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Solid-phase extraction–gas chromatography–mass spectrometry using a fullerene sorbent for the determination of inorganic mercury(II), methylmercury(I) and ethylmercury(I) in surface waters at sub-ng/ml levels

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Abstract

A novel, straightforward solid-phase extraction system for the determination of inorganic mercury and organomercury compounds in water is proposed. The analytes, in a buffer medium at pH 4.5, are sorbed as diethyldithiocarbamate complexes on a C_{60} fullerene column an subsequently eluted and derivatized with sodium tetra-*n*-propylborate in ethyl acetate. Following elution, 1 μl of extract is injected into a gas chromatograph–mass spectrometer system. The proposed gas chromatography–mass spectrometry speciation method exhibits a linear range of 4–1 ng/ml, and a detection limit of 1.5 ng/l (sample volume, 50 ml). Its repeatibility, as relative standard deviation (RSD) (from 11 standards containing 50 ng/l for each analyte), is ca. 7%. No interferences from metals ions, such as Zn^{2+}, Fe^{3+}, Sb^{3+}, As^{3+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Sn^{2+}, Co^{2+}, $Mn^{2+}$and Cd^{2+} were encountered at concentrations 1000 times higher than those of the mercury compounds. The method was used for the speciation of inorganic mercury, methylmercury and ethylmercury in various types of water including sea and waste water.

Keywords: Atomic fluorescence spectrometry; Gas chromatography; Solid-phase extraction

1. Introduction

The speciation of metals and organometallic compounds continues to be a major challenge for analysts. For example mercury is found in the environment as mercurious (Hg^{+}) and mercuric (Hg^{2+}) cations, and occurs as methylmercury ($MeHg^{+}$), dimethylmercury (Me_2Hg) and ethylmercury ($EtHg^{+}$) formed by biological conversion in organic systems [1]. Organomercury compounds differ significantly in bio-physicochemical properties, such as toxicity, solubility and rate of bioaccumulation by organisms, among others. $MeHg^{+}$, which the most toxic species of mercury, can accumulate in living organisms and damage their central nervous system [1,2]. $MeHg^{+}$ can be of anthropogenic origin, however, inorganic mercury can be biologically transformed into $MeHg^{+}$ by methylation. It is usually encountered at higher levels in sediment and biota than in water by effect of its accumulation in the fomer [3]. Inorganic mercury and $MeHg^{+}$ seem preconcentrate in sediments and are found at relatively high levels in fish.

The great concern about the determination of mercury and organomercury compounds in environmetal samples using different analytical methods is reflected in the number of papers published on this topic over the past decade [4–10]. Several reviews about mercury and organomercury speciation in food [1] and environmetal samples [2,3] have been published. The methods currently employed to determine

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mercury and organomercury compounds in environmental matrices usually involve several steps, the analytes usually being extracted or preconcentrated from the samples by acid/alkaline digestion and solvent extraction [11,12], acid volatilization [3], solid-phase extraction [4,5,13] or, more recently, solid-phase microextraction [7,8,14]. Current methods for this purpose use a separation technique (GC or LC) in combination with highly sensitive, element-specific detection methods, such as mass spectrometry [6,15], cold vapour atomic absorption spectrometry [13], cold vapour atomic fluorescence spectrometry [16], microwave inductively coupled plasma atomic emission spectrometry [6,7] or inductively coupled plasma mass spectrometry [17]. The gas chromatography–atomic fluorescence spectrometry hyphenated technique is emerging as an effective choice for mercury analysis on account of its high sensitivity and selectivity [6]; although gas chromatography–mass spectrometry (GC–MS) is rarely used to determine mercury [18,19], it is still very useful for structural confirmation. Organomercury compounds must be derivatized to volatile species for GC analysis. One commonly used derivatization method for this purpose is aqueous alkylation with tetraethylborate [20] and, more recently, tetrapropylborate [21] or tetraphenylborate [6]. However, tetraethylborate does not distinguish between ethylmercury and inorganic mercury, so the latter is preferable when $EtHg^+$ or Hg^{2+} is to be determined.

