Review

Preconcentration of contaminants in water analysis

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Abstract

Among the environmental areas, in this review attention will be focused on water matrices and both on organic (e.g., pesticides, herbicides, phenols, polycyclic aromatic hydrocarbons), inorganic species and anion pollutants, since these kinds of substances include a wide number of compounds with different physical and chemical properties and different effects on human health. Analytical methods for control of quality of waters are required to be highly specific and possibly highly sensitive for the determination of even low amounts of pollutants. The main problems encountered during the analysis are the separation of matrix components from the pollutants of interest and the achievement of low detection limits. Therefore an overview on different materials and techniques available for sample concentration and/or matrix removal will be provided and discussed according to the chemical characteristics of the pollutant that has to be enriched.   © 2000 Elsevier Science B.V. All rights reserved.

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Contents

1. Introduction

Pollution in different environmental compartments (water, soil and air), that has arisen as a consequence of the industrialisation processes or simply from human activity, is one of the main problems, that man has to solve or at least to control. Contaminants can have different chemical characteristics and, in a preliminary classification, they can roughly be divided into organic, inorganic and metal species pollutants.

Among the environmental areas, this review will

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focus on water matrices and purely organic [e.g., pesticides, herbicides, phenols, polycyclic aromatic hydrocarbons (PAHs)], inorganic and species on the border of these two families will be considered, giving wider emphasis to the organic pollutants.

With respect to the past, the multi-component determination of organic contaminants in environmental waters is nowadays made more difficult as a much larger number of target compounds has to be monitored and the demand is for methods of greater sensitivity. Chromatography provides a unique tool for the analysis of environmental water samples which most times are extremely complex and often contain many different classes of compounds in varying amounts. Different chromatographic procedures suitable for different classes of pollutants have been developed and are currently available for researchers and laboratories. The main problems encountered during the analysis are the separation of matrix components from the pollutants of interest, the achievement of low detection limits and the identification of unknown pollutants. Since conventional detection methods coupled with separation techniques do not provide the sensitivity required for low amounts of pollutants, enrichment and matrix removal procedures are needed.

Preconcentration of contaminants from water samples, and generally sample preparation steps, are often accomplished by extraction techniques, based on enrichment on liquid (liquid–liquid extraction) or solid (solid–liquid extraction) phases [1,2]. Extraction procedures, optimised prior to chromatographic separation, can be coupled on- or off-line to the analysis which is mainly performed by liquid (LC) or gas chromatographic (GC) methods. An overview on different materials and techniques available for analyte concentration and/or matrix removal will be provided and discussed according to the chemical characteristics of the pollutant that has to be enriched.

Another relevant topic, related to environmental pollutants, is the analysis of their degradation products. Independently of the large amount of literature available, in this review they will only be briefly mentioned when involved in the detection and identification of priority classes of pollutants.

Improvements in the detection of low amounts of both known and unknown pollutants by powerful hyphenation approaches (e.g., MS, MS–MS) will be recalled throughout this review.

2. Organic compounds

2.1. Phenols

This is a class of analytes of major environmental importance since phenols can be found in the aquatic environment as biodegradation products of humic substances, lignins and tannins or as derivatives of plastics, dye industries and pulp processing. Chlorophenol, for example, can be present in environmental compartments as compounds coming from industrial activities (e.g., chemicals, conservation agents) or as degradation of other pollutants like pesticides and herbicides.

Due to their toxicity the European Union (EU) and the US Environmental Protection Agency (EPA) listed several phenol compounds as priority pollutants in the aquatic medium and thus highly sensitive techniques usually coupled with preconcentration steps, are employed. Historically, liquid–liquid extraction was the procedure followed to enrich phenols from water samples. More recently, due to the poor recoveries of solvent extraction, which varies from compound to compound, the extraction of phenols was performed by solid-phase methods using adsorbing materials, mainly of the reversed phase [3–5], anion exchange [6,7] and graphitised carbon black (GCB) [8–10] types.

Extraction of phenols has been extensively performed by GCB by Di Corcia and co-workers [8–10] who made detailed studies on this kind of substrate. After extraction, a portion of eluate containing phenols has been injected in a chromatographic system and eluted on a C_{18} stationary phase by 0.01–0.025% trifluoroacetic acid and mixtures of methanol–acetonitrile or acidified acetonitrile.

GCB (commercially referred to as Carbopack B or Carbograph 1) is a non-specific, non-porous sorbent, having surface areas between 8 and 100 m^2/g. Retention of phenols has been ascribed to anion-exchange and non-specific interactions with the GCB surface. In fact, graphitic carbons have an oxygen complex having a chromene-like structure [11] that

in the presence of acidified water rearranges to form benzpyrylium salts, according to the reaction:
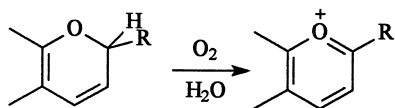
GCB has been proven successful in the selective extraction of 2,4-dichlorophenol, *p*-nitrophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2-*sec.*-butyl-4,6-dinitrophenol, 2,4-dinitro-*o*-cresol, 2,4-dinitrophenol from water [8]. It has been shown that *p*-nitrophenol (pK_a 7.2), 2,4,6-trichlorophenol (pK_a 7.0) can be quantitatively eluted by a 20 mM tetramethylammonium hydroxide (TMAOH) solution of CH_2Cl_2–CH_3OH (90:10, v/v), with the recovery being dependent upon the conditioning procedure used for GCB before extraction of phenols. Phenols of higher pK_a, like 2,4-dichlorophenol (pK_a 8.0), can be almost eluted with an organic solution containing methanol. This solvent has been reputed necessary to rapidly elute any kind of neutral adsorbate from the GCB surface. The contribution of TMAOH to the elution of phenols has been ascribed to a synergic action played by OH^- ions (adsorption and ion exchange competition for the fixed cationic sites) and tetraalkylammonium cation for the formation of stable ion pairs highly soluble in the organic eluent phase. The extraction and the recoveries of phenols have been found to be independent of the presence of large amounts of inorganic ions ($I = 0.6\ M$), due to the higher affinity of organic in respect to the inorganic ions for the benzpyrylium-containing GCB surface. Moreover, organic matter, mainly present in water samples as fulvic acids, can saturate the ion-exchange sites of GCB, thus limiting to the *unspecific* ones the interactions between phenols and the carbon surface, while fulvic acids of water can associate with acidic compounds thus reducing their retention in the substrate.

The interference in the selective elution of weakly ionised phenols when the water sample also contains neutral species has been reduced by the use of a two-trap tandem extraction system [9]. The coupling of the GCB cartridge and a strong anion-exchange (SAX) material ensured that phenols were distributed between the two cartridges, with the most acidic phenols adsorbed on the GCB surface, while the least acidic phenols were washed away from the GCB cartridge and readsorbed by the SAX cartridge. Elution of phenols from the two sorbent beds is performed by 0.25 M formic acid in CH_2Cl_2–CH_3OH (90:10, v/v). Recoveries of 17 phenols of environmental concern added to a drinking water sample at concentration levels between 0.2 and 2 µg/l were higher than 90%, with detection limits below 0.1 µg/l which represents the maximum admissible individual concentration for organic contaminants in drinking waters. Interference originated by fulvic acids on the recovery of phenols has also been highlighted. This system allows the possibility of analysing high-ionic-strength water samples (e.g., sea waters) that could not be otherwise processed in a merely ion-exchange-based system. The GCB system proved to be more efficient than C_{18} material in the recovery of phenolic substances.

Another substrate GCB-based, Carbograph 4, used by Di Corcia et al. [10] was suitable for extracting phenol, *p*-nitrophenol, 2-chlorophenol, 2,4-dinitrophenol, 2-nitrophenol, 2,4-dimethylphenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 4,6-dinitro-2-methylphenol, 2,4,6-trichlorophenol, pentachlorophenol. Recoveries for a river water sample are between 93 and 99% with the relative standard deviation (RSD) not higher than 3.5, with recovery independent of phenol concentrations. Phenol spikes concentrations made throughout that work were between 1 and 2 µg/l.

GCB, as well as styrene–divinylbenzene polymeric sorbents have been used and compared by Rodríguez and Cela [12] for preconcentration of 16 mono-, di- and trichlorophenols. When the polymeric sorbent is used, these analytes have been preconcentrated by simple acidification of the water samples until pH 2.5–2.8 is achieved. Elution is simply performed with methanol. After acetylation of the concentrated extract, chlorophenols have been analysed and quantified by gas chromatography. Derivatization of chlorophenols in their acetylated form was performed on GCB. In this case, a backflush elution (3 ml hexane + 1% TMAOH) was able to remove chlorophenols from 0.25 g GCB, accomplishing a complete recovery for pentachlorophenol too, whose interactions with positively charged benzpyrylium groups are very strong, due to the high

acidity of pentachlorophenol. Good gas chromato-grams obtained for the determination of chloro-phenols in tap waters with different hyphenation techniques [microwave-induced plasma spectros-copy, Fourier transform infrared spectrometry (FT-IR), and tandem mass spectrometry (MS–MS)] are shown, as well as a comparison among the limits of quantitation with the different gas chromatographic hyphenated techniques. Liquid chromatographic de-termination by reversed-phase (RP) was employed after extraction by off- and on-line solid-phase extraction (SPE) of 18 phenols of different nature [13]: catechol, phenol, 4-methylphenol, 2,4-di-methylphenol, 2-nitrophenol, 4-nitrophenol, 2,4-ni-trophenol, 2-amino-4-chlorophenol, 4-chloro-3-methylphenol, 2-chlorophenol, 3-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichloro-phenol, 2,3,5-trichlorophenol, 2,3,4-trichlorophenol, 3,4,5-trichlorophenol, pentachlorophenol. The au-thors provide a stability study for the compounds selected spiked in a water sample from the River Ebro to a final concentration of 10 μg/l. Under the storage conditions followed, those recommended by the US EPA, the study, performed over a period of 30 days under laboratory conditions, confirmed that polychlorinated are more persistent than mono chlorinated phenols, owing to the lower reactivity of carbon–chlorine bonds in the former. The off-line enrichment of phenols was performed on polystyrene and C_{18} extraction disks, while the on-line enrich-ment was performed on C_{18}, C_8, C_2, cyanoyl, phenyl, cyclohexyl and styrene–divinylbenzene sor-bents. Some comparative limits of detection are reported in Table 1 for off- and on-line extractions for some sorbents. A confirmation of peaks of interest, after liquid chromatographic separation, has been made by thermospray mass spectrometry in the single ion monitoring (SIM) mode, that allowed the identification of phenol compounds in complex samples and to avoid interference from humic sub-stances usually present in river water.

