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Review

Selected procedures for the monitoring of polar pesticides and related microcontaminants in aquatic samples

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Abstract

There is an increasing need to monitor trace-level concentrations of organic micropollutants in water, especially in surface and tap water. In the present review, attention is mainly devoted to the determination of polar pesticides. After an introduction which briefly explains the reasons to select this group of analytes, the advantages of on-line monitoring procedures for early-warning and rapid-screening purposes are outlined. The main part of the paper is devoted to a discussion of selected papers from the recent literature, which combine sample treatment by means of solid-phase extraction (SPE), and a liquid (LC) or gas (GC) chromatographic separation-cum-detection procedure in one set-up. Aspects of special interest include (i) the variety of detectors in use with both SPE–LC and SPE–GC procedures, (ii) the increasing popularity of (on-line and off-line) SPE–LC–MS techniques, and (iii) the high potential of SPE–GC as well as alternative sample treatment–GC procedures.

Contents

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1. Introduction

Over the past twenty years, increasingly stringent regulations have been set on the production, transport, use and discharge of toxic substances, and the number of industrial and waste water treatment plants that has been installed has increased dramatically. These regulations and a much better control of surface water quality have induced a general reduction of the pollution load. An interesting overview of the scope, impact, and also limitations, of such regulations and directives within the European Community/Union (EC/EU) has been published recently [1]. The quoted paper only discusses organic micropollutants, which seems to be a good choice, because in the last decade there has been growing concern about the presence of such trace-level contaminants in, especially, water, and also soil and food or foodstuffs, and their impact on environmental quality. Groups of compounds which have received much attention include polyaromatic hydrocarbons, phthalate esters, amines, alkyl and aryl sulphonates, and organochlorine and other pesticides. The need to monitor these groups of compounds in surface, tap and ground water is increasingly being recognized, and novel procedures for their determination are being published continuously. For divergent reasons, the class of compounds attracting most attention today are the pesticides —not the older-generation, non-polar and highly persistent organochlorines, but the current, more water-soluble, less persistent and often more or less polar organophosphorus pesticides, triazines, phenylureas, carbamates and phenoxyalkanoic acids.

Because of the environmental impact of pesticides, several priority —also called "black" or "red"— lists have been published to protect the quality of surface and tap water. In the Netherlands, for example, the Institute for Inland Water Management and Waste Water Treatment (RIZA) consults an extensive survey including some 40 different national and international priority lists [2], which cover several hundreds of pesticides in use today. A recent paper [3] on the determination of such priority pesticides, and their transformation products, in water reported 39 pesticides listed in the 76/464 EEC Council Directive on pollution caused by certain dangerous substances discharged into the aquatic environment of the community (Table 1). Another highly relevant priority list which was published some two years ago [4] considers the, over 500 (!), pesticides used in Europe in amounts of over 50 000 kg per annum and their capacity for probable or transient leaching. The "leaching" group comprises 55 compounds; for over 20 of these, the annual production is even at least 10-fold higher (cf. Ref. [3]). In addition, one should consider that several other, rather notorious pesticides were not included in the study because of insufficient relevant physicochemical data, such as, e.g., thiram (rapid degradation in aqueous environment), glyphosate (analytical methodology) and zineb (polymeric product); our comments in parentheses may provide an explanation of the problems encountered.

Table 1
Pesticides listed in 76/464/EEC council directive on pollution caused by certain dangerous substances discharged into the aquatic environment of the community (black list) [3]

Aldrin	Disulphoton	Monolinuron
Atrazine	Endosulphan	Omethoate
Azinphos-ethyl	Endrin	Oxydemeton-methyl
Azinphos-methyl	Fenitrothion	Parathion-ethyl
Chlordane	Fenthion	Parathion-methyl
Coumaphos	Heptachlor	Phoxim
2,4-D	Hexachlorobenzene	Propanil
DDT	Linuron	Pyrazon
Demeton	Malathion	Simazine
Dichlorprop	MCPA	2,4,5-T
Dichlorvos	Mecoprop	Triazophos
Dieldrin	Metamidophos	Trichlorfon
Dimethoate	Mevinphos	Trifluralin

Finally, in addition to the above, one should clearly state that a very large majority of all earlier, and also of most current studies, deal with the parent compounds only, or, in other words, do not consider the degradation/transformation products of the pesticides at all. It is rather obvious that, when reliable determination of the pesticides themselves still causes problems, inclusion of the transformation products is a real challenge (highly polar low-molecular-mass analytes, i.e. early elution and interfering

matrix). However, the well-known fact that, for several pesticides, (one of) the transformation products is more toxic than the parent compound indicates that more attention should be given to this aspect. Relevant examples include 1-naphthol (from carbaryl), fenitrooxon (from fenitrothion) and ethylenebisthiourea (ETU; from several ethylenebisthiocarbamates; see Fig. 1; cf. Ref. [5]). Another topic which is of distinct interest here, is that of pesticide stability [6]. A list of pesticides which did not meet the US Environmental Protection Agency National Pesticide Survey (EPA NPS) criteria, and were therefore discarded, is shown in Table 2. Somewhat surprisingly, several of these compounds appear in the 76/464/EEC Council Directive list referred to above. Actually, today it starts to become quite common to study the stability of pesticides in water, and to examine the effects of water type, biological inhibitors, and storage conditions [temperature, residual water, storage on solid-phase extraction (SPE) cartridges or membrane extraction disks, etc.]. Compounds which in addition to those of Table 2 show rapid degradation include several carbamates, coumafuryl and fenamidosulf and benomyl. Under suitable conditions, the latter pesticide degrades almost immediately to carbendazim, and both are often determined together as the latter compound [7].

1.1. Goal of the present review

The brief discussion presented above clearly indicates that there is a distinct need to develop state-of-the-art analytical procedures for the monitoring of a wide variety of often moderately polar pesticides (but, as a group, covering a rather wide polarity range) and also for early-warning purposes. Since increasing concentrations of toxic substances due to, e.g., accidental spills or washouts shortly after the start of the spraying season, should be detected as rapidly as possible, because immediate action may be required to protect water reservoirs, on-line and, preferably, fully automated analytical systems are required to serve the latter purpose. If monitoring is the main goal, that is, if the overall quality of water and/or long-term trends have to be measured, off-line procedures are a good approach. However, considerations such as cost-effectiveness and reduction of the consumption of chemicals (see also below) make analytical chemists increasingly aware of the beneficial effects of utilizing on-line procedures. The close similarity, if not identity, of the early-warning and monitoring systems which will then ensue, self-evidently is another advantage.

On the basis of considerations such as those presented above, many workers in governmental, research and related laboratories try to develop analytical procedures that will enable the detection of 0.1 μg/l of individual pesticides (and related products, probably their transformation products; cf. Ref. [3]) in drinking water and, typically, of 1 or 3 μg/l as the alert and alarm threshold values, respectively, in surface water. Such systems should preferably also provide some structural information and be sufficiently robust to allow their routine use and, even

Table 2
Pesticides that have been withdrawn from the EPA NPS because they suffer 100% loss when stored at 4°C for 14 days after the water has been biologically inhibited [6]

Aspon	Disulphoton sulphoxide	Malathion
Azinphos-methyl	EPN	Methyl-parathion
Chlorpropylate	Ethion	MGK 326
Demeton	Ethyl-parathion	Phorate
Diazinon	Fampur	Phosmet
Dicloran	Fenitrothion	Pronamide
Diclofenthion	Fensulfothion	Terbufos
Disulfoton	Fenthion	
Disulfoton sulphone	Fonophos	

EPN = O-Ethyl O-4-nitrophenyl phenylphosphonothioate; MGK 326 = dipropyl pyridine-2,5-dicarboxylate.

better, unattended operation. It is not surprising that systems which meet these criteria almost invariably combine a sample treatment unit for trace enrichment of the analytes of interest and sample clean-up, a liquid chromatographic (LC) or capillary gas chromatographic (GC) separation module, and a sufficiently selective detection device such as a UV–Vis absorbance, thermionic (N/P-selective) or mass-selective detector.

As an illustration of the great steps forward that have been made in the past few years, some interesting recent developments in the area of on-line monitoring of aqueous samples will be highlighted. Both LC- and GC-based methods will be discussed, with special emphasis on the former approach because of its good compatibility with aqueous samples. Attention will be devoted both to studies performed in our laboratory in the framework of the international Rhine Basin Program [8], and to work carried out by other groups.

2. On-line monitoring systems

As was explained in some detail above, the trace-level determination of a wide variety of pesticides —which may well involve identification, quantification *and* confirmation by an independent check method— requires the use of sophisticated instrumentation and adequate analytical procedures. With the number of samples being offered for analysis showing a rapid increase, and legislation concerning threshold values becoming stricter, it is not surprising that the keywords in trace-level environmental analysis are *speed*, *selectivity* and *sensitivity*. To our opinion a fourth keyword, *solvents*, should be added. Because of the very concern for the quality of our environment, state-of-the-art analytical procedures should meet the criterion that the consumption of (toxic) organic solvents is kept as low as possible. Modern developments in the area of monitoring, and early warning, consequently are in the direction of designing fully on-line —and, therefore, automatable— systems, which combine sample preparation and separation-cum-detection in one analytical set-up. Examination of the recent literature reveals that, with such on-line methods, sample preparation generally involves liquid–solid sorption or, in other words, SPE. Compared with more traditional methods of sample treatment such as liquid–liquid (LLE) or Soxhlet extraction, or even off-line SPE, on-line SPE is less laborious and time-consuming. Besides, because of the "closed" nature of an on-line system, contamination of the sample and/or sample extract during handling is seriously reduced, and analyte losses due to evaporation do not occur. Further, the complete sample rather than an aliquot of, typically, 1–5% of the final extract, is analysed. A considerable increase in analyte detectability (in terms of concentration units) is thereby effected, part of which can be sacrificed in order to reduce sample sizes from the conventional 0.5–1 l to about 100 ml (LC) or a mere 10 ml (GC). Finally, because no LLE step is involved, in GC instead of the frequently encountered 100–300 ml of dichloromethane, less than 1 ml of organic solvent is often required per analysis in the on-line procedures.

In the past five years, much work has been carried out to design on-line SPE–LC- and SPE–GC-based analytical systems equipped with, mainly, diode array UV–Vis detection (DAD) or thermospray (TSP) or particle beam (PB) MS detection in the case of LC, and with selective GC or MS detection in the case of GC. These approaches will be discussed below. An extensive review on the use of SPE in multiresidue pesticide analysis of water, with tables giving the nature of the sorbents and the samples, has been published recently [9].

