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On-line coupling of equilibrium-sorptive enrichment to gas chromatography to determine low-molecular-mass pollutants in environmental water samples

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Abstract

On-line combination of equilibrium sorptive enrichment and gas chromatography is used for the analysis of a group of pollutants varying widely in polarity and volatility in aqueous samples at trace levels. For the ESE process open-tubular traps were used. The newly developed hyphenated method shows a high sensitivity for all the compounds under study. The detection limits were typically between 0.1 and 1 μg/l. The sample volumes required for the compounds to reach equilibrium with the stationary phase are in the range of 20 ml for the aromatic hydrocarbons included in the study (benzene, toluene and *p*-xylene), to 200 ml for epichlorohydrin and dichlorohydrin. Within- and between-day precision of the absolute peak areas varied between 3 and 16%. The performance of the new method was tested by the analysis of different environmental water samples.

Keywords: Water analysis; Environmental analysis; Equilibrium sorptive enrichment; Sample preparation; Benzene; Toluene; Xylenes; Ethoxyethanol; Epichlorohydrin; Dichlorohydrin; Amines

1. Introduction

The analysis of organic contaminants in water samples by gas chromatography (GC) is complicated by a number of problems. One of them is the low concentration level at which these compounds are present in the water. In addition to this, water transfer onto the GC column has to be avoided.

In order to overcome the above mentioned complications, several methods for water analysis by GC have been developed. Most of these methods are based on phase-switching. In phase-switching methods the analytes are transferred from a large volume of water to a small volume of an organic solvent that is eventually introduced into the GC system [1,2]. The most common methods for phase switching are liquid–liquid extraction (LLE) [3–5] and solid-phase extraction (SPE) [6–8]. SPE is nowadays preferred to LLE because it minimizes or eliminates some of the drawbacks of LLE such as the need to use large amounts of organic solvents. Moreover, SPE is easier to automate and can be coupled on-line to both LC and GC [9–15]. Unfortunately, SPE also has some limitations. In particular in the analysis of polar solutes the breakthrough volumes and the capacity of

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the cartridge can be too low to meet the required detection limits.

In recent years, the general trend is to replace conventional sample preparation techniques, such as the above mentioned LLE or SPE, by more environmentally beneficial and less laborious methods. Different solvent-less extraction techniques have been applied such as the recently developed solid-phase microextraction (SPME) technique [16,17] or methods using open-tubular trapping (OTT) columns for the extraction step [2,18–23].

OTT columns for pretreatment of aqueous samples consist of a short length of a column coated with a thick film of a GC stationary phase. The main advantage of using these columns for extraction is that the residual water remaining in the column after sampling can be rapidly and completely removed by simply purging a short plug of gas through the capillary enrichment column. Another advantage of OTT is the high inertness of the trap.

When OTT columns are used for water enrichment, the water sample is pumped through the column where the components are retained. Retention of the analytes from the water is based on partitioning into the stationary phase [2,24]. The micropollutants retained in the OTT can be either solvent extracted with a small volume of a suitable solvent [2,21–23] or can be thermally desorbed [20]. The last approach is a truly solvent-free sample preconcentration technique. The first method uses a small volume of an organic solvent.

In this paper a novel approach for sample enrichment of aqueous samples using OTT columns is described, the equilibrium sorptive enrichment (ESE) technique. This technique was originally developed for the enrichment of air samples [25–27]. In the present work it is applied to aqueous samples. In this new method, sampling of the aqueous sample through the OTT column is continued until all analytes have reached equilibrium with the stationary phase. In this way, maximum enrichment can be obtained for each analyte. With this new sample enrichment technique, a homogeneously enriched sample is generated and any part of it is representative for the entire sample thereby enabling reproducible injection into the GC system and eliminating the need to transfer the entire sample to the analytical column. If sensitivity permits, only a time-slice of the enriched sample is transferred to the column and the use of a cryogenic refocusing step is no longer necessary.

The aim of this paper is to explore the use of OTT columns in the ESE technique for the extraction from water samples of different compounds covering a wide range of polarities. The scope of the work is to establish a rapid, simple and solvent-less alternative to traditional methods for sample preparation of aqueous samples.