The high variability of breakthrough volumes for phenols, when reversed-phase sorbents are used, mainly dependent on the polarity of the compounds

Table 1
Detection limits (μg/l) of phenols for off- and on-line procedures[a]

Compound	SDB	C_{18}	PLRP-S	Cyclohexyl
	Off-line[b]		On-line[c]	
Phenol	2	>4	3	4
2-Nitrophenol	0.5	>4	0.05	0.5
4-Nitrophenol	0.5	>4	0.7	1
2,4-Nitrophenol	0.1	>4	0.01	0.5
2,4-Dimethylphenol	3	2	0.05	0.3
4-Chloro-3-methylphenol	4	3	0.1	0.7
2-Chlorophenol	2	>4	0.4	0.8
2,4-Dichlorophenol	1	2	0.2	0.5
2,4,6-Trichlorophenol	0.5	0.1	0.1	0.1
Pentachlorophenol	1	0.3	0.01	0.05
Catechol	–	–	4	4
4-Methylphenol	–	–	0.7	1
2-Amino-4-chlorophenol	–	–	7	n.d.
3-Chlorophenol	–	–	0.4	0.8
4-Chlorophenol	–	–	0.5	0.8
2,3,5-Trichlorophenol	–	–	0.1	0.1
2,3,4,-Trichlorophenol	–	–	0.1	0.1
3,4,5-Trichlorophenol	–	–	0.1	0.1

[a] Detection: UV 280 nm. Data taken from Ref. [13].
[b] Eluent: three aliquots of methanol (10+5+5 ml).
[c] Eluent: 75% (water+1% acetic acid) and 25% (methanol–acetonitrile, 1:3).
SDB=Styrene–divinylbenzene.
PLRP-S=Polymeric reversed-phase.

considered, as well as the low breakthrough volumes of C_8, C_{18} silica-based, polymeric resins and some carbon black types sorbents led to an increase in the kinds of materials tested. Masqué et al. [14] provide a comparison of a carbon black (Carbopack B, Supelco), a functionalised polymeric resin (Bond Elut PPL, 125 μm, Varian), and a higher cross-linking polymer resin (HYSphere-1, 5 μm, Spark Holland) for SPE of groups of phenolic compounds (phenol, 4-nitrophenol, 2,4-dinitrophenol) from surface and drinking waters in the presence of some polar pesticides. On-line enrichment was performed, with the use of a column-switching device, after adjusting the pH of tap water samples to 2.5 by HCl, and adding Na_2SO_3 (to prevent further production of chlorophenols by the free chlorine). Phenols were desorbed in a backflush mode by acetonitrile in order to reduce the band broadening effect. Analyte separations were performed by reversed-phase LC with a Spherisorb ODS2 with an acidic eluent and a linear gradient of acetonitrile, while detection was performed at 280 nm. Detection limits were found to range between 0.03 and 0.17 μg/l. In Fig. 1, we plotted the recoveries obtained [14] for the three substrates studied and for the phenols considered. Due to its higher degree of cross linking, which increases the specific surface area, and to its smaller particle size, which increases the surface area between the water sample and the sorbent and allows more interactions between the analytes and the resin
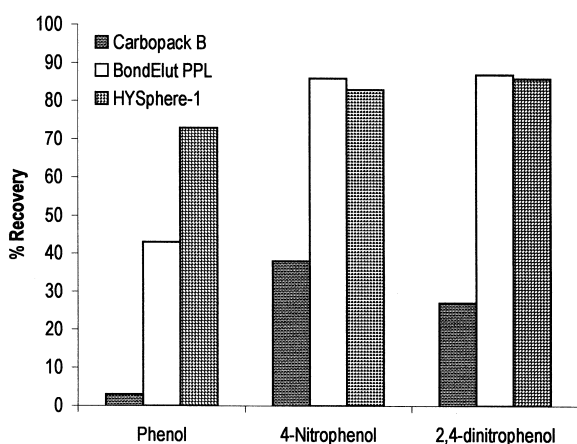

Fig. 1. Recovery values obtained preconcentrating phenols on different substrates. Sample volumes: 100 ml, analyte concentrations: 2 μg/l. Data obtained from Ref. [14].

surface, HYSphere-1 has greater capacity than Bond Elut PPL. Further improvements and comparison of synthetic (based on *o*-carboxybenzoyl structure) and commercial resins are shown [15] in respect to humic and fulvic acids interferences.

A dual-column set set-up has been proposed by Brouwer and Brinkman [16] for the monitoring of large series of phenolic compounds in surface waters. Selectivity is increased through the use of the different breakthrough of phenols in the two different pre-columns (PLRP-S and ENVI-Chrom P). By using a diode array detector, detection limits ranging between 0.05 (4-chlorophenol, 195 nm) and 1 (phenol, 195 nm) μg/l have been achieved.

It is worth mentioning that extensive work on extraction and enrichment of phenols and other organic pollutants (e.g., pesticides) has been performed by Brinkman and his group of co-workers.

Not solely related to phenolic species (2-nitrophenol), but also to aniline, 2-chloroaniline, atrazine and diuron (chosen as analytes of different polarity and acidities), Liska et al. [17] studied capabilities and limitations of 10 sorbents (C_{18}, phenyl-, diol-bonded silica, C_{18} bonded polymers with neutral, weak anion- and cation-exchange properties, styrene–divinylbenzene polymers and carbon phases). Experimental results showed that the styrene–divinylbenzene copolymer was the best sorbent for the enrichment of analytes of different properties. Styrene–divinylbenzene copolymer containing quaternary ammonium groups (PRP-X 100, 125×4 mm) has been used for preconcentration of phenols at μg/l levels [18]. Since sample pH was kept at 2.0, non-polar interactions between aromatic rings of both sorbent copolymer and phenols are acting. Polar-type interactions can occur due to the polarizability of the phenols increased by the presence of chlorine and nitro substituents. Enrichment factors of 100 are reached and recovery of nine priority pollutants phenols, evaluated in Manzanares River water, ranged from 92% (4,6-dinitro-2-methylphenol) to 105% (2,4-dichlorophenol). A recent procedure involving modification of the C_{18} surface with cationic surfactants such as cetyltrimethylammonium bromide has been shown [19]. Thirty-two phenolic compounds can be thus determined by gas chromatography–flame ionisation detection (GC–FID). The suitability of the method

has been tested in several samples of natural and waste waters with good recovery results.

A method for the preconcentration and simultaneous determination of priority pollutant chlorophenols (2-chlorophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) by flow-injection analysis (FIA) has been developed [20]. The sorbent used for preconcentration was 1.2 g of XAD-4 polymeric resin packed into a 60×5 mm I.D. column. Acidified water sample can be drawn through the column and chlorophenols eluted by methanol. After methanol evaporation, the sample is dissolved in a borate buffer (pH 9.1) and injected into the FIA system. In this system, chlorophenols form ion pairs with tetrabutylammonium ion and are extracted by chloroform to be then detected by a diode-array spectrophotometer (200–430 nm). The limitation of FIA is mainly on the simultaneous determination of analytes, but can be overcome by using multivariate analysis. It has been shown [20] that chlorophenols recoveries depend upon the multivariate calibration method applied (better than 95% for classical least-squares – CLS – and Kalman filter, better than 87% for partial least-squares – PLS). As shown in Fig. 2, the comparative study show the best results, expressed as SEP (standard error of prediction), for the CLS method.

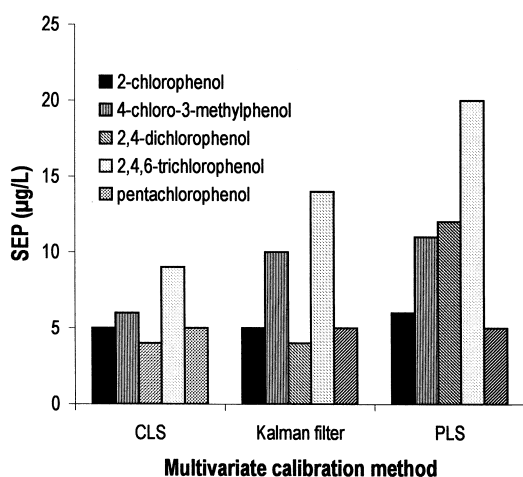A procedure for trace enrichment of phenols, and

Fig. 2. Standard error of prediction (SEP) for spiked tap water (µg/l). CLS = Classical least-squares; PLS = partial least-squares. Data taken from Ref. [20].

generally for ionogenic compounds, based on dynamic ion-exchange has been shown by Li and Lee [21]. By adsorbing long-carbon-chain ionic surfactants on C_{18} silica surface, ion-exchange and hydrophobic interactions take place between solutes and sorbent. Higher extraction efficiency, less influence on recovery by inorganic ions and humic substances than RP bonded-, ion-exchange-, carbonaceous- or polymer adsorbents-based materials used throughout literature, are claimed.

Automated on-line trace enrichment of phenols and reversed-phase LC separation with electrochemical detection (glassy carbon electrode: 0.8 V for 2,4,6-trichlorophenol and pentachlorophenol; 1.1 V for phenol, 4-nitrophenol, 2,4-dinitrophenol, 2-chlorophenol, 2-nitrophenol, 2,4-dimethylphenol, 2-methyl-4,6-dinitrophenol, 4-chloro-3-methylphenol, 2,4-dichlorophenol) has been developed and applied to environmental waters by Pocurull et al. [22]. Enrichment was performed on a 10×2 mm I.D. column packed with styrene–divinylbenzene copolymer (PLRP-S) on samples at pH 9.0 and added with 5 m*M* tetrabutylammonium (to increase breakthrough for most polar compounds). Desorption was performed in the backflush mode by water:methanol eluents. Recoveries higher than 85% (except for 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol) and detection limits of 0.01–0.1 µg/l are shown.

Based on enrichment on polymeric-based material (SDB1), chlorophenols have been enriched from natural water samples with quantitative recovery values [23]. The material studied showed increased retentive properties if compared with conventional silica-based materials.

Capillary electrophoresis (CE) gained success as a separation technique in the environmental trace analysis of phenols and other organic compounds [24] (e.g., herbicides, inorganic cations and anions, PAHs). A preconcentration step with a highly cross-linked styrene–divinylbenzene copolymer (Envi-Chrom P) was applied before capillary zone electrophoresis and high-performance liquid chromatography (HPLC) to determine 11 priority US EPA phenols in Ebro River water [25]. The 100-fold preconcentration allowed a reduction of matrix effect. The commercial sorbents PLRP-S and Li-Chrolut EN have been laboratory packed for on-line SPE of the 11 US EPA priority phenolic compounds and determination by supercritical fluid chromatog-

raphy with diode-array detection (DAD) [26] from tap and river water. Through the addition of tetra-butylammonium bromide, breakthrough volumes in the extraction process have been increased. Detection limits ranging from 0.4 to 2 µg/l are achieved. A comparison of performance of different sorbents for enrichment of phenols from industrial effluents at different total organic carbon content has been presented by Lacorte et al. [27].

2.2. Pesticides and herbicides

Polar pesticides and herbicides, like other polar micro pollutants, are difficult to enrich since they cannot always be trapped efficiently on the most frequently applied non-polar sorbents.

Among the herbicides, simazine and atrazine, applied for a wide variety of crops, have been enriched from tap and surface water samples by graphitised carbon black Carbopack B [28]. Using 50 mg of sorbent, the authors show the effect of sample volume preconcentrated on the recovery of simazine and atrazine from tap and surface water. It is shown that recovery for 1 µg/l simazine is reduced from 98.3% to 88.5% when 200 ml and 800 ml of surface water is preconcentrated, probably due to partial sorbent saturation by substances other than the two herbicides considered. Claimed limits of detection, evaluated by a C_{18} reversed-phase system, with UV detection at 220 nm, are 0.07 and 0.15 ng. In a further development of the method [29], the group of analytes has been enlarged to nine species of herbicides: 2-methoxy-3,6-dichlorobenzoic acid (Dicamba), 2,4-dichlorophenoxyacetic, 4-chloro-2-methylphenoxyacetic, 2-(2,4-dichlorophenoxy)-propionic, 2,4,5-trichlorophenoxyacetic, 2-(4-chloro-2-methylphenoxy)propionic, 4-(2,4-dichloro-phenoxy)butyric, 4-(4-chloro-2-methylphenoxy)-butyric, 2-(2,4,5-trichlorophenoxy)propionic acids. Widely used for their relative cheapness and effectiveness, they belong to the family of phenoxy acid herbicides. Extraction has been performed in one cartridge containing 50 mg of Carbopack B and, in the lower side, 70 mg of a silica-based SAX. After the sample is passed through the two-adsorbent trap, quite a long procedure is required to remove herbicides from the trap. In fact, inorganic anions of real samples are displaced from SAX resin by 1 M

sodium acetate. Salt excess is then removed with deionised water, which is in turn removed by acetonitrile. Phenoxy acids and Dicamba are then eluted from Carbopack B to SAX by CH_2Cl_2–CH_3OH (80:20, v/v) containing 1 mM NaOH. The elution of analytes from SAX resin is finally accomplished by water–methanol (50:50, v/v) containing 0.5% trifluoroacetic acid.

