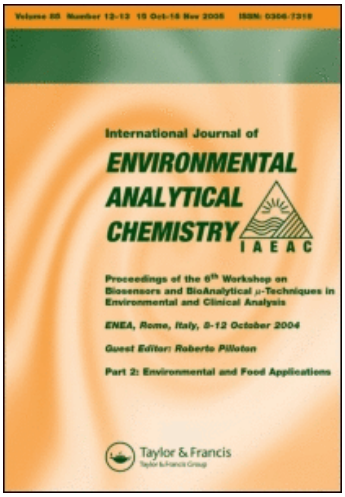

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Coupling Pervaporation-Gas Chromatography for Speciation of Volatile Forms of Selenium in Sediments

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COUPLING PERVAPORATION-GAS CHROMATOGRAPHY FOR SPECIATION OF VOLATILE FORMS OF SELENIUM IN SEDIMENTS

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A method for speciation of dimethylselenide (DMeSe), dimethyldiselenide (DMeDSe) and diethylselenide (DEtSe) in sediments based on a coupling between a pervaporation module, a preconcentration sorptive trap and a gas chromatograph-mass spectrometer is reported. The coupling is performed through a high pressure injection valve which allows two different operational modes: (a) analysis without preconcentration, in which analytes are directly driven from the pervaporation chamber to the injection port of the chromatograph, and (b) analysis with preconcentration in a trap, in which the analytes from the pervaporation chamber are first trapped on a Tenax minicolumn and then thermally desorbed and driven to the GC. This second approach improves the sensitivity compared to the direct coupling, reaching estimated absolute detection limits lower than 0.6 ng Se for each tested species. The method is applied to the determination of volatile organic selenium species in several sediments collected from different areas in the Southwest of Spain.

Keywords: Selenium volatile compounds; pervaporation; gas chromatography; mass spectrometry; sediments

INTRODUCTION

Although the organic species of selenium are less toxic than the inorganic ones[1], they can be easily absorbed by human producing serious diseases. However, methylation can be an effective detoxification mechanism. There is evi-

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dence of the production of volatile organic species of selenium, mainly dimethylselenide (DMeSe) and dimethyldiselenide (DMeDSe) from inorganic selenide salts, as well as from selenocystine and selenomethyonine by fungi, plants and animals in the environment[2,3], and DMeSe has also been found at levels ranging from 0.08 to 0.98 $\mu g\ m^{-3}$ in human breath[4]. As a consequence analytical methods for the chemical speciation of volatile selenium compounds in environmental samples are necessary.

Volatile organic selenides[5] have been analyzed by gas chromatography, especially in air samples, which were directly injected into the chromatograph or trapped on a sorbent for subsequent desorption by both solvent elution and temperature programming of the trap. A number of coupled GC-AAS systems with a previous purge and trap isolation technique have also been proposed for DMeSe, diethylselenide (DEtSe) and DMeDSe[3,6]. Jiang et al.[7], using GC-GF-AAS, determined up to 0.1 ng of DMeSe and DEtSe and 0.2 ng of DMeDSe. The same detection limit (0.1 ng) was achieved by Chau et al.[8], for both DMeSe and DMeDSe, using GC-QF-AAS. Cutter[9] could determine up to 0.5 ng of DMeSe and DMeDSe using HG-QF-AAS with an air-hydrogen flame. Lower detection limits have been obtained for DMeDSe (0.015 ng) and for DEtDSe (0.012 ng) using GC-AES[10].

The proposed methods for the determination of volatile compounds in solid samples usually involve gas chromatography coupled with dynamic[11–16] or static[17–21] headspace. However, these techniques present several drawbacks. The dynamic headspace technique, adopted by the US Environmental Protection Agency, USEPA, for solid samples[22] does not agree with the quality targets for environmental measures. Hiatt[23] mentioned that the EPA methods are unacceptable because of providing low recoveries of the spiked analytes in fish and sediment samples. Others reports[24,25] confirmed that the recoveries for sediment samples could be improved using elevated temperatures and long purge times. The difficulty for applying the static headspace methods to soil samples lies in the unfavorable partition equilibrium of the analytes between the sample matrix and the gas phase, since the sampled amount is a function of the gas/matrix partition coefficient of the sample. The method can be calibrated for selected matrices but it is hardly applicable for the most environmental samples with a high organic matter content[26].

