluated. Detection limits in the low $ng\,l^{-1}$ level, linearity over three orders of magnitude and repeatability in the range of 3–20% were achieved for all compounds under study. The accuracy of the method in terms of average percentage recovery of the compounds in spiked river water and seawater samples was better than 90%. Finally, application of the proposed method to real natural aqueous samples enabled the simultaneous determination of all the compounds under study in seawater samples obtained from the marina area of Gijón (Asturias, Spain).


*Keywords:* Water analysis; Speciation analysis; Solid-phase microextraction; Organometallic compounds; Mercury; Lead; Tin

## 1. Introduction

The presence of organometallic compounds in the environment has increased in recent decades owing to anthropogenic activities [1]. The toxicity and bioavailability of these compounds, in addition to their mobility and their environmental impact, is highly dependent on their chemical form. Therefore, metal speciation analysis has become an important topic of present day analytical research for organometallics [2,3].

The most important and abundant organometallic species in the environment so far are organomercury, organolead and organotin compounds. Thus, the determination of such compounds in different environmental samples has been one of the goals of metal speciation analysis in recent years. The most common approaches for this purpose used a separation technique, mainly gas chromatography (GC), coupled to an atomic spectroscopic element specific detector [4], particularly as inductively coupled plasma-mass spectrometry (ICP-MS) [5–10] or microwave-induced plasma atomic emission spectrometry (MIP-AES) [11–14]. Although less popular for such determinations, GC–MS, a well-established analytical technique, has demonstrated also to be useful for organometallic speciation [15–18].

Using GC, ionic organometallic compounds have to be extracted from the sample matrix and derivatized to volatile species. Aqueous in situ ethylation with sodium tetraethyl borate ($NaBEt_4$) followed by liquid–liquid extraction with an organic solvent has been demonstrated to be a suitable method for this purpose [19]. An alternative approach to liquid–liquid extraction is the solid phase microextraction (SPME) technique. This technique involves the extraction of the volatile or semivolatile organic analytes directly from aqueous or gaseous samples onto a fused-silica fiber that is coated with a suitable stationary phase. While the fiber is exposed to the sample, the analytes partition from the sample matrix into the stationary phase until equilibrium is reached. The fiber is then directly transferred into a GC injector for thermal desorption and analysis. Therefore, SPME is a simple, fast, solvent-free technique, which combines sampling, extraction, con-

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centration and sample introduction in one single device [20,21].

To date, SPME has been mainly used for the analysis of different organic pollutants and only in recent years this technique has been also employed for speciation of organometallic compounds of mercury, lead and tin [22]. Few papers, however, can be found in the literature dealing with its application to multielemental speciation studies of the above mentioned compounds [15,23–25].

Therefore, the aim of this work was to develop a fast, simple and sensitive method for the simultaneous determination of inorganic mercury, methylmercury, trimethyllead, triethyllead, monobutyl-, dibutyl- and tributyltin in aqueous samples and to evaluate its possibilities and limitations. The method is based on in situ aqueous phase ethylation with $NaBEt_4$ followed by SPME and then GC–MS determination. This new method has been successfully applied to the analysis of natural water samples (river water and coastal seawater).

## 2. Experimental

### 2.1. Apparatus

The SPME device used for manual extraction, a holder assembly and several replaceable fibers, was purchased from Supelco (Madrid, Spain). Two different fiber types were compared, polydimethylsiloxane (PDMS, 100 μm) and divinyl-benzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 50 μm/30 μm). The fibers were conditioned before use, as recommended by the manufacturer, by heating them in the injection port of the gas chromatograph for 1–4 h at 250–270 °C, depending on the fiber coating. Ten milliliters glass vials closed with PTFE-coated silicone septa were used for sampling. Proper mixing of the sample solutions during the SPME was achieved with a magnetic stirrer.