Chromatographic analysis has been then performed by a C_{18} column, a water–methanol (41:59, v/v) mixture containing 0.08% trifluoroacetic acid and an UV detection at 230 nm. The high recovery values obtained for herbicides (e.g., 95–99% for two 50-ml samples of river and sea waters containing 2 µg/l of each analyte) were ascribed to the anion-exchange properties of Carbopack B, since the strong anion exchanger has low affinity for organic anions. Interestingly, the authors pointed out that with the increase in preconcentrated sample volume, only the recovery of Dicamba is affected, reducing from 98 to 32% in river water and from 99 to 49% in sea water, when 200 ml of sample are enriched. Recovery is enhanced to about 97% if the sample is acidified at pH 2. The use of Carbopack B has also been tested by the same authors for the extraction of 14 phenyl-urea herbicides [30], alone and in presence of their main degradation products (anilines). Fenuron, metoxuron, monuron, monolinuron, fluometuron, chlortoluron, metobromuron, difenoxuron, iso-proturon, diuron, linuron, chlorbromuron, chloro-uxoron, neburon were recovered and detected at about 1 ng/l for a 2-l river water sample. In presence of anilines, the Carbopack B needs to be coupled with a strong cation exchanger that retains basic compounds.

Recoveries for atrazine and linuron, together with methyl- and chlorophenols derivatives have been compared on different commercial sorbents [31]: activated carbon (Envi-Carb, Supelco), mixed C_8/anion-exchange resin (Certify II, Varian) and amino- and diamino-bonded silicas (Baker) and on synthesised hydroxymethyl and acetyl derivatives of Amberchrom 161M resin (Supelco) according to Sun and Fritz [32]. The separation and determination of analytes have been performed by gas chromatography, coupled to an ion trap detector. Best recoveries of herbicides were obtained with acetyl-modified resin, even if poor recovery of more polar, anionic species has been noted. The combination of

acetyl resin and amino-bonded silica gave the best results among all the material tested. Unfortunately, the paper, which appears to be a preliminary screening of suitable enrichment materials, does not provide either the chromatograms obtained nor the detection limits achieved. Still based on the use of GCB, Di Corcia and Marchetti show good examples of enrichment and RP separation with UV detection for 35 pesticides with base/neutral and acidic properties [33] with stepwise elution. Comparison with C_{18} cartridge recoveries is provided and the advantages over the use of reversed-phase sorbents are detailed. Detection limits range between 3 and 70 ng/l. As a further improvement of the method developed, Di Corcia et al. [34] describe the advantages of back-flush over forward desorption of 27 polar pesticides and metabolites. Pesticide residues and their metabolites have also been enriched on SPE disks and determined by GC techniques with flame thermionic, electron-capture and mass-selective detection systems [35]. Several compounds like alachlor, atrazine, deethylatrazine, metolachlor, molinate, propanil, simazine, carbofuran, diazinon, methylparathion, propazine, trifluralin, malathion, ethylparathion, lindane, heptachlor have been determined in river water samples.

Organophosphorus pesticides (e.g., fenamiphos, fenthion, disulfoton, diazinon) and some of their transformation products have been enriched with C_{18} pre-columns, desorbed with a water–acetonitrile mixture containing ammonium formate and detected by thermospray mass spectrometry [36] with selected ion monitoring. By loading 100 ml of sample, pesticides have been detected at concentrations as low as 0.01–0.1 μg/l. The paper is mainly devoted to MS detection and identification of transformation products such as 3,5,6-trichloro-2-pyridinol, which according to the authors, was for the first time detected in natural waters. Recovery data are not available. As regards P-containing pesticides, a fast procedure for their determination in aqueous samples based on on-line extraction with membrane disks (C_{18} and polymer XAD) and GC analysis has been developed by Kwakman et al. [37]. Recoveries for most of the pesticides considered were higher than 95%. This method appears virtually suitable for enrichment of any analyte that shows affinity for the hydrophobic extraction disk and is amenable to GC analysis.

Based on MS analysis after HPLC separation, base/neutral and acid herbicides in natural waters after enrichment on GCB have been determined at ppt level by D'Ascenzo et al. [38].

C_{18} silica sorbent performance has been studied for extraction of triazines, organochlorine, carbamates and acidic pesticides from ground waters and compared with that of liquid–liquid extraction [39]. The determination method [GC–electron-capture (ECD) and nitrogen–phosphorous detection (NPD)] allowed the achievement of detection limits of 3–60 ng/l.

A detailed study on the presence of pesticides of different polarity phosphorous, organochlorine, nitrophenol, phenoxyalkanoic and chloroalkanoic acids pesticides, as well as other organic micropollutants in the River Elbe (Mid-Europe) has been presented by Pietsch et al. [40]. Analyses have been performed by four different methods comprising solid-phase and liquid–liquid extraction both with and without derivatization by GC–ECD, NPD and MS. The aim of the paper is primarily the evaluation of River Elbe pollution and the distribution of pollutants in the different region of the river.

Based on liquid–liquid enrichment with dichloromethane procedure, a method for characterisation of triazine (atrazine, simazine, ametryne, cyanazyne, deetylatrazine, deisopropylatrazine), phenylurea (chlortoluron, isoproturon, diuron, linuron, difluben-zuron) derivatives, alachlor and metolachlor is shown [41]. The method developed has been applied to trace enrichment of the different herbicides in estuarine water samples from the Elorn River (France), with limits of detection ranging from 10 to 500 pg obtained with an RPLC separation coupled with high-flow pneumatically-assisted electrospray mass spectrometry. A SPE procedure, claimed to be fast and with automation possibilities has been presented [42]. A group of 29 pesticides in 400 ml of water sample has been enriched with Envi-Carb substrates, separated by RP chromatography and detected in the UV region at 225 nm. Detection limits ranged from 0.1 to 0.5 μg/l. Automation of enrichment and separation steps follow the development of new analysis techniques. Slobodník and co-workers [43,44] optimised a fully automated column liquid separation system using on-line enrichment (with PLRP-S cartridges), gradient elution and DAD. The system has been optimised for the analysis of 18

polar pesticides [43], through the control of pH, volume and ionic strength of the sample and the flow-rate of the enrichment step. The method developed has been applied for analysis of tap and river (Rhine) water samples, achieving detection limits below 0.1 μg/l for all the analytes considered (carbendazim, metamitron, chloridazon, aldicarb, bromacil, simazine, 2-chloroaniline, atrazine, diuron, monolinuron, warfarin, linuron, 3,3-dichlorobenzidine, barban, dinoterb, dinoseb, pentachlorophenol and phoxim). Developments in the area of on-line enrichment–LC separation–detection/identification have also been discussed [45]. The automated systems using SPE coupled on-line to LC–DAD, LC–MS, and GC–MS developed by the group of Brinkman [43–45] are known under the acronym SAMOS (system for automated measurements of organic micropollutants in surface water). The SAMOS concept and the analytical process involved can be divided into an extraction/enrichment and a separation/detection step. A known volume of a water sample is pumped through SPE pre-column(s) where sorption and enrichment of compounds of interest occurs. Their desorption is performed by suitable solvent mixture for introduction into LC or GC instruments. The SAMOS-LC system is mainly designed for automated on-line determination of polar pesticides in water after enrichment on PLRP-S pre-column. SAMOS-LC–MS and SAMOS-GC have been developed following SAMOS-LC design and testing [46]. In particular, SAMOS-GC is essentially the implementation of an on-line LC–GC technique for the sub-ppb level determination of a wide range of (semi) volatile compounds in water. Software for complete automation has also been designed.

A further improvement of these automated procedures consisted in the selection of three SAMOS systems (SPE–LC–DAD UV, SPE–LC–particle beam MS and SPE–GC–MS) for a 2-year regular monitoring programme of the Nitra River (Slovak Republic) [47]. Interesting results in term of detection limits, reproducibility, identification of unknown pollutants by at least one technique, and provisional overview of the type and classes of pollutants of the River Nitra are shown throughout the study. As an application in the Rhine Basin Program, SAMOS technology has been considered in a report of the *Journal of Analytical Chemistry* [48]. A modified SAMOS system has been recently intro-

duced [49] in order to allow the determination of ionic and polar compounds that otherwise show breakthrough from SPE cartridge prior to complete the loading of the sample.

As an application for environmental screening, where in most instances few compounds of interest occur at a certain point in time, Hupe et al. [50] simplified the configuration previously optimised [43] to a new system in which a single column (Hypersil ODS, 5 μm, 60$\times$4.6 mm or 20$\times$4.6 mm) is used for extraction–enrichment and separation of a mixture of seventeen polar pesticides. A diode-array detector is coupled. The procedure can be assimilated to a FIA-like system which still possesses chromatographic properties including accessibility to any kind of detection and identification devices. Great attention has been devoted in applying single and/or double short columns for the rapid analysis and study of pesticide degradations [51–56]. With such an approach, some selectivity is sacrificed, but through the use of only few ml of aqueous sample, analyte detectability can be compared to those levels achieved by systems that use sample volumes as high as 100 ml. The single-short column approach has been recognised advantageous especially when expensive spectroscopic detectors (MS, MS–MS) have to be used and short run times are required.

A fully-automated and software-controlled on-line SPE–GC–MS system (PROSPEKT) by using PLRP-S sorbent, has proved successful in the identification and quantification of wide variety of pollutants in surface and waste water samples at 0.01 μg/l levels, using 10 ml of aqueous sample [57]. A loop-type interface for on-line SPE (PLRP-S)–GC has been evaluated in combination with ion-trap MS–MS detection for analysis of pesticides in real-life water samples in concentration as low as 0.5 (desethylatrazine)–0.01 (trifluralin) ng/l [58].

Still based on on-line coupling of SPE (PLRP-S) to GC–MS, a method for determination of pesticides at 2–20 ppt levels has been optimised by Pocurull et al. [59] through the study of parameters affecting the transfer of analytes from the pre-column to the GC system. Recently, Hankemeier et al. [60] improved an automated at-line SPE–GC–MS system that allows determination of micropollutants at the low ng/l level without interferences from impurities extracted from the septa of the vials of commercial cartridges.

A different approach also using enrichment procedure consists in GC water analysis by direct injection of large sample volumes in programmed temperature vaporizer (PTV) injector [61] with adsorbent inside the insert of the PTV. Among the substrates investigated, Tenax TA [porous poly(2,6-diphenyl-*p*-phenylene oxide)], Tenax GR (porous polymer+23% graphite), Chemopack C_{18} (silica C_{18}), Carbopack F and C (graphitized thermal carbon black) and Carbotrap (graphitized carbon black), Tenax TA proved to be the best sorbent in terms of breakthrough volumes and inertness to the analytes to be determined. Injections of 500 µl samples gave detection limits between 10 ng/l (dieldrin by ECD) and 0.5 µg/l (aldimorph by NPD). Further improvements exploiting the capabilities of the PTV–GC–MS coupling for target (SIM mode) and non-target (scan mode) analysis has been shown [62].