The aim of this work was the optimization of methods for the extraction, based on pervaporation, of DMeSe, DMeDSe and DEtSe from sediments, using GC-MS for speciation.

EXPERIMENTAL

Standard solutions and reagents

The solvents used in the experiments were pesticide grade 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.

Organoselenium stock solutions were prepared at a concentration of 500 mg l^{-1} (as Se) in pentane from DMeDSe (Aldrich, Gillingham, Dorset, UK), DEtSe and DMeSe (Pfaltz and Bauer, Waterburg, CT). Intermediate solutions were prepared by dissolving appropriate volumes of stock solutions in 1 ml of methanol and bringing the volume to 50 ml with water. Working solutions were daily prepared by dilutions of the intermediate solutions with water.

Instrumentation

The two different approaches for the extraction of the organic selenium species from sediments are shown in Figure 1. They consisted of a high pressure injection valve (Análisis vínicos, Ciudad Real, Spain), the unit of pervaporation (home-made device) and the GC-MS (Varian Ibérica, Barcelona, Spain) and differed in the presence of a purge and trap system for preconcentration.

The pervaporation module consisted 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 membrane, 40 mm diameter and 1.5 mm thickness, 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. The two chambers were aligned with the membrane support using two metallic bars. The whole module was placed between two aluminum supports and four long screws closed the system tightly.

Selenium species analyses were carried out using a Varian 3800 gas chromatograph coupled to a Varian Saturn 2000 mass detector via a capillary direct inlet. Selenium species were separated on a fused-silica capillary column, 25 m×0.20 mm I.D. with a film thickness of 0.33 μm HP-1 crosslinked methylsilicone gum.

Injection was performed in splittless mode (purge time = 0.5 min off). Helium was used as carrier gas at a head pressure of 100 kPa (14.5 p.s.i.) resulting in a flow-rate between 0.5 and 1 ml min^{-1}. The interface temperature was kept at 260°C. Electron impact (EI) ionization mass spectrometry was used for detec-

tion. A scan time of 1.0 s was used over a mass range from 40 to 220 *m/z*. The electron multiplier was set at autotune value; the emission current at 0.4 mA and the electron energy at 70 eV. Mass calibration of the GC-MS was performed with perfluorotributylamine. Data were stored as total ion chromatogram (TIC) and quantification was performed by using SIM (single ion monitoring) mode.

Purity of the organoselenium standards

The purity of the individual compounds was evaluated by gas chromatography-mass detection. The chromatographic determination of each compound showed the presence of only one peak, whose nature was confirmed by the fragmentation pattern[5,8]. The characteristic fragments were as follows: for dimethylselenide, base peak and the molecular ion at *m/z* 110; for dimethyldiselenide, base peak and the molecular ion at *m/z* 188; for diethylselenide, molecular ion at *m/z* 138 and base peak at *m/z* 110.

In addition, the total selenium content in each standard was checked by flame AAS after an acid digestion method and by using a 1000 mg l^{-1} inorganic selenium Titrisol standard (Merck) for calibration. A suitable portion (10 µl) of each organoselenium compound was digested with 2 ml of concentrated nitric acid and diluted to 10 ml[8]. Purities of 97±3 %, 98±2 % and 98±3 % were assessed for dimethylselenide, dimethyldiselenide and diethylselenide, respectively.

Procedure

Extraction without preconcentration (Fig. 1A)

A defined amount of sample (5 g) was weighed in the lower chamber of the pervaporation module putting a spacer between this compartment and the membrane support in order to leave some distance between the sample surface and the membrane. The module was closed after placing the membrane and the upper chamber. The analytes and the internal standard were injected in the lower compartment via the injection port using a syringe equipped with a hypodermic needle and the mixture was stirred by a magnetic stirrer. Finally, the pervaporation module was placed in a water bath at 70 °C.

