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Journal of Chromatography A, 912 (2001) 151–161

JOURNAL OF CHROMATOGRAPHY A

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New method for rapid solid-phase extraction of large-volume water samples and its application to non-target screening of North Sea water for organic contaminants by gas chromatography–mass spectrometry

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Received 8 August 2000; received in revised form 12 December 2000; accepted 3 January 2001

Abstract

A method has been developed that allows the solid-phase extraction of microorganic compounds from large volumes of water (10 l) for non-target analysis of filtered seawater. The filtration–extraction system is operated with glass fibre filter candles and the polymeric styrene–divinylbenzene sorbent SDB-1 at flow-rates as high as 500 ml/min. Recovery studies carried out for a couple of model substances covering a wide range of polarity and chemical classes revealed a good performance of the method. Especially for polar compounds (log K_{OW} 3.3–0.7) quantitative recovery was achieved. Limits of detection were between 0.1 and 0.7 ng/l in the full scan mode of the MS. The suitability of the method for the analysis of marine water samples is demonstrated by the non-target screening of water from the German Bight for the presence of organic contaminants. In the course of this screening a large variety of substances was identified including pesticides, industrial chemicals and pharmaceuticals. For some of the identified compounds their occurrence in marine ecosystems has not been reported before, such as dichloropyridines, carbamazepine, propyphenazone and caffeine.

Keywords: Seawater; Organic pollutants; Pesticides; Pharmaceuticals; Dichloropyridines

1. Introduction

Solid-phase extraction (SPE) has gained major importance in the analysis of aqueous environmental samples. A broad variety of organic chemicals has been enriched from drinking [1,2], ground [3,4], waste [5,6], surface [7–9], estuarine [10,11], coastal [12] and marine [13,14] waters by SPE. Thus far, emphasis was placed upon organochlorine pesticides [15], organophosphorus and -nitrogen pesticides [16,17], chlorophenols [18], explosives [19], phthalates [20], aromatic sulfonates [21,22] and polycyclic aromatic hydrocarbons (PAHs) [23]. The sorbents used in SPE include graphitized carbon black (GCB) [1,24,25], reversed-phase (RP) materials (modified silica gels) and polymeric materials. The most widely used RP material (and SPE sorbent in general) is the

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0021-9673/01/$ – see front matter
PII: S0021-9673(01)00529-5

octadecyl (C_{18}) phase, but ethyl, butyl, cyclohexyl, octyl, phenyl, propylamino, dimethylaminopropyl and cyanopropyl reversed-phases have been applied as well [26–28]. With respect to polymeric sorbents, the best known are styrene–divinylbenzene co-polymers (Polysorb S, Amberlite XAD-2 and XAD-4) and polyacrylates (Amberlite XAD-7 and XAD-8). Unsatisfactory recovery rates [26] and poor reproducibility [29] were observed for XAD resins. Especially for the XAD resins excessive cleaning procedures are required prior to their use [30]. The development of a new generation of polystyrene-based sorbents did not only overcome the problems associated with XAD resins. However, the sorptive capacity of these styrene–divinylbenzene or divinylbenzene–ethylvinylbenzene co-polymers has risen immensely. It is specified to be 10-fold higher than that of C_{18} RP sorbents. Polymeric sorbents of this type, e.g., SDB-1 or LiChrolut EN, have been used successfully for the extraction of the whole range of organic contaminants (e.g., Refs. [22,31,32]). They proved to be especially suitable for medium to highly polar substances, where they showed substantially higher recovery rates than alkylsilica RP sorbents [5,33] or liquid–liquid extraction (LLE). Even acidic pesticides like dicamba, 2,4,5-trichlorophenoxy acetic acid (2,4,5 T) and dinoterb [34] as well as chlorophenols [35] were extracted quantitatively without acidification of the sample.

In marine analytical chemistry, standard SPE methods can only be applied to estuarine or highly polluted coastal water samples of around 1 l volume. On the open sea, concentrations of most organic pollutants are low, as compared to limnic systems. Concentrations are typically in the lower ng/l range (e.g., lindane [36]) or even in the low pg/l range (e.g., polychlorinated biphenyls, PCBs [37]). A conceivable possibility to meet the requirements for low detection limits is to rise the volume of the sample to 10, 100 or more litres. Basic needs for large-volume SPE are (i) efficient online filtration, (ii) high flow-rates (to keep the extraction time within acceptable limits), (iii) low flow resistance (both of the filter and the extraction unit), (iv) mechanical stability of the sorbent package.