A review dealing on methods for the analysis of aqueous samples with GC has been presented [63]. The direct (water introduced in the GC column) and the indirect (elimination of water via solid or liquid extraction) approaches have been discussed, with emphasis pointed on methods in which on-line combinations of sample preparation and GC analysis are performed. A survey on multidimensional gas and liquid chromatographic approaches to trace-level environmental analysis has been done by Brinkman [64].

Recently, a major experimental and theoretical study has been performed and presented by Hennion et al. [65] who give a method development for predicting the main SPE parameters for polar analytes poorly extracted using popular C_{18} silicas. From the knowledge of the sample volume needed to obtain the required detection level, the prediction of the necessary retention factor in water (log K_w) has been done in order to achieve recoveries of at least 85%. The selection of type and amount of sorbent to predict log K_w values has been discussed for common reversed-phase sorbents (C_{18} silicas, apolar copolymers, carbon-based sorbents). By this study, the high potential of polystyrene–divinylbenzene (PS–DVB) and carbonaceous sorbents for the extraction of polar pesticides (oxamyl, deisopropyl-atrazine, deethylatrazine, carbendazim, aldicarb, simazine) has been shown.

Trace enrichment of polar pesticides as well as phenolic compounds from river water has been performed by Masqué et al. [66,67] by modification of a PS–DVB resin with 2-carboxy-3/4-nitrobenzoyl and with 2,4-dicarboxybenzoyl and *o*-carboxybenzoyl moieties. Best results are showed to be achieved by the nitro-modified resin with recoveries for pesticides higher than 80%.

Besides traditional methods of using sorbents, membrane-extraction disks made of a matrix of 10% PTFE and 90% sorbent (e.g., C_{18}-modified silica, polymer, cation exchanger) have also been used for polar pollutant enrichment [68]. The authors show how a special constructed holder containing both C_{18} and cation-exchange disks can enrich pollutants (e.g., bentazon, metamitron, chloridazon, aldicarb, dinoseb, simazine, 2-chloroaniline atrazine, diuron) from 20-ml surface water samples. Desorption was performed at 60°C using reversed-phase gradient elution. Detection limits of 0.5–2 µg/l are shown. Some advantages of the use of disks rather than the traditional sorbents are the absence of channelling (sorbent particles are immobilized), high capacity (more homogeneous sorbent bed) and possibility of use different kinds of sorbents in the same cartridge holder. On-line trace enrichment (by Bondesil C_{18}, Analytichem) in combination with gradient reversed-phase separation and a luminol chemiluminescence detection system based on on-line photochemical production of organic hydroperoxides has been presented by Niederländer et al. [69]. Detection limits of 0.2–0.7 µg/l for warfarin, chloridazon, bromacil have been found.

The preconcentration of hydrophilic organic compounds like cationic herbicides cannot be performed by liquid–liquid extraction, due to their water solubility and low volatility and therefore SPE techniques are generally employed. Conditions for extraction of paraquat, diquat and difenzoquat by silica cartridges with the addition of a cationic surfactant have been optimised with respect of pH and cationic surfactant type and concentration [70]. The method, applied to natural water samples analysis partially resolve the problem of interference of humic substances on recovery, but is unfortunately ineffective for the interferences of inorganic salts.

A comparative study for solid-phase extraction–preconcentration of paraquat, diquat, and difenzoquat

by silica and porous graphitic carbon has been recently proposed [71]. Advantages and limitations of the two sorbents are highlighted taking into account the determination techniques used for the analysis of herbicides (CE and reversed-phase ion pair chromatography with UV detection); the procedure has been applied on tap and river water samples. Recovery values obtained vary according to the sample matrix, the sorbent and separation techniques used as shown in Fig. 3.

An analytical method based on combination of SPE and field-amplified concentration with micellar electrokinetic chromatography has been developed for extraction, concentration and separation of organonitrogen pesticides from drainage water with recoveries >85% and detection limits of 0.8 ppb [72].
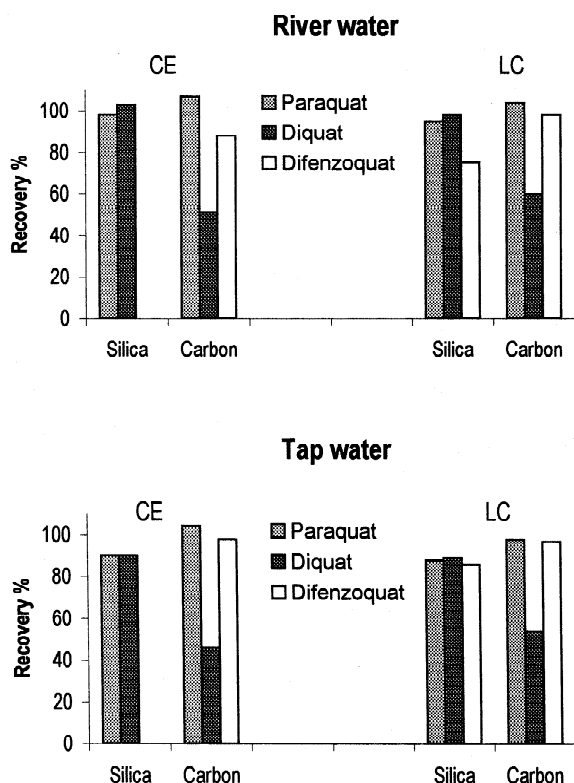
The preconcentration and removal of organic (e.g.,

Fig. 3. Recoveries, %, of spiked (5 μg/l) cationic herbicides from river and tap water samples using silica (Sep-Pak, Waters) and porous graphitic carbon (Shandon) after determination by capillary electrophoresis (CE) and LC. Data taken from Ref. [71].

pesticides, phenols, aromatic hydrocarbons) and inorganic (metal ions) analytes of environmental concern from aqueous media by surfactant-based separation techniques exploiting the solubilization power of micelles and other amphiphilic aggregates towards the analytes has been summarised by Pramauro and Bianco Prevot [73]. The number of published papers concerning the development and application of analysis of pesticides in water matrices has increased enormously and has resulted in an extensive bibliography. In particular, MS detection of polar thermally labile (not GC amenable) pesticides coupled to LC separations for environmental applications has received great attention. The development of different interface systems {e.g., thermospray [74,75], particle beam, electrospray, APCI (atmospheric pressure chemical ionisation) [76–78]} for solving the incompatibility between HPLC and MS introduced power coupling hyphenated techniques that provide adequate sensitivity and structural information for the detection of a broad range of pollutants of environmental interest. MS detection of polar pesticides has been reviewed by Ferrer and Barceló [79] and by Slobodník et al. [80] and, in recent times, a method for determination of polar pesticides (e.g., triazines, phenylurea herbicides, phenoxy acids) based on SPE and APCI-MS–MS and gradient liquid chromatography, has been published [81]. On-line SPE followed by GC separation and coupled with atomic emission (AED)/mass spectrometric detection has been used by Hankemeier et al. [82] for the non-target screening of hetero-atom-containing compounds in drinking water samples. Other examples of atomic emission detection (microwave induced plasma, MIP-AED) for the screening analysis of aqueous samples have been proposed by Frischenschlager et al. [83,84]. MIP-AED proved to be highly selective over other elements simultaneously present with the analyte and enables the calculation of empirical formulas of the detected compounds as well as quantitation of identified analytes.

The complexity of aqueous matrix compositions often lead to co-extraction and co-elution with the pollutants of interest present at trace levels. Therefore there is a considerable interest in developing class-selective methods to extract and isolate groups of components, from complex matrices, in one step. Materials with antibodies covalently bonded form the

so-called immunosorbents that can be packed into a solid-phase extraction cartridge or pre-column. Through antigen–antibodies interaction, analytes can be individually quantified after extraction, desorption, and separation. Immunosorbents have been designed and applied for the extraction of groups such as triazine and phenylurea pesticides or PAHs [85–88]. Examples of on-line coupling of immunoaffinity-based sorbents with LC [89,90] and GC [91] techniques have also been shown.

For the sake of completeness, we also mention reviews on chromatographic techniques for pesticides and their residues in water [92,93], and a capillary electrophoretic application for the characterisation of photodegradation of atrazine [94]. CE coupled with a continuous flow system to automatically carry out calibration, preconcentration, elution and injection has been presented by Hinsmann et al. [95]. Finally, supported liquid membrane extraction for continuous extraction and enrichment of ionisable organic pollutants from aqueous environmental samples should be mentioned [96].

2.3. Polycyclic aromatic hydrocarbons

PAHs are ubiquitous environmental pollutants of anthropogenic origin, mainly formed by incomplete combustion of organic matter. Their mutagenic and carcinogenic nature has been widely recognised by several researchers. Due to the complexity of the matrix, PAH determination in environmental samples is often a difficult task, even after fractionation of sample extracts, therefore good chromatographic selectivity, both in separation and in detection are required during environmental analysis. Moreover, since their concentration in water samples is extremely low due to their low solubility, the determination of PAHs is rather difficult.

Among environmental compartments, the marine system has received great attention and chromatographic separation as well as sampling, clean-up and enrichment procedures of marine samples have been reviewed [97]. In this collection, enrichment procedures based on flotation, extraction by light petroleum–diethyl ether mixture and determination procedures based on HPLC coupled with different detectors (e.g., fluorescence, MS, UV-diode array)

are listed. Since great problems are encountered during sampling and storage of PAHs due to their sorption, solubilisers like organic solvents or surfactants are required to increase their solubility. An on-line RPLC system for the determination of PAHs has been developed by Brouwer et al. [98] who studied the solubilising properties of several ionic and non-ionic surfactants to solve the problems arising from the low solubility of PAHs in water and their sorption to surfaces. Surfactants above the critical micelle concentration (cmc) dissolve hydrophobic substances. It has been shown that polyoxyethylene lauryl ether, Brij-35 has a positive influence on analyte recovery even below its cmc $(1.0 \cdot 10^{-4}$ $M)$ especially for late-eluting compounds (Fig. 4). Above the cmc, breakthrough occurs since micelles act as modifier.

On-line micelle mediated preconcentration and reversed-phase separation with fluorescence detection for 16 PAHs in River Rhine water (spiked at concentrations of 0.1 µg/l) are shown. Octadecyl-modified silica sorbent (Zorbax ODS1) has been used by Renner et al. [99] for on-line enrichment of PAHs in water, with separation and detection performed by RPLC and fluorescence. Thermally as-
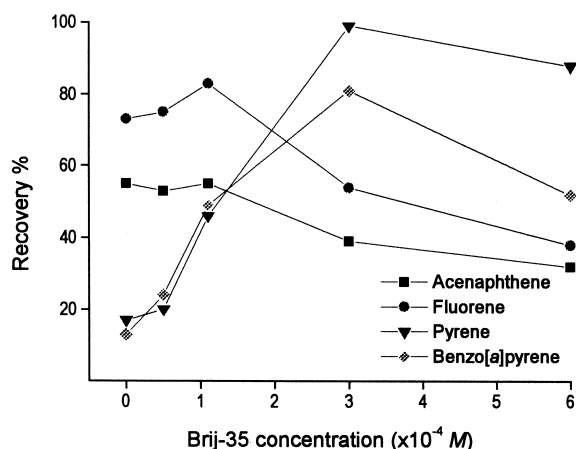

Fig. 4. Effect of surfactant concentration (polyoxyethylene lauryl ether, Brij-35) on recovery of PAHs (25 µg/l). Preconcentrated volume: 10 ml. Preconcentrator column: diol-modified silica (20 µm, 10×3 mm I.D.) modified with copper phthalocyanine trisulfonic acid moiety. Desorption eluent: water–CH$_3$CN (60:40). Data taken from Ref. [98].

sisted desorption has been shown to increase the recovery of analytes. Loss of PAHs for adsorption on surface of tubing and materials made of polymeric materials has been evidenced.