After 3 min, the three-way-valve was switched and a He stream drove the pervaporated analytes to the gas chromatograph.

Extraction with solid-phase preconcentration (Fig. 1B)

During the extraction, a N_2 stream through the upper chamber drove the analytes to the Tenax-filled sorptive column placed in an ice-water bath (0 °C). After 7

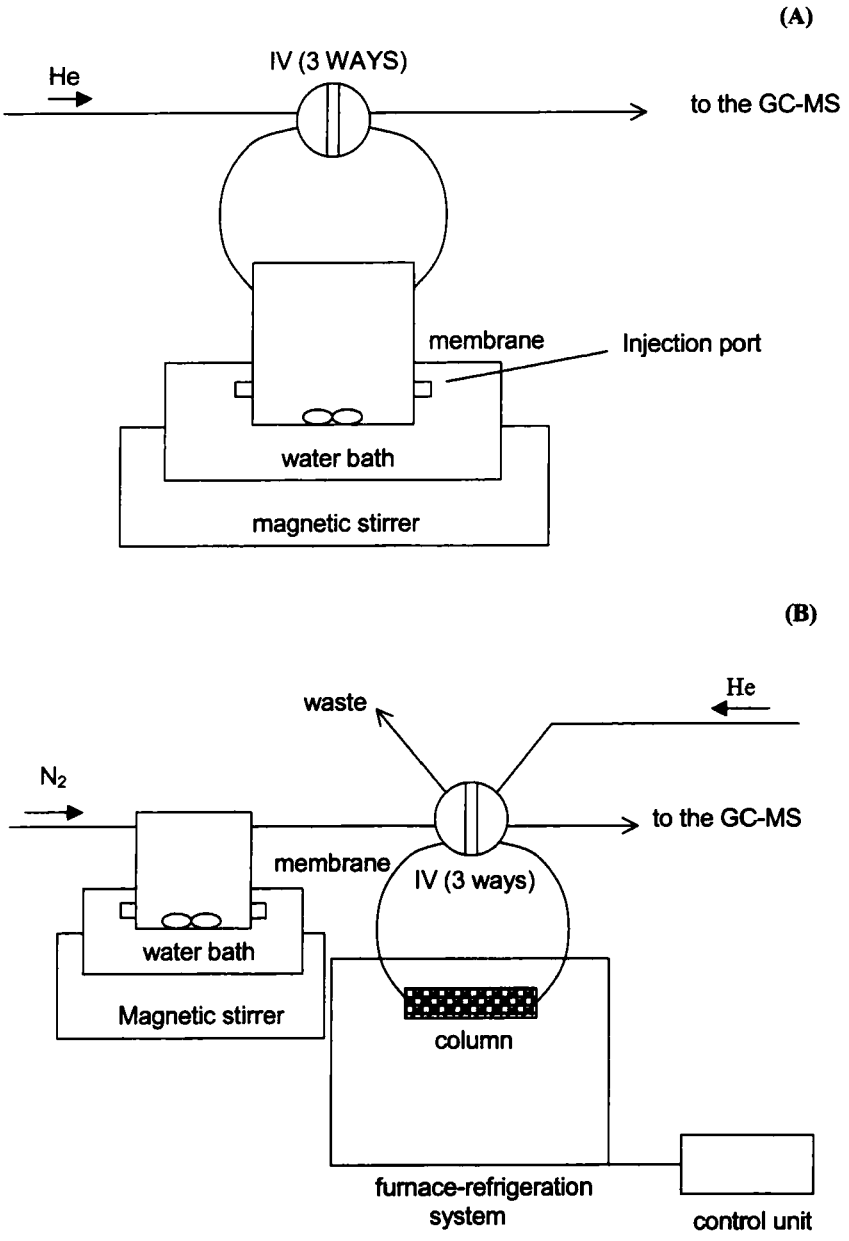

FIGURE 1 Scheme of instrumental coupling of the pervaporation module to the GC-MS. A) approach without preconcentration, B) approach with preconcentration

min, the valve was switched on, the preconcentration column was electrically heated to 150 °C and the analytes were back desorbed and drove to the gas chromatograph by an He stream for the chromatographic analysis.