3. SPE–LC–diode array UV systems

The general set-up of a typical fully automated LC-based analyser for water monitoring is shown in Fig. 1. Next to the pumps, the key parts of the on-line SPE–LC system are the disposable cartridge containing a small precolumn (typically 5–10 mm length × 2–3 mm I.D.), the alkyl-bonded silica analytical column and the DAD

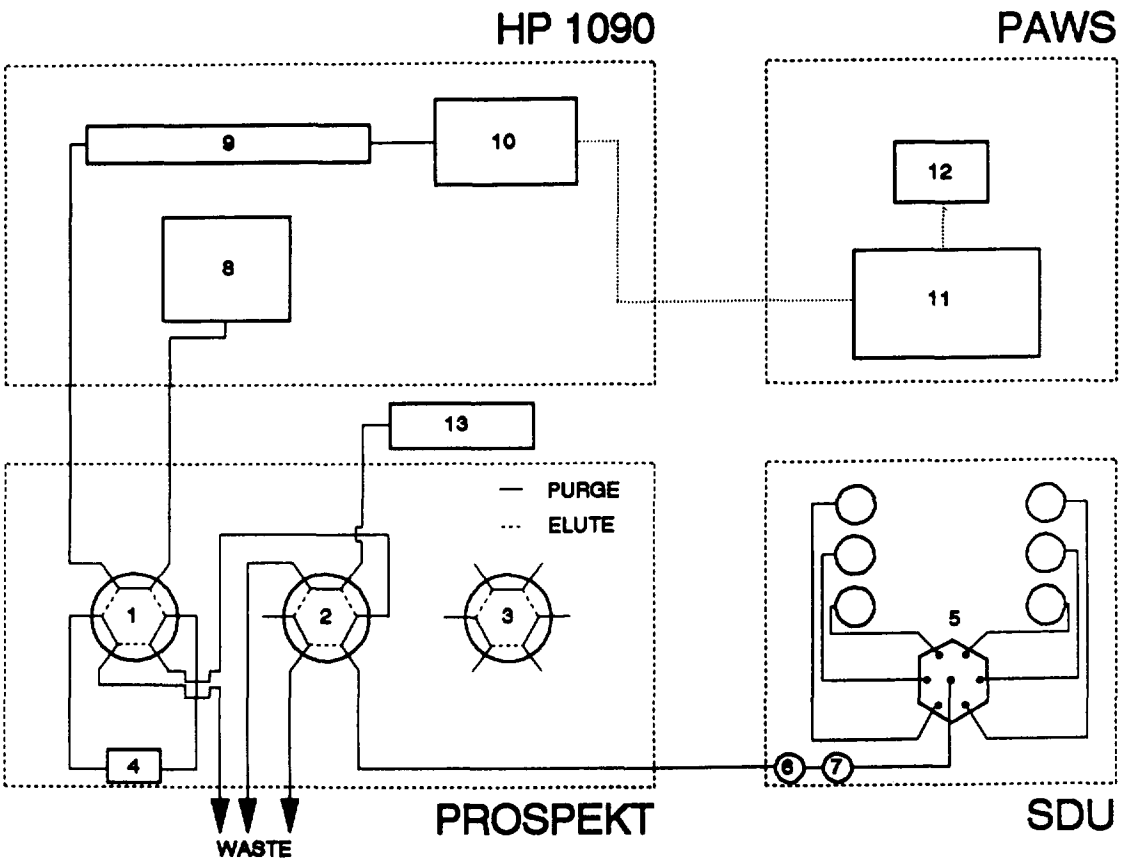

Fig. 1. Automated on-line trace enrichment–LC system for water samples (SAMOS). 1, 2, 3 = High-pressure valves of the Prospekt; 4 = trace-enrichment cartridge of the Prospekt; 5 = solenoid valve; 6 = pulse dampener; 7 = purge pump; 8 = solvent-delivery system of HP 1090 liquid chromattograph; 9 = analytical column; 10 = diode array detector; 11 = Pascal Workstation (PAWS) computer; 12 = printer; 13 = preparative pump for sample loading; SDU = solvent-delivery unit [10].

system. During an analysis, a suitable volume of the aqueous sample, often approx. 100 ml, is loaded onto the precolumn at a flow-rate of 5–10 ml/min. The analytes of interest are retained on the precolumn, which is usually packed with a C_{18}-bonded silica or an even more hydrophobic styrene–divinylbenzene copolymer (PLRP-S, PRP-1) to ensure efficient analyte trapping (trace enrichment); the solution itself passes to waste. After rapid clean-up with a few millilitres of HPLC-grade water, desorption is performed by coupling the precolumn on-line with the analytical column and starting a suitable organic solvent–aqueous buffer mobile phase gradient.

With polar pesticides, near-optimum UV detection conditions for a large number of analytes are found by monitoring at, for example, 210/220/245/280 or 220/230/245/270/300 nm. Data handling includes searching for target analytes within the proper LC retention time windows, matching the experimentally observed and library DAD spectra, quantification and printing of a report [10,11]. The whole procedure can be automated. It is possible to identify and quantify some 100 organic micropollutants at concentrations (in the water sample) of 0.5–1 μg/l [12]. That is, the alert and alarm levels for individual pesticides in surface water, quoted above, can be

met. Several examples which illustrate the performance of on-line SPE–LC–DAD, are presented in the next paragraphs.

The on-line SPE–LC–DAD approach combined with multicomponent analysis (MCA) has been used to examine a large number of pesticides from different classes in a single run [12]. Using conventional DAD, the extremely wide range of pesticides can pose a difficult problem for LC when purity determinations and identification are needed. Additional compounds can co-elute with other sample constituents giving problems with quantification. MCA, a technique that deconvolutes and quantifies known UV-absorbing substances in an unknown solution, has been adapted to identify 36 pesticides and some degradation products in drinking water. With an on-line preconcentration of 200 ml of drinking water detection limits typically were in the low (10–50) ng/l range.

Today, several laboratories use the SAMOS approach depicted in Fig. 1 above. With this system, the analytes of interest are trapped on a PLRP-S precolumn from 100–150 ml of surface water loaded at a flow-rate of 5 ml/min. Desorption from this precolumn and separation on a C_{18}-bonded silica analytical column are carried out with an acetonitrile–aqueous phosphate buffer (pH 3) gradient. The analysis itself takes about 60 min. The system has been extensively validated [10] using a test set of 25–30 pesticides which covered the total retention time window. The results were rather gratifying, with R.S.D. values of 0.2–1.5% ($n = 20$) for the retention times, and of 1–9% ($n = 8$) for peak area measurements in the low μg/l range. Calibration plots were linear over the concentration range of interest (0.1–10 μg/l) in all but two cases, and the detection limits in real-life samples were at or below the alert level of 1 μg/l for all but two of the test analytes. There were virtually no maintenance problems during the 6-month validation period. The system has been used to determine many pesticides at the trace level in the rivers Rhine and Meuse, and in other European rivers. Compounds that were detected included simazine, atrazine, 3,3-dichlorobenzidine, alachlor and diuron. An interesting example [13] of the use of the SAMOS approach is shown in Fig. 2 which deals with a recent study on the presence of the phenylurea herbicide, isoproturon, in river Rhine water.

Recently, a valuable complementary validation study of SPE–LC–DAD has been published

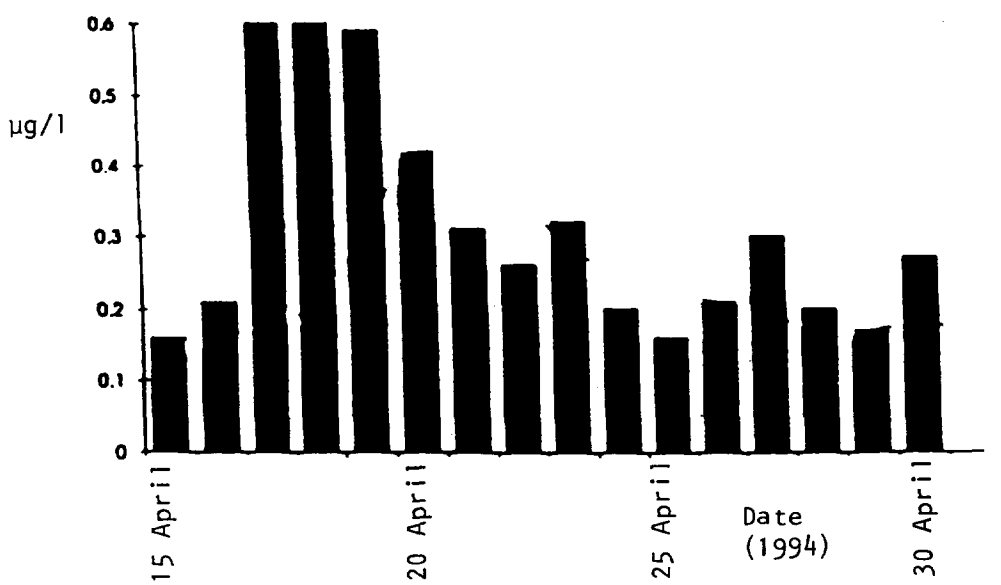

Fig. 2. Concentration profile of isoproturon determined in river Rhine (Lobith, Netherlands), 15–30 April 1994 [13].

[14]. The data confirm that the set-up (with a Prospekt sample preparation module) is rather robust. Using C_{18}-bonded silica rather than a copolymer as the precolumn sorbent, highly satisfactory analytical data were obtained for eleven pesticides determined in drinking and ground water. Detection limits typically were 0.02–0.2 μg/l (150-ml samples). It is interesting to add that analytical problems essentially were encountered only with pesticides known to be unstable in water under the conditions used in such studies. Additionally, it is worthwhile to note the baseline-separated elution of *cis*- and *trans*-mevinphos, and the higher retention of the extremely polar cyanazine acid on C_{18}-bonded silica as compared to that on copolymer PLRP-S material.

In another study, Reupert et al. [15] used SPE–LC–DAD for the on-line screening of river Rhine water, and reported data on metamitrone in surface water. The authors emphasize that the proper choice of the sorbent in the precolumn and the sample volume used for trace enrichment are of critical importance. Fourteen stationary phases were tested for their retention power. Although Bakerbond C_{18} ($d_p = 48$ μm) was found to be somewhat better with respect to sorption power, the second best, Spherisorb ODS I ($d_p = 3$ μm), was finally chosen because less band broadening was observed, especially with the early-eluting compounds. The band broadening caused by inserting a 14 × 4 mm I.D. precolumn containing this material, was shown to be negligible, but increasing the sample volume from 5 to 10 ml did result in additional band broadening in the final separation. With the optimized system, the authors could obtain detection limits of below 1 μg/l for many pesticides in surface water, even when using 5-ml samples only (cf. Fig. 3).