Commercially available standard SPE systems are often incapable of handling these volumes. However, some approaches to SPE of large-volume (>10 l) seawater samples were reported in the literature. For example, Gómez-Belichòn et al. [38] extracted hydrocarbons, PAHs, PCBs and fatty acids from seawater with XAD-2, PUF and by LLE. Volumes ranged from 42 to 1000 l at flow-rates of 100–1900 ml/min. Ehrhardt and Burns [39] extracted 221 to 435 l of coastal and inshore waters with an Seastar Infiltrex sampler and 100 ml XAD-2 resin for the analysis of *n*-alkanes, alkylbenzenes and PAHs. Schulz-Bull and co-workers [37,40] continuously filtered and extracted seawater for analysis of PCBs from board of a ship at a flow-rate of 500 ml/min, using GF/C filters (120 mm) and XAD-2 filled glass columns (100 and 120 ml). Extracted volumes ranged from 50 to 1140 l. The same group developed a submersible in situ filtration–extraction system (KISP) [41]. The system was tested at flow-rates between 1250 and 1500 ml/min with a XAD-2 volume of 250 ml and extracted water volumes of 210–700 l. The limiting factor, apart from energy supply, was found to be the clogging of the filter with suspended particulate matter (SPM). Sturm et al. [42] extracted samples of 100 l of coastal water with an Infiltrex II sampler and 30 g of C_{18} material for the determination of PAHs and organochlorines. Generally, the loaded sorbents were back-extracted in a Soxhlet or Ehrhardt apparatus, which is time consuming, prone to contamination and requires considerable amounts of solvents.

Most investigations in marine analytical chemistry focus on classical lipophilic target compounds like organochlorines and PAHs. However, large uncertainties exist with regard to the inventory of polar organic pollutants in marine systems, which may reflect the lack of a method to extract and identify a sufficiently broad variety of substances. Within this work a sampler was constructed that allows the on-line filtration and extraction of large volumes (10 l) of coastal and offshore waters at high flow-rates. Furthermore, an analytical method for the application of this filtration–extraction unit to non-target screening of seawater for a wide range of organic pollutants was developed. In contrast to the cited large-volume methods, modern principles of SPE were adopted, i.e., glass cartridges packed with relatively small amounts (2 g) of sorbent were used and the trapped analytes were directly eluted from the car-

tridge. Thus, the method extends the applicability of common SPE procedures to large volume samples and, by the use of the polymeric sorbent, to highly hydrophilic compounds.

In order to assess the overall threat from organic pollutants to aquatic ecosystems it is crucial to set up inventories of the chemicals present in the respective compartment by a non-target screening. This had been realised rather completely for the River Elbe and its tributaries [43]. Further investigations were carried out, for example, for effluents of Swedish sewage treatment plants [44], for the Elbe estuary [45] as well as part of some toxicity identification evaluation (TIE) approaches (e.g., in the River Rhine delta [46]).

However, no systematic experiment based on this approach has been reported for the North Sea, although results for single ''non-target compounds'' were published (e.g., Ref. [47]). In this work, the results of non-target screening of North Sea water performed with the newly developed method will be presented.

2. Experimental

2.1. Chemicals and materials

The filtration–extraction unit was manufactured by the mechanical workshop of the Department of Chemistry, University of Hamburg, from stainless steel 4301 (Schoch, Germany) and PTFE (Wegener, Hamburg, Germany), respectively. The respective glass cartridges were made by the Institute's glassblowers from glass tubes and glass frits (pore size 40–100 μm) (Winzer, Germany). Glass fibre filter candles (exclusion size 0.5 μm) were obtained from Voigt (Wernau, Germany). They were cleaned prior to filtration by heating 72 h at 693 K (420°C) and duplicate Soxhlet extraction (200 ml *n*-hexane–ethyl acetate, 4:1, v/v, 6 h). Glass fibre filter disks GF/C (diameter 47 mm, exclusion size 0.45 μm) were supplied by Whatman (Maidstone, UK). The commercially available sorbent Bakerbond SDB-1 (styrene–divinylbenzene co-polymer, particle size 40–120 μm, pore size 27 nm) was obtained from Baker (Griesheim, Germany).