An interesting and well performed study has been shown by Sturm et al. [100] who evidenced that the entity of interactions between humic substances and PAH (fluorene, pyrene, benzo[*a*]pyrene) in the adsorption involved during SPE by a reversed-phase system becomes considerable for analyte concentrations lower than 200 ng/l. Commercial humic acid solutions (model substance) exhibited greater interference than natural ones (samples from coastal waters of the southern North Sea) showing that the level of interference depends on the type of humic substance. According to the results obtained, interesting correlations between octanol–water distribution coefficients (polarity of compounds) and type of extraction procedure (liquid–liquid or solid–liquid) that has to be chosen are gathered.

The problem of interference by compounds present in the environment has been detailed by Madichie et al. [101] who focused their attention on the effect of surfactants (biodegradable alcohol ethoxylates) on the analysis of some PAHs in natural waters after preconcentration on an ODS2 column. Severe interference from surfactants in the recovery of PAHs from the reversed-phase sorbent has been evidenced. Concentration and length of chain of surfactant, pH, ionic strength of sample solutions have been recognised to be the more crucial parameters governing recovery of PAHs.

A method for extraction of PAHs based on different principles is the cloud point extraction methodology. This approach exploits the extraction properties of surfactants, mainly of the non-ionic and zwitterionic types, when they are present at concentrations above their cmc value. By heating the solution two phases are formed. The surfactant-rich phase is able to extract organic hydrophobic and hydrophilic compounds (e.g., organophosphorous pesticides [102] and fungicides [103]).

A procedure based on micellar extraction aimed to the extraction of the PAHs classified as priority pollutants by the US EPA has been presented [104]. After extraction, removal of surfactant by a clean-up with silica gel, separation has been performed by

RPLC with fluorescence detection. Triton X-114 (cloud point temperature 25°C) has been used as extractant. Results obtained for determination of PAHs after extraction by cloud point with 1% (w/w) surfactant are shown in Fig. 5. Some of the drawbacks of this methodology lies in the need of removal of surfactant that, due to its non-polar character and to its aromatic moieties (if any), can interfere in the separation and in the fluorescence detection of PAHs.

The anionic surfactant sodium dodecane sulfonic acid (SDSA) has been studied and proposed for the first time for the extraction and preconcentration of the 16 PAHs [105] listed as priority pollutants by the US EPA from water system by the cloud point extraction. This approach is a promising alternative to the most widely used extraction procedures (liquid–liquid and solid–liquid) and for preservation, desorption of PAHs from containers of samples.

The application of carbon sorbents to the preconcentration of organic pollutants (e.g., PAHs, pesticides) from environmental samples is listed by Matisová and Škrabáková [106], while an extraction procedure has been applied for an investigation of concentration of PAHs in Lake Balaton (Hungary) [107]. A method based on SPE with Isolut Env+ has been optimised by Toribio et al. [108] for the determination of 35 common contaminants (including also pesticides and phenols) by supercritical fluid
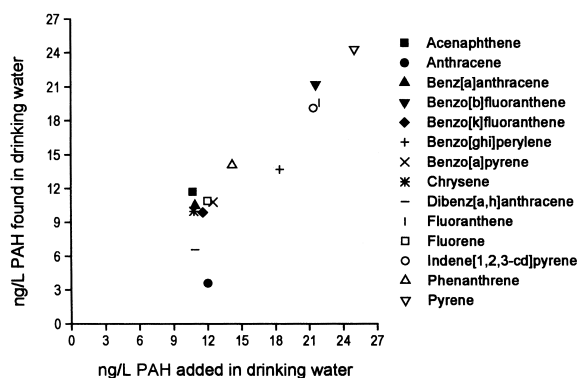

Fig. 5. Correlation between concentrations of PAH added and found in a drinking water sample. Recovery percentage after preconcentration, clean-up and LC determination: mean 85.9%, minimum 30.0% (anthracene), and maximum value 109.4% (acenaphthene). Data according to Ref. [104].

chromatography, obtaining detection limits of 0.4–2.6 µg/l.

Immunosorbents have been recently used in the extraction of organic pollutants (PAHs as well as pesticides and their degradation products) from environmental waters. The advantages of the use of this material [109] over the conventional ones (C_{18} or polymeric) are discussed. One of the last applications of SPE of organic pollutants from surface waters has been presented by Lacorte et al. [110]. Through the use of an *N*-pyrrolidone styrene–divinylbenzene sorbent (Oasis, Waters) and GC–MS with electron impact ionization, they provide a wide number of experimental data aimed at the determination of 109 priority organic compounds listed in the 76/464/CEE Council Directive. Besides PAHs, the analytes considered belong to the family of benzidines, chloroanilines, chloronitrobenzenes, chloronitrotoluenes, chlorophenols, chloronitrotoluidines, polychlorinated biphenyls (PCBs), pesticides, phenylurea and triazine herbicides. Oasis cartridges proved to be effective in retention of basic, neutral analytes and compounds in their ionic form with recoveries between 70 and 120% and detection limits of low ng/l (for a preconcentration volume of 200 ml).

Even if not directly related to PAH preconcentration, but to PAH analysis, the study of Szolar et al. [111] is worthy of mention, since separation of neutral PAHs is achieved by CE through the addition of cyclodextrin mixture to the buffer phase.

2.4. Surfactants

Usually classified into four main families: anionic (e.g., linear alkylbenzenesulfonates, LASs), cationic, zwitterionic and non-ionic (e.g., polyethoxylates), surfactants find their application in industry (e.g., pesticides synthesis), processing technology and science. Due to their physical chemical properties, the non-ionic surfactants are used when detergency, (de)foaming, (de)emulsification, dispersion and solubilisation effects are required [112]. Their widespread applications imply their direct use and discharge into water with a certain risk of entering natural waters. Classically, determination of surfactants is performed by the cumulative parameter method with direct determination after extraction. Anionic surfactants are determined as methylene blue active substance (MBAS) and non-ionic surfactants are determined according to the bismuth active substance method. In any case, positive interferences are often encountered. The less recent literature dealing with determination of LAS surfactants proposes determination methods based on spectrophotometry [113], GC [114], GC–MS [115]. Enrichment procedures using C_{18} silica cartridges (Sep-Pak, Supelclean and Bond-Elut) developed for LASs and alkylphenol polyethoxylates have been shown by Marcomini et al. [116]. Applications of the method developed to the analysis of sewage effluents, raw, mechanically, biologically treated waste waters by RPLC and fluorescence detection are shown. High recoveries (e.g., >80% for biologically treated waste waters) can be obtained according to the experimental conditions used. Additional application of SPE of non-ionic poly(ethylene oxide)-type surfactant mixtures by C_{18}-bonded silica cartridges is described by Desbène et al. [117]. By the procedure developed concentrations of analytes below 1.0 µg/l can be determined in water with quantitative recovery of the surfactants from the stationary phase. Reversed-phase extraction has been used by Maruyama et al. [118] with HPLC to evaluate the presence of poly-(oxyethylene)alkylphenyl ether non-ionic surfactants in three main rivers of Tokyo. By the use of electrospray ionization mass spectrometry, poly(oxyethylene)nonylphenyl ether was recognised to be the dominant pollutant.

In order to simultaneously determine anionic, cationic and non-ionic surfactants, a combination of the anion-exchange resin XAD-4 and C_{18} reversed-phase materials has been employed [119] and applied to surfactants determination in River Elbe water.

C_{18} reversed-phase and XAD-4 extraction steps have been used for pre-treatment of industrial waste water for determination of LASs (C_{10}, C_{11}, C_{12}, C_{13}) by CE [120]. Recoveries ranging from $93\pm24\%$ (C_{13}) to $107\pm4\%$ (C_{10}) have been obtained. The high relative standard deviation (RSD) values have been ascribed to matrix influences.

Specifically devoted to determination of cationic surfactants, a membrane liquid–liquid extraction method coupled on-line with LC in the normal phase has been recently proposed by Norberg et al. [121].

In this work, Dodigen 226 homologues (alkyldimethylbenzylammonium chloride), chosen as model compounds, have been ion-paired with heptanoic acid and extracted into chlorobutane by means of microporous membrane liquid–liquid extraction. Detection limits of 0.7–5 µg/l in river water samples and an enrichment factor of 250 have been obtained. Samples of waste waters have also been considered.

Supercritical fluid extraction (SFE) has been presented as selective method for extraction of non-ionic surfactant without interference from anionic and cationic ones. Kane et al. [122] compare two methods (direct and continuous) for extraction of an alcohol phenol ethoxylate non-ionic surfactant. By coupling a SPE disc, preconcentration of analyte is achieved. Removal of analyte from the disk is performed by SFE. Though simple in design, with little sample preparation required, continuous extraction looks kinetically limited with recoveries of about 40–60% even at relatively long extraction times (2 h).

Based on a flow injection system, an application of chromatomembrane cells (size $3.0 \times 0.5 \times 1.0$ cm^3, free volume of each phase 0.2 ml, macropores 200 µm, micropores 0.3 µm) to the critical step of ion-pair extraction intended for the methylene blue method has been presented [123]. Referring to the preconcentration and extraction cycle proposed by the authors and shown in Fig. 6, the ion-pair complex between dodecylsulfate and methylene blue is pumped through the macropores of the cell, with micropores filled with pure chloroform in condition of a stationary chloroform phase. The ion pair is adsorbed at the interface boundary of the liquids and retention volume is inversely proportional to its concentration. The break point occurs when the interface boundary has been saturated. Extraction by chloroform should start before saturation takes place. This computer-operated procedure allows to determine anionic surfactants corresponding to the methylene blue method and it is claimed to warrant good recovery and accuracy.

Among spectrophotometric approaches, a method for determination of sodium dodecylsulfate (SDS) by ion pair association with Rhodamine 6G and adsorption on the walls of a PTFE vessel has recently been presented [124]. Methyl cellosolve is then used
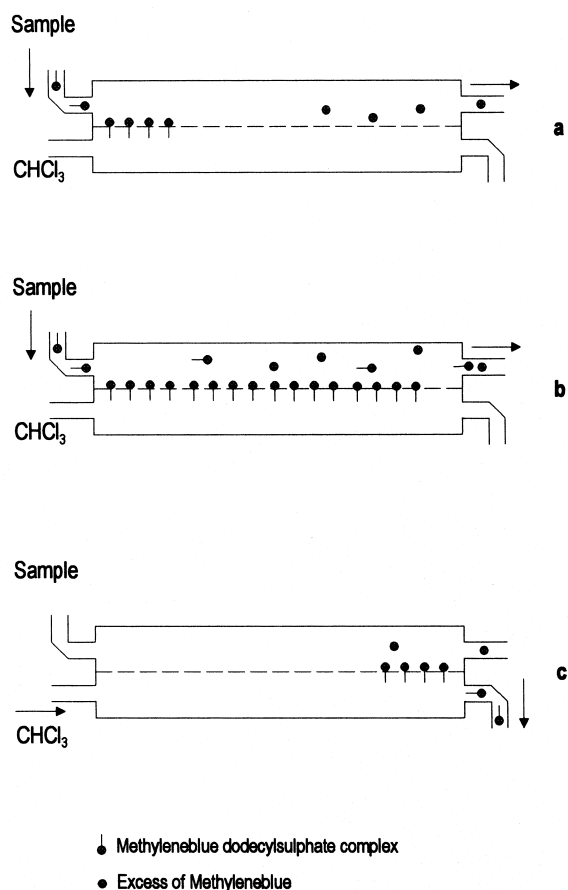

Fig. 6. Detail of model of preconcentration cycle inside the chromatomembrane cell. (a) Adsorption at the phase boundary water–CHCl$_3$. (b) Saturated phase boundary. (c) Desorption into the organic cell. Reprinted from Ref. [123] with permission.

to dissolve the ion associates and as reference for absorbance measurement at 534 nm. Although parameters for characterisation of the ion associate are given (e.g., stability constant $= 3.71 \cdot 10^5$ and stoichiometry dye-to-SDS $= 1:1$) as well interference effects from Na$^+$, Ca^{2+}, Mg^{2+}, Fe^{3+}, NH$_4^+$, Cl$^-$, SO$_4^{2-}$, NO$_3^-$, CO$_3^{2-}$ (to simulate the composition of natural waters), no experiments were performed to evaluate the interference from other anionic surfactants. The method developed has a good linearity for SDS amounts of 0–15 µg.