Recently, another group of workers reported results on river Seine water [1]. Using a copolymer sorbent with its typically ca. 30-fold higher retention for most analytes of interest than long-chain-alkyl-bonded silicas, and 150-ml samples, many phenylureas and triazines could be detected down to the 0.1 μg/l level. The sample volume could not be increased to 300 ml, as was done for drinking water, because the peaks of the early-eluting analytes were masked by a large matrix peak. A typical result is shown in Fig. 4. As with many other rivers, atrazine

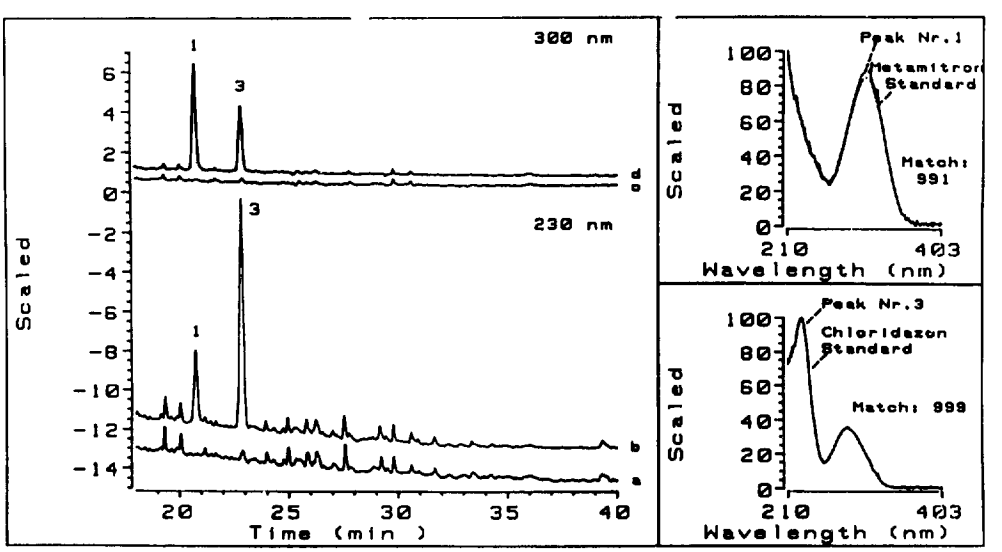

Fig. 3. On-line SPE–LC–DAD analysis of a river water sample with (traces b and d) and without (traces a and c) spiking with 5 μg/l metamitrone (1) and 5 μg/l chloridazone (3). Sample volume: 5 ml; detection at 230 nm (traces a and b) and 300 nm (traces c and d). Compound identification and confirmation performed by comparison with spectral library [15].

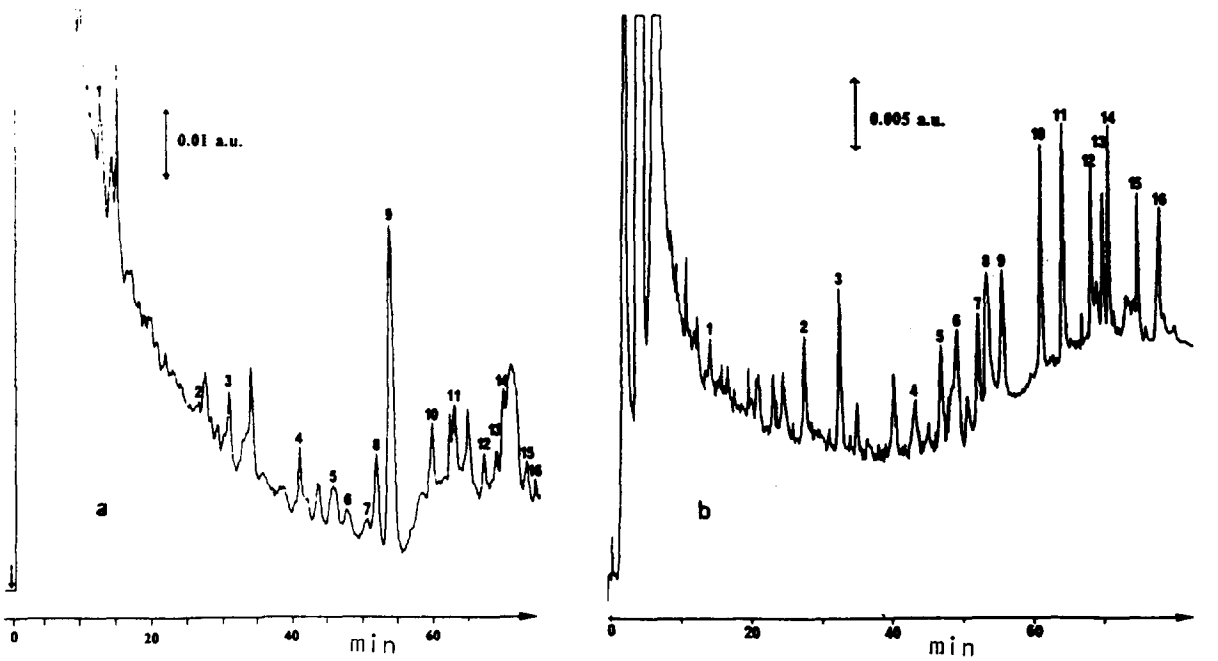

Fig. 4. On-line SPE–LC–UV analysis of (a) 150 ml of surface water (Seine) spiked with 0.1 μg/l of each phenylurea and (b) 300 ml of drinking water spiked with 0.1 μg/l of phenylureas. Peaks: 1 = fenuron; 2 = methoxuron; 3 = monuron; 4 = methabenzthiazuron; 5 = chlortoluron; 6 = fluometuron; 7 = monolinuron; 8 = isoproturon; 9 = diuron; 10 = difenoxuron; 11 = buturon; 12 = linuron; 13 = chloroxuron; 14 = chlorbromuron; 15 = diflubenzuron; 16 = neburon. Precolumn: PLRP-S cartridge (1 cm × 2 mm I.D.) from the Prospekt. Analytical column: Varian ODS (25 × 0.46 cm I.D.) Acetonitrile gradient with phosphate buffer at pH 7: 20 to 35% acetonitrile from 0 to 52 min, 35 to 70% from 52 to 77 min. UV detection at 249 nm [1].

and diuron were among the pesticides frequently detected at relatively high levels.

Additionally it should be realized that systems such as those discussed here, can of course easily be modified and adapted to the determination of rather different classes of compounds. To quote an example, ion-pair-based separations have been used to detect a series of aromatic sulphonic acids in river Rhine water at the 1–10 μg/l level. For one acid, 4-nitrotoluene-2-sulphonic acid, the occurrence of an accidental spill was demonstrated [16]. Another aromatic sulphonic acid, naphthalene-1,5-disulphonic acid (NDS), was found to be present in Amsterdam drinking water at the 1 μg/l level. The same acid was found to be an appropriate tracer in studies on effluents from industrial waste water treatment plants [17,18]. A SAMOS ion-pair-based SPE–LC system with, in this instance, both DAD and fluorescence detection, was used to study the fate of several sulphonates in the course of different water-treatment steps. It was demonstrated that NDS could not be effectively be removed, in other words, these results are in agreement with those mentioned above. With the final analytical system detection limits were well below 0.5 μg/l for all eleven sulphonates studied. One further study should be quoted here, although it deals with SPE combined with LC off-line rather than on-line. Zerbinati et al. [19] determined 23 aromatic sulphonates in natural waters using two sets of fluorescence wavelengths, viz. 250/455 nm and 240/660 nm (λ_{ex}/λ_{em}); consequently, two injections per sample were required to monitor all the investigated compounds. Despite this drawback, only 30 min were needed to perform the double chromatographic run. Ten aromatic sulphonates were tentatively identified in river Bormida (Italy) at levels of between 1 μg/l and 1500 mg/l.

A final aspect of interest concerns the use of off-line rather than on-line approaches if, e.g. precolumn packing materials such as graphitized carbon are used. Such sorbents are often recommended when the analyte polarity range that has to be bracketed is very wide and/or when highly polar analytes are of primary interest. When such precolumns are combined on-line with a conventional reversed-phase LC system, the additional band broadening created during analyte desorption is excessive. As an alternative, desorption can be performed with a pure organic solvent such as ethyl acetate; however, this precludes on-line operation [20]. To quote an example, DiCorcia and Marchetti [21] used a 250-mg Carbopack B cartridge to trap basic, neutral and acidic pesticides from 2 l of drinking water. The presence of positively charged centres on the Carbopack B surface allowed separation of the basic and neutral pesticides from the acidic ones using stepwise desorption. Without additional clean-up detection limits in drinking water were of the order of 3–70 ng/l.

4. SPE–LC–MS

Whenever concentrations of pesticides, or other relevant compounds, are suspected to be close to or above threshold values such as the alert level for surface water, confirmation and/or identification make it mandatory to use MS-based techniques. The same is true when relatively large, unidentified peaks show up in a chromatogram. In other words, confirmation of the identity of target compounds, and identification of non-target analytes, is an important aspect of modern water analysis. Today, LC–MS has certainly been shown to be a highly rewarding technique in divergent fields of interest such as, e.g., biomedical, pharmaceutical and environmental chemistry. Although most of the technical problems of LC–MS have been solved by now, analyte detectability still often leaves much to be desired, both with the popular TSP and even more so, with the PB interface. There are high expectations that the situation will markedly improve with the advent of electrospray and other atmospheric pressure ionization interfaces, but the number of papers published so far is too limited to draw definitive conclusions. In order to meet the current demands of environmental analysis, it is therefore necessary to perform trace enrichment prior to the separation-cum-detection step, and in our opinion to do so on-line. In current research, increasing interest is indeed devoted to the set-up and optimization of SPE–LC–MS procedures, although it should be added that most of these are not yet utilized for routine analysis, and, although on-line, are not fully automated. In these studies, generally speaking, both sample sizes (50–250 ml) and separation conditions are quite similar to those commonly used in SPE–LC–DAD.

4.1. SPE–LC–TSP-MS

In an early study, Bellar and Budde [22] explored the possibility of developing a broad-spectrum method for the determination of non-volatile target compounds in aqueous environmental samples, using off-line LLE and SPE prior to LC–TSP-MS. Gradient LC of samples containing a wide range of pesticides such as carbamates, sulfonylureas, triazines, phenylureas and organophosphorus pesticides (OPPs), spiked at the 2–50 and 20–500 μg/l level for LLE and SPE, respectively, was performed. Co-elution of a few analytes was considered to be acceptable because very few analytes will actually be present in each single run. With preconcentration by means of LLE detection limits varied from 0.2 μg/l for cyanazine to 16 μg/l for carbaryl. Detection limits obtained when using SPE were about 10-fold higher, mainly because of the limited capacity of the commercial extraction cartridges used in the study, i.e. because of the limited amount of sample volume processed (100 ml). A typical chromatogram obtained using filament-off TSP-MS in the positive ionization mode is shown in Fig. 5. More recently, the work of Bellar and Budde has been extended to include analysis of fruits and vegetables [23,24].