Chemicals for the recovery experiments and verification of the non-target screening results were obtained from Merck (Darmstadt, Germany) [2,5-dichloroaniline, dichlorobenzenes, caffeine, chloroaniline, chloronitrobenzenes, di-*n*-butylphthalate, *N,N*-diethyl-3-toluamide (DEET), nitrobenzene], Sigma–Aldrich (Steinheim, Germany) (3-chloro-4-fluoronitrobenzene, 2,4-dibromoanisol, dichloropyridines, triphenylphosphinoxide), Promochem (Wesel, Germany) [desethylatrazine, HCHs, hexachlorobenzene (HCB), octachlorostyrene, parathion-methyl, pirimicarb, propoxur, terbutylazine], Synopharm (Barsbüttel, Germany) (carbamazepine, propyphenazone), Dr. Ehrenstorfer (Augsburg, Germany) (atrazine, desethylterbutylazine, dimethoate, metolachlor, simazine, trichlorobenzene), Fluka (Neu Ulm, Germany) (tri-*iso*butylphosphate, tri-*n*-butylphosphate) and ABCR (Karlsruhe, Germany) (2,6-dichlorobenzonitrile=dichlobenil). All solvents used were of organic trace analysis grade and supplied by Merck, as well as HPLC-grade water. Sodium sulfate (granulated, organic trace analysis grade, Merck) was heated for 6 h at 873 K (600°C) before use. For fractionation, columns were prepared from glass cartridges (8 ml), PTFE frits (pore size 20 μm) and 2 g silica (particle size 40 μm, pore size 6 nm, analytical grade) (all from Baker). The silica was activated prior to use by heating for 12 h at 393 K (120°C). Ultrapure water was prepared with a Seral-Pur Pro 90C apparatus (Seral, Ransbach, Germany).

The standard stock solution of ca. 200 mg/l was prepared by dissolving about 20 mg (range from 12 to 64 mg) of the pure compounds in 100 ml acetone. The working standard solutions were obtained by further dilution with acetone (for spiking) or *iso*-octane (for external quantification). All solutions were stored at 277 K (4°C) in the dark.

2.2. Sampling

Water samples were taken using a 10-l glass-sphere-sampler as described by Gaul and Ziebarth [48]. Two samples from the River Elbe were taken for recovery and screening studies on 23 March 1998, at Hamburg–Neumühlen (km 627, right bank, depth: 2 m). The North Sea water sample used for screening purposes was taken from board of the research vessel *RV Gauss* on 27 June 1998, at the

position 54° 13.50′ N, 8° 23.00′ E, sampling depth 5 m.

2.3. Filtration–extraction

After sampling the water was pumped from the sampler via PTFE-tubing through the filtration and the extraction unit by a gear pump (Model MCP-Z, pump head Z-120 with PTFE gears, magnet 66; Ismatec, Wertheim, Germany). For the determination of recovery rates from purified water the pump was placed behind the extraction unit. The pump had to be placed between filtration and extraction unit for the handling of environmental samples with a high load of particulate matter, because with rising flow resistance air was drawn in at the exit of the extraction unit. This led to malfunctioning of the pump. Rearrangement of the pump before the extraction unit did not cause contamination as checked by procedural blanks.

2.3.1. Filtration

For on-line filtration of the sample glass fibre filter candles (height 82 mm, outer diameter 26 mm, inner diameter 14 mm) were used in a stainless steel housing (see Fig. 1).

2.3.2. Extraction

Extraction was performed in a specially designed and constructed device (see Fig. 2). Into the PTFE-housing a glass cartridge (height 57 mm, inner diameter 45 mm) was inserted. The bottom was covered with a glass fibre filter sheet (GF/C). A 2-g (ca. 6 ml) amount of the sorbent was filled in as suspension in *n*-hexane and covered with another filter sheet, resulting in a bed height of approximately 5 mm. The package was fixed for mechanical consistency by introducing the PTFE-cylinder and locked by the screw-ring. Uniform thickness of the sorbent layer was checked by the resulting position of the fixing screw ring. The sorbent was rinsed with 50 ml *n*-hexane and 50 ml ethyl acetate by application of aspirator vacuum at the exit of the extraction unit. The column was conditioned by passing through 50 ml of methanol and 50 ml of HPLC-grade water.

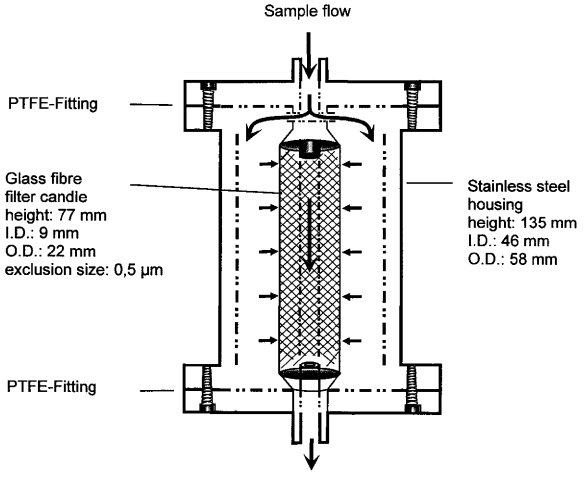

Fig. 1. Filtration unit for use with filter candles (schematic view).