2. Experimental

2.1. Reagents and standards

Methanol, HPLC grade, was purchased from Merck (Darmstadt, Germany). Deionized water was prepared using a Milli-Q water purification system (Millipore, Bedford, MA, USA). Benzene, toluene and *p*-xylene (BTX) were obtained from Merck and were of >99% purity. A BTX mixture of 100 mg/l each was prepared in methanol. This solution was used to prepare dilute solutions and to spike water samples to the required concentrations. 2-Ethoxyethanol (oxitol), epichlorohydrin and dichlorohydrin and the amine compounds studied, ethylamine, pentylamine and hexylamine, were also purchased from Merck. Each of these compounds was first diluted in Milli-Q water to a concentration of 100 mg/l and then these solutions were used to spike water samples to different concentration levels.

2.2. Equipment

A schematic diagram of the instrumental set-up used for the experiments is shown in Fig. 1. The instrument partly resembles that used in previous work for equilibrium enrichment of air samples [27]. The GC instrument used for the chromatographic separations was a Varian 3400 GC (Sunnyvale, CA, USA) equipped with a flame ionisation detection (FID) system. The FID system was operated at 250°C. The chromatographic column was a CP Wax 52 CB capillary column (Chrompack, Middelburg, The Netherlands) of 21 m×0.25 mm I.D. with a film thickness of 0.22 μm. CLASS VP data acquisition

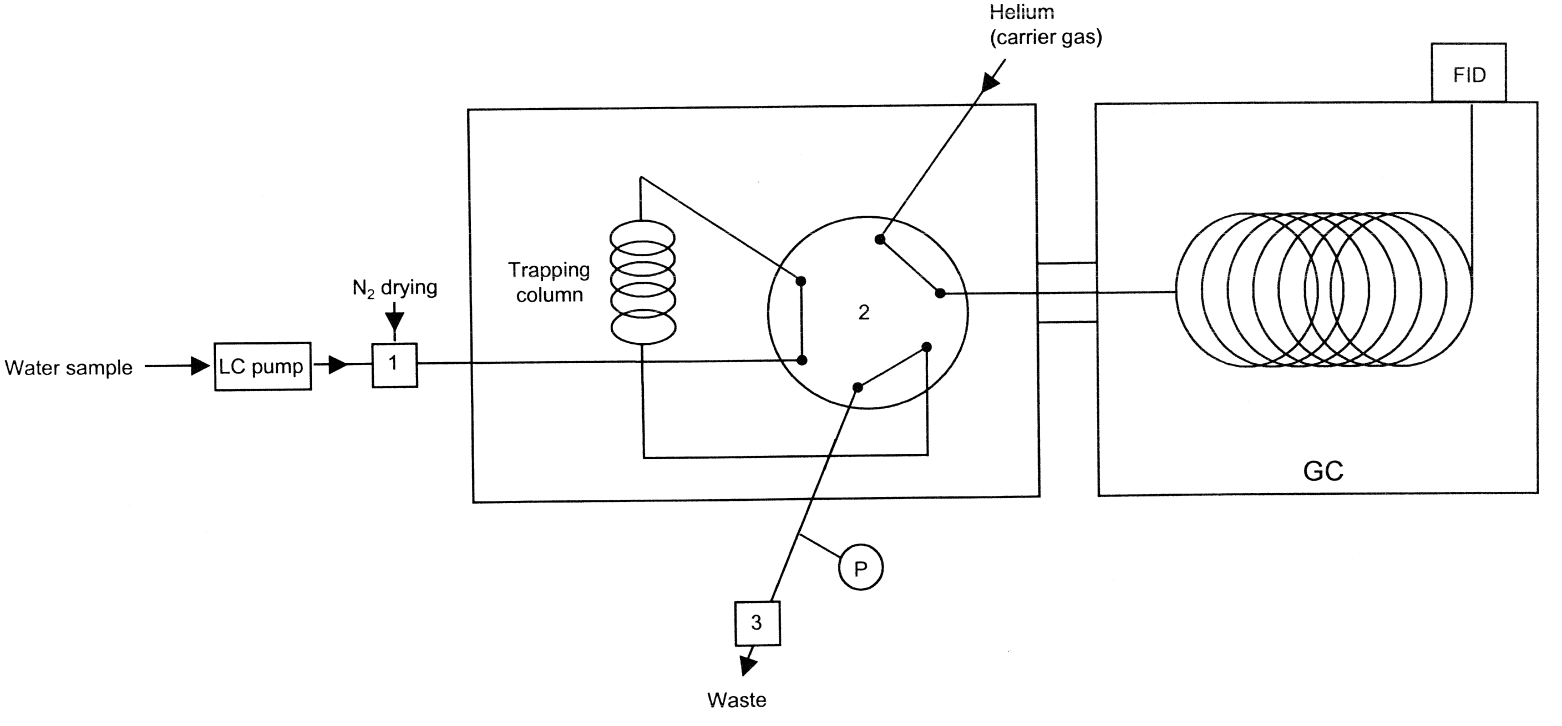

Fig. 1. Schematic diagram of the set-up used for the experiments. (1) Three-way flow selection valve (2) six-port switching valve (3) on/off valve and P is a pressure gauge. The six-port switching valve is in the sampling position.

software (Shimadzu, Kyoto, Japan) was used for data acquisition.