Solid-phase extraction (SPE) and solid-phase microextraction (SPME) [22] are rapidly growing in popularity as a choice for preconcentrating organometallic compounds. Thus, In SPE cotton sulphydryl minicolums have been used to preconcentrate Hg^{2+} and $MeHg^+$ in water [3]. Also, various complexing agents including dithiocarbamates and dithizone have been employed to neutralize cationic mercury compounds prior to retention on polymers [5] and, more frequently, RP-C_{18} sorbents [4,13]; the chelates formed were eluted with benzene or methanol. However, the extensive manipulation involved in transfer operations for the subsequent reaction introduce some hazards through uncontrolled evaporation losses. In this context, the use of an on-line SPE system for sorption, elution and derivatization prior to GC separation/determination is crucial as it avoids losses during concentration and alterations in the chemical composition of the analytes.

This work was part of a research project concerning the analytical potential of fullerene as a sorbent for organometallic compounds in environmental samples; so far, fullerene has exhibited excellent sorbent properties for neutral chelates of organolead [23] and butyltin [24] compounds. In this work, we extended the analytical uses of C_{60} fullerene to the sorption of mercury and organomercury compounds by using a system similar to one reported elsewhere [23] on account of its simplicity. The compounds were derivatized with tetrapropylborate to enable injection into the GC–MS system. The ensuing method was applied to the analysis of water samples.

2. Experimental

2.1. Reagent and standard solutions

Stock standard solutions of Hg^{2+}, $MeHg^+$, Et_2Hg (internal standard) and $EtHg^+$ were prepared by dissolving appropriate amounts of mercury(II) nitrate monohydrate, methylmercury chloride (99%), diethylmercury (Sigma–Aldrich, Madrid, Spain) and ethylmercury chloride (LGC Promochem, Barcelona, Spain) in methanol. All standards were stored in PTFE bottles at 4 °C. A buffer solution of pH 4.5 was prepared by mixing appropriate amounts of sodium acetate (99%) 2 M and acetic acid (>99%) 4 M in water doubly deionised (18.2 MΩ) with a Milli-Q water system (Millipore, Madrid, Spain). Working-strength standard solutions were prepared daily from the stock solutions by dilution with the buffer solution (0.2 M acetate/0.4 M acetic acid). Solutions containing 3.5×10^{-3} M sodium diethyldithiocarbamate (NaDDC, Sigma–Aldrich) in water Milli-Q and 1.2 M sodium tetra-*n*-propylborate (98%, Galab, Geesthacht, Germany) in ethanol were also prepared. Aqueous solutions of other metals (Zn^{2+}, Fe^{3+}, Sb^{3+}, As^{3+} Pb^{2+}, Ni^{2+}, Cu^{2+}, Sn^{2+}, Co^{2+}, Mn^{2+}, Cd^{2+}) at a 1 g/l concentration were prepared for the interference tests. Organic solvents and all other chemicals were analytical reagent grade or better and purchased from Scharlau (Barcelona, Spain). C_{60} fullerene (>99.4% purity) was obtained from Dynamic Enterprises (Berkshire, UK).

2.2. Apparatus

The speciation of mercury and organomercury compounds was accomplished by using a Fison GC8000/MD800 gas chromatograph/mass spectrometer from Thermo-Quest (Madrid, Spain) based on a quadrupole analyzer and a photomultiplier detector and governed via MASSLAB software (also from Thermo-Quest). Analytes were separated on an HP-5-MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness), using a stationary phase of 5% phenyl–methylpolysiloxane from Supelco (Madrid, Spain). The system was operated in the constant flow mode (1 ml/min), using helium (6.0 grade, Air Liquide, Seville, Spain) as the carrier gas. The GC temperature programme was as follows: 40 °C (held 2 min), 15 °C/min to 250 °C (held 10 min). The injection port, transfer line and ion source temperature were maintained at 200, 250 and 200 °C, respectively. Mass spectra were obtained in the electron impact ionization mode at 70 eV; the mass spectrometer was operated in the selective ion monitoring mode (SIM or SIR) and sample injections were done in the split mode (split ratio 1:25). The optimum GC–MS conditions were established by using a mixture containing a concentration of 1 μg/ml of each analyte with sodium tetra-*n*-propylborate ($NaBPr_4$) and the internal standard (Et_2Hg, 0.1 μg/ml) in ethyl acetate; the injected volume was 1 μl. Each derivative compound was identified from three characteristic ions (in all cases, the

boldfaced base peaks were used for quantification): $MeHg^+$ 202, **217**, 260; $EtHg^+$ 202, 231, **274**; Hg^{2+} 202, 245, **288**.