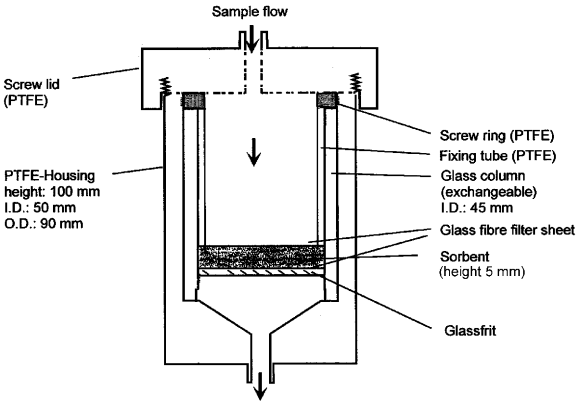

Fig. 2. Solid-phase extraction unit (schematic view).

After having filled all parts of the filtration–extraction unit with water it was connected to the pump and the sample was pumped through the experimental set at a flow-rate of 500 ml/min. After the extraction step the wet extraction cartridges and filter candles were removed and stored in screwtop glasses at 255 K (−18°C) until elution.

2.4. Elution

After defrosting the loaded cartridges were inserted and fixed in the extraction unit (Fig. 2) as described above. The solid phase was eluted by three portions of 30 ml ethyl acetate, followed by 50 ml *n*-hexane–ethyl acetate (4:1, v/v). A gentle vacuum

was applied to suck the solvent through the cartridge, the combined eluates were collected in a 250-ml round-bottomed flask. Relatively high amounts of ethyl acetate were used for elution, in order to repel residual water from the sorbent. This approach avoided excessive drying of the cartridge and thus reduced potential contamination or losses of analytes. After phase separation the aqueous phase (ca. 5 ml) was pipetted off and re-extracted twice with 1 ml *n*-hexane. The combined organic phases were dried over sodium sulfate. The solvent was pipetted off and the residual sodium sulfate slurry re-extracted three times with 10 ml *n*-hexane–ethyl acetate (4:1, v/v). The combined organic phases were reduced to a final volume of approximately 150 μl in a rotary evaporator after addition of *iso*octane as a keeper.

The filter candles loaded with SPM were not extracted since the main interest of this work was focused on polar analytes. However, extraction in a Soxhlet apparatus can be performed thus including the organic fraction adhering to particles.

2.5. Clean-up

No clean-up was necessary for the recovery studies from purified water, and it was thus not performed in this case. The intention was to check the performance of the new SPE approach rather than that of the clean-up. This means that the recovery rates presented herein do not include any clean-up steps.

In contrast, a clean-up was improving the proper identification of trace organics in the course of non-target screening of environmental samples. In this case, a silica clean-up–fractionation similar to that described by Specht and Tilkes [49] was applied. In an 8-ml glass cartridge 2 g silica were packed between two PTFE frits and conditioned with 10 ml *n*-hexane. After application, the sample was eluted with 6-ml portions of first *n*-hexane, followed by *n*-hexane–dichloromethane (9:1, v/v), *n*-hexane–dichloromethane (4:6, v/v), dichloromethane, dichloromethane–ethyl acetate (1:1, v/v), ethyl acetate, acetone and finally 12 ml methanol. The eluates were reduced to a final volume of approximately 150 μl in a rotary evaporator after addition of *iso*octane as a keeper.

2.6. Gas chromatography–detection

For the recovery studies and non-target screening of environmental samples a Magnum ITD (Finnigan MAT, Bremen, Germany) ion trap mass spectrometer was used under the following conditions: electron impact (EI) ionisation at 70 eV, manifold temperature 473 K (200°C), emission current 10 μA, scan range 100–420 u. It was coupled to a Varian 3400 GC system (Sunnyvale, CA, USA) [split/splitless injector 1075, 60 s splitless, 523 K (250°C); column DB5-MS (J&W Scientific, Folsom, CA, USA), 25 m×0.20 mm I.D., film thickness 0.33 μm; carrier gas helium 5.0 (75 kPa); transfer-line 523 K (250°C)] run with an A 200 SE autosampler (CTC Analytics, Zwingen, Switzerland) (injected volume 2 μl). Temperature programmes were usually 333 K (60°C) (2 min)→(10 K/min)→533 K (260°C) (20 min) for recovery studies and 333 K (60°C) (2 min)→(7 K/min)→533 K (260°C) (20 min) for environmental samples.