RESULTS AND DISCUSSION

Chromatographic separation and choice of the internal standard

Several temperature ramps ranging from 5 to 20 °C min^{-1} were tested. The initial and the final temperatures were 35 and 250 °C. The injector was heated at 280 °C and the injection of 5 µl of the headspace of a mixture of the three organic selenium species was performed in the splitless mode (purge time, 0.5 min off). A ramp of 10 °C min^{-1} was selected as optimum since the species were base line resolved.

Several reagents were studied in order to choose the most convenient internal standard. They were checked for their retention times. 1-bromopentane was chosen as a suitable internal standard since it produced a base-line resolved peak eluting close to those of to the selenium species. Moreover, the repeatability of the measured concentration changed from more than 15% RSD to less than 7%, when the internal standard was considered for quantification.

Optimization of variables

For all the experiments, portions of 5 g of diatomaceous earth as a general solid matrix were introduced in the lower chamber and spiked with 15 ng of DMeSe, 25 ng of DEtSe and 20 ng of DMeDSe in distilled water.

Approach A

All the studied variables relevant for the extraction of the organic selenium species, and both the ranges and the optimum values are shown in Table I.

The pervaporation module was coupled to the chromatographic system and its upper compartment was introduced into the loop of the injection valve (Fig. 1A). The pervaporation process was assisted by heating the module in a water bath at temperatures ranging from 30 to 85 °C. Peak areas increased with temperature reaching a maximum at 70 °C (Table II). Higher temperatures did not improve the extraction and moreover, the precision decreased, probably due to the less stable water bath temperature.

TABLE I Optimisation of variables

Parameter	*Studied range*	*Optimum Value*
Rath temperature, °C	30 – 85	70
Preconcentration time, min[a]	0 – 10	3
Preconcentration time, min[b]	0 – 15	7
Trap temperature, °C	–75 – 25	0
Purge temperature, °C	50 – 250	150
He flow, ml min^{-1}	14 – 52	52
N_2 flow, ml min^{-1}	4 – 50	35

a. Approach A
b. Approach B

TABLE II Results obtained when the pervaporation process was assisted by heating the module in a water bath

Temperature (°C)	*Relative peak area[a] ± SD (%)*		
	DMeSe	*DEtSe*	*DMeDSe*
30	75 ± 4.0	52 ± 3.6	51 ± 4.4
40	80 ± 3.8	72 ± 4.8	70 ± 3.9
50	89 ± 5.2	81 ± 2.9	80 ± 4.5
60	98 ± 3.7	95 ± 4.1	92 ± 4.2
70	97 ± 3.9	99 ± 3.7	98 ± 4.1
80	100 ± 5.1	97 ± 6.0	100 ± 5.5
85	99 ± 5.8	100 ± 5.7	98 ± 6.6

a. Relative peak area = (peak area/maximum peak area) × 100

The time necessary to preconcentrate the analytes in the static gas volume in the upper compartment was also optimized. Signal was obtained even without preconcentration because of the high volatility of the analytes. Several preconcentration times ranging from 0 to 10 min were tested (Table I). An optimum value of 3 min was obtained and longer times did not improve the extraction efficiency.

The Figure 2A shows the chromatogram obtained for a sample spiked with 20 ng Se of each analyte and internal standard