Chromatographic analysis was performed with an Agilent 6890 Network gas chromatograph equipped with a mass spectrometric detector (Agilent 5973 Network MSD). A split/splitless injector (2 mm i.d. glass liner) was used in the splitless mode, and maintained at 260 °C and 1 min. desorption time was used for all fiber injections. The separation was achieved on a 30 m × 0.25 mm i.d., 0.25 μm film thickness, HP-5MS (5% phenyl/methylsiloxane) fused-silica column. The column temperature was initially held at 50 °C for 1 min., increased at 30 °C $min^{-1}$ to a final temperature of 250 °C. Helium was used as carrier gas at a flow rate of 1.2 ml $min^{-1}$.

The MSD transfer-line and ion source temperatures were 280 and 150 °C, respectively. Electron-impact ionization was performed at an electron energy of 70 eV; the electron multiplier potential was 1200 V. A mass range from *m/z* 50–400 was recorded in the full-scan mode. The *m/z* values used for selective ion monitoring (SIM) mass detection are listed in Table 1.

Table 1
List of ions and time windows used for selective ion monitoring mass detection

| Compound | Starting time (min) | *m/z* |
|---|---|---|
| (1) Methylmercury | 1.00 | 217, 246 |
| (2) Trimethyllead | 3.05 | 231, 260 |
| (3) Inorganic mercury | 3.50 | 223, 253 |
| (4) Triethyllead | 4.70 | 237, 295 |
| (5) Monobutyltin | 5.08 | 179, 235 |
| (6) Dibutyltin, tributyltin | 5.80 | 149, 179 |

### 2.2. Reagents

Monobutyltin trichloride (MBT), dibutyltin dichloride (DBT) and tributyltin chloride (TBT) were obtained from Aldrich (Steinheim, Germany). Trimethyllead (TML) chloride and triethyllead (TEL) chloride were purchased from ABCR (Karlsruhe, Germany). Methylmercury (MeHg) chloride was obtained from ICN Biochemicals (Cleveland, Ohio, USA) and mercury(II) nitrate was from Merck (Darmstadt, Germany). Stock solutions of 1000 mg $l^{-1}$ organometallic compounds were separately prepared in methanol (Merck, Darmstadt, Germany). Mixed working solutions were prepared daily before analysis by dilution of the stock solutions with Milli-Q water (Millipore, Molsheim, France) and stored in the dark at 4 °C.

Sodium tetraethyl borate was obtained from Strem Chemicals (Bischheim, France). A fresh $NaBEt_4$ solution of 2% (w/v) was prepared daily in 0.1 M NaOH solution (obtained from Merck, Darmstad, Germany).

A buffer solution at pH 5.3 was prepared by mixing appropiate volumes of 0.2 M acetic acid (Merck, Darmstad, Germany) and 0.2 M sodium acetate (Merck, Darmstad, Germany) solutions.

All other chemicals and solvents were of analytical-reagent grade or better. Glassware was cleaned over night in chromic acid and then rinsed with Milli-Q water. The PTFE-coated magnetic stirring bars were used only once and were disposed after each analysis.

### 2.3. Derivatization and SPME procedure

Derivatization with $NaBEt_4$ was achieved in aqueous solutions at pH 5.3. The effect of the pH on the efficiency of $NaBEt_4$ to derivatize alkylmetals has been evaluated by others [23]. Highest derivatization yields for all compounds under study were obtained at pH 5.3, which is in agreement with results obtained previously in our laboratory. For headspace SPME sampling 5 ml of the organometallic standard solution and 1 ml of acetate buffer solution (pH 5.3) were placed in a 10 ml glass vial. Hundred microliters of 2% (w/v) $NaBEt_4$ were added and the vial was then immediately closed with a PTFE-coated silicon rubber septum. The SPME needle was pierced into the septum and the fiber was exposed to the solution headspace for 30 min. The solution was intensively stirred with a PTFE-coated magnetic stirring

bar with constant velocity. Finally, the fiber was withdrawn into the needle and transferred to the GC injector for thermal desorption at 260 °C during 1 min. During HS-SPME the temperature was controlled by immersing the sample vials in a water bath.