Since the GC–MS system showed a poor performance for dimethoate, confirmational measurements were carried out by GC–phosphorus–nitrogen detection (PND) as follows: GC 8130 (Fisons Instruments, Milan, Italy), split/splitless injector 30 s splitless (injected volume 2 μl), column NB 54 (HNU-Nordion, Helsinki, Finland) 25 m×0.25 mm I.D., film thickness 0.25 μm, carrier gas helium 5.0 (125 kPa); detector NPD 800 (Fisons Instruments), base temperature 553 K (280°C), detector gases: air (140 kPa), hydrogen (90 kPa), make-up gas: helium (85 kPa). Temperature programme: 343 K (70°C) (2 min)→(10 K/min)→533 K (260°C) (20 min).

3. Results and discussion

3.1. Mechanical performance of the filtration–extraction unit

The use of filter candles in the filtration unit proved to be highly effective. Due to the high capacity of the filter candle as compared to the usual membrane filters, clogging occurred only to a small extent. Even samples of 10 l water from the River Elbe, containing high loads of SPM (typically 20–40

mg/l), were filtered with the system at a routine flow-rate of 500 ml/min.

The construction of the extraction unit combines the advantages of extraction disks and extraction columns. The high, disk-like diameter lowers the flow resistance. The column-like packing of the sorbent not only raises the overall capacity of the cartridge but also decreases the risk of breakthrough. The extent of breakthrough for a given sorbent is directly depending on the polarity of the analytes, the extracted volume of water and the sorbent bed height. Furthermore, a sufficient bed height (capacity) is especially important for surface and seawater since dissolved organic carbon competes with the analytes for adsorption. Compared to common SPE approaches, the achieved flow-rates are exceptionally high without decreasing recovery. This is a product of the efficient on-line filtration achieved by filter candles in contrast to membrane filters, the diameter of the extraction cartridge and the hydrodynamic and sorptive properties of the solid phase used. C_{18} material would have required the use 20 g of sorbent to reach the same capacity as 2 g SDB-1 and exhibited a higher flow resistance.

During the processing of river water samples with a high SPM load, an increase in the flow resistance was observed, probably caused by the advancing clogging of the filter candle and/or the filter sheet covering the sorbent. This resulted in the entering of air at the connection between the extraction unit and the pump. For this reason, the pump was placed between the filtration unit and the extraction unit for the processing of environmental samples.

3.2. Solid-phase extraction

Recovery experiments were executed for the determination of the performance, the reproducibility, the recovery rates and the linearity of the method. Since the aim of the work was to develop a non-target screening method, a standard solution was used that represented a broad range of compounds. It included pesticides of different classes as well as industrial chemicals and additives (plasticisers), varying in polarity from octachlorostyrene (log K_{OW} 7.7) to dimethoate (log K_{OW} 0.7) [50,51]. The compounds were chosen in a way that co-elutions were avoided. Fig. 3 shows a chromatogram of the

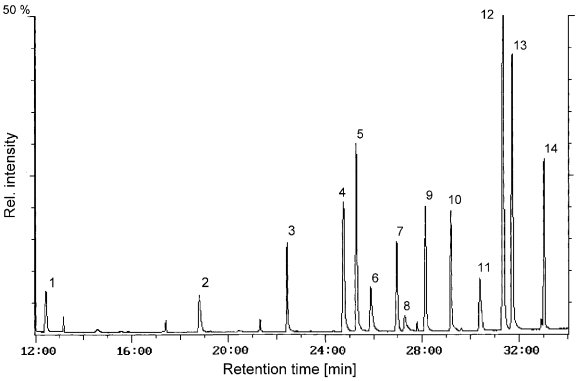

Fig. 3. Gas chromatogram of a standard solution, column DB5-MS (25 m×0.20 mm, 0.33 μm), temperature programme: 333 K (60°C) (2 min)→(6 K/min)→533 K (260°C) (20 min), mass spectrometric detection (full scan mode); 1=nitrobenzene, 2=2,5-dichloroaniline, 3=tri-*iso*butylphosphate, 4=propoxur, 5=tri-*n*-butylphosphate, 6=desethylatrazine, 7=hexachlorobenzene (HCB), 8=dimethoate, 9=terbutylazine, 10=pirimicarb, 11=parathion-methyl, 12=dibutylphthalate, 13=metolachlor, 14=octachlorostyrene (OCS).

standard solution. The parameters obtained for the test compounds were intended to serve as a framework for the evaluation of the method with respect to non-target screening with emphasis on polar analytes rather than for the quantitative determination of these substances.