The sample enrichment system, which consisted of a 2 m×0.32 mm, 1.1 μm CP Sil-5 CB (Chrompack) OTT column and a high temperature six-port switching valve (VICI Valco, Schenkon, Switzerland), was placed inside the oven of an HP 5890 GC (Hewlett-Packard, Little Falls, DE, USA). A Waters (Milford, MA, USA) M45 HPLC pump (P1) was used to pump the water sample through the trap. Valve 1 in Fig. 1 is a three-way flow selection valve which directs either the water sample, or the nitrogen drying gas to the trapping column. An on/off valve (valve 3) in the waste line can be used to obtain stop-flow conditions during the heating step of the trap. A pressure gauge (P) is installed in the waste line to be able to measure the pressure drop over the enrichment trap.

2.3. Sampling and desorption process

Water samples were pumped through the OTT by the HPLC pump at a flow-rate of 1.5 ml/min. The sampling time required to reach equilibrium was determined experimentally (see below). After the sampling step, the trap was dried by purging it with nitrogen at a flow-rate of 1 ml/min for 5 min to completely remove the water. Afterwards, the trap is ready for thermal desorption of the retained analytes. To do so it is heated under stop flow conditions. The compounds are now released by the stationary phase and transferred into the void volume of the column. Next, the six-port valve is switched to the inject position in order to transfer the analytes to the analytical column by a flow of carrier gas. The amount injected can be varied by varying the time that the six-port valve is left in the inject position. In the present work, the valve was left in the inject position for just a few seconds except in case of desorption profiles studies. In these experiments it was open for few minutes. Finally, the analytes were separated on the GC column.

River water samples were filtered through a 0.45-μm filter prior to analysis to remove any particulate matter. During this step losses of volatile compounds can occur. In the present situation, however, no significant losses were observed for the analytes under study. After the filtration step, blank real samples were analysed. Following this, tap and river water samples spiked with the analytes at different concentration levels were studied.

2.4. Chromatographic conditions

For the analysis of BTX and 2-ethoxyethanol, the GC oven temperature was held at 40°C during the enrichment of the aqueous samples and for 2 min afterwards. Next, the temperature was programmed to 200°C at a rate of 10°C/min. For the analysis of epichlorohydrin and dichlorohydrin the GC temperature programme was as follows: initial temperature 40°C (2 min) and then to 160°C at 50°C/min. The final temperature was held for 8 min. For the amines the GC temperature was held at 40°C for 2 min and then increased to 250°C at 15°C/min. The carrier gas was helium at a flow-rate of 1 ml/min.

For studying the linearity range, real water samples were spiked with the compounds under study at different concentration levels. For each sample three replicate analyses were performed. For every family of compounds studied, the short- and long-term repeatabilities of the method were checked for tap water samples spiked with the analytes. The data found were expressed as relative standard deviations. The short-term repeatability was evaluated by performing five different analyses of the sample on 1 day under identical experimental conditions. The long-term repeatability was evaluated by analyzing the spiked samples on different days ($n=5$).

3. Results and discussion

3.1. ESE process

In a first series of experiments the performance of the ESE technique in the analysis of water pollutants was evaluated through the preconcentration of a simple test mixture that contained the following three compounds: benzene, toluene and *p*-xylene.

In order to establish the optimum conditions for the ESE procedure, the influence of different parameters was investigated. The first parameter studied was the volume of sample that had to be sampled through the open trap to reach full equilibrium. Because the ESE technique is an equilibrium process in which the analytes partition between the sample

matrix and the stationary phase, a minimum volume is required to achieve equilibrium. This parameter was studied by sampling increasing volumes containing the three aromatic hydrocarbons at a concentration level of 10 μg/l through the trap. Fig. 2 shows the chromatogram obtained for the analytes under investigation. The conditions for recording this chromatogram were chosen in such a way that maximum information on the desorption profile was obtained. In these experiments, the trap temperature during the sampling process was kept at 30°C. The desorption process was performed at 200°C. These temperatures were chosen on the basis of previous results [27]. A sample volume of approximately 24 ml was necessary to ensure that the three aromatic hydrocarbons are in equilibrium with the CP Sil-5 CB stationary phase. For other solutes larger or smaller volumes will be required depending on the stationary phase–water partitioning coefficient.