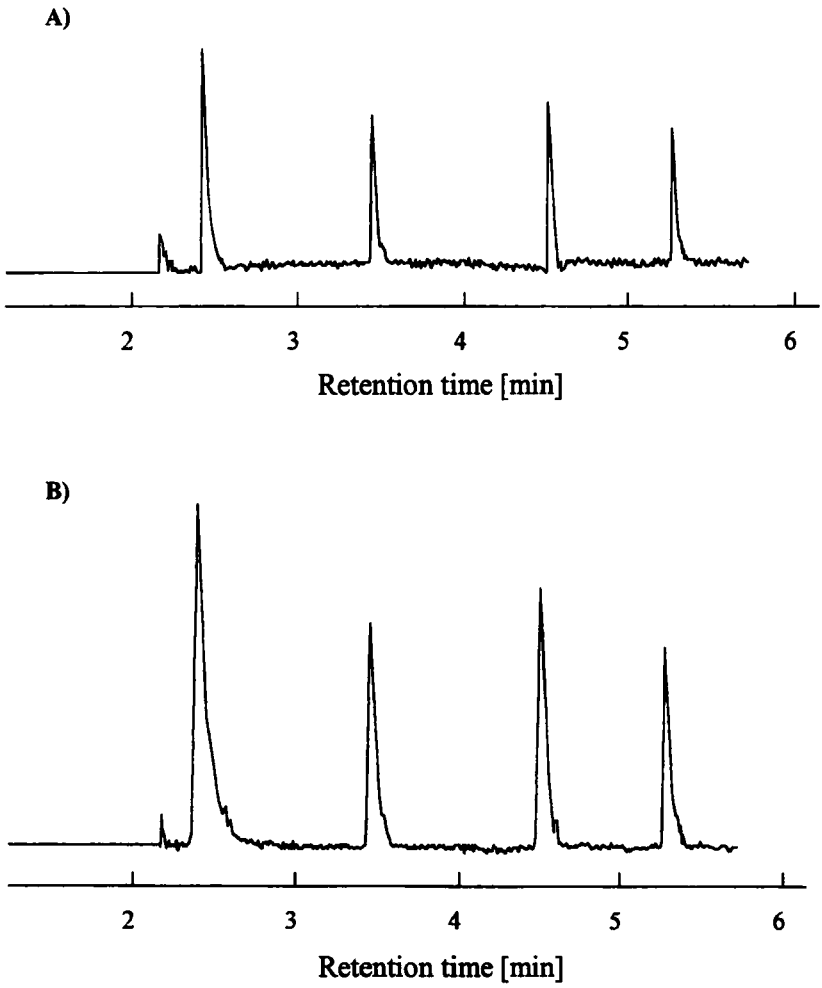

FIGURE 2 A) Chromatogram obtained for the without preconcentration method (sample spiked with 20 ng Se of each analyte). B) Chromatogram obtained for the with preconcentration method (sample spiked with 20 ng Se of each analyte)

Approach B

N_2 flows ranging from 4 to 50 ml min^{-1} for 10 min were tested in the pervaporation chamber heated at 70 °C. The sorbent trap was initially kept at 0 °C and desorption was performed at 200 °C with He at 52 ml min^{-1}. The flow control was performed with a needle valve placed in the tubing system, which regulated the gas flow from the N_2 cylinder. Results are shown in Table III. An optimum value

of 35 ml min^{-1} was selected. Lower flow rates did not completely transfer the analytes to the trap and higher flow rates did not allow them to be sorbed.

TABLE III Results obtained with different N_2 flows

N_2 flow rate (ml min^{-1})	Relative peak areas[a] ± SD (%)		
	DMeSe	DEtSe	DMeDSe
4	79 ± 4.0	48 ± 3.4	54 ± 3.5
10	87 ± 3.8	70 ± 4.2	73 ± 4.6
20	97 ± 4.9	80 ± 2.9	81 ± 3.9
30	98 ± 3.7	97 ± 4.7	96 ± 5.1
35	97 ± 3.9	100 ± 4.1	98 ± 3.7
40	100 ± 4.3	94 ± 5.2	100 ± 3.8
50	90 ± 5.6	87 ± 4.6	92 ± 5.7

a. Relative peak area = (peak area/maximum peak area) × 100

Preconcentration times in the Tenax column from 0 to 15 min were tested. The highest peak areas were obtained for 7–10 min, and a value of 7 min was selected as optimum.