Samples (10 l) of purified water were spiked with 1 ml of the respective standard solution in acetone. They were pumped through the filtration–extraction unit at a standard flow-rate of 500 ml/min, i.e., the extraction was completed within 20 min. Further treatment was carried out as described above. Quantification was routinely performed by GC–MS, except for dimethoate, which showed unsatisfactory chromatographic behaviour and poor response on the GC–MS system. In this case, quantification was additionally effected by GC–PND.

Recovery rates and reproducibility were determined at an environmentally relevant concentration level (~20 ng/l) by triplicate extractions. The results are given in Table 1. Quantitative recovery was observed for polar analytes, whereas the highly non-polar organochlorines were recovered in the 60–70% range. Interestingly, a good correlation was observed between polarity (given as log K_{OW}) and recovery of the analytes (Fig. 4). This effect has to be attributed

Table 1
Recovery rates and standard deviations (SDs) of the method as determined from triplicate extractions from spiked purified water (10 l) at the 20 ng/l level (* in parentheses: quantification by PND, $n=2$)

Analyte	Log K_{OW} [50,51]	Recovery (%)	SD (%)
Octachlorostyrene	7.7	62	1
Hexachlorobenzene	6.4	67	4
Di-*n*-butylphthalate	4.9	132	7
Tri-*n*-butylphosphate	3.7	99	12
Tri-*iso*-butylphosphate	3.5	80	8
Metolachlor	3.4	95	1
Terbutylazine	3.0	96	3
Parathion-methyl	3.0	95	2
2,5-Dichloroaniline	2.9	86	17
Chlorobenzene	2.8	29	15
Nitrobenzene	1.8	66	6
Pirimicarb	1.8	98	3
Propoxur	1.6	107	10
Desethylatrazine	1.5	102	11
Dimethoate	0.7	184 (112)*	41 (6)*

either to an irreversible sorption to the solid phase or to incomplete extraction. Low recovery of chlorobenzene (29%) and, to a lesser extent, of nitrobenzene (66%) are due to their high volatility. Especially for chlorobenzene, evaporation procedures and solvent change to *iso*octane led to severe losses and high standard deviation, which makes the method unsuitable for this compound. In case of interest in highly volatile analytes, a respective modification of the elution and the further treatment (e.g., elution with small volumes of dichloromethane) would raise recoveries. For dibutylphthalate a reliable determination was not possible due to contamination from the laboratory environment.

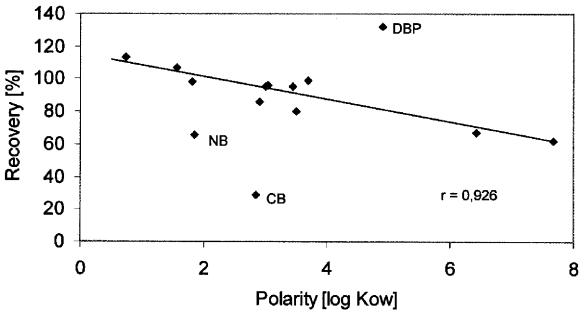

Fig. 4. Correlation between polarity of the investigated compounds and their recovery by the presented SPE method. Di-*n*-butylphthalate (DBP), nitrobenzene (NB) and chlorobenzene (CB) are not included in the regression for the reasons given in the text.

The recovery rates were checked for the influence of an environmental matrix by spiking and extracting a water sample from the River Elbe (7.5 l, spiking level 800 ng/l). The thus obtained recovery rates were within the standard deviation of those from purified water for most analytes. Only octachlorostyrene showed a significant decrease in recovery (from 62 to 40%), which can be explained by its partitioning to SPM (whereas no decrease was observed for HCB). This behaviour is well known for other highly chlorinated compounds, e.g., PCBs [37]. Thus, the missing amount might be found by extraction of the SPM-loaded filter candles. The investigation of the SPM load will be subject of further studies.