The next parameter studied was the effect of the sampling flow-rate. Different values in the range 0.05–5 ml/min were tested. The sample volume sampled through the OTT was 24 ml. No significant influence of the flow-rate on the peak areas of the analytes was observed in the flow-rate range 0.05–1.5 ml/min. In further experiments 1.5 ml/min was selected to minimize the required sampling time. For higher sampling flow-rates, a decrease in the area responses was observed, most likely due to insufficient contact time between the sample and the stationary phase.

Purging of the trap with nitrogen prior to desorption is an essential step to prevent water reaching the chromatographic column. Even trace amounts of water can result in deterioration of the performance of the system. The influence of the drying step on the recovery of volatile analytes was studied in a separate series of experiments. Different drying gas flow-rates were examined. The drying time was fixed at 5 min. The flow-rate was varied in the range 0.1–5 ml/min. As expected, a decrease in the response of the compounds was observed at higher flow-rates. At flow-rates above 1 ml/min volatile analytes were lost. For further experiments a drying flow-rate of 1 ml/min was chosen. This resulted in good drying of the trap without causing losses of the volatiles.

The ESE method is an equilibrium distribution technique. Equilibrium techniques are somewhat more prone to matrix effects than ‘total extraction’ or breakthrough methods. To evaluate whether the water matrix affected the component distribution in ESE, tap and river water samples were spiked with the BTX mixture again at a concentration level of 10 μg/l. These samples were then analysed under the conditions previously identified to be optimum conditions for ESE enrichment of BTX from Milli-Q water. No significant differences were observed in comparison to those obtained for Milli-Q water

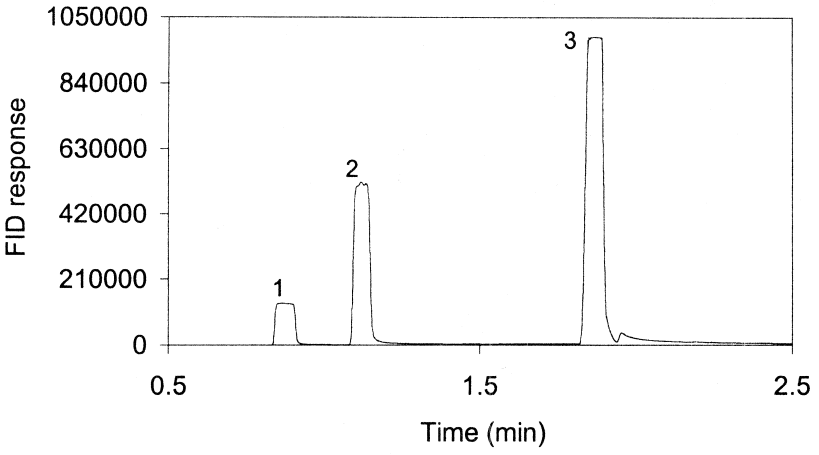

Fig. 2. Desorption profiles of benzene, toluene and *p*-xylene at a concentration of 10 μg/l after equilibrium (ab)sorptive enrichment on a 2 m×0.32 mm×1.1 μm CP Sil-5 CB trapping column. The volume sampled was 24 ml at 30°C. The desorption temperature was 200°C. Peaks: 1=benzene, 2=toluene, 3=*p*-xylene.

indicating that no matrix effects occurred. For this kind of water samples the organic carbon content is known to be much lower than for other kinds of samples such as e.g. groundwater. Whether displacement effects occur for these samples was not studied in detail.

The linearity of the method was assessed by preconcentrating tap water samples spiked with the BTX mixture at different concentration levels ranging from 0.5 to 10 μg/l. The sample volume was 24 ml for all concentration levels. The correlation coefficients for the calibration lines were >0.999. The limits of detection, defined at a signal-to-noise ratio of three, were in the range of 0.5 μg/l for benzene and 0.1 μg/l for *p*-xylene. The results are presented in Table 1. The results found here are comparable with those reported in literature obtained using other enrichment processes such as SPME with polydimethylsiloxane fibers [34,35] or membrane extraction [36].

The short- and long-time repeatability ($n=5$) was evaluated by studying the peak area obtained in the analysis of tap water spiked with the three test analytes at a concentration of 1 μg/l. The values obtained, expressed as relative standard deviations (RSDs) were between 3 and 6% for the short-term repeatability and between 5 and 9% for the long-term repeatability (Table 1). Hence, the method has a good quantitative accuracy for the analysis of BTX in water.