## 3. Results and discussion

### 3.1. Effect of the fiber coating nature

In HS-SPME the affinity of the analytes for the three phases (fiber coating, headspace and sample solution matrix) involved in the extraction process determine the extraction yield. Therefore, the choice of an appropriate fiber coating is extremely important. In this work, two coated fibers available commercially, PDMS (100 μm) and DVB/CAR/PDMS (50 μm/30 μm) were tested for the extraction of the derivatized organometallic compounds. The results obtained are shown in Fig. 1. As can be seen, for all the organometallic compounds under study, the extraction yield using the mixed fiber coating (DVB/CAR/PDMS) was much higher than that observed for the PDMS coating, specially for the most volatile compounds (methylmercury, trimethyllead and inorganic mercury).

### 3.2. Temperature effect

The HS-SPME process involves two equilibrium steps: the first step is the partitioning of the analyte between the fiber coating and the headspace gas phase, with a partitioning coefficient $K_1$; The second step involves analytes partitioning between the gas phase and the liquid sample phase, with a partitioning coefficient $K_2$. To some extent, heating is a convenient method to improve extraction efficiency since heating the sample helps to release analytes from matrix to headspace. Of course, lower temperature facilitates the physical adsorption process on the fibers coating. If temperature increases, the ability of fibers to adsorb analytes will decrease. Therefore, the total extraction efficiency depends on both, the fiber (its affinity character) and the compound (volatility) [26].

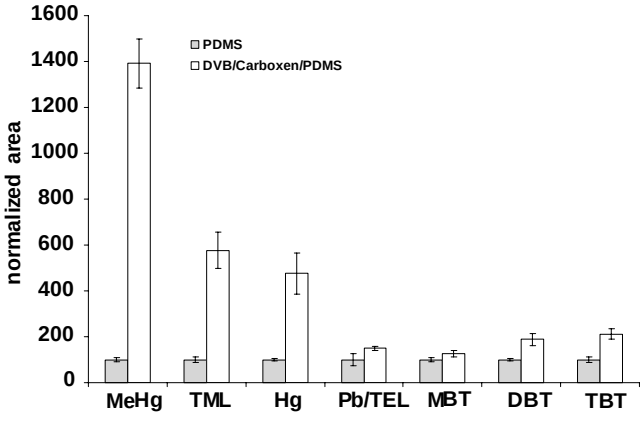


Fig. 1. Comparative performance of two different fiber coatings for SPME.