A further illustration of the potential of LC–TSP-MS to identify target compounds is the

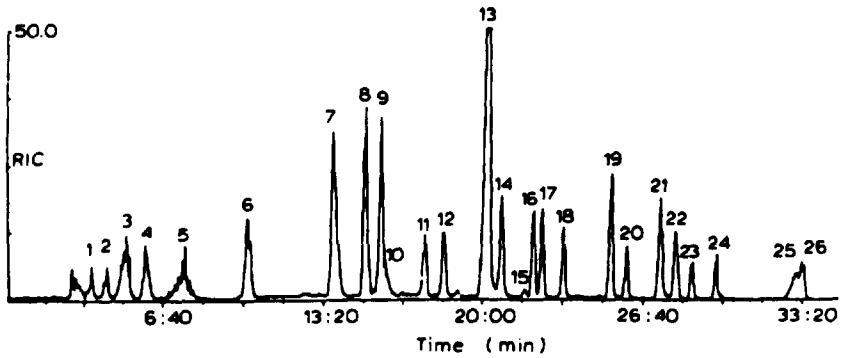

Fig. 5. Total ion current profile from the LC–filament off TSP-MS determination of a mixture of 34 compounds of environmental interest. Peaks: 1 = aldicarb sulphoxide; 2 = caffeine; 3 = aldicarb sulphone + oxamyl; 4 = methomyl; 5 = coumafuryl; 6 = atrazine, dealkylated; 7 = metribuzin, deaminated; 8 = N-(1-naphthyl)thiourea; 9 = fenamiphos sulphoxide + warfarin; 10 = carboxin sulphone + aldicarb; 11 = monuron; 12 = cyanazine; 13 = D_6 and D_4 dimethyl phthalate + propoxur; 14 = carbofuran; 15 = D_5 atrazine; 16 = fluometuron; 17 = thiofanox + carbaryl; 18 = diuron; 19 = propachlor; 20 = propham; 21 = siduron; 22 = BPMC (Osbac) + methiocarb; 23 = linuron; 24 = mexacarbate; 25 = alachlor; 26 = rotenone [22]. RIC = Reconstructed ion chromatogram.

analysis of river water [25]. Concentration of 1-l samples spiked at the 5 μg/l level by means of SPE, with subsequent desorption with methanol and the injection of 20 μl of the extract onto the analytical column enabled the detection of several triazine and phenylurea pesticides at the low μg/l level under full-scan conditions. As a real-life example, the presence of isoproturon was confirmed in the dichloromethane extract of a polluted river water sample: a major peak exhibiting an ion at m/z 207 had the same retention time as an isoproturon standard and gave a similar mass spectrum.

The feasibility of including trace enrichment and sample clean-up, i.e. SPE, on-line into the analytical system, was described by Bagheri et al. [26] for the determination of a large number of phenylureas in surface and drinking water. With 50-ml samples, and using either a copolymer-packed precolumn or membrane extraction disks, and linear-gradient LC with methanol–0.1 M ammonium acetate, time-scheduled selected ion monitoring (SIM) of spiked river Rhine samples gave detection limits of 5–15 ng/l for all but two of the fifteen analytes tested. It was shown that a non-spiked water sample contained low levels of monuron and isoproturon. Further work has revealed that, next to the phenylureas, a large number of triazines, N-methylcarbamates, OPPs and chlorophenols can be detected down to 0.01–1 μg/l in surface water [27] (cf. Fig. 6).

Another interesting paper on SPE combined off-line with LC–TSP-MS deals with the multiresidue determination of 128 polar pesticides in aqueous samples [28]. From among these pesticides, 95 were chosen as target compounds to develop a method with identical experimental parameters for all compounds. Special attention was paid to compounds with low UV absorbance such as aldicarb, methomyl, oxamyl, triallate, allidochlor and several organophosphorus compounds. The post-column addition of aqueous 175 mM ammonium acetate was found to improve sensitivity. In order to prevent the flow-rate of the final carrier stream to exceed critical values (1.5 ml/min) and allow the ammonium acetate flow-rate to be changed over a wide range, a 3 mm I.D. analytical column with a typical flow-rate of 0.5 ml/min was selected. Using both negative ionization and positive ionization detection limits of 0.1–100 ng were obtained for all compounds under full-scan conditions (m/z 130–450). With the published off-line SPE procedure (1 l concentrated to 1 ml; 20-μl injection), detection limits have to be 2 ng or lower for all compounds to meet the drinking water regulations of 0.1 μg/l of an individual

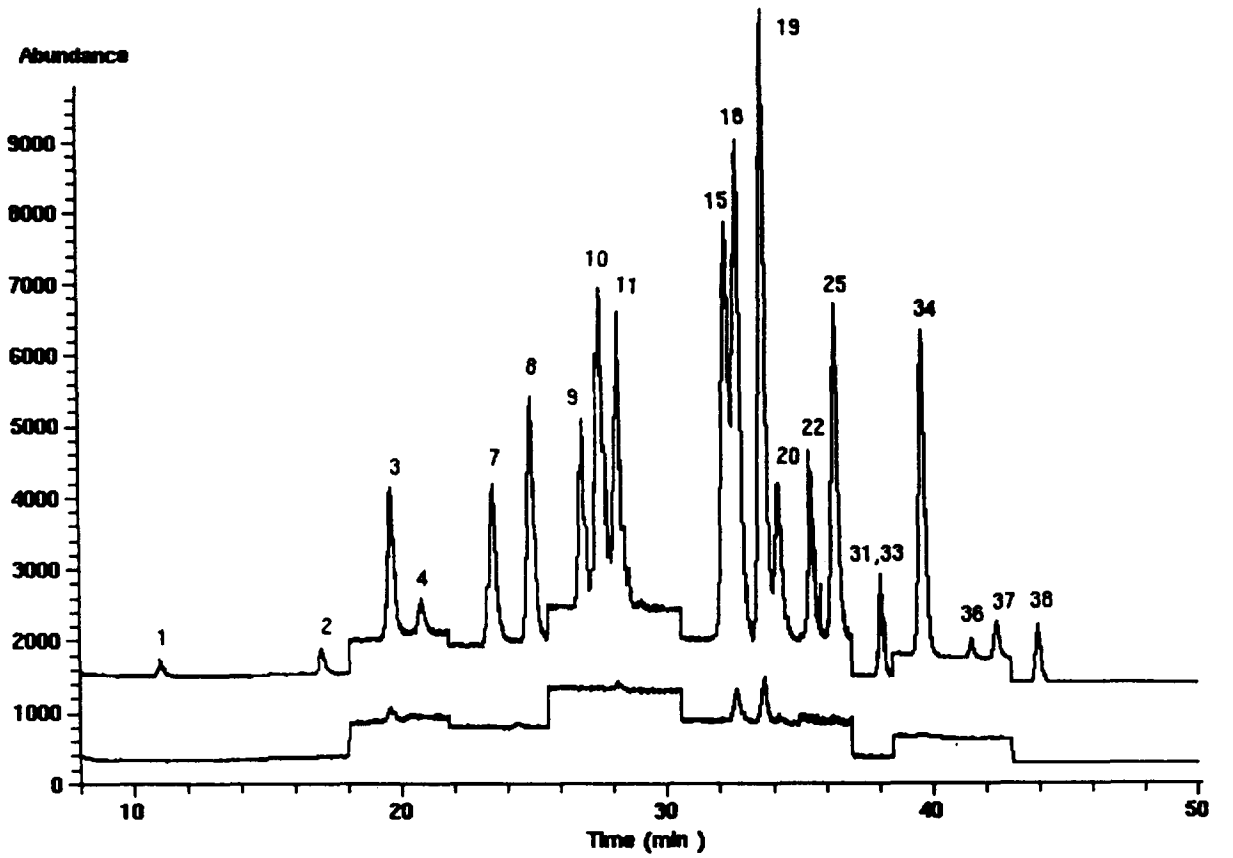

Fig. 6. On-line trace enrichment–LC–TSP-MS trace for 50 ml of (bottom) river Rhine and (top) river Rhine water spiked with a mixture of 21 polar pesticides at 1 μg/l. Column, 250 mm × 4.6 mm I.D. stainless-steel containing 5-μm C_{18}-bonded silica; eluent, linear methanol–0.1 *M* ammonium acetate gradient [10:90 to 90:10 (v/v) in 45 min]; MS, discharge positive ionization mode. Peaks: 1 = aldicarb sulphone; 2 = 1-(3-chloro-4-hydroxyphenyl)-3,3-dimethylurea; 3 = dimethoate; 4 = desmethylmetoxuron; 7 = monomethylmetoxuron; 8 = metoxuron; 9 = cyanazine; 10 = monuron; 11 = simazine; 15 = atraton; 18 = atrazine; 19 = isoproturon; 20 = diuron; 22 = azinphosmethyl; 25 = propazine; 31 = malathion; 33 = trietazine; 34 = prometryn; 36 = parathion-ethyl; 37 = diazinon; 38 = disulfoton [27].

pesticide. Obviously, the off-line procedure should be replaced by an on-line method. In principle, this will effect 50-fold improved detection limits. On the other hand it should be emphasized that the present procedure is highly suitable for target analysis: time-scheduled SIM enhanced analyte detectability 8–100-fold! The paper contains much relevant MS information.

Another interesting recent study [29] deals with the trace-level determination of pollutants in drinking water and in effluents from municipal and industrial sewage treatment plants. One approach used was SPE combined off-line with LC–TSP-MS and LC–TSP-MS–MS. Although identification is usually achieved by combining retention time and mass spectral data, the author found that even low levels of surface-active compounds caused a shift of the retention times. The potential problems such as misinterpretation of LC–UV results or the necessity to introduce a time-consuming clean-up procedure, were solved by using tandem MS, generating daughter-ion spectra by means of collision-induced dissociation. Many pollutants in drinking and waste water were found to be surface-active compounds of anthropogenic origin or their bio-

chemical degradation products. Although the paper does not directly address the determination of pesticides, the information provided is highly interesting for the topic at hand.

4.2. SPE–LC–PB-MS

The lack of structural information generally provided by TSP-MS ("confirmation" rather than "identification") has encouraged several groups of workers to use PB-MS, or both TSP-MS *and* PB-MS, for detection [30,31]. The distinct advantage of the latter alternative is that electron-impact (EI) mass spectra are generated, which provide a wealth of structural information and can be compared with spectra from GC–EI-MS libraries. The main drawback is that analyte detectability in LC–PB-MS is rather poor, which is mainly due to the low analyte transport efficiency through the interface —an aspect that starts to receive more attention [32].

A good example is provided by a study [30] on over 100 analytes from the EPA NPS, which showed the practicability of LC–PB-MS for the identification and quantification of non-volatile polar pesticides in ground water. On the basis of detection limits estimated for selected pesticides —which ranged from 5 to 50 ng— the authors concluded that with this single interface, and when using published procedures for analyte concentration and clean-up [33], about half of the pesticides on the quoted list can be confirmed at the 0.1 μg/l level. Obviously, for the other analytes, the method must be combined with TSP, and atmospheric pressure ionization modes of MS detection.

LC–PB-MS has also been used for the identification of non-target analytes in effluents from treatment plants. In this instance, 10-l samples were concentrated off-line to 1 ml, and an aliquot was injected [34]. Quite a number of non-ionic surfactants, plasticizers and plastic additives were detected, as well as the phenylurea triclocarban. Detection limits often were in the low μg/l range.

It will be evident that, as an alternative to using various interfaces and/or very large sample sizes, applying more advanced procedures for trace enrichment will, of course, also alleviate the problems, as becomes clear from a recent study on the use of on-line SPE–LC–PB-MS for target analysis of real-life samples [31]. With 100–250-ml samples, several phenylureas could be detected at the 30–50 ng/l level (full-scan mode). In addition low levels of various microcontaminants were identified in surface and drinking water samples, using both EI-mode, and negative ion chemical ionization (NCI)- and positive ion chemical ionization (PCI)-mode PB-MS. As an example Fig. 7 shows pertinent data concerning the identification of benzenesulphonamide in river Ob (Siberia) water. As a continuation of this work, an SPE–LC–UV–PB-MS system has been set up, and used for the trace-level detection of, amongst other compounds, oxamyl, monuron, atrazine and barban. The overriding importance of on-line trace enrichment is also evident from a study by Prosen et al. [35] who used 500-ml samples to detect sub-μg/l levels of bromacil in drinking water.