3.2. Determination of 2-ethoxyethanol in water

The ESE method is of particular interest for the analysis of small, polar analytes in water. The analysis of such compounds in aqueous samples is extremely complicated as the analytes are very difficult to extract from the water. In techniques that rely on sampling until breakthrough, such as SPE, the volume of water that can be sampled is very low. Due to their high water solubility the analytes exhibit rapid breakthrough. This problem is absent in the ESE method for water analysis. Each analyte shows maximum enrichment. The ESE system developed here was employed to determine small, polar compounds with a high water solubility in water samples.

The first compound studied was 2-ethoxyethanol, a compound that is widely used as a solvent and as an anti-icing additive in brake fluids, and aviation and automobile fuels. This compound is hazardous to aquatic life. Hence, there is a need for analytical procedures for its determination [28]. Different experiments were performed to determine the optimum conditions for the preconcentration process.

The response obtained in the ESE enrichment of 2-ethoxyethanol was very low. In order to elucidate whether this was due to an unfavourable partitioning coefficient of the analyte or due to adsorption of the compound in tubing, valves, etc., an organic modifier, methanol, was added to the water. Methanol was added to the water samples at different concen-

Table 1
Sample volume, linear range, correlation coefficients, r^2, limits of detection (LODs) and short- and long-term repeatability (RSD) ($n=5$) obtained by on-line ESE–GC–FID for the compounds studied

Analyte	Sample volume (ml)	Linear range (μg/l)	r^2	LOD (μg/l)	Repeatability (RSD,%)	
					Short-term	Long-term
Benzene	24	1–10	0.999	0.5	6	6
Toluene	24	0.5–10	0.999	0.2	4	5
p-Xylene	24	0.5–10	0.999	0.1	3	9
2-Ethoxyethanol	50	2–50	0.997	0.5	6	11
Epichlorohydrin	200	2–50	0.998	0.5	4	7
Dichlorohydrin	200	2–50	0.996	1	6	5
Ethylamine	40	2–50	0.998	1	10	13
Pentylamine	40	2–50	0.999	1	8	15
Hexylamine	40	2–50	0.998	1	16	17

Table 2
Peak areas obtained by adding different percentages of methanol to the water sample before the preconcentration step

Methanol (%)	Peak area[a]
0	2640
5	8729
10	16 334
20	19 827
30	21 288
40	20 916

[a] Results are the average of three experiments.

trations ranging from 5 to 40%. The results are shown in Table 2. It was found that the addition of methanol improved the 2-ethoxyethanol response significantly. An addition of 30% of methanol was chosen for further experiments because higher percentages did not result in a further increase of the response. The exact cause of the positive effects of the methanol addition is as yet unclear. It is likely that part of the methanol partitions into the stationary phase thereby altering the stationary phase polarity and the affinity of the polar analytes for the stationary phase. Based on the octanol–water partitioning coefficient of methanol [29,30] it is estimated that a concentration of 30% of methanol in the water will result in a methanol concentration of roughly 4.5% in the stationary phase.

Different experiments were performed to investigate the required sample volume and the desorption profile for 2-ethoxyethanol. Sample volumes ranging from 2 to 100 ml were preconcentrated. Fig. 3a shows the peak area response as a function of the sample volume. From this figure it can be seen that in the first part of the curve, from 2 to 50 ml, the response (peak area) is directly proportional to the sample volume. From 50 ml upwards, peak areas are no longer affected by the sample volume. Apparently equilibrium has been reached. The sample volume used in further experiments was 50 ml. Fig. 3b shows the chromatogram obtained for 2-ethoxyethanol after sampling 50 ml of a Milli-Q water sample containing 20 μg/l of this compound through the trap.

A 50-ml volume of a solution containing 2-ethoxyethanol at a concentration of 10 μg/l was preconcentrated at different sampling temperatures ranging from 30 to 100°C to study the influence of the sampling temperature. As expected, these experiments clearly showed decreasing enrichment factors with increasing sampling temperature. Further experiments were performed at 30°C.

The effect of the temperature used for the desorption of the analytes retained in the trap was also evaluated. In these experiments, different desorption temperatures in the range between 75 and 250°C were tested. From the data obtained it can be concluded that again, as expected, the desorption temperature has a marked influence on the response. The results of this series of experiments are plotted in Fig. 4. The enrichment factor increases with increasing desorption temperature until it reaches a constant value at 150°C. This value was used for further experiments.