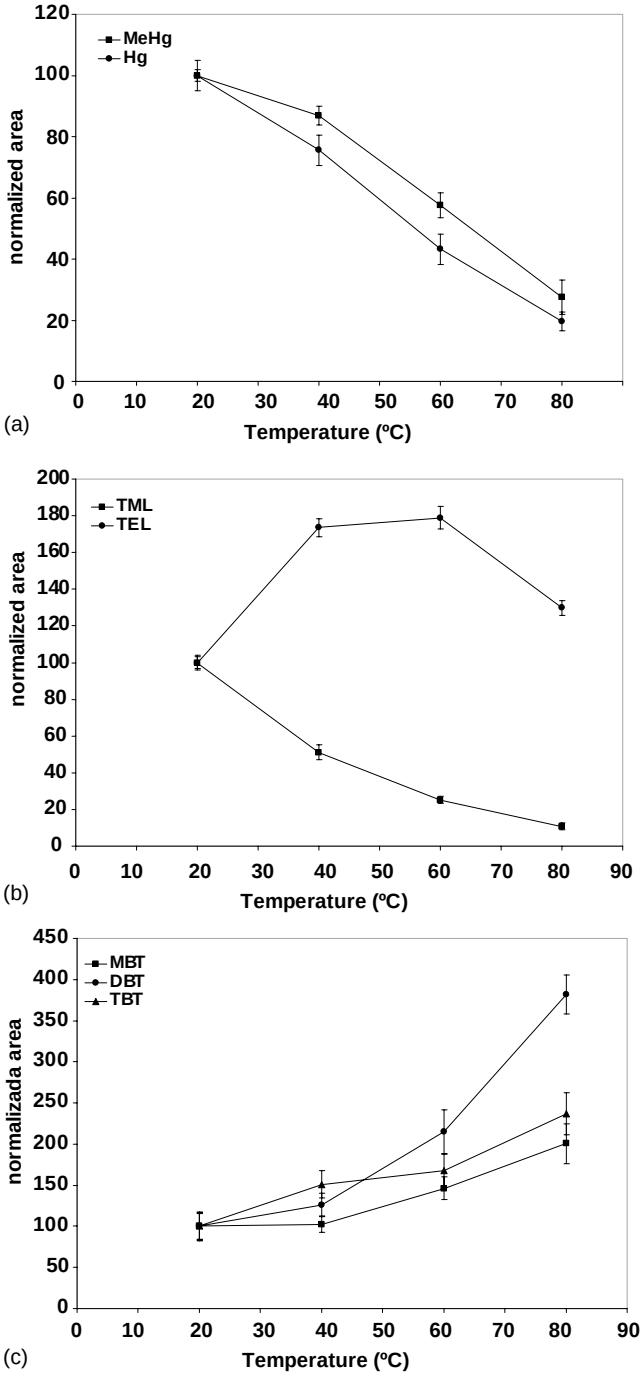


Fig. 2. Effect of extraction temperature on the extraction efficiency for: (a) Hg and methylmercury; (b) TML and TEL; and (c) MBT, DBT, TBT.

The temperature effect between 20 and 80 °C was studied with the PDMS and the DVB/CAR/PDMS fibers. Fig. 2 shows the results obtained using the DVB/CAR/PDMS fiber (similar results were obtained with the PDMS fiber). As shown in Fig. 2, with increasing temperature, the amount of MeHg, TML and Hg, extracted by the fiber, decreases mainly due to the shift of the gas phase/fiber coating par-

titioning coefficient towards the gas phase with increasing temperature. Since these are the most volatile compounds, an increase in temperature will mainly affect their first equilibrium step ($K_1$), but hardly the second one ($K_2$). However, the amount of MBT, DBT and TBT extracted increased with the temperature due to their higher boiling points, i.e. the increase of $K_2$ values with increasing temperatures is much higher than the decrease of $K_1$ values. These results are in agreement with results reported by other authors [23]. Because extraction at higher temperatures is more tedious (and time consuming), extractions were accomplished at 20 °C in subsequent experiments.

### 3.3. Effect of extraction time

The derivatized organometallic compounds are volatile and apolar, therefore they have a greater affinity for the apolar fiber coating (PDMS or DVB/CAR/PDMS) than for the polar aqueous sample matrix. As the mass transfer from headspace to the fiber goes fast, it is expected that the limiting transfer step to reach equilibrium between fiber coating, headspace and sample solution is the mass transport from the sample to headspace, which depends on the analyte's volatility. In Fig. 3, the effect of the extraction time on the extraction yield for the derivatized organometallic compounds obtained by using the DVB/CAR/PDMS fiber at room temperature (20 °C) is demonstrated: equilibrium is reached after 30 min for the more volatile compounds MeHg, Hg and TML. However, for TEL, DBT and TBT more than 60 min. were needed to reach equilibrium (similar results were obtained with the PDMS fiber). A sampling time of 30 min was considered a suitable compromise between maximising the extraction yield and minimizing the extraction time. The observed behavior of the organometallic compounds under study was similar to those reported in the literature, however, extraction times in this study are larger than those reported previously.

Finally, it was found that after 1 min. at a temperature of 260 °C, complete desorption from both fibers (PDMS and DVB/CAR/PDMS) was obtained for all the organometallic compounds studied. Table 2 shows the experimental conditions finally selected after such optimization experiments for the HS-SPME procedure. A chromatogram of a simultaneous HS-SPME–GC–MS determination of the organometallic compounds under study using the optimized operating conditions is shown in Fig. 4. All the analytes appear sufficiently separated to be reliably determined.