Linearity of the whole procedure was investigated at four points over a concentration range from 2 to 200 ng/l water (2, 10, 20, 200 ng/l). The correlation between concentration and recovery was generally good (correlation coefficients 0.9994 or higher) for this range. Limits of detection (LODs) were estimated from the smallest peak area that could be quantified reliably, which corresponds to a signal-to-noise ratio of 10. The LODs thus obtained for the instrumental performance were connected to recovery rates and sample volume to give overall LODs for the entire procedure. They were in the range of 0.1 to 0.7 ng/l except for dimethoate (ca. 5 ng/l). It has to be pointed out here that the method

was developed for non-target screening purposes in the full scan mode of the MS system. For quantitative investigations the given parameters (LOD, SD, linearity) would have to be determined more thoroughly for the analytes of interest. Additionally, other detection modes (e.g., selected ion monitoring) would basically lower the LODs.

3.3. Screening of North Sea water for organic compounds

After the present method had proven its aptitude for the investigated test compounds, its performance in non-target screening was tested with a sample of 8 l river water. The detection and identification of a large number of compounds, ranging from highly lipophilic organochlorines to readily water soluble compounds like caffeine demonstrated its suitability for this purpose.

The newly constructed gear as well as the co-developed analytical method were then routinely applied to the extraction and screening of water samples from the German Bight and the entire North Sea. In order to demonstrate the power of this approach, the results from the station DB30 (Fig. 5) will also be presented here. It should be noted though, that, facing the enormous number of microorganics present in the North Sea, the intention was not to elucidate every peak/substance, but to provide a fast screening for anthropogenic and potentially harmful substances. Identification was achieved by comparison of the obtained spectra with the NIST library. The large number of identified substances included PAHs, oxo-PAHs, alkylbenzenes, ethers, alcohols, aldehydes, ketones, esters, anilines, amides, nitro-compounds, *N*-heterocycles, sulfonamides, thiophenes, benzothiazoles, alkyl- and chloroalkyl phosphates as well as various halogenated compounds like, e.g., chloroanilines and chlorinated bispropylethers. Since identification by (low-resolution) spectra alone may lead to false assignments, library proposals for a couple of substances were verified by injection and measurement of the respective reference compounds. For some of the substances hitherto not reported to occur in the North Sea, concentrations were estimated by comparison with external standards of these compounds (not corrected for recovery rates). None of them were detected in the procedural blanks. The verified compounds are listed in Table 2. For the dichloropyridines, of which the occurrence in the environment has not been reported so far to our knowledge, spectra obtained from a North Sea water sample extract and from the pure substance are depicted in Fig. 6a and b, respectively.

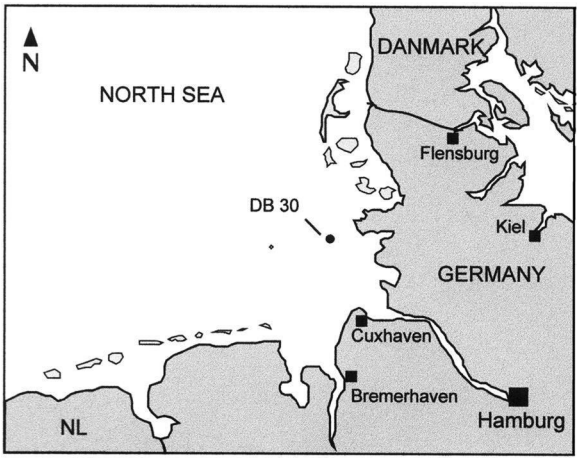

Fig. 5. Position of the sampling location DB30 within the German Bight.

Further research on the occurrence and distribution of the newly identified compounds in the North Sea is currently being carried out since their presence, especially of those compounds known for their biological activity (pesticides, pharmaceuticals), poses a potential threat to marine ecosystems.

4. Conclusions

The SPE apparatus and the method reported herein were shown to be a valuable tool for the extraction of trace organics from large volumes of water, as typically required for the analysis of marine samples. Hitherto, the system has been tested for 10-l samples. An extension to higher volumes (e.g., 100 l) as well as higher flow-rates seems possible and would further lower the achievable detection limits. The high diameter of the extraction cartridges and the small amount of sorbent (resulting in a relatively thin bed) in combination with the high-capacity filtration system allows high flow-rates, which significantly

Table 2
Compounds identified in sample DB30 by library search (NIST) and verified by comparison with reference substances[a]