After optimization of the preconcentration parameters, the method was applied to the analysis of tap and river water samples. The first step was the analysis of blank samples. No peaks appeared in the chromatograms at the retention time of 2-ethoxyethanol. Moreover, no significant differences were observed when compared with the results obtained for Milli-Q water indicating that the method, at least for these samples, is free of matrix effects. Fig. 5 shows the chromatogram corresponding to the preconcentration of tap water spiked with 2-ethoxyethanol at 0.5 μg/l.

3.3. Epichlorohydrin and dichlorohydrin

The viability of the evaluated preconcentration method was also tested for the analysis of epichlorohydrin (ECH) and dichlorohydrin (DCH), two compounds used in the production of epoxy resins, glycerol and various other intermediates. ECH and DCH are also used as solvents for natural and synthetic resins, gums, paints and varnishes. Both compounds have been demonstrated to be carcinogens so it is necessary to develop methods for their determination [31]. Analysis of these compounds is, however, by no means trivial as they are highly unstable.

The influence of different parameters on the

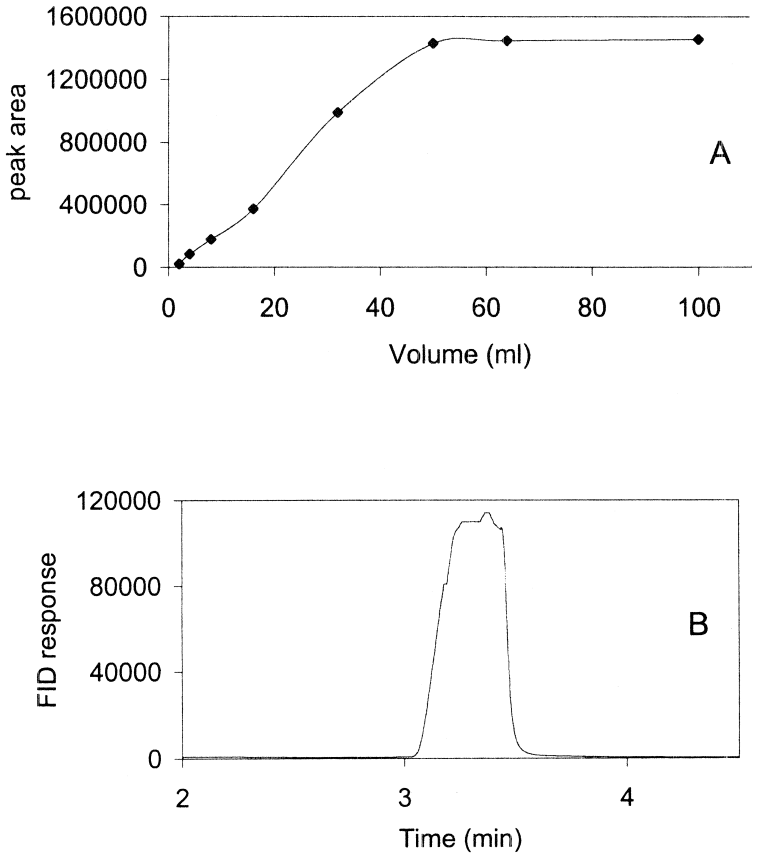

Fig. 3. (a) Peak area of 2-ethoxyethanol versus sample volume. (b) Desorption profile of 2-ethoxyethanol at a concentration of 20 μg/l after equilibrium (ab)sorptive enrichment on the same trapping column as that reported in Fig. 2. The volume sampled was 50 ml at 30°C. Desorption was performed at 150°C.

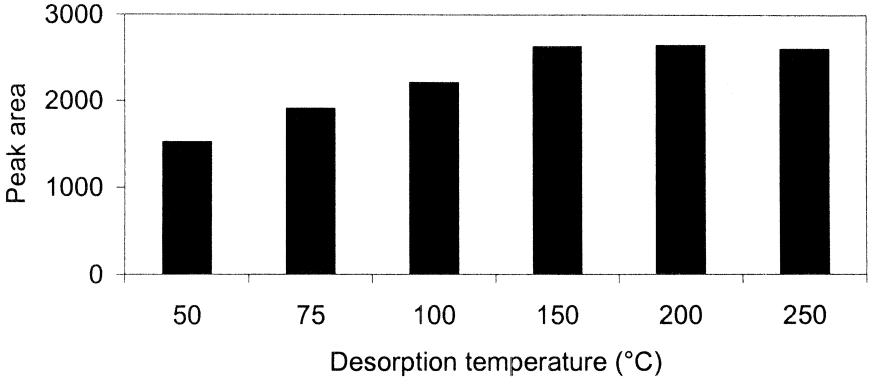

Fig. 4. Peak area of 2-ethoxyethanol at various desorption temperatures.