4.3. Other options in SPE–LC

Next to SPE–LC–DAD with its wide application range and good robustness, and SPE–LC–MS with its identification potential, there are of course other options. These mainly involve fluorescence (FL) or electrochemical (ED) detection, and sometimes include pre- or post-column derivatization or reaction detection procedures. In principle, the use of more or less selective methods of detection restricts the number of analytes that can be determined. It is therefore primarily utilized for the monitoring of selected classes of microcontaminants rather than for general monitoring purposes. Still, such techniques can well play a role in the on-line SPE–LC screening of environmental water samples, as will be discussed below.

On-line SPE–LC–ED/UV has successfully been used [36] for the determination of aniline, chloroanilines and other substituted anilines —which are both degradation products of the phenylureas, and industrial chemicals— using cation exchangers for trace enrichment. Since the direct pumping of real-life surface water

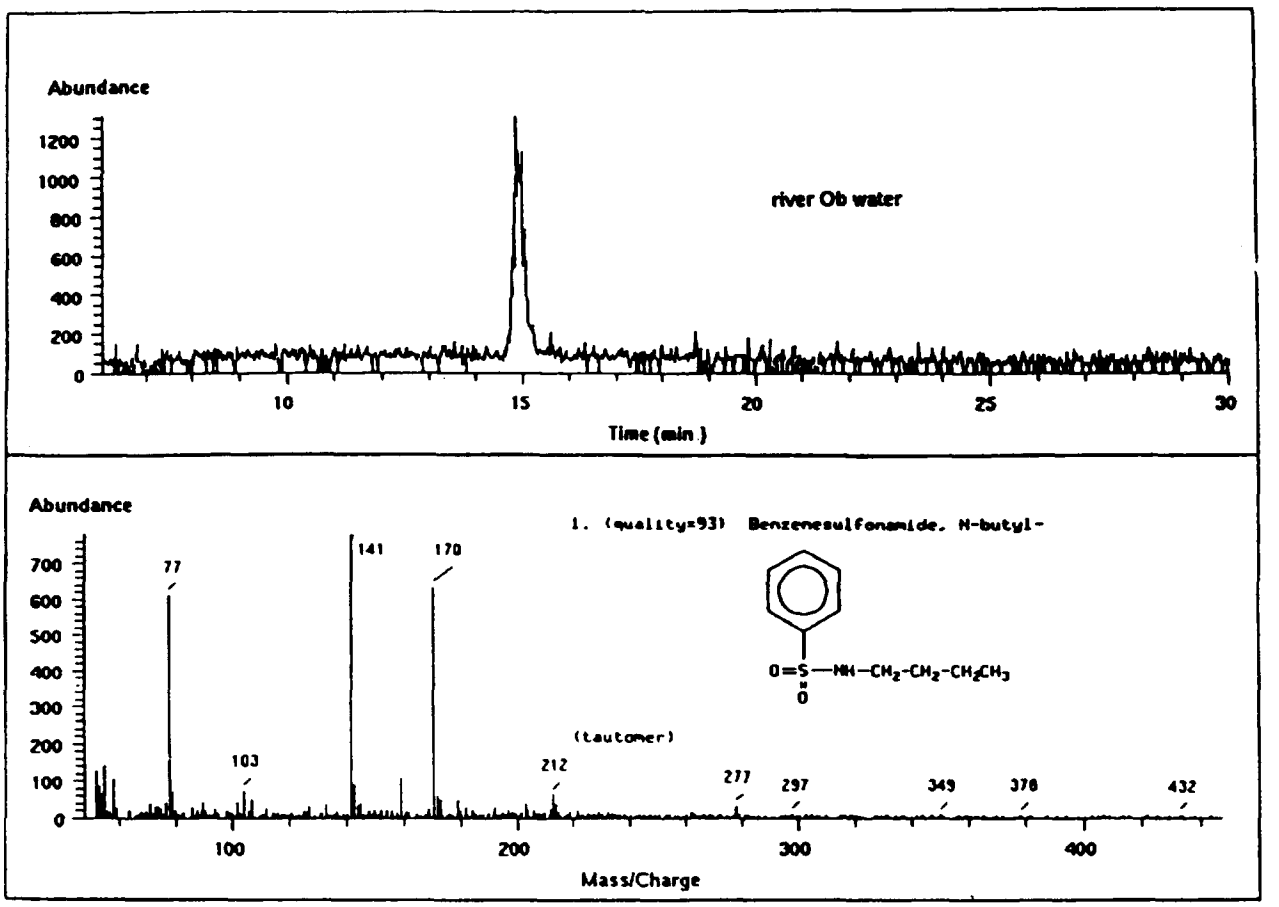

Fig. 7. On-line trace enrichment–LC–PB-MS extracted ion chromatogram (m/z 141) of 100 ml of Ob water and mass spectrum of the major peak [31].

samples has to be avoided owing to the high amount of inorganic cations in surface waters, a two-step preconcentration was performed. The analytes were first trapped in their neutral form on a polymer-based precolumn; next, the aniline derivatives were desorbed from this precolumn with a small amount of 20% aqueous acidic acetonitrile, redirected to a second precolumn which contained a cation exchanger. Finally, the analytes were on-line desorbed by the appropriate LC eluent. The combination of selective trace enrichment and sensitive ED allowed the determination of chloroanilines from 150 ml of river water, with detection limits below 30 ng/l. A typical example of the on-line analysis is shown in Fig. 8.

Another promising approach has been described by Miles [37]. In this paper, selectivity was obtained by post-column photolysis, and three detectors (FL, ED and conductivity) were used to detect over 100 analytes from the EPA NPS. Because of the large number of analytes tested, various gradient profiles had to be applied. LC–FL and LC–ED were found to be complementary with the former responding to several S-containing, and the latter to many N-containing pesticides. About half of the analytes tested had detection limits of 10 ng or below. Considering the fact that most of the test analytes can easily be concentrated on a suitable sorbent, on-line SPE–LC–FL/ED should enable their detection at the 0.1 μg/l level.

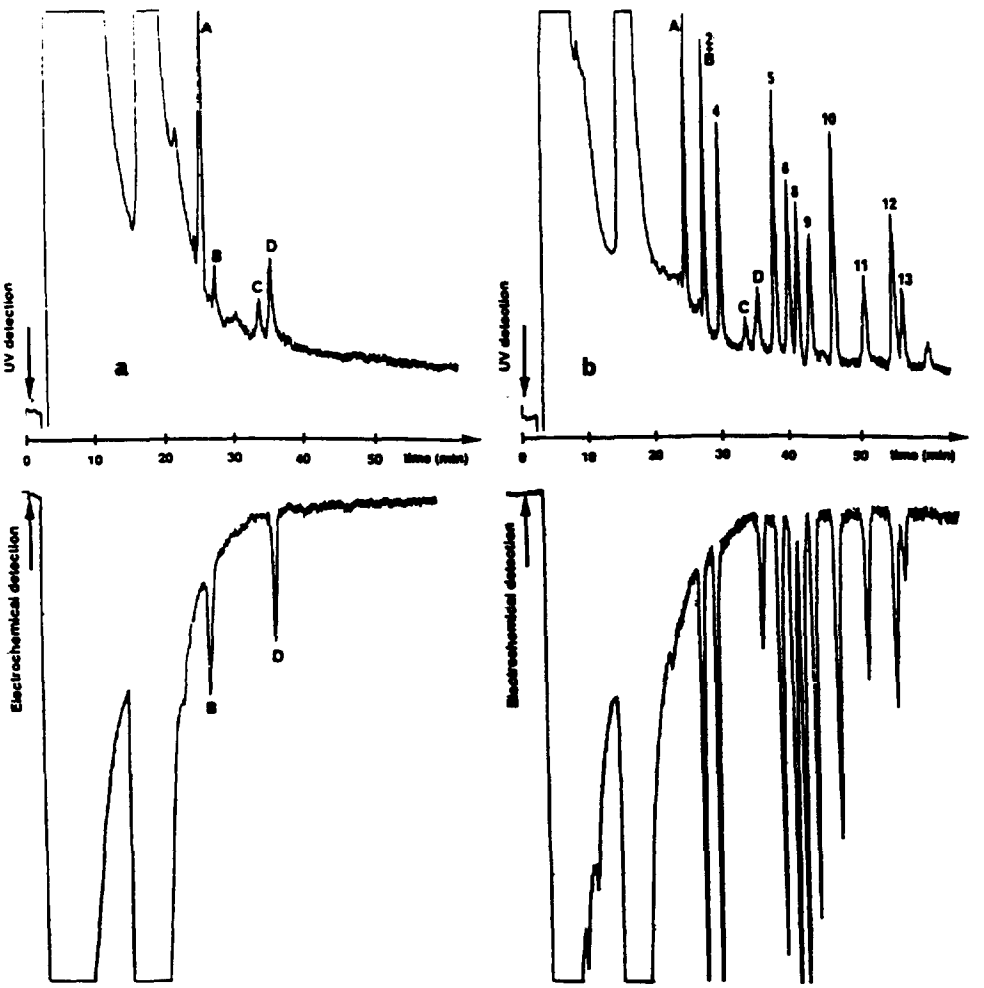

Fig. 8. Preconcentration and on-line analysis of a 500-ml sample of river Seine water: (a) non-spiked and (b) spiked with 0.5 μg/l of each aniline derivative. Peaks: 2–4 = monochloroanilines; 5–9 = chloromethylanilines; 9–13 = dichloroanilines. UV detection at 245 nm (0.02 AUFS); ED at 0.95 V (vs. Ag/AgCl), 5 μA FS [36].

It will be obvious that LC–FL, which is generally considered more robust than LC–ED for real-life sample analysis, is most advantageous when the microcontaminants of interest display native fluorescence. Such compounds include the aromatic sulphonates extensively referred to above and, of course, the polynuclear aromatic hydrocarbons (PAHs). An extensive review on the analysis of the latter class of compounds has been published recently [38]. It is interesting to add that the well-known problem of sorption of PAHs to connective tubing and inner walls apparently has been solved for fully on-line SPE–LC–FL by the addition of Brij-35, a neutral surfactant, above its critical micelle concentration, to the sample solution [39]. By disrupting the micelles just before the precolumn by adding water via a T-piece, unwanted peak broadening was prevented, without destroying the beneficial solubilizing effect during preconcentration. The combination of micelle-mediated sample preparation and time-scheduled FL allowed the trace-level determination of sixteen EPA-priority PAHs from 10 ml of surface water,

with detection limits at the low- to sub-ng/l level.