Besides surfactants, the attention of researchers is also focused on analytical methods for the determination of their metabolites, in order to follow their environmental fate and effects. Kanz et al. [125]

presented a laboratory study on the biodegradation of *p*-sulfophenyl-3-butyrate enantiomers (chiral metabolites of LASs). Qualitative and quantitative measurements have been performed in a primary sewage effluent by high-performance capillary electrophoresis after enrichment on graphitized carbon black (Carbopack B). Detection limits at the ppb levels can be reached. Longer chain sulfophenyl carboxylate compounds (>5 carbon atoms), have been isolated by two-step extraction by C_{18} and SAX columns and identified by LC–ion spray MS [126]. Detection limits of 2–20 ng/l have been obtained after preconcentration of 250 ml of coastal water.

Some reviews on the analysis of non-ionic surfactants are available [112,127].

3. Inorganic compounds: metal species and anions

Trace metal ion determinations are receiving particular attention due to the strong environmental impact of these kinds of analytes. Preconcentration methods including enrichment of analytes and removal of matrix interferences aimed mainly to the analysis of water samples have been recently extensively reviewed and, in most cases, principles of the mainly employed preconcentration techniques are detailed [128–132]. Some applications of determination of inorganic anions at trace levels in environmental water samples will be finally described hereafter.

On-line preconcentration and determination of Cu, As, Se, Cd, In, Hg, Tl, Pb and Bi by *o,o*-diethyldithiophosphoric acid on C_{18} silica-based minicolumns has been optimised for inductively coupled plasma (ICP) MS analysis of different aqueous and solid matrices [133]. The use of small volumes of methanol, as the eluent, minimises the problems produced by introduction of organic solvent into plasma encountered during ICP analysis. Detection limits from 0.43 ng/l (Bi) to 33 ng/l (Cu) can be achieved with enrichment factors of 5–61 depending on the analyte.

Pre-treatment and preconcentration methods aimed at analysis by CE and ion chromatography have been reviewed by Fritz et al. [134] focusing on the suitability of chelating resins (e.g., iminodiacetic acid

and dithiocarbamate types) to concentrate metal ions. The use of ligands such as dithiocarbamate for complexation of metal ions and for their further extraction by SPE on a XAD-4 anion exchanger is shown. Literature experiences are referred to as good applications to water samples analysis.

Specifically devoted to the determination of Hg (organic and inorganic), a technique using EDTA as a complexing agent for inorganic mercury and a crosslinked chitosan for preconcentration of the complex formed has been presented [135]. The method involves enrichment on the resin, filtration, and transfer of the chitosan on the detection system which includes acidification of the solution and reduction of Hg. Enrichment factors of 100 and detection limits of 12 ng/l (with the cold vapour atomic absorption spectrometry detection) have been obtained and applications on tap, rain, and lake water samples are shown. The FT-IR spectrum of chitosan is available and a mechanism for preconcentration of inorganic Hg (based on anion-exchange interactions) is proposed.

The use of sorbents containing an immobilized ligand for SPE of several metal ions represents a valid approach for preconcentration. A historical overview on the preparation of these materials is supplied by Manzoori et al. [136] who describe the use of dithizone immobilized on surfactant (SDS)-coated alumina for preconcentration of inorganic and methylmercury cations from aqueous solutions (synthetic, river and tap water). Back extraction of mercury species has been obtained by 1 *M* HBr that, with respect to solutions of HCl and HNO_3 of higher concentrations, provides quantitative recovery and does not give SDS release and therefore foam that would interfere during mercury detection by cold vapour atomic absorption spectrometry. The method allowed one to determine concentrations as low as 28 ng/l in tap water samples (Tabriz City, Iran). Attention to speciation topics in environmental problems is widespread. As a recent application, an anion-exchange resin (SAX) has been used for preconcentration of anionic complexes of Cr^{6+} and Cr^{3+} with EDTA [137], at 1.1 and 0.4 µg/l levels, after elution with a high ionic strength solution (0.5 *M* NaCl) and analysis by atomic absorption spectroscopy. Interferences from the main ions occurring in natural waters (e.g., Mg^{2+}, Mn^{2+}, Sn^{2+}, Fe^{3+},

Ba^{2+}, Al^{3+}, Ca^{2+}, Cl^-, I^-, Br^-, F^-, SO_4^{2-}, PO_4^{3-}, HCO_3^-, NO_3^-) have been considered.

A different approach for the selective enrichment of metal ions from various complex matrices is the supported liquid membrane (SLM) technology that is gradually replacing conventional liquid–liquid techniques in large-scale operations. An enrichment procedure based on the use of SLM containing 40% (w/w) di-2-ethylhexyl phosphoric acid (DEHPA), tested for preconcentration of Cu^{2+}, Cd^{2+} and Pb^{2+} from river water samples, has been presented [138]. A pH gradient across the membrane who separates a donor and an acceptor (the sample and a HNO_3 solution, respectively) is the driving force for the mass transport of the analytes. Extraction efficiency as a function of pH differences across the membrane as well as long-term stability are discussed. Detection limits achieved, using atomic absorption spectroscopy (AAS), ranged from 0.09 to 0.19 µg/l.

Flotation procedures, consisting in collection of single particles on the surface of gas bubbles with the aid of collectors, surfactants or organic solvents [130], have been used for spectrophotometric (430 nm) and atomic absorption determination of Ni(II) in fresh and river waters at concentration levels of 0.5–4.0 µg/g [139]. In this work, Ni has been extracted with sodium diethyldithiocarbamate and oleic acid has been used as a surfactant for the flotation procedures. Cloud point preconcentration, previously described for the enrichment of the organic pollutants, has also been applied for determination of low amounts of Ni and Zn followed by flame atomic absorption spectrometry [140]. 1-(2-Pyridylazo)-2-naphthol (PAN) and Triton X-114 have been used as hydrophobic ligands and surfactant, respectively. Since the method has been aimed at the analysis of river, sea and mineral drinking water samples, attention has been focused on interferences from other cations [e.g., Al, Cd, Ca, Co(II), Cu(II), Fe(III), Mg, Pb(II)] at different metal-to-interferent ratios (1:1, 1:10, 1:100), thus observing that interferences encountered at the highest metal-to-interferent ratio is easily avoided increasing ligand concentration. Anionic interferences (mainly Cl^- and SO_4^{2-}) were found to be negligible, while ammonia and EDTA, due to their complexation ability cause severe interference. Concentration levels of humic acids higher than 5 ppm (overcome by prior treat-ment by peroxodisulfate) can interfere during the preconcentration step.

Recently, solvent-soluble membrane filters have been proposed for preconcentration of trace metal ions after precomplexation with suitable ligands able to pair with a species of opposite charge and to be retained by the filters. Detection limits of 30 ng/l for Fe(II) (after spectrophotometric detection at 560 nm) have been obtained using Ferrozine as a selective ligand and cetylpyridinium as cationic pairing ion [141]. The nitrocellulose membrane filter collects the Fe(II) complex and is simply dissolved in a small volume of ethoxyethanol. Natural and sea water samples have been considered for verification of the suitability of the method proposed.

The use of simple devices, such as membrane disks modified with proper ligands, allows the enrichment of metal species. Disks made of 90% (w/w) octadecyl-bonded silica and 10% (w/w) PTFE fibres modified with a 2O–2N donating Schiff's base have been used for selective enrichment of Cu^{2+} and further determination by AAS in tap, rain, and sea water samples up to 4 ng/l concentration levels [142]. Although the method seems attractive if interference from other transition metal ions have to be avoided (up to 100 mg in 50 ml water samples), obviously the method is of lower validity for simultaneous determination of metal species in the same matrix.

Based on precipitation as preconcentration step, determination of ultra-trace amount of cobalt in sea water, by direct graphite furnace AAS measurement on precipitates, has been recently shown by Zhang et al. [143]. The 30 000-fold preconcentration required to detect concentrations of Co as low as 1 ng/l has been achieved by co-precipitation with a combination of 30 mg 8-quinolinol, 5 mg nickel as a carrier element and 10 mg 1-nitroso-2-naphthol as an auxiliary complexing agent added to 1-l portions of aqueous sample. This last reagent is known to be a specific precipitant for cobalt in precipitation gravimetry. A very different approach for preconcentration of metal ions, aided by complexing agents, is represented by the direct measurement of the reflection of the species in the solid phase. One of these applications has been recently applied by Ershova and Ivanov [144] using Eriochrome cyanine R as a ligand for Al determination. Interesting results, such

as the best affinity of the resulting anionic complex for a cellulose sorbent (100–250 μm) with respect to an anion exchanger and the best sensitivity and precision results obtained with the use of chromaticity characteristics (e.g., colour lightness, saturation, brightness, etc.) rather than with the diffuse reflection coefficient are discussed. Detection limits of 4 μg/l and applications to analysis of surface waters are shown.

Analysis of low levels of ionic impurities is of particular importance when power plant waters or other high-purity water samples have to be used. The analytical determination of anions is often accomplished by ion chromatography with on-line sample preconcentration performed by a concentrator column made of a material with anion-exchange properties. Like any enrichment procedure, efficiency of recoveries is the most crucial parameter especially for those anions with low ion-exchange affinities. Since sample preconcentration is a complex process whose yield depends on appropriate choice of sample parameters, Toofan et al. [145] discussed the factors affecting the preconcentration behaviour of inorganic anions (flow-rate, sample volume, sample matrix ions and concentrator column selectivity) in order to provide a preconcentration method for the analysis of high purity waters. The preconcentrator used, AC10 (Dionex), proved to have appropriate selectivity and capacity to permit quantitative recoveries for all ions in 10–15 ml of a sample containing 100 μg/l each of F^-, CH_3COO^-, $HCOO^-$, Cl^-, NO_2^-, SO_4^{2-}, $C_2O_4^{2-}$, but showed low recoveries for larger volume samples containing weakly retained solutes in the presence of mid-to-low μg/l levels of strongly retained anions. Specifically devoted to the improvement of the combination of ion chromatography and particle beam mass spectrometry, a method for determination of periodate, iodide, nitrate, bromide, nitrite, chloride and iodate, applied to drinking water analysis has been shown by Buchberger and Haider [146]. Since the detection limits have been found poorer (e.g., 80 ng for sulfate, 65 ng for nitrate) than those commonly obtained by a traditional conductivity detection, a preconcentration step is required when real samples have to be analysed. For this reason, an on-line preconcentration with a loop packed with a silica-based anion-exchange material, that allows to lower the detection limits to the μg/l

range, is shown. An interesting application of combination of sample preparation capabilities offered by flow injection systems with separation and determination provided by capillary electrophoresis has been shown by Arce et al. [147]. In such a work, automated technologies have been developed for monitoring of both anionic (Cl^-, NO_2^-, NO_3^-, SO_4^{2-}, PO_4^{3-}) and cationic (Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Fe^{3+} Mn^{2+}, Al^{3+}, Cd^{2+}, Pb^{2+}) species in a water purification plant to provide continuous control of water quality. An on-line preconcentration step can be introduced for heavy transition metals by a Chelex-100 minicolumn (iminodiacetic-based chelating resin, widely employed for transition metals preconcentration) when they have to be analysed at concentration levels required by legislation.