Table 2
Optimized experimental conditions for HS-SPME

| | |
|---|---|
| Fiber coating | 50/30 μm DVB/CAR/PDMS |
| Extraction time (min) | 30 |
| Extraction temperature (°C) | 20 |
| Desorption time (min) | 1 |
| Desorption temperature (°C) | 260 |
| Vial volume (ml) | 10 |
| Sample volume (ml) | 5 |

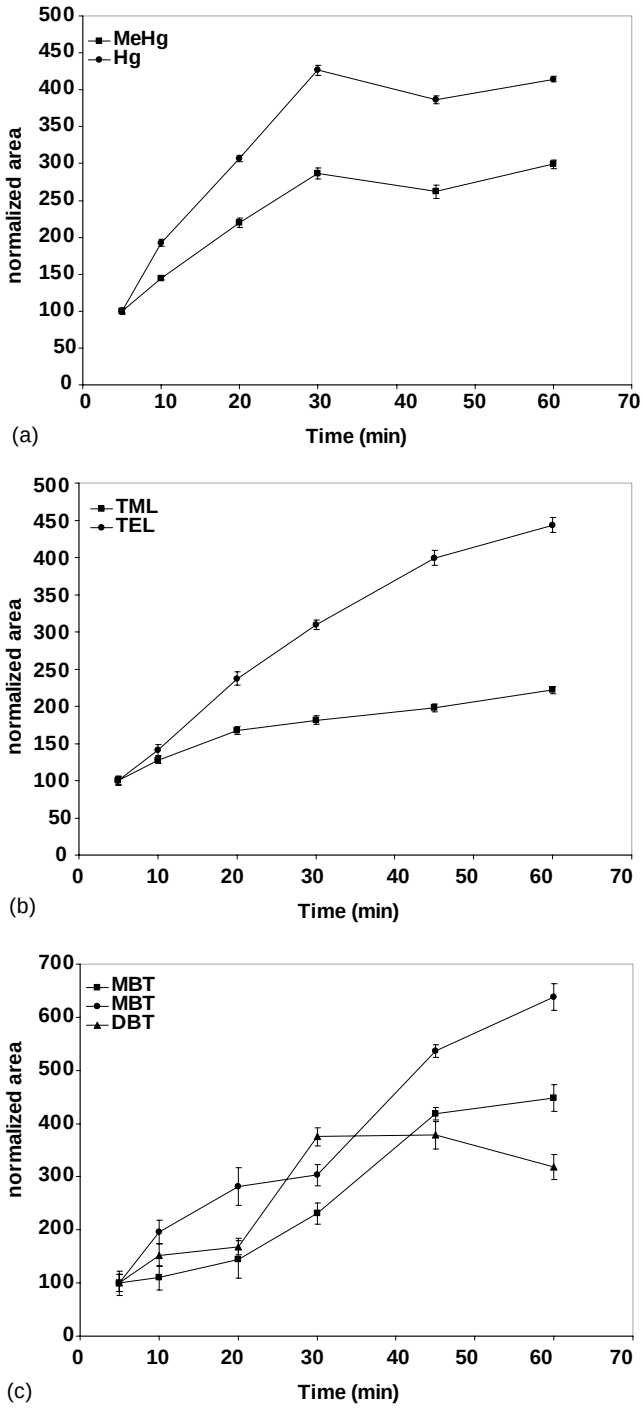


Fig. 3. Effect of extraction time on the extraction efficiency for: (a) Hg and methylmercury; (b) TML and TEL; and (c) MBT, DBT, TBT.

### 3.4. Analytical characteristics

The studies described above showed that different organometallic compounds have different conditions under which optimum HS-SPME occurs. However, even under the

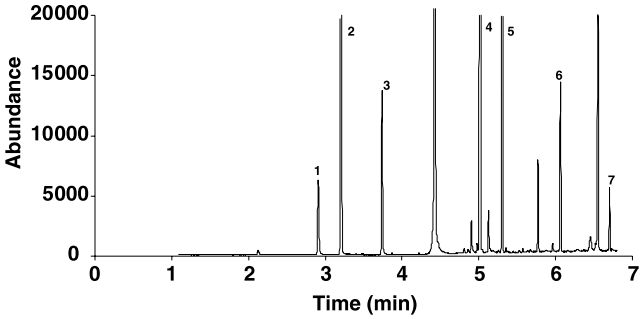


Fig. 4. HS-SPME–GC–MS chromatogram in SIM mode of an ethylated standard mixture (in 5 ml water) of: 1, methylmercury; 2, trimethyllead; 3, inorganic mercury; 4, triethyllead; 5, monobutyltin; 6, dibutyltin; 7, tributyltin.

compromise conditions selected (see Table 2) the detection limits of the developed HS-SPME method are in the sub ng $l^{-1}$ level. Those limits of detection calculated as three times the baseline noise are presented in Table 3.