Finally, some attention should be devoted to post-column reaction detection. A recent review [40] states that there is a trend favouring post-column over pre-column derivatization, as evidenced by the fact that only 25% of the reviewed methods (on pesticide analysis) reported up to 1982, but 70% of those reported since then, employed post-column derivatization. The author repeats some well-known advantages of post-column operations: (i) they are invariably carried out on-line and are therefore easily automated and (ii) the LC separation of the analytes of interest is not affected. From among the examples discussed in the quoted review, there apparently is only a single one which merits attention in a paper primarily devoted to the on-line monitoring of environmental pollutants in aquatic samples. This is the use of *o*-phthalaldehyde/2-mercaptoethanol (OPA/MERC) for the determination of N-methylcarbamates (although one should add that phenylureas, glyphosate and nabam, an ethylenebisthiocarbamate, have also been determined using this procedure). Initially, the analytes were hydrolysed by means of the post-column addition of sodium hydroxide, the OPA/MERC solution being introduced next in order to quantitatively convert the methylamine formed into the highly fluorescent 1-hydroxyethylthio-2-methylisoindole. This method, introduced by Moye et al. [41] and repeatedly been refined since then [42], now is a well established EPA procedure [43].

An interesting alternative to simplify the complex method, and to reduce additional band broadening, is to effect hydrolysis in a solid-phase reactor containing an anion exchanger, or magnesium oxide. The applicability of such a system for the determination of a large group of carbamates and also many of their sulphoxide and sulphone degradation products in surface water, was shown recently by De Kok et al. [44,45]. A 50-ml water sample is passed through a disposable SPE cartridge packed with a low-carbon C_{18}-bonded silica (C_{18}/OH), which selectively retains polar compounds. The trapped analytes are eluted with acetonitrile, and 100 μl of the final extract (1 ml) are injected into the analytical system. Detection limits for all N-methylcarbamates and transformation products were 20–30 ng/l. In a sequel to this work, a fully automated on-line SPE procedure was developed to make the method more suitable for monitoring purposes [46]. The major advantages of this method are the reduced sample size required (typically 3–5 ml), a high sample throughput (30 samples per hour) and the absence of cross-contamination from one sample to the next. During a 6-month monitoring period of the river Rhine, no detectable amounts of N-methylcarbamates or their degradation products were found. However, occasionally some unknown, and as yet unidentified, peaks showed up. A typical chromatogram of a 5-ml surface water sample spiked at the 0.1 μg/l level is shown in Fig. 9.

5. SPE–GC

Analytes which are amenable to direct analysis by means of GC, i.e. without prior derivatization or conversion procedures, should preferably be determined by means of this separation technique because of three advantages: high separation efficiency, high speed of analysis, and the availability of many selective and sensitive detectors. However, integrated GC-based analytical procedures have one weak spot, sample pretreatment and/or introduction. Briefly, trace enrichment of the analytes of interest is generally carried out by means of off-line LLE or SPE, and a rather small proportion of the final extract —typically 1–5 μl out of 0.1–1 ml— is injected into the GC system. One way to alleviate the problem of insufficient sensitivity is to use large-volume injection techniques which enable the introduction of at least ca. 100 μl of a sample extract in an appropriate organic solvent. This approach which typically deals with the optimization of the GC part of one's system, and is well documented [47,48], will not be discussed here. Another way to look at the problems, which is especially interesting for aqueous samples, is to use the well-tried LC-type approach, that is, SPE, in order to simultaneously effect the usual

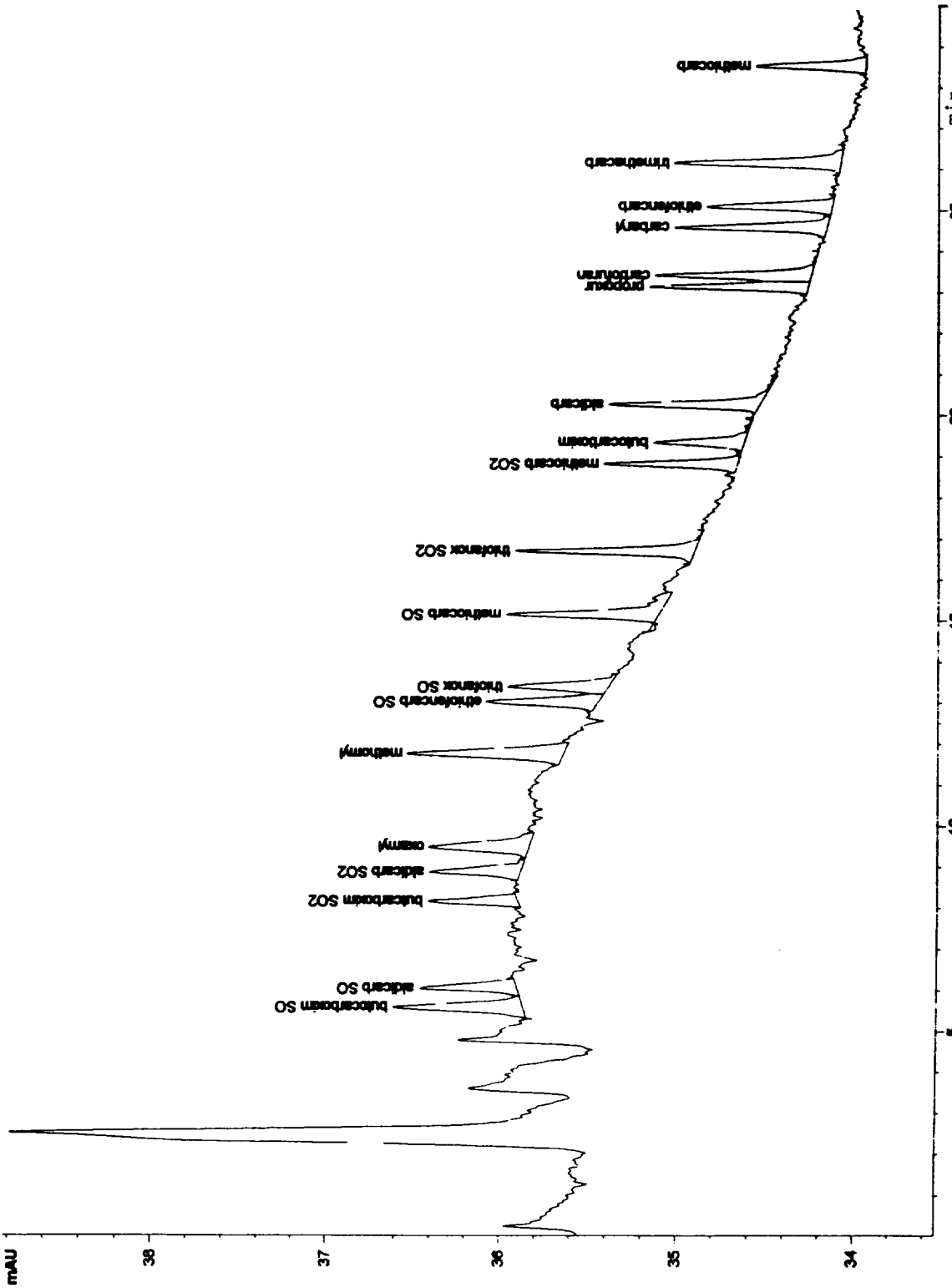

Fig. 9. SPE–LC–post-column reaction detection–FL (340/445 nm, $\lambda_{ex}/\lambda_{em}$) chromatogram of a 5-ml surface water sample, fortified with 18 N-methylcarbamates and degradation products at the 0.1 μg/l level, after on-line trace enrichment on a 10×4.0 mm I.D. C_{18}/OH precolumn, using an OSP-2 for on-line sample preparation. Trimethacarb was used as an internal standard [46].

analyte trace enrichment *and* the complete removal of the solvent, water, which of course should not enter the GC system.

In the recent literature on the on-line GC-based water analysis, rather much attention has been devoted to SPE–GC procedures. Since, in addition, this is the approach which is most closely parallel to the SPE–LC procedures discussed above, the main emphasis in the remainder of this section will be on SPE–GC. This is not because the present authors are of the opinion that SPE–GC will turn out to be the best or only solution. It is much more realistic to assume that several mutually, rather different, approaches will turn out to each have their own area of application, or, in other words, to be complementary.

5.1. Options for on-line "aqueous sample" GC

One alternative to combine SPE and GC would be to use on-line SPE–LC–GC. However, since with aqueous samples LC would have to be reversed-phase LC with its partly aqueous eluents, this apparently does not provide a simple solution. Quite apart from that, it will only enable one to transfer fractions of the LC eluent to the GC system or, in other words, to carry out heart-cut operations. The few papers devoted to on-line reversed-phase LC–GC clearly demonstrate that very small injection volumes [49] and a restricted range of LC eluent composition [50] are major drawbacks.

In principle, better results can be expected from reversed-phase LC–LLE–GC. The LLE part of the system is essentially the same as that often described for post-column extraction detection in LC analysis. In some studies, extraction and derivatization have been combined to achieve better detection sensitivity and selectivity [51,52]. A typical set-up of a reversed-phase LC–LLE–GC system, which has been used for the determination of fenpropimorph in an aqueous cereal extract [53], is depicted in Fig. 10. To all probability, disadvantages such as the absence of a real trace-enrichment potential, the complexity of the total set-up, and the limited polarity range of analytes that can be extracted in a single run (which especially is a drawback with general screening procedures!) are main obstacles for the introduction of this technique for routine purposes.

A third option is the use of open tubular trap (OTT)–GC. The procedure involves the retention of the analytes of interest from 1–2.5-ml water samples on the swollen stationary phase inside the OTT (typical dimensions: 5 m × 0.53 mm I.D.; 5 μm stationary phase). Swelling the stationary phase with, e.g., hexane or chloroform, considerably increases retention for non-polar and medium-polar analytes, respectively, and breakthrough volumes often are at least 5–10 ml [54]. Interesting results have been published for, e.g., spiked river water (Fig. 11). The approach certainly has its merits, but these will probably be for non- to weakly polar rather than medium-polar analytes.