Analysis of both organic (fumarate and maleate) and inorganic anions (bromide and nitrate) by CE with a large-volume sample stacking technique has been shown by He and Lee [148]. In this technique, the sample at neutral pH conditions is injected to almost fill the capillary and an acidic buffer, used as the electrolyte, is displaced towards the outlet. Due to the difference of pH and of resistance between the sample and the background electrolyte regions, the electroosmostic force (directed towards the cathodic inlet) is higher for the sample rather then for electrolyte in the same manner as the electrophoretic mobility of an anion (towards the outlet). In such a way, the aqueous sample matrix emerges from the inlet, while the analyte anions become stacked at the interface between the sample and background electrolyte regions. The stacked anions move towards the inlet until all the sample matrix has been removed and then they start to migrate towards the outlet as normally happens in CE. The method allows one to achieve enrichment factors higher than 300 and hence to improve detection capabilities. CE with sample stacking has also been used for determination of trace levels anions (Cl^-, Br^-, NO_2^-, NO_3^- and SO_4^{2-}) in melted snow samples [149]. Although separation of the anions was achieved in 3 min with high reproducibility, RSDs of about 13% were found for peak areas, due to the effect of ionic strength on enrichment factor. The use of bromide as internal standard and as ionic strength adjuster allowed to obtain quantitative results in agreement with those

obtained by ion chromatography, with detection limits of 0.1 µmol/l for chloride, sulfate and nitrate.

Finally a study of the effect of a passive neutral membrane introduced in an electrodialyser unit into the conducts of a flow injection system, on the permeability of selected anions has been shown [150]. The results obtained by application of the method for determination of chloride in industrial effluents were in agreement with those obtained by standard titration procedures.

Acknowledgements

References

[1] J. Horack, R.E. Majors, LC·GC Int. 6 (1993) 208.

[2] L.A. Berrueta, B. Gallo, F. Vicente, Chromatographia 40 (1995) 474.

[3] C.E. Werkhoven-Goewie, U.A.Th. Brinkman, R.W. Frei, Anal. Chem. 53 (1981) 2072.

[4] J. Gawdzik, B. Gawdzik, U. Czerwinska-Bil, Chromatographia 25 (1988) 504.

[5] G. Achilli, G.P. Cellerino, G. Melzi d'Eril, S. Bird, J. Chromatogr. A 697 (1995) 357.

[6] L. Renberg, Anal. Chem. 46 (1974) 459.

[7] C.D. Chriswell, R.C. Chang, J.S. Fritz, Anal. Chem. 47 (1975) 1325.

[8] A. Di Corcia, S. Marchese, R. Samperi, J. Chromatogr. 642 (1993) 163.

[9] A. Di Corcia, S. Marchese, R. Samperi, J. Chromatogr. 642 (1993) 175.

[10] A. Di Corcia, A. Bellini, M.D. Madbouly, S. Marchese, J. Chromatogr. A 733 (1996) 383.

[11] L. Campanella, A. Di Corcia, R. Samperi, A. Gambacorta, Mater. Chem. 7 (1982) 429.

[12] I. Rodríguez, R. Cela, Trends Anal. Chem. 16 (1997) 463.

[13] D. Puig, D. Barceló, Chromatographia 40 (1995) 435.

[14] N. Masqué, R.M. Marcé, F. Borrull, J. Chromatogr. A 793 (1998) 257.

[15] N. Masqué, E. Pocurull, R.M. Marcé, F. Borrull, Chromatographia 47 (1998) 176.

[16] E.R. Brouwer, U.A.Th. Brinkman, J. Chromatogr. A 678 (1994) 223.

[17] I. Liska, E.R. Brouwer, H. Lingeman, U.A.Th. Brinkman, Chromatographia 37 (1993) 13.

[18] C. Elvira-Cozar, P. Cano-Faura, L.V. Pérez-Arribas, M.E. León-Gonzales, L.M. Polo-Diez, Chromatographia 40 (1995) 91.

[19] F. Abu-Shammala, Anal. Lett. 32 (1999) 3083.

[20] F. Navarro-Villoslada, L.V. Pérez-Arribas, M.E. León-González, L.M. Polo-Díez, Anal. Chim. Acta 308 (1995) 238.

[21] N. Li, H.K. Lee, Anal. Chem. 69 (1997) 5193.

[22] E. Pocurull, G. Sánchez, F. Borrull, R.M. Marcé, J. Chromatogr. A 696 (1995) 31.

[23] R. Schilling, P.J. Clarkson, M. Cooke, Fresenius' J. Anal. Chem. 360 (1998) 90.

[24] D. Martínez, F. Borrull, M. Calull, Trends Anal. Chem. 18 (1999) 282.

[25] D. Martínez, E. Pocurull, R.M. Marcé, F. Borrull, M. Calull, Chromatographia 43 (1996) 619.

[26] J.L. Bernal, M. Nozazl, L. Toribio, M.L. Serna, F. Borrull, R.M. Marcé, E. Pocurull, Chromatographia 46 (1997) 295.

[27] S. Lacorte, D. Fraisse, D. Barceló, J. Chromatogr. A 857 (1999) 97.

[28] A. Di Corcia, M. Marchetti, R. Samperi, J. Chromatogr. 405 (1987) 357.

[29] A. Di Corcia, M. Marchetti, R. Samperi, Anal. Chem. 61 (1989) 1363.

[30] A. Di Corcia, M. Marchetti, J. Chromatogr. 541 (1991) 365.

[31] M.W. Powell, J. Chromatogr. A 697 (1995) 101.

[32] J.J. Sun, J.S. Fritz, J. Chromatogr. 590 (1992) 197.

[33] A. Di Corcia, M. Marchetti, Anal. Chem. 63 (1991) 580.

[34] A. Di Corcia, R. Samperi, A. Marcomini, S. Stelluto, Anal. Chem. 65 (1993) 907.

[35] T.A. Albanis, D.G. Hela, T.M. Sakellarides, I.K. Konstantinou, J. Chromatogr. A 823 (1998) 59.

[36] S. Lacorte, D. Barceló, J. Chromatogr. A 712 (1995) 103.

[37] P.J.M. Kwakman, J.J. Vreuls, U.A.Th. Brinkman, R.T. Ghijsen, Chromatographia 34 (1992) 41.

[38] G. D'Ascenzo, A. Gentili, S. Marchese, A. Marino, D. Perret, Chromatographia 48 (1998) 497.

[39] I. Vassilakis, D. Tsipi, M. Scoullos, J. Chromatogr. A 823 (1998) 49.

[40] J. Pietsch, W. Schmidt, F. Sacher, S. Fichtner, H.J. Brauch, Fresenius J. Anal. Chem. 353 (1995) 75.

[41] C. Molina, G. Durand, D. Barceló, J. Chromatogr. A 712 (1995) 113.

[42] C.L. Ritland, S. Cohen, C.J. Mason, The Reporter, Vol. 15, Supelco, 1996, No. 4.

[43] J. Slobodník, E.R. Brouwer, R.B. Geerdink, W.H. Mulder, H. Lingeman, U.A.Th. Brinkman, Anal. Chim. Acta 268 (1992) 55.

[44] J. Slobodník, M.G.M. Groenewegen, E.R. Brouwer, H. Lingeman, U.A.Th. Brinkman, J. Chromatogr. 642 (1993) 359.

[45] U.A.Th. Brinkman, J. Slobodník, J.J. Vreuls, Trends Anal. Chem. 13 (1994) 373.

[46] P.J.M. van Hout, U.A.Th. Brinkman, Trends Anal. Chem. 13 (1994) 382.

[47] J. Slobodník, A.J.H. Louter, J.J. Vreuls, I. Liška, U.A.Th. Brinkman, J. Chromatogr. A 768 (1997) 239.

[48] W. Pipkin, P.J.M. van Hout, Anal. Chem. News Features 1 (1997) 21A.

[49] M. Purvis, S.J. Gledhill, B.E. Drage, A.C. Hogenboom, D.A. Jolly, R.J.J. Vreuls, U.A.Th. Brinkman, Int. J. Environ. Anal. Chem. 74 (1999) 135.

[50] K.P. Hupe, M. Riedmann, G. Rozing, Chromatographia 40 (1995) 631.

[51] A.C. Hogenboom, J. Slobodnik, J.J. Vreuls, J.A. Rontree, B.L.M. van Baar, W.M.A. Niessen, U.A.Th. Brinkman, Chromatographia 42 (1996) 506.

[52] A.C. Hogenboom, U.K. Malmqvist, K. Nolkrantz, J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 759 (1997) 55.

[53] A.C. Hogenboom, P. Speksnijder, R.J. Vreeken, W.M.A. Niessen, U.A.Th. Brinkman, J. Chromatogr. A 777 (1997) 81.

[54] A.C. Hogenboom, R.J.C.A. Steen, W.M.A. Niessen, U.A.Th. Brinkman, Chromatographia 48 (1998) 475.

[55] A.C. Hogenboom, W.M.A. Niessen, U.A.Th. Brinkman, J. Chromatogr. A 794 (1998) 201.

[56] A.C. Hogenboom, W.M.A. Niessen, U.A.Th. Brinkman, J. Chromatogr. A 841 (1999) 33.

[57] A.J.H. Louter, C.A. van Beekvelt, P. Cid Montanes, J. Slobodnik, J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 725 (1996) 67.

[58] K.K. Verma, A.J.H. Louter, A. Jain, E. Pocurull, J.J. Vreuls, U.A.Th. Brinkman, Chromatographia 44 (1997) 372.

[59] E. Pocurull, C. Aguilar, F. Borrull, R.M. Marce, J. Chromatogr. A 818 (1998) 85.

[60] Hankemeier, P.C. Steketee, J.J. Vreuls, U.A.Th. Brinkman, Fresenius J. Anal. Chem. 364 (1999) 106.

[61] S. Müller, J. Efer, W. Engewald, Chromatographia 38 (1994) 694.

[62] S. Müller, J. Efer, W. Engewald, Fresenius J. Anal. Chem. 357 (1997) 558.

[63] H.G.J. Mol, H.G.M. Janssen, C.A. Cramers, J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 703 (1995) 277.

[64] U.A.Th. Brinkman, Chromatographia 45 (1997) 445.

[65] M.C. Hennion, C. Cau-Dit-Coumes, V. Pichon, J. Chromatogr. A 823 (1998) 147.

[66] N. Masqué, M. Galia, R.M. Marcé, F. Borrull, Chromatographia 50 (1999) 21.

[67] N. Masqué, M. Galia, R.M. Marcé, F. Borrull, J. Chromatogr. A 803 (1998) 147.