The repeatability (relative standard deviation R.S.D.) of the proposed method is also given in Table 3. As can be seen, the observed %R.S.D. for a standard solution mixture of 50 μg $l^{-1}$ in each of the seven compounds ranged between 3 and 5% ($n = 5$) for Hg and Pb compounds and increased (up to 20%) for organotin derivatives.

The linear dynamic range was found to be between 50 ng $l^{-1}$ and 250 μg $l^{-1}$ (maximum concentration assayed) with correlation coefficients between 0.9945 and 0.9999 (see Table 3).

### 3.5. Recovery experiments

The accuracy (expressed as percent recovery) of the developed method was investigated by analyzing uncontaminated river water and coastal seawater samples (with tested organometallic concentrations below the detection limits) both spiked with a known amount of a standard mixture of the compounds under study. The results obtained were compared with those obtained by similar analysis of the mixed standard solution made up just in Milli-Q water. The spiking level was 0.5 μg $l^{-1}$. The results obtained are collected in Table 4, which shows that the mean recoveries for each compound in the river water sample ranged from 86 to 115%. However, in the more complex seawater sample matrix interferences were observed, as the recoveries obtained were poorer (below 70%, see Table 4).

Table 4
Recovery experiments

| Compound | Recoveries (%) | | |
|---|---|---|---|
| | River water | Seawater[a] | Seawater[b] |
| Methylmercury | 93 | 34 | 105 |
| Trimethyllead | 104 | 43 | 108 |
| Inorganic mercury | 115 | 54 | 104 |
| Triethyllead | 108 | 65 | 90 |
| Monobutyltin | 91 | 68 | 109 |
| Dibutyltin | 96 | 41 | 116 |
| Tributyltin | 93 | 76 | 100 |

[a] Calibration standards without NaCl.
[b] Calibration standards with NaCl.

It is known that addition of a soluble salt increases the ionic strength of the solution. This makes organic compounds less soluble, and the analytes partitioning coefficients, between the sample and the headspace, can increase several times. However, this effect was not observed when standard calibration solutions were prepared in a 4% (w/v) sodium chloride solution, since the derivatization reaction is also influenced by the high salt content. This results are in agreement with results reported by other authors [23,16]. In any case, matrix interferences could be compensated in this simple way and quantitative recoveries could be obtained for the seawater sample also (90–116%, see Table 4).

Nowadays, it is well-established that the use of appropriate internal standards may compensate for matrix effects or changes in the sensitivity during the analysis and also correct instrumental drift. Therefore, several elements that can be ethylated in aqueous solutions (Ge, Bi, Sb, As) were studied as possible internal standards. However, none of those potential elements could be derivatized adequately under the conditions used here for the ethylation of the organometallic compounds of mercury, lead and tin. Therefore, standard addition calibration procedure was used for the analysis of seawater samples.

Table 3
Analytical characteristics of the HS-SPME–GC–MS method proposed

| Compound | DL (ng $l^{-1}$)[a] | Repeatability (%R.S.D.)[b] | Linear range up to (μg $l^{-1}$) | Relative standard deviation of the method (%) |
|---|---|---|---|---|
| Methylmercury | 3.1 | 5 | 250 | 1.6 |
| Trimethyllead | 0.4 | 3 | 250 | 3.1 |
| Inorganic mercury | 2.3 | 3 | 250 | 3.2 |
| Triethyllead | 0.2 | 5 | 250 | 1.7 |
| Monobutyltin | 1.4 | 20 | 250 | 4.9 |
| Dibutyltin | 7.0 | 14 | 250 | 4.3 |
| Tributyltin | 16.8 | 20 | 250 | 3.3 |

[a] DL calculated as three times the baseline noise.
[b] $n = 5$ (50 μg $l^{-1}$).