5.2. On-line SPE–GC

Next to the techniques discussed above and other related options such as solid-phase microextraction–GC and SPE–thermal desorption GC (see, e.g., Refs. [55] and [56]), there obviously is a need for a procedure which is a close parallel of SPE–LC. The scheme of a completely on-line set-up is shown in Fig. 12; with this design, full automation has been achieved. The sample volume generally is 1–10 ml rather than the 100 ml used with LC systems because of the better performance of GC detectors. Although exceptions have been noted, it is generally of crucial importance to remove all traces of water after loading of the aqueous sample. One option is drying with nitrogen gas (15 min; ambient temperature; no losses of medium volatile analytes; cf. Ref. [57]). The use of several small (3–4 mm diameter) membrane extraction disks stacked in a holder rather than a conventional precolumn facilitates drying. An alternative is to use a drying cartridge containing anhydrous sodium sulphate or silica [58,59] which is inserted between the precolumn outlet and the inlet to the GC part of the system. On-line desorption of the analytes from the precolumn or disks holder is often performed with ethyl ace-

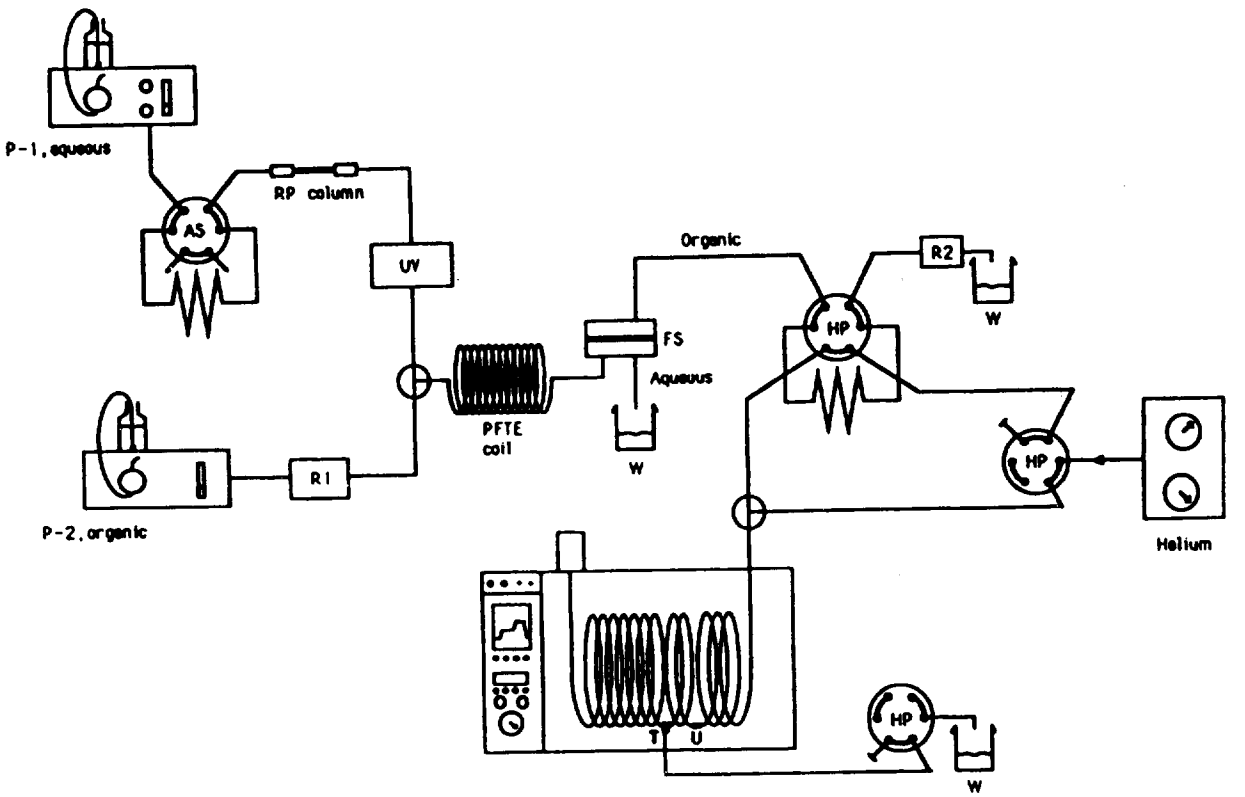

Fig. 10. Schematic representation of the reversed-phase (RP) LC–GC equipment. P = LC pumps; AS = autosampler with 20-μl sample loop; UV = UV detector; FS = phase separator; HP = six-port high-pressure valve of which one is equipped with a 1000-μl storage loop; R-2 = needle valve restrictor; W = waste, U = connection between retention gap and retaining column; T = connection between retaining column, separation column and early vapour exit [53].

tate at a flow-rate of, typically, 50–100 μl/min. The total desorption volume is on the order of 50–150 μl or, in other words, introduction into the GC part of the system will cause no problems (cf. discussion on large-volume injections above).

In the past few years, quite a number of applications of on-line SPE–GC have been reported, using both flame ionization (FID), thermionic (NPD), flame photometric (FPD), MS and atomic emission (AED) detection. Because of the relative novelty of the approach, proper validation has not yet been performed and practical experience still is limited. The brief overview presented in the next paragraphs should, however, suffice to illustrate that SPE–GC-based water analysis can provide excellent results in terms of analyte detectability and selectivity.

In an early study, SPE–GC–NPD [57] (with nitrogen drying) was found to be a rewarding approach for the analysis of surface water samples from several European rivers. With 2.5-ml samples detection limits for fourteen OPPs were at or below the 0.1 μg/l level. More recently, SPE–GC–NPD and SPE–GC–MS were shown to give nicely agreeing results in the sub-μg/l determination of atrazine and simazine in river Rhine water [60]. The EI-MS spectra recorded enabled unambiguous identification of the two triazines. SPE–GC–MS has also been used to confirm the presence of benzothiazole in river water [61].

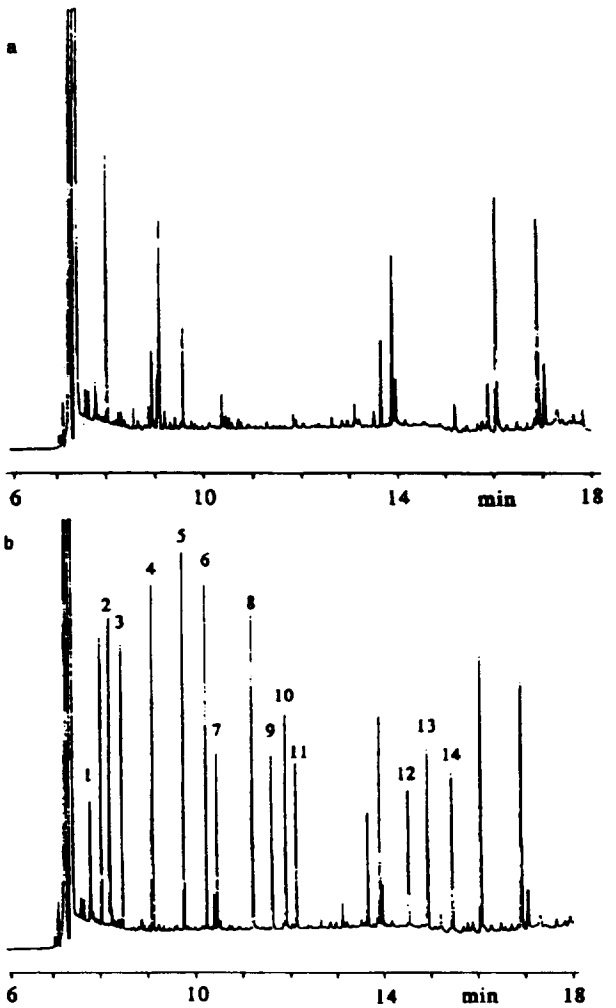

Fig. 11. On-line OTT–GC of river Dommel water: (a) 2.25 ml river water, (b) 2.25 ml river water spiked at a 5 μg/l level with: 1 = toluene; 2 = ethylbenzene; 3 = methoxybenzene; 4 = *p*-dichlorobenzene; 5 = dimethylphenol; 6 = dimethylaniline; 7 = chloroaniline; 8 = indole; 9 = dichlorobenzonitrile; 10 = trichlorophenol; 11 = dinitrobenzene; 12 = unknown; 13 = atrazine; 14 = phenanthrene (ca. 40 ng/compound). Trapping details: 2m × 0.32 mm I.D. trap with a 5-μm stationary phase swollen with CH_2Cl_2; sampling flow-rate 100 μl/min, desorption with 75 μl CH_2Cl_2 [54].

In two papers on the re-use of drying cartridges, OPPs, triazines and organosulphur compounds could be detected down to the 0.1 μg/l level, even with SPE–GC–FID (10-ml drinking water samples) [59,62]. A more selective approach using NPD or FPD was required with surface water. Fig. 13 shows results of the analysis of several types of water samples spiked with 0.03–0.1 μg/l of triazine and OPPs. The blank run demonstrates that, even at this low concentration level, there are no memory effects. In another study, SPE–GC–FID was used to analyse over 100 real-life samples spiked with nine chlorophenols [56]. Even with 1-ml samples, the limits of detection were about 1 μg/l. No maintenance problems were encountered.

Next to GC–MS, GC–AED can also be used to provide (limited) structural information. After earlier studies had shown that, contrary to general belief, GC–AED can also be combined with large-volume injections [63], completely on-line SPE–GC–AED was set up [64]. With, admittedly, rather large sample volumes of 50–100 rather than 10 ml, detection limits for, especially, organosulphur and organophosphorus compounds, in real-life samples and without any clean-up but that provided by the SPE procedure, are at or below the 0.1 μg/l level. One interesting example is depicted in Fig. 14. In the quoted studies, SPE–GC–AED has been used for the analysis of drinking, surface and waste water samples.

6. Conclusions

In the past few years great strides have been made with regard to the use of procedures, and systems, for the trace-level analysis of microcontaminants in aqueous samples. An increasing number of these is based on the on-line combination of SPE-type analyte trace enrichment (and sample clean-up) and LC or GC separation, plus detection. The application of such on-line, and frequently semi- or fully automated set-ups has helped to increase sample throughput and to improve analyte detectability in terms of sensitivity and selectivity. In addition, with many of the recently introduced GC-based procedures (on-line as well as at-line and off-line), there is a dramatic decrease in the consumption of organic solvents during sample preparation.

Both when early warning and when wide-rang-

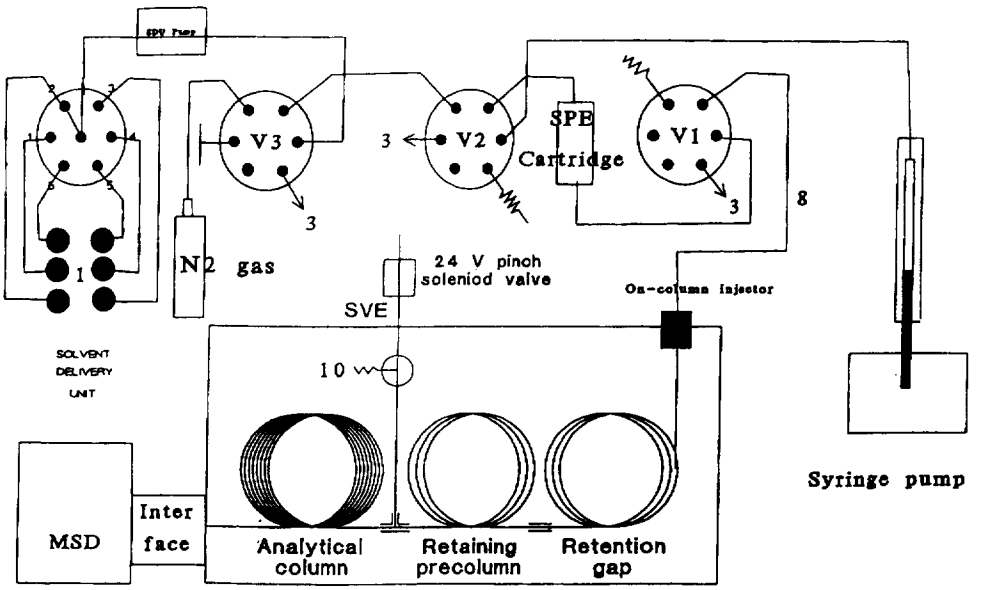

Fig. 12. Schematic diagram of an on-line SPE–GC–MS system consisting of three six-port switching valves (V1–V3), two pumps, and a GC system equipped with a solvent vapour exit, a retention gap, a retaining precolumn, an analytical column and a mass spectrometer (MSD) [67].

ing monitoring is the main purpose, there are three main options: (i) SPE–LC–UV or SPE–LC combined with other conventional detection principles, (ii) SPE or LLE combined off-line or on-line with LC–TSP-MS or LC–PB-MS, and (iii) SPE–GC and related GC-based procedures. Today, SPE–LC–DAD is being used in quite a number of laboratories. Fully integrated systems are commercially available; alternatively, combining commercial sample preparation units such as the Prospekt (Spark Holland, Emmen, Netherlands) or OSP-2 (Merck, Darmstadt, Germany), or even an additional pump and switching valve, with conventional LC–DAD systems in one's own laboratory will not cause any undue problems. With water samples of up to about 100 ml, detection limits of 0.5–1 μg/l, or better, can be obtained for a wide range of polar pesticides and related microcontaminants. In most instances, full absorbance spectra can be recorded at about the same concentration level. It is the general experience that the SPE–LC–DAD systems are rugged and do not cause serious maintenance problems. Actually, a main improvement in performance may well come from the general consideration that in most early-warning and monitoring programmes, the number of microcontaminants showing up at concentrations sufficiently close to or above pertinent threshold values to justify further action, will be very low on a *per analysis* basis. In other words, provided that analyte detectability (sensitivity) is maintained at the proper level, chromatographic resolution (selectivity) may well be reduced. One can therefore envision the design of less expensive single-column LC systems, in which trace enrichment and separation are carried out on one, possibly even rather short, analytical column. First attempts in this direction appear promising [65] (Fig. 15).