[68] E.H.R. van der Wal, E.R. Brouwer, H. Lingeman, U.A.Th. Brinkman, Chromatographia 39 (1994) 239.

[69] H.A.G. Niederländer, C. Gooijer, N.H. Velthorst, Anal. Chim. Acta 285 (1984) 143.

[70] M. Ibanez, Y. Pico, J. Manes, J. Chromatogr. A 823 (1998) 137.

[71] M.C. Carneiro, L. Puignou, M.T. Galceran, Anal. Chim. Acta 408 (2000) 263.

[72] Y. He, H.K. Lee, Electrophoresis 18 (1997) 2036.

[73] E. Pramauro, A. Bianco Prevot, Pure Appl. Chem. 67 (1995) 551.

[74] H. Bagheri, E.R. Brouwer, R.T. Ghijsen, U.A.Th. Brinkman, J. Chromatogr. A 647 (1999) 121.

[75] E. Benfenati, P. Pierucci, R. Fanelli, A. Preiss, M. Godejohann, M. Astratov, K. Levsen, D. Barceló, J. Chromatogr. A 831 (1999) 243.

[76] I. Ferrer, E.M. Thurman, D. Barceló, Anal. Chem. 69 (1997) 4547.

[77] C. Aguilar, I. Ferrer, F. Borrull, R.M. Marcé, D. Barceló, J. Chromatogr. A 794 (1998) 147.

[78] M. Castillo, M.C. Alonso, J. Riu, D. Barceló, Environ. Sci. Technol. 33 (1999) 1300.

[79] I. Ferrer, D. Barceló, Analusis 26 (1998) 118.

[80] J. Slobodník, B.L.M. van Baar, U.A.Th. Brinkman, J. Chromatogr. A 703 (1995) 81.

[81] R.B. Geerdink, A. Kooistra-Sijpersma, J. Tiesnitsch, G.M. Paul, U.A.Th. Brinkman, J. Chromatogr. A 863 (1999) 147.

[82] Hankemeier, J. Rozenbrand, M. Abhadur, J.J. Vreuls, U.A.Th. Brinkman, Chromatographia 48 (1998) 273.

[83] H. Frischenschlager, M. Peck, C. Mittermayr, E. Rosenberg, M. Grasserbauer, Fresenius J. Anal. Chem. 357 (1997) 1133.

[84] H. Frischenschlager, C. Mittermayr, M. Peck, E. Rosenberg, M. Grasserbauer, Fresenius J. Anal. Chem. 359 (1997) 213.

[85] V. Pichon, M. Bouzige, M.C. Hennion, Anal. Chim. Acta 376 (1998) 21.

[86] V. Pichon, M. Bouzige, C. Miège, M.C. Hennion, Trends Anal. Chem. 18 (1999) 219.

[87] S. Pérez, I. Ferrer, M.C. Hennion, D. Barceló, Anal. Chem. 70 (1998) 4996.

[88] B. Hock, A. Dankwardt, K. Kramer, A. Marx, Anal. Chim. Acta 311 (1995) 393.

[89] M. Bouzige, V. Pichon, M.C. Hennion, Environ. Sci. Technol. 33 (1999) 1916.

[90] M. Bouzige, V. Pichon, M.C. Hennion, J. Chromatogr. A 823 (1998) 197.

[91] J. Dallüge, T. Hankemeier, R.J.J. Vreuls, U.A.Th. Brinkman, J. Chromatogr. A 830 (1999) 377.

[92] A. Balinova, J. Chromatogr. A 754 (1996) 125.

[93] G.R. van der Hoff, P. van Zoonen, J. Chromatogr. A 843 (1999) 301.

[94] Ph. Schmitt, D. Freitag, Y. Sanlaville, J. Lintelmann, A. Kettrup, J. Chromatogr. A 709 (1995) 215.

[95] P. Hinsmann, L. Arce, A. Rios, M. Valcarcel, J. Chromatogr. A 866 (2000) 137.

[96] L. Chimuka, N. Megersa, J. Norberg, L. Mathiasson, J.Å. Jönsson, Anal. Chem. 70 (1998) 3906.

[97] H. Hühnerfuss, R. Kallenborn, J. Chromatogr. 589 (1992) 191.

[98] E.R. Brouwer, A.N.J. Hermans, H. Lingeman, U.A.Th. Brinkman, J. Chromatogr. A 669 (1994) 45.

[99] T. Renner, D. Baumgarten, K.K. Unger, Chromatographia 45 (1997) 199.

[100] B. Sturm, H.D. Knauth, N. Theobald, G. Wünsch, Fresenius J. Anal. Chem. 361 (1998) 803.

[101] C. Madichie, G.M. Greenway, T. McCreedy, Anal. Chim. Acta 392 (1999) 39.

[102] C.G. Pinto, J.L. Pérez Pavón, B. Moreno Cordero, Anal. Chem. 67 (1995) 2606.

[103] R. Carabias Martínez, E. Rodríguez Gonzalo, M.G. García Jiménez, C. García Pinto, J.L. Pérez Pavón, J. Hernández Méndez, J. Chromatogr. A 754 (1996) 85.

[104] R. Ferrer, J.L. Beltrán, J. Guiteras, Anal. Chim. Acta 330 (1996) 199.

[105] D. Sicilia, S. Rubio, D. Pérez-Bendito, N. Maniasso, E.A.G. Zagatto, Anal. Chim. Acta 392 (1999) 29.

[106] E. Matisová, S. Škrabáková, J. Chromatogr. A 707 (1995) 145.

[107] G. Kiss, Z. Varga-Puchony, A. Gelencser, Z. Krivacsy, A. Molnar, J. Hlavay, Chromatographia 48 (1998) 149.

[108] L. Toribio, Ma.J. del Nozal, J.L. Bernal, J.J. Jimenez, Ma.L. Serna, J. Chromatogr. A 823 (1998) 163.

[109] I. Ferrer, D. Barceló, Trends Anal. Chem. 18 (1999) 180.

[110] S. Lacorte, I. Guiffard, D. Fraisse, D. Barceló, Anal. Chem. 72 (2000) 1430.

[111] O.H.J. Szolar, R.S. Brown, J.H.T. Luong, Anal. Chem. 67 (1995) 3004.

[112] A.T. Kiewiet, P. de Voogt, J. Chromatogr. A 733 (1996) 185.

[113] Standard Methods for the Examination of Water and Wastewater, 16th ed., American Public Health Association, Washington, DC, 1985, Section 512A.

[114] Q.W. Osburn, J. Am. Oil Chem. Soc. 63 (1986) 257.

[115] J. McEvoy, W. Giger, Environ. Sci. Technol. 20 (1986) 376.

[116] A. Marcomini, S. Capri, W. Giger, J. Chromatogr. 403 (1987) 243.

[117] P.L. Desbène, F.I. Portet, G.J. Goussot, J. Chromatogr. A 730 (1996) 209.

[118] K. Maruyama, M. Yuan, A. Otsuki, Environ. Sci. Technol. 34 (2000) 343.

[119] A. Kreißelmeir, M. Schoester, G. Kloster, Fresenius J. Anal. Chem. 353 (1995) 109.

[120] K. Heinig, C. Vogt, G. Werner, Analyst 123 (1998) 349.

[121] J. Norberg, E. Thordarson, L. Mathiasson, J.Å. Jönsson, J. Chromatogr. A 869 (2000) 523.

[122] M. Kane, J.R. Dean, S.M. Hitchen, C.J. Dowle, R.L. Tranter, Analyst 120 (1995) 355.

[123] L.N. Moskvin, J. Simon, P. Löffler, N.V. Michailova, D.N. Nicolaevna, Talanta 43 (1996) 819.

[124] M. Kamaya, Y. Tomizawa, K. Nagashima, Anal. Chim. Acta 362 (1998) 157.

[125] C. Kanz, M. Nölke, T. Fleischmann, H.P.E. Kohler, W. Giger, Anal. Chem. 70 (1998) 913.

[126] J. Riu, E. Gonzalez-Mazo, A. Gomez-Parra, D. Barceló, Chromatographia 50 (1999) 275.

[127] A. Marcomini, M. Zanette, J. Chromatogr. A 733 (1996) 193.

[128] C. Sarzanini, E. Mentasti, J. Chromatogr. A 789 (1997) 301.

[129] C. Sarzanini, J. Chromatogr. A 850 (1999) 213.

[130] C. Sarzanini, in: A. Gianguzza, E. Pelizzetti, S. Sammartano (Eds.), Marine Chemistry, Water Science and Technology Library, Vol. 25, Kluwer, Dordrecht, 1997, p. 131.

[131] C. Sarzanini, in: A. Gianguzza, E. Pelizzetti, S. Sammartano (Eds.), Chemical Processes in Marine Environments, Springer, Berlin, 2000, p. 339.

[132] C. Sarzanini, in: P.R. Brown, E. Gruska (Eds.), Advances in Chromatography, Vol. 41, Marcel Dekker, New York, 2000, in press.

[133] L. Valderi Dressel, D. Pozebon, A.J. Curtius, Spectrochim. Acta 53B (1998) 1527.

[134] J.S. Fritz, R.C. Freeze, M.J. Thornton, D.J. Gjerde, J. Chromatogr. A 739 (1996) 57.

[135] M. Wang, G. Huang, S. Qian, J. Jiang, Y. Wan, Y.K. Chau, Fresenius J. Anal. Chem. 358 (1997) 856.

[136] J.-L. Manzoori, M.H. Sorouraddin, A.M. Haji Shabani, J. Anal. Atom. Spectrom. 13 (1998) 305.

[137] D.M. Adria-Cerezo, M. Llobat-Estelles, A.R. Mauri-Aucejo, Talanta 51 (2000) 531.

[138] N.K. Djane, K. Ndung'u, F. Malcus, G. Johansson, L. Mathiasson, Fresenius J. Anal. Chem. 358 (1997) 822.

[139] M.A. Kabil, S.E. Ghazy, M.R. Lasheen, M.A. Shallaby, N.S. Amar, Fresenius J. Anal. Chem. 354 (1996) 371.

[140] M.C. Cerrato Oliveros, O. Jimenez de Blas, J.L. Pérez Pavón, B. Moreno Cordero, J. Anal. Atom. Spectrom. 13 (1998) 547.

[141] Y. Chen, C.M. Ding, T.Z. Zhou, D.Y. Qi, Fresenius J. Anal. Chem. 363 (1999) 119.

[142] M. Shamsipur, A.R. Ghiasvand, H. Sharghi, H. Naeimi, Anal. Chim. Acta 408 (2000) 271.

[143] Q. Zhang, H. Minami, S. Inoue, I. Atsuya, Anal. Chim. Acta 407 (2000) 147.

[144] N.I. Ershova, V.M. Ivanov, Anal. Chim. Acta 408 (2000) 145.

[145] M. Toofan, C.A. Pohl, J.R. Stillian, P.E. Jackson, J. Chromatogr. A 775 (1997) 109.

[146] W. Buchberger, K. Haider, J. Chromatogr. A 770 (1997) 59.

[147] L. Arce, A. Ríos, M. Valcárcel, J. Chromatogr. A 791 (1997) 279.

[148] Y. He, H.K. Lee, Anal. Chem. 71 (1999) 995.

[149] Y.T. Yang, J.W. Kang, H.J. Lu, Q.Y. Ou, F. J Liu, J. Chromatogr. A 834 (1999) 387.

[150] J.F. van Staden, C.J. Hattingh, Talanta 45 (1998) 485.