Table 5
Results of real sample analysis

| Compound | Pigüeña river | Trubia river | Marina Gijón[a] |
|---|---|---|---|
| Methylmercury | n.d. | n.d. | 35 ± 1 |
| Trimethyllead | n.d. | n.d. | 179 ± 5 |
| Inorganic mercury | n.d. | n.d. | 210 ± 8 |
| Triethyllead/Lead | n.d. | n.d. | 25000 ± 1000 |
| Monobutyltin | n.d. | n.d. | 50 ± 7 |
| Dibutyltin | n.d. | n.d. | 100 ± 10 |
| Tributyltin | n.d. | n.d. | 110 ± 20 |

n.d.: not detectable.
[a] Concentrations in ng $l^{-1}$.

### 3.6. Analysis of real samples

Natural water samples from two rivers in Asturias (Spain), including a river in a "clean" area (Pigüeña river) and a river in an industrial area (Trubia river), and coastal seawater from the marina of Gijón (Asturias) were analyzed by the proposed method using standard additions to counteract matrix effects.

Table 5 shows the results obtained. The compounds under study were not detected in the river water samples. However, all of them were present in the coastal seawater sample, in concentrations between 35 ng $l^{-1}$ for methylmercury to 210 ng $l^{-1}$ for inorganic mercury. Organotins were present at 100 ng $l^{-1}$ and very high levels of lead were apparent. Fig. 5 illustrates the type of HS-SPME–GC–MS chromatogram obtained for the coastal seawater analysis in SIM detection mode. With respect to the results obtained for lead it is necessary to point out that derivatization by ethylation results in a loss of information about the original identity of some ethyllead species. It is only useful for methylated lead compounds, since both inorganic and ethylated species yield $PbEt_4$ [27]. Therefore, the results obtained for tetraethyllead are only reflecting the sum of all ethyllead compounds plus inorganic lead. The use of sodium tetrapropyl borate (or tetraammonium tetrabutyl borate) permits to overcome this problem. An alternative is the use of deuterium-labeled $NaBEt_4$ to distinguish between ethylated inorganic lead and ethyllead species, because isotope-labeled ethylgroups are not present in the environmental samples [15].

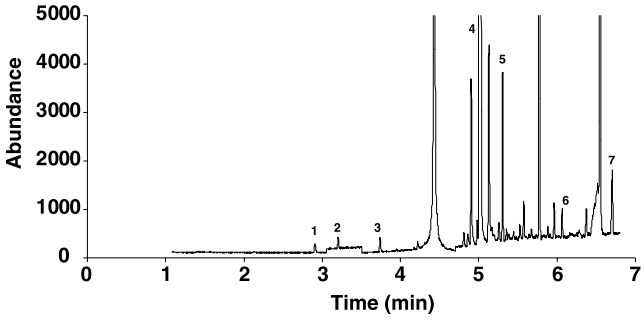


Fig. 5. HS-SPME–GC–MS chromatogram in SIM mode for the ethyl-derivatives of a marina sample: 1, methylmercury; 2, trimethyllead; 3, inorganic mercury; 4, lead/triethyllead; 5, monobutyltin; 6, dibutyltin; 7, tributyltin.

## 4. Conclusions

A method to increase the sensitivity of GC–MS to perform simultaneous speciation and determination of organometallic compounds of mercury, lead and tin has been developed by in situ volatile species formation and headspace-solid phase microextraction. It has been shown that the developed HS-SPME–GC–MS method presents good analytical performance characteristics in terms of detection limits and precision (see Table 3). It is important to note that the detection limits obtained for the analytes under study by the HS-SPME–GC–MS technique described are only around one order of magnitude higher than those reported using HS-SPME–GC–ICP-MS (a more expensive methodology) [24].

The proposed methodology is simple, rapid, solvent-free and has proved to be suitable for multielemental speciation analysis of the environmental relevant species: inorganic mercury, methylmercury, trimethyllead, triethyllead, monobutyl-, dibutyl and tributyltin, at sub-ppb levels in natural waters. Therefore, this technique could be considered as an interesting and practical alternative for simultaneous multi-element speciation analysis which otherwise is performed with costly and not generally available instrumentation such as GC–ICP-MS. Furthermore, the use of GC–MS permits the identification and verification of molecular species, which is not possible using element-specific detection by ICP-MS.

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