The SPE system consisted of a Gilson Minipuls-2 peristaltic pump (Villiers-le-Bel, France) fitted with poly(vinyl chloride) tubes, two Rheodyne 5041 injection valves (Cotati, CA, USA), PTFE tubing of 0.5 mm i.d. for coils and a laboratory-made sorption column packed with C_{60} fullerene. The column was constructed by packing a PTFE column of 30 mm × 3 mm i.d. with 80–160 mg of sorbent; small cotton plugs were used on both ends to prevent packing losses. An Omnifit 3303 PTFE filter (chamber inner volume, 100 μl; filtration area, ca. 3 cm^2) furnished with a paper disk (Whatman no. 1) was also used whenever filtration was required.

2.3. Sampling procedure

The factors affecting the stability of inorganic mercury and methylmercury in environmental samples during storage were recently reviewed [10]. Both compounds can be stable in PTFE and glass containers for a longer time than in other materials. The addition of preservatives has also been proposed to prevent losses of mercury species during storage; however, the results have been controversial. In addition, samples must be stored in clean containers. Based on the foregoing all PTFE containers used in this work were cleaned by soaking in 10% (v/v) HNO_3 for 48 h, rinsing five times with water and filling with water until use. Samples were collected in opaque PTFE bottles of 1 l without headspace and placed in a portable freezer for transfer to the laboratory, where they were stored at 0–4 °C until analysis. All samples were analysed within 1 week after collection in order to avoid storage losses.

If any sample requires filtration, this should be done at the time of sampling [3] because freezing and filtration after defreezing result in the loss of both inorganic and organic mercury. Samples requiring filtration should therefore be passed through a commercial PTFE filter furnished with a paper disk (Whatman no. 1) before they are frozen.

2.4. Speciation procedure

The flow system used in the speciation method is depicted in Fig. 1. Volumes of 50 ml of standards or water samples containing 0.2 and 50 ng of mercury species in 0.2 M acetate–0.4 M acetic acid buffer at pH 4.5 were fed into the system and merged with the chelating reagent (3.5×10^{-3} M NaDDC). Chelates were immediately formed in the reaction coil (150 cm long) and retained on the sorbent column (160 mg of C_{60}) located in the loop of the preconcentration valve (IV_1) while the sample matrix was sent to waste. After preconcentration, an air stream was passed through the column at 5.0 ml/min for 30 s in order to remove residual aqueous phase from the column and connections. Simultaneously, the loop of the elution valve (IV_2) was filled with 200 μl of ethyl acetate (eluent) containing the derivatizing reagent (1.8×10^{-2} M $NaBPr_4$) and diethylmercury (0.1 μg/ml) as internal standard. The extract was collected in an Eppendorf vial an allowed to settle for 7.5 min to ensure complete derivatization. Finally, 1 μl of the extract was injected into the GC–MS system. The C_{60} column was flushed with 200 μl of *n*-hexane and 200 μl of methanol after each working day.

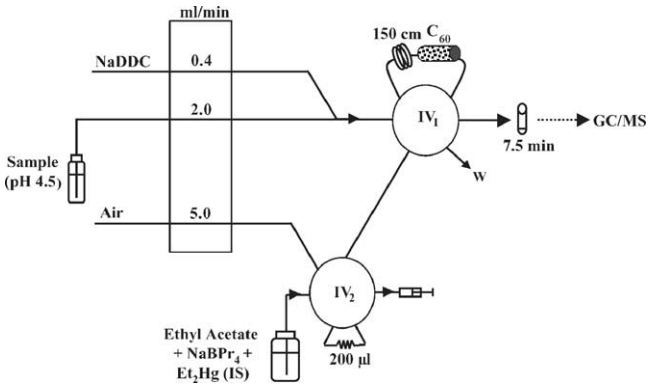

Fig. 1. Continuous-flow manifold for the preconcentration/derivatization of inorganic mercury and organomercury compounds in water. IV = Injection valve; W = waste; GC/MS = gas chromatograph–mass spectrometer.

3. Results and discussion

3.1. Optimisation of the SPE system

In previous work we developed an SPE system for the extraction of organolead compounds in rainwater [23]. The previously reported system, similar to that depicted in Fig. 1, was initially used to examine the effect of the sample pH and select the most suitable sorbent, eluent and derivatizing conditions. For this purpose, further tests were carried out by aspirating 10 ml of ultrapure water containing a 1 ng/ml concentration of each species (Hg^{2+}, $MeHg^+$ and $EtHg^+$) into the SPE unit. A column packed with 80 mg of C_{60} fullerene was also employed.