In order to optimize the trap temperature, three different alternatives were assayed. The preconcentration column was submerged in either a CO_2(s)/ethanol bath (about −75 °C), an ice/water bath (about 0 °C) or was let at room temperature (about 25 °C). It could be noticed that the same peak areas were obtained in the first two cases while the area was lower in the third case, therefore the cheapest option, the second one, was chosen as optimal.

The temperature for the desorption was studied between 50 and 250 °C and the signal increased with the temperature up to a final constant value above 150 °C, this value being taken as optimal. In order to find the best value for the He flow the range between the minimal and the maximal flows with which the column pressure was stable (50–250 ml min^{-1}) were studied and it was concluded that the highest flow produced the largest peak areas.

The Figure 2.B shows the chromatogram obtained for a sample spiked with 20 ng Se of each analyte and internal standard using the described preconcentration procedure.

Features of the method

In order to check the efficiency of the pervaporation, the preconcentration and the desorption systems, a calibration corresponding to each studied species was

performed by direct injection into the chromatograph. These were compared to those obtained injecting the standards in the pervaporation module and using both approaches without and with preconcentration (Table IV).

TABLE IV Features of the pervaporation method

Analyte	*Linear range (ng Se)*	*Sensitivity (calibration slope)*	*r*	*Detection limit (ng Se)*
A) Without preconcentration approach				
DMeSe	<72	76.4	0.996	2.8
DMeDSe	<71	181	0.997	3.3
DEtSe	<96	78.2	0.995	2.9
B) With preconcentration approach				
DMeSe	<32	98.2	0.998	0.3
DMeDSe	<40	246	0.999	0.5
DEtSe	<51	112	0.998	0.6
C) Features of the direct injection method				
Analyte	*Linear range (ng Se)*	*Sensitivity (calibration slope)*	*r*	*Detection limit (ng Se)*
DMeSe	<41	95	0.998	0.5
DMeDSe	<37	253	0.998	0.5
DEtSe	<61	106	0.997	0.7

A careful selection of the solvent must be considered in order to avoid its coelution with the analytes. Therefore, several solvents were tested by injecting 5 µl aliquots of their headspace. None of the tested solvents could be used for all the analytes and therefore two calibration curves from organoselenium standard solutions in *n*-pentane (for DMeSe and DEtSe) and *n*-decane (for DMeDSe) were constructed (Table IV). The precision was improved by using 1-bromopentane as internal standard, which was added to the sample via the injection port. The detection limits were computed as [3×standard deviation of the mean +the value for the mean standard blank], for n=7 standard blanks runs.

Aliquots of 1 µl were injected into the chromatograph and analyzed by GC-MS. The calibration curves were linear for selenium amounts (as elemental Se) less than 41 ng (correlation coefficient, r = 0.998) for DMeSe, 61 ng (r = 0.997) for DEtSe and 37 ng (r = 0.998) for DMeDSe. The detection limits

were estimated to be 0.5 ng, 0.7 ng and 0.5 ng for DMeSe, DEtSe and DMeDSe, respectively. The sensitivities (slope of the calibration curve) were 95.3±3.1, 106±3.3 and 253±4.3 μg^{-1} of Se for DMeSe, DEtSe and DMeDSe, respectively. The solutions were analyzed at least five times with relative standard deviation lower than 8% when peak height was used. The relative standard deviation of the detector was usually lower than 5% when using peak area. For this reasons peak area was used throughout.

The calibration curves using the approach without preconcentration (Table IV A) obtained by using standards at five different concentrations (in three replicates each one) were linear for selenium (as elemental Se) amounts less than 72 ng (r = 0.996) for DMeSe, 96 ng (r = 0.995) for DEtSe and 71 ng (r = 0.997) for DMeDSe. The detection limits were estimated to be 2.8 ng, 2.9 ng and 3.3 ng for DMeSe, DEtSe and DMeDSe, respectively. The sensitivities (slope of the calibration curve) obtained by this method were 76.4±2.5, 78.2±4.3 and 181±5.2 μg^{-1} of Se for DMeSe, DEtSe and DMeDSe, respectively. Reproducibilities of better than 9% were obtained by analysis of five samples spiked with 20 ng of each organoselenium species in different days.