Until recently in LC–MS-based procedures not much attention was devoted to either the monitoring of large numbers of microcontaminants in one run, or to the evaluation of properly designed on-line SPE–LC–MS set-ups. Combined with the well known deficiencies of the TSP and PB interfaces, this often caused the attitude towards the usefulness of these techniques in trace-level environmental analysis to be one of scepticism. Fortunately, it is increasingly

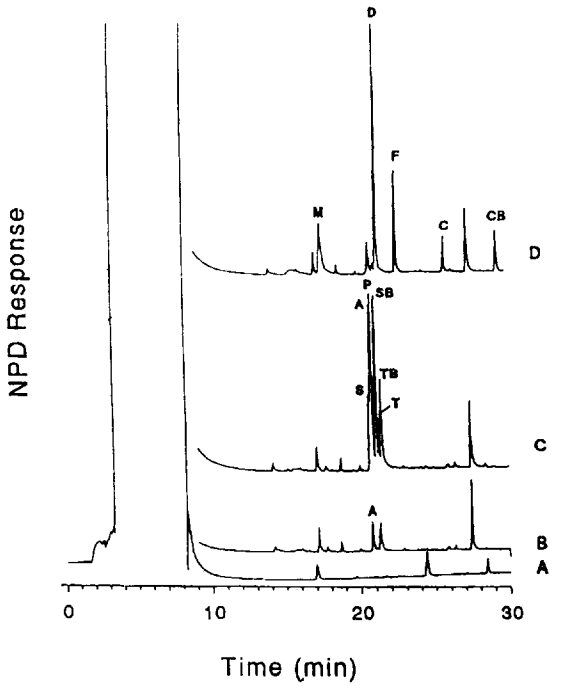

Fig. 13. SPE–GC–NPD chromatograms obtained after preconcentration of 10 ml of (A) HPLC-grade water, (B) Amsterdam drinking water, and drinking water spiked with (C) triazines (0.1 μg/l) and (D) OPPs (0.03 μg/l). Peaks: S = simazine; A = atrazine; P = propazine; SB = secbumeton; T = trietazine; TB = terbutylazine; M = mevinphos; D = diazinon; F = fenitrothion; C = coumaphos; CB = carbophenthion. Drying cartridge contained silica. GC programme: 75°C during sample introduction, ten to 300°C at 15°C/min; held at 300°C for 5 min [59].

being realized that it is the on-line SPE–LC approach which largely solves the problems of too high limits of detection. Simultaneously, papers start to appear which deal with wide ranges of micropollutants. Besides, more attention is given to novel interfacing options, notably atmospheric pressure ionization. Finally, and this will no doubt become increasingly important in the near future, SPE–LC–MS techniques are being used to evaluate the nature of the, generally rather polar, transformation products of the microcontaminants of interest [31,66].

Finally, SPE–GC and other approaches which combine sample treatment and GC in an on-line or at-line fashion have seen a marked development in the recent past and several papers dealing with the direct analysis of water samples have been published. Still, most of them are in their infancy and it is too early to make a definitive statement concerning their relative merits. A rather attractive aspect of SPE–GC is that sample pretreatment proceeds in essentially the same way as with the LC procedures. This will help to combine LC and GC operations in one set-up, and will facilitate the comparison of experimental results. For the rest, both SPE–GC *and* the other approaches share the advantage, compared with LC techniques, that both the sensitivity and selectivity are distinctly superior. Therefore, 1–10 ml of sample will often suffice to achieve limits of detection of 0.1 μg/l. With SPE–GC–MS and SPE–GC–AED one has, moreover, two techniques which provide complementary structural information which will frequently lead to unambiguous identification rather than confirmation.

In summary, analytical methods do exist and/or are being developed which enable the determination of a large number of organic microcontaminants, and already some of their breakdown products, at levels of 0.05–5 μg/l in a variety of water samples. Aspects which are related to the cost-effectiveness —another important keyword today— of the procedures are increasingly being considered by analytical chemists, charged with the development of proper procedures and strategies: it is probably correct to say that sample sizes should preferably be small, separation should be adequate, and detection should be continuously improved. Due attention still has to be given to validation of the methods presently in use, and to related quality assurance aspects. With some imagination, the latter category should also comprise a proper selection of the microcontaminants that should really be monitored in, e.g, surface water. As has recently been aptly remarked [1] 39 pesticides are included in the 76/464 EEC Council Directive; however, many of these are used no longer, or only in small quantities. Or, to quote another example, from the list of widely used, probable or transient leaching compounds, only eight appear in the 76/464 Directive. Even updated lists should, of course, be used with

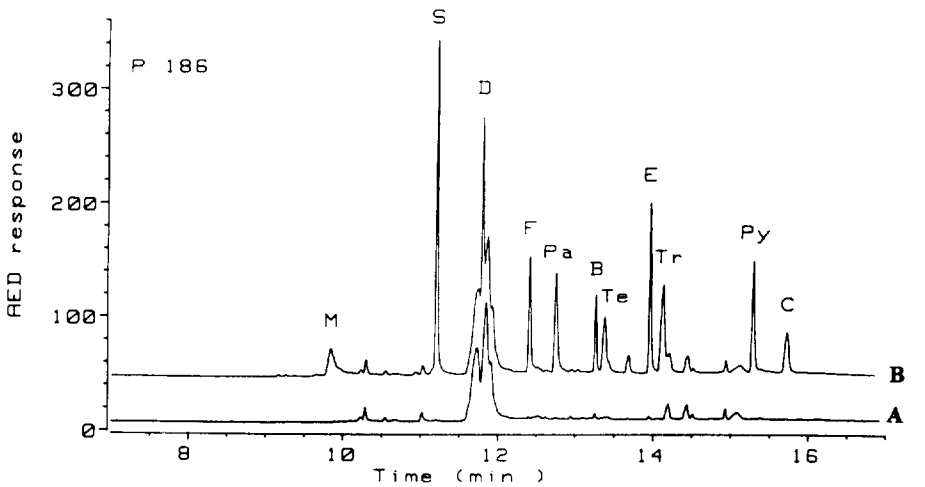

Fig. 14. On-line SPE–GC–AED (P channel) of (trace A) 50 ml of river Meuse water and (trace B) 50 ml of river Meuse water spiked with OPPs at the 0.1 μg/l level. Peaks: M = mevinphos; S = sulfotep; D = diazinon; F = fenchlorphos; Pa = parathion-ethyl; B = bromophos-ethyl; Te = tetrachlorvinphos; E = ethion; Tr = triazophos; Py = pyrazophos; C = coumaphos [64].

care: data on agricultural, industrial and other activities for a particular region or river basin can help to finalize one's set of target compounds. Obviously, in such a situation as depicted here, the rather rigid approach of the EPA certainly has its advantages, especially when the same set of rules has to be applied in a large number of countries, as in the EU. On the

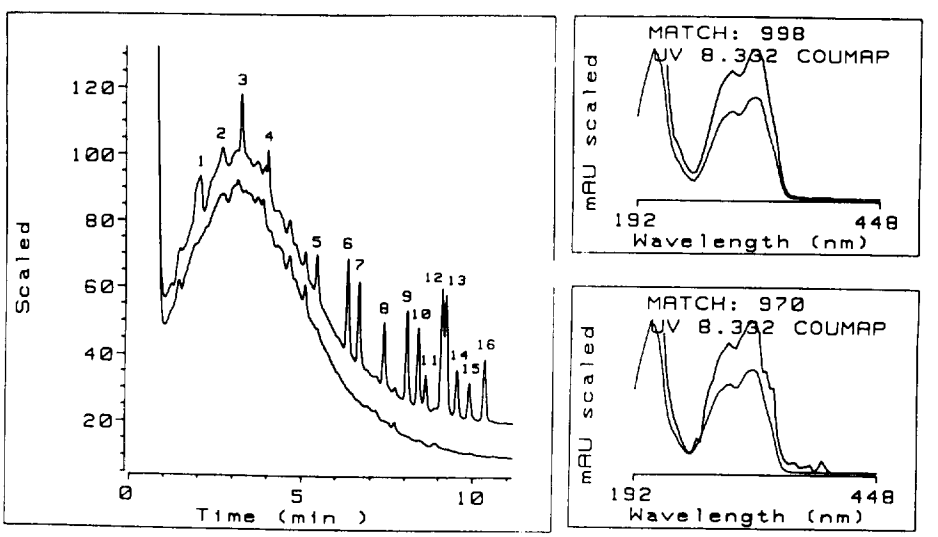

Fig. 15. Single short-column (20 mm × 4 mm I.D.) LC–DAD of 15-ml samples from the river Meuse without and with a 4 μg/l spike of sixteen OPPs. Inserts on the right-hand side: UV spectra of coumaphos (peak 10) at 4 μg/l (top) and 1 μg/l (bottom) compared with library spectra. Eluent: 15-min linear acetonitrile–aqueous phosphate buffer gradient; UV detection at 210 nm. Peaks: 1 = monocrotophos; 2 = dimethoate; 3 = mevinphos; 4 = phosphamidon; 5 = paraoxon; 6 = azinphos-methyl; 7 = fenamiphos; 8 = fenitrothion; 9 = fenthion; 10 = coumaphos; 11 = phoxim; 12 = fenchlorphos; 13 = bromophos-methyl; 14 = chlorpyryfos; 15 = carbophenothion; 16 = bromophos-ethyl [65].

other hand, allowing workers to use their individual skills, and stimulating their interest in evaluating novel analytical strategies, optimization of the final result not being the least of these, certainly has its attractions.

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