The first variable studied was the sample pH as the retention of species on the sorbent depends on the formation of neutral chelates (with a 3×10^{-3} M NaDDC solution), which was only possible if the complexation reaction was favoured over the hydrolysis of the organomercury compounds. The effect of pH on chelate sorption was different in each case; thus, sorption was maximal at pH 1–7 for Hg^{2+} and 4–7 for organomercury compounds. Formation of the inorganic chelates prevailed over protonation of the ligand, NaDDC, below pH 1 as a result of the high sortion constant for fullerene. On the other hand, the signal for alkylmercury species decreased below pH 4 as the likely result of the hydrolysis of the alkymercury species to Hg^{2+}; this was confirmed by the fact that the peak area for Hg^{2+} increased with decreasing peak area for organic mercury. In addition, the signals for all compounds were lower under alkaline conditions, probably as consequence of the precipitation of HgO. Because $MeHg^+$ was the most toxic species, the method was optimized for its determination; thus, the sample pH

was adjusted to 4.5 with sodium acetate–acetic acid buffer. The buffer concentration had not effect, so a 0.4 M acetic acid–0.2 M sodium acetate buffer (pH 4.5) was selected for further testing. Compared to conventional liquid–liquid extraction [11,12] or SPE [6,7,13], the optimum pH range of the proposed method was fairly narrow (4.5–6.0) for most of the species studied; back-extracting the mercury species from the benzene or toluene phase to an aqueous phase for cleaning and preconcentration and eluting with 2 M HCl from sorbents prior to manual extraction provided low recovery and precision, and was time-consuming. The use of C_{60} fullerene as sorbent circumvented these shortcomings.

The most common complexing agents for mercury compounds include ammonium pyrrolidine dithiocarbamate (APDC) and NaDDC. Both reagents were tested, at a 3×10^{-3} M concentration and their performance compared. NaDDC provided a slightly increased peak area, so it was selected for further work. The concentration of NaDDC used was found to have no effect over the range 1×10^{-3} to 6×10^{-3} M; a concentration of 3.5×10^{-3} M was selected to ensure the presence of an adequate excess of complexing agent to avoid potential interferences of other metals present in real water samples.

Organic solvents of variable polarity (viz. *n*-hexane, ethyl acetate and methanol) were tested as eluents; all were supplied with an identical amount of $NaPBr_4$ (the derivatizing reagent). A volume of 10 ml of a standard solution containing 1 ng/ml of each compound at pH 4.5 was passed through the sorbent column; after retention, the column was dried with air (30 s) and the retained chelates eluted with 200 μl of eluent (propelled by an air stream) as depicted in Fig. 1. Ethyl acetate and methanol were found to be more effective eluents for these compounds (the average efficiency was ca. 100%) than was *n*-hexane (average efficiency ca. 65%); ethyl acetate was selected as eluent as it was more selective and less toxic than methanol (and also immiscible with water). The effect of the volume of eluent (ethyl acetate) was studied over the range 100–300 μl; obviously, the desorption efficiency increased with increasing eluent volume, which also increased analyte dilution, however; an injected volume of 200 μl was chosen. Concerning the derivatizing reagent, $NaBPr_4$ was selected on the grounds of the satisfactory results previously reported in literature [21] for inorganic and organomercury compounds (it effectively discriminated Hg^{2+} and $EtHg^+$). Concentrations over the range 0.9×10^{-2} to 2.4×10^{-2} M were evaluated [25]. The peak area increased with increasing concentration of derivatizing reagent up to 1.8×10^{-2} M; a solution of 1.8×10^{-2} M $NaBPr_4$ in ethyl acetate was selected as eluent/derivatizing reagent. The reaction time was also varied by allowing the vial contents to stand for 5–20 min. Quantitative derivatization of all compounds was achieved within 7.5 min, beyond which the signal decreased as a result of the volatile derivatives reaching the headspace of the Eppendorf vial.

The sample and reagent flow rates were set at 2.0 and 0.4 ml/min, respectively, to avoid sample dilution. Formation of the chelates was instantaneous, so the length of the reaction coil was not a significant variable; the range studied was between 50 and 250 cm, and the signal remained constant above 150 cm (selected value). The flow rate of the carrier (air) was also especially relevant in this case as the carrier was use not only to lead the eluent/derivatizing reagent through the sorbent column, but also to remove residual water from the system tubing. This variable had no effect between 2.0 and 6.0 ml/min, so a flow rate of 5.0 ml/min was adopted.