The calibration curves using the approach with preconcentration (Table IV B) obtained by using standards at five different concentrations (in three replicates each one) were linear for selenium (as elemental Se) amounts less than 32 ng (r = 0.998) for DMeSe, 51 ng (r = 0.998) for DEtSe and 40 ng (r = 0.999) for DMeDSe. The estimated detection limits were 0.3 ng, 0.6 ng and 0.5 ng for DMeSe, DEtSe and DMeDSe, respectively. The sensitivities (slope of the calibration curve) achieved by this method were 98.2±2.7, 112±3.7 and 246±3.9 μg^{-1} of Se for DMeSe, DEtSe and DMeDSe, respectively. Reproducibilities of less than 7% were obtained by analysis of five samples spiked with 20 ng of each organoselenium species in different days.

Comparative values were obtained for the features of the direct injection method (Table IV.C) and the preconcentration pervaporation method. 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 limits.

Application to natural samples

The proposed method was validated studying recoveries in spiked samples since to our knowledge, no reference materials for volatile organic selenium species

are currently available. Five sediments and a sewage sludge collected from areas of Southwest Spain were selected as representative environmental samples. However, levels in all the sediments were below the detection limit. Two possible reasons supporting these results were the absence of bioalkylation microorganisms in the sediments and the normally high temperatures in the Southern Spain summer (higher than 35 °C) which may cause volatilization of the alkylselenides. However, DMeSe at a maximum concentration of 1 ng g^{-1} and DMeDSe at a maximum concentration of 2.1 ng g^{-1} have been evaluated in sediment samples of different locations of a river in Germany[27].

Therefore, recovery experiments were carried out on these samples, which were spiked with 15 ng of DMeSe, 25 ng of DEtSe and 20 ng of DMeDSe. Results were obtained by external calibration and are summarized in Table V. Recoveries were higher than 83% for all the organic selenium species.

CONCLUSIONS

Pervaporation can be used for the determination of volatile analytes in complex samples, since there is no contact between the sample and the membrane. In this way, a possible obstruction in the pores of the polymer is prevented.

The main advantages of the method proposed here, as compared to the dynamic and static headspace methods, is the fact that it can be easily automated with a minimum equipment investment and maintenance, as well as better recoveries and repeatability. In comparison to the static mode, the analysis time decreases, since it is not necessary to reach equilibrium conditions.

Comparing to the purge and trap mode, the two main advantages here proposed are the following: On the one hand, with pervaporation the removal of water vapor is unnecessary, since the water does not pass through the hydrophobic membrane. On the other hand, the sample can be introduced in the separation module in an automatic way, continuously or by injection.

The number of methods proposed for volatile organoselenium compounds in sediment samples is scarce, because of the transfer of this compounds to the atmosphere which reduces their presence in natural solid samples and makes sensitive speciation procedures with preconcentration stages necessary.

TABLE V Application to spiked natural samples[a]

Sample	DMeSe			DMeDSe			DEtS		
	Added (ng Se)	Found (ng Se)	Recovery, % (RSD,%)b	Added (ng Se)	Found (ng Se)	Recovery, % (RSD,%)[b]	Added (ng Se)	Found (ng Se)	Recovery, % (RSD,%)[b]
Tinto river		14.2	94.6 (4.6)		22.0	110 (3.4)		25.3	101 (5.3)
Ayamonte city		13.0	86.7 (4.8)		19.1	95.5 (4.1)		26.2	105 (4.1)
Portil boatyard		16.1	107 (5.1)		18.7	93.5 (3.8)		23.5	94.0 (3.4)
Portil lake	15	15.2	101 (4.3)	20	19.0	95.0 (5.1)	25	24.3	97.2 (3.0)
Rompido boatyard		13.1	87.3 (3.9)		20.9	104 (4.0)		23.7	94.8(4.6)
Puntaumbria boatyard		16.3	108 (3.2)		16.6	83.0 (3.9)		22.3	89.2(1.9)

a. Results obtained using the pervaporation module with preconcentration in column.
b. n = 3.

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