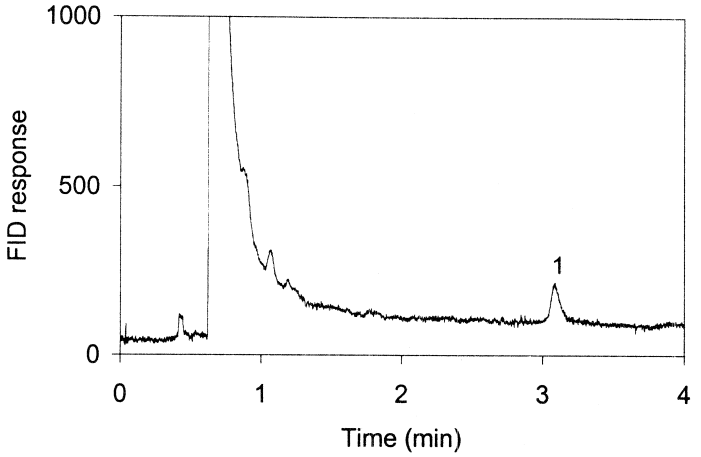

Fig. 5. Chromatogram obtained in the preconcentration of tap water containing 2-ethoxyethanol (1) at a concentration of 0.5 μg/l after enrichment. The trapping column was the same as in Fig. 2. Sample volume: 50 ml, sorption temperature: 30°C, desorption temperature: 150°C. For chromatographic conditions see Experimental.

responses obtained for ECH and DCH was studied. The sample volume required for the two compounds to reach equilibrium with the sorbent was 200 ml. Fig. 6 shows the desorption profiles obtained for epichlorohydrin and dichlorohydrin after the preconcentration of 200 ml of a Milli-Q water sample containing 25 μg/l of each compound.

The addition of methanol to the water samples containing the two compounds was also studied. In this study different percentages of methanol ranging from 5 to 20% were evaluated. The general trend was a decrease in the response with increasing concentration of methanol in the sample, most likely as a result of the improved solubility of ECH and DCH in methanol–water mixtures.

In order to test the influence of the sampling temperature, 200-ml water samples containing the two compounds at 10 μg/l were preconcentrated at different temperatures ranging from 30 to 70°C. Increasing the sampling temperature was again found to result in a decrease of the area response. The temperature chosen for further experiments was 30°C.

Finally, the effect of the desorption temperature

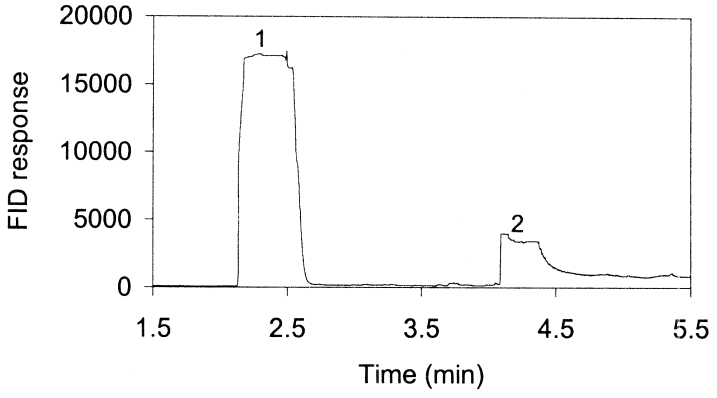

Fig. 6. Equilibrium sorption profiles of epichlorohydrin and dichlorohydrin (25 μg/l each) after equilibrium (ab)sorptive enrichment. Trapping column as in Fig. 2. The sample volume was 200 ml at 30°C and the desorption temperature was 150°C. Peaks: 1 = epichlorohydrin, 2 = dichlorohydrin.

was evaluated. Different temperatures were tested in the range from 75 to 250°C. The optimum temperature was found to be 150°C. When higher temperatures were used, a decrease in the response was observed, especially for ECH. In the corresponding chromatograms obtained at higher desorption temperatures, additional peaks were observed, probably as a result of degradation of the compounds at higher temperatures.