Table 1
Figures of merit for the speciation of Hg^{2+}, $MeHg^+$ and $EtHg^+$

	Hg^{2+}	$MeHg^+$	$EtHg^+$
Retention time (min)	8.66	6.05	7.74
m/*z*[a]	288	217	274
Detection limit (ng/l as Hg)[b]	1.0	1.5	1.5
Linear range (ng/ml as Hg)[b]	0.003–0.8	0.004–1.0	0.004–1.0
Correlation coefficient (r^2)	0.997	0.998	0.997
Precision (RSD, %)	6.3	7.0	7.6

[a] *m*/*z* quantitation value.
[b] Sample volume, 50 ml.

3.2. Sensitivity and selectivity of the method

A 1.1 cm × 3 mm column packed with 80 mg of C_{60} allowed up to 25 ml of sample to be preconcentrated (larger volumes caused signals to drop as a result of the chelates being eluted from the end of the column). Longer columns were used to increasing the sample breakthrough volume and hence the sensitivity. A 2.3 cm × 3 mm column containing 160 mg of C_{60} sufficed to preconcentrate up to 50 ml of sample, so it was selected for further work.

The performance and reliability of the proposed method (Fig. 1) were assessed by determining the regression equation, linear range, analyte detectability and relative standard deviation (RSD) for Hg^{2+}, $MeHg^+$ and $EtHg^+$. For this purpose, 50 ml of ultrapure water spiked with variable amounts of the mercury compounds (0.2–50 ng as Hg^{2+}) was adjusted to pH 4.5 and processed as described in Section 2.4. Detection limits were calculated as three times the standard deviation of the blank divided by the slope of each calibration graph; the lowest concentration levels used in constructing the calibration model were prepared by spiking reagent water (blank, $n = 12$) owing to the absence of background signal. The results are listed in Table 1. The precision of the method, expressed as RSD, was checked on 11 standards containing a 50 ng/l concentration of the analytes and found to be ca. 7% (within day). The C_{60} fullerene column remained serviceable for at least 6 months (e.g. 15–25 samples/day).

The influence of metals that might react with NaDDC and replace mercury in the original chelates was investigated in order to identify potential interferences. Most reported preconcentration methods have not been tested for interferences as GC methods usually employ specific atomic detectors. However, chemical interferences do not arise in the detection system, but in the previous extraction/preconcentration step,

which usually involves complexing reagents; this is equally the case with liquid–liquid extraction and liquid–solid extraction, where the metal of interest must compete with other metals (usually at higher concentrations) present in water samples. The literature about the determination of mercury species in water seemingly includes only two methods that were subjected to a rigorous study of potential interferences. In one, all mercury compounds were complexed with APDC and then preconcentrated on RP-C_{18} sorbent; the separation/determination was carried out by LC, with amperometric and coulometric detection [4]. Only Cu^{2+}, Ni^{2+} and Co^{2+}, at concentration levels similar to those of the analytes, were found to interfere. The other method used a similar preconcentration procedure and separation/determination by LC cold vapour atomic absorption spectrometry [13]; a volume of 300 ml of water at pH 6.5 was preconcentrated and none of the nine heavy metals studied (which, surprisingly, excluded the analyte mercury) was found to interfere at concentrations below 5 mg/l. Therefore, the same sorbent RP-C_{18} provided contradictory results in these two applications.

Major elements commonly encountered in waters (viz. Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) were discarded as they do not react with the chelate reagent, thus, only trace elements, such as Zn^{2+}, Fe^{3+}, Sb^{3+}, As^{3+}, Pb^{2+}, Ni^{2+}, Cu^{2+}, Sn^{2+}, Co^{2+}, $Mn^{2+}$and Cd^{2+} were studied, at concentrations up to 0.5 μg/ml. Ten of these metals was found to interfere with the determination of 0.5 ng/ml of each mercury compound (as Hg^{2+}); by exception, Sb^{3+} interfered at concentration 800 times higher than that of mercury compounds. Therefore, the proposed method is highly selective as if tolerates the metals studied at concentrations 1000 times higher than those of the analytes. The increased selectivity achieved with C_{60} fullerene can be ascribed to its high specific surface area (ca. 3000 m^2/g which would allow both dissolved and precipitated chelate to be adsorbed) relative to RP-C_{18} (ca. 600 m^2/g), in addition to its high interstitial volume (which ensures more uniform distribution of the chelate throughout the column and hence readier elution). Because the other sorbent (RP-C_{18}) had a small surface area and preferentially retained the chelates of the major element to the detriment of mercury and/or its interstitial volume was lower, the chelate was not adsorbed uniformly on the minicolumn, so its subsequent elution was more difficult.