Substance	Verification
Pesticides	
α-HCH	Qualitatively
β-HCH	Qualitatively
γ-HCH	Qualitatively
Atrazine	Qualitatively
Simazine	Qualitatively
Terbutylazine	Quantitatively (0.7 ng/l)
Desethylatrazine	Quantitatively (1.6 ng/l)
Desethylterbutylazine	Qualitatively
Metolachlor	Quantitatively (0.3 ng/l)
Dichlobenil	Quantitatively (0.1 ng/l)
DEET (*N*,*N*-diethyl-3-toluamide)	Quantitatively (0.6 ng/l)
Industrial chemicals	
1,3-Dichlorobenzene	Qualitatively
1,4-Dichlorobenzene	Qualitatively
1,2,4-Trichlorobenzene	Qualitatively
1-Chloronaphthalene	Qualitatively
2,6-Dichloropyridine	Quantitatively (0.2 ng/l)
3,5-Dichloropyridine	Quantitatively (0.1 ng/l)
Nitrobenzene	Quantitatively (0.7 ng/l)
Chloronitrobenzene (*o*- and/or *p*-isomer)	Qualitatively
3-Chloro-4-fluoronitrobenzene	Quantitatively (1.2 ng/l)
2-Chloroaniline	Qualitatively
2,5-Dichloroaniline	Quantitatively (0.7 ng/l)
Triphenylphosphinoxide	Quantitatively (53 ng/l)
Pharmaceuticals	
Propyphenazone	Quantitatively (0.6 ng/l)
Carbamazepine	Quantitatively (2 ng/l)
Caffeine	Quantitatively (2 ng/l)
Brominated compounds	
2,4-Dibromoanisol	Qualitatively

[a] Concentrations of selected compounds were estimated by comparison with external standards (not corrected for recovery rates).

lowers the extraction time. In contrast to former approaches to large-volume SPE in marine analytical chemistry, the analytes can directly be eluted from the cartridge. The polymeric sorbent used in this work proved to be apt to extract analytes of a wide polarity range (log K_{OW} 7.7–0.7). It is especially suitable for medium to highly polar compounds (log K_{OW} range 3.5 to 0.7), which often are poorly recovered by LLE or C_{18}-SPE. The possibility of extracting large volumes within a reasonable time enables high enrichment factors and thus very low LODs.

The application of the method to riverine and marine water samples demonstrated its strength in the analysis of organic compounds in environmental samples, even at concentrations in the pg/l range. Non-target screening of sample extracts from the German Bight revealed the presence of a large variety of potentially harmful substances, part of which are known as pollutants in river systems, but have not been mentioned yet to occur in the North Sea.

Acknowledgements

This work was funded by the German Federal Environmental Agency (UBA) through the project

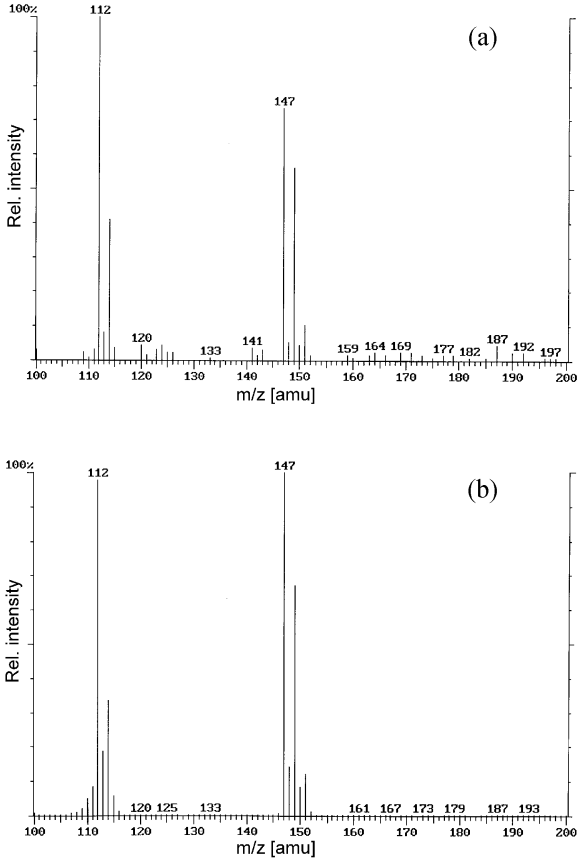

Fig. 6. (a) Mass spectrum of 2,6-dichloropyridine obtained from a North Sea water sample. (b) Mass spectrum of 2,6-dichloropyridine obtained from a standard solution.

ALOSON and by the Fonds der Chemischen Industrie. The authors wish to express their gratitude to N. Theobald (BSH, Germany) for many enlightening discussions.

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