The method was applied for the analysis of tap and river water samples. The blank chromatograms obtained for these samples showed no peaks at the retention times of ECH and DCH. Afterwards, the samples were spiked with the analytes and no significant differences were observed in comparison with the results previously found for Milli-Q water samples. The corresponding values found for the linear range, detection limits and short- and long-term repeatibilities ($n=5$) are shown in Table 1. The repeatability of the method was determined by the analysis of a tap water sample that contained the compounds at a concentration of 5 μg/l. Low RSD values, typically <8%, provide proof of the good performance of the method for the two compounds.

3.4. Determination of amines

The use of the ESE technique was also investigated for the preconcentration of amines from aqueous samples. The selected compounds were three short-chain aliphatic amines, ethylamine, pentylamine and hexylamine. Due to their excellent water solubility these compounds are particularly difficult to detect in water samples. Extraction is virtually impossible. Among different applications, the short aliphatic amines are used as solvents or as starting products in organic synthesis [32,33].

Different experiments were carried out to study the effect of the various operational parameters on the response obtained for the amine compounds under study. Different volumes ranging from 2 to 75 ml were preconcentrated for studying the sample volume needed to reach equilibrium. The required sample volume was found to be 40 ml. Sampling was performed at 30°C. Elevated sampling temperatures were again found to result in lower peak areas. The quantitative transfer of the amines from the OTT to the GC column required a desorption temperature of 275°C. Despite the fact that this is close to the maximum allowed column temperature (300°C) no problems with trap bleeding were encountered.

The optimized on-line-ESE–GC procedure was applied to the analysis of tap water samples spiked with the amines. For these samples also there were no significant differences observed in comparison with the results for Milli-Q water. The linearity of the method was determined by analyzing tap water samples spiked with the three amines in the range 2–50 μg/l. Linearity turned out to be satisfactory for all analytes with correlation coefficients >0.997. The detection limits for the compounds were approximately 1 μg/l as is shown in Table 1. The quantitative performance of the method was similar to that reported for the analysis of short aliphatic amines in

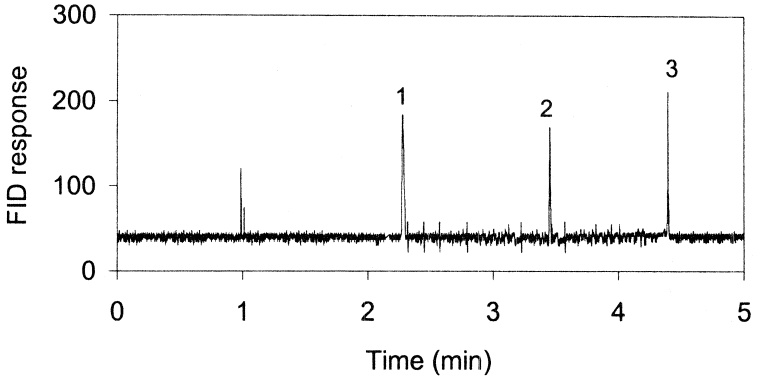

Fig. 7. Chromatogram obtained after preconcentrating a river water sample containing ethylamine, pentylamine and hexylamine at a concentration of 2 μg/l after enrichment on the trapping column. Sample volume: 40 ml; sorption temperature: 30°C; desorption temperature: 275°C. For chromatographic conditions see Experimental. Peaks: 1=ethylamine, 2=pentylamine, 3=hexylamine.

aqueous solutions using other preconcentration methods such as SPME [37]. Our method does not use a derivatization step before the extraction procedure, thereby reducing the analysis time.

The method precision was determined by analyzing five replicate tap water samples spiked at a concentration level of 5 μg/l. Table 1 shows the results obtained.

The performance of the method was also validated for the analysis of Dommel river water samples. The linearity of the response, correlation coefficients, limits of detection and precision were similar to those obtained for tap water. Fig. 7 shows the chromatogram obtained for a river water sample spiked with the amine compounds at a concentration of 2 μg/l.

All experiments described in the present article were performed with one OTT column. At least 400 water samples were analysed without noting any change in the trap properties, so the traps can be used without problems over prolonged periods of time.

4. Conclusions

In this contribution, a new method for the analysis of organic pollutants in water samples is described. The proposed ESE method was evaluated for the analysis of various compounds. The ESE method carried out using OTT columns is eminently suited to the analysis of small, polar molecules in water. Due to their high water solubility these compounds are very difficult to analyze using traditional methods. Low-molecular-mass compounds that can be enriched using ESE in OTT columns are 2-ethoxyethanol, epichlorohydrin, dichlorohydrin and different amines. The detection limits for most of the compounds studied are around 1 μg/l (1 ppb) using FID detection. The method does not require sophisticated instrumentation. The lifetime of the enrichment traps is at least 400 analyses.

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