3.3. Analysis of water samples

The robustness of the proposed method was checked by performing recovery tests on various types of uncontaminated water including drinking, river, rain, sea and waste water (no certified reference material was available). Each type of water was spiked with variable amounts of Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ at low (0.05 ng/ml), medium (0.1 ng/ml) and high (0.5 ng/ml) concentrations. River and waste water were filtered after spiking. Each type of water was spiked three times at each of the three levels (n = 9) and then analysed using the proposed SPE method (two GC–MS determinations were made on each replicate). All compounds were determined with average recoveries of 85–95 for Hg^{2+} and $EtHg^{+}$, and 80–95% for $MeHg^{+}$ (waste water provided the lowest recoveries for all compounds, probably as a result of the presence of organic matter). In addition, sea water provided higher recoveries (98–105%) owing to the saline effect. For application to sea water, the influence of saline solutions on the retention of mercury compounds on C_{60} fullerene was examined by using synthetic sea water the composition of which, according to the specifications [26] was 27.9 g/l NaCl, 1.4 g/l KCl, 2.8 g/l $MgCl_2$, 0.5 g/l NaBr and 2.0 g/l $MgSO_4$. A synthetic and an uncontaminated sea water spiked with 0.05, 0.1 and 0.5 ng/ml of each mercury species provided similar signals. Therefore, the method can be applied to sea water, albeit with recoveries slightly higher than 100%.

Table 2
Determination of mercury compounds (expressed as Hg) in water by SPE–GC–MS

Compound	Concentration found ± S.D. (ng/l)[a]			
	River 1	River 2	Sea	Waste
Hg^{2+}	100 ± 7	140 ± 9	120 ± 8	200 ± 14
$MeHg^{+}$	<4	<4	60 ± 4	14 ± 1
$EtHg^{+}$	<4	<4	70 ± 5	<4

[a] n = 3; 95% confidence level.

Recently reported estimates of total mercury in natural waters range from 0.2 to 100 ng/l, whereas $MeHg^{+}$ levels are much lower (ca. 0.05 ng/l) [10]; higher values can be found in water from heavily industrialized areas. The European Community has also included total mercury on the list of 33 priority pollutants of waters and established an MCL of 1 μg/l for total mercury in drinking water [27]; the detection limits of the proposed method (i.e. 1.5 ng/l) are adapted according to current guidelines.

The proposed method was applied to the determination of Hg^{2+}, $MeHg^{+}$ and $EtHg^{+}$ in various types of water including four drinking, five river, two rain, four sea and five waste water samples. First, a volume of 50 ml of each sample at pH 4.5 was aspirated into the SPE system (using a sorbent column with 160 mg of C_{60} fullerene); then, the analytes were eluted with 200 μl of eluent (preconcentration factor, 250) to ensure the highest possible sensitivity. Of the 20 water samples studied, only two river, one sea and one waste water sample were found to contain mercury compounds at concentrations above 4 ng/l (the quantification limit). The results are listed in Table 2. As can be seen, organomercury compounds were undetected or found at the lowest levels, probably because they were degraded to inorganic mercury in the environment.

4. Conclusions

From the foregoing it follows that C_{60} fullerene is an effective sorbent material for preconcentrating mercury compounds, also, it is preferable to the conventional sorbent RP-C_{18} on account of its large specific surface area and

volume, which endow it with an increased physical sorption capacity. The SPE manifold used minimizes evaporation of the derivative compounds as it is a closed system. The proposed GC–MS method is less sensitive than is GC with atomic or analytical plasma detection methods (viz. microwave-induced plasma atomic emission spectrometry, inductively coupled plasma mass spectrometry); despite its lower sensitivity, GC–MS is intrinsically the most specific option: organometallic compounds can be detected in their molecular chemical forms upon derivatization. Moreover, the analytes can be identified not only from their retention time, but also on the basis of distinctive features of their fingerprint mass spectra. In addition, the interface between the gas chromatograph and the detector is simpler for MS than for other hyphenated techniques [6].

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