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Review

Fifty years of solid-phase extraction in water analysis – historical development and overview

I. Liška*,[1]

Water Research Institute, Nábrezie Svobodu 5, 812 49 Bratislava, Slovakia

Abstract

The use of an appropriate sample handling technique is a must in an analysis of organic micropollutants in water. The efforts to use a solid phase for the recovery of analytes from a water matrix prior to their detection have a long history. Since the first experimental trials using activated carbon filters that were performed 50 years ago, solid-phase extraction (SPE) has become an established sample preparation technique. The initial experimental applications of SPE resulted in widespread use of this technique in current water analysis and also to adoption of SPE into standardized analytical methods. During the decades of its evolution, chromatographers became aware of the advantages of SPE and, despite many innovations that appeared in the last decade, new SPE developments are still expected in the future. A brief overview of 50 years of the history of the use of SPE in organic trace analysis of water is given in presented paper.

Keywords: Reviews; Solid-phase extraction; Water analysis; Environmental analysis

Contents

1. Introduction

The growing extent of pollution of the environment as a result of human activities initiated a wide complex of legislative measures. Any assessment of efficiency of environmental protection policy, however, necessitated availability of relevant and reliable data on concentrations of pollutants in the environment. The largest problems were encountered in the case of organic micropollutants, where the analysts had to cope with many different compounds occurring at trace concentrations. Thus, the need for

*Fax: +431-260-60-5895.

E-mail address: igor.liska@unvienna.org (I. Liška)

[1]International Commission for the Protection of the Danube River, Vienna Int. Center, Building D 0443, Postfach 500, 1400 Vienna, Austria.

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reliable data on occurrence of organic micropollutants in the environment was an important driving force initiating the development of modern analytical techniques and procedures. With certain degree of approximation, two major target areas of interest can be distinguished in the process of development of environmental organic trace analysis. The first area that was given major attention in the past was analytical separation and detection. In this field remarkable progress has been achieved during several decades. The initial analytical set-up including, e.g., column chromatography, colorimetry and IR spectroscopy changed gradually to achieve the present status characterized, e.g., by automated hyphenated chromatographic systems or by selective immunoaffinity systems. The second field – sample preparation – has always been in the shadow of the first one, often being considered as a boring, inevitable part of the whole analytical method. Only after the highly sensitive analytical systems had become a common standard for environmental analysts it was realized that the preparation of samples was an important braking factor in the general progress in environmental analysis. It became apparent that any mistake occurring in collecting and processing a water sample could lead to a substantial error in the final result regardless of the excellent performance of the state-of-the-art analytical technique applied subsequently. Moreover, the result of the survey among analysts indicated that, for all respondents, two-thirds of the analysis time was spent on collection and preparation of the sample [1]. Hence, sample-handling techniques were shifted into the spotlight of the attention of environmental analysts and, consequently, they started to attract an increased interest from manufacturers as well. At that time the boom also started for solid-phase extraction (SPE). In the last decade this sample handling technique became the method of choice in many environmental analytical applications and it has been gradually included also into standardized methods. This resulted in SPE becoming familiar to a wide analytical public.

At present, when SPE is being described, it is often referred to some 15–20 years of its history, obviously concentrating on the period of the above-mentioned boom. However, the first experimental applications of SPE started five decades ago in the very beginnings of the organic trace analysis of water. Since then hundreds of papers have appeared in the scientific journals describing various developments and applications of SPE in water analysis and many articles reviewing the use of SPE for trace enrichment of organic compounds from water can be found in literature, as well [2–9]. Since these reviews give a thorough description of SPE methodology as well as comparison of different materials, procedures and configurations, to avoid useless redundancy, the intention of this paper is to present a brief reminiscence of 50 years of SPE development. In the presented overview, the development of SPE has been divided into several periods or ‘ages’. This division has not been based on exact discrete time periods but rather on major research targets attracting the attention of SPE experimenters in a particular age.

2. First attempts – the age of active carbon

The property of solid surfaces to bind molecules of organic compounds via different affinity mechanisms has been known for many decades. The analytical possibilities offered by this phenomenon were gradually recognized during long-term development of chromatographic techniques first introduced by Tswett at the turn of the twentieth century. Differences in affinity of various molecules to active sites located on the surface of the sorbent material resulted in separation of mixtures of different molecules, thus enabling their detection as single species. Experiments with separation of molecules on sorbent materials gave rise to chromatographic techniques.

On the other hand, the sorption properties of solid materials were recognized to also be useful in water treatment technologies, especially those used for drinking water purification. Granulated active carbon (GAC) had already been a popular sorption material in water treatment technologies when it was tested also for recovery of organic compounds from water samples prior to further analysis and identification. The pioneering work was made by the group in the US Public Health Service (Cincinnati, OH, USA). Braus et al. [10] used an iron cylinder packed with 1200–1500 g of granular activated carbon for the concentration of organic compounds from raw and filtered surface waters. Using these carbon filters

they sampled at six water plants along the Ohio River from Midland, PA, USA, to Louisville, KY, USA, during the spring of 1949. After a metered volume of water had passed through the carbon filters, the filters were returned to the laboratory, the carbon was removed, air-dried and extracted with diethyl ether in a large-capacity modified Soxhlet extractor. The organic residue was separated into five groups and certain specific chemicals were identified. Later on, Rosen and Middleton continued in testing of carbon filter method. In their method for identification of petroleum refinery wastes in surface waters, thousands of gallons of surface or waste water were pumped through the carbon filter, which was then extracted with chloroform, the extract was fractionated using column adsorption chromatography and petroleum pollutants were measured by infrared spectroscopy [11]. This method was able to provide evidence of the presence of low (ppm) concentrations of petroleum refinery wastes in surface waters. The same authors applied carbon filter sampling in connection with adsorption chromatography and infrared spectrometry for the development of a general monitoring procedure that could detect a variety of common insecticides in surface waters [12]. Also, in this application of carbon filter sampling, thousands of gallons of water samples were forced through a 18×3 in I.D. (1 in=2.54 cm) inches column of active carbon and pesticides were recovered by chloroform. The authors examined the efficiency of adsorption and of recovery for several chlorinated insecticides and found it satisfactory. They also reported that the practical application of a carbon filter method in a program of monitoring organic chemicals in surface water systems had led to the detection of DDT in five large rivers at concentrations below those toxic to aquatic life. These pioneering efforts led to the increased use of activated carbon for analytical purposes which may be documented by many representative citations [4].

Except of the use in classical SPE procedures, the high capacity of activated carbon made it the most popular sorbent for the closed-loop-stripping analysis. This sample handling technique, which is related to SPE (the main difference is that analytes are stripped from the water sample with an inert gas and then are sorbed onto the solid sorbent), had been introduced by Grob [13] and found to be very efficient for volatile organics. To safeguard high recovery efficiency in this case, carbon disulfide was used as eluting solvent.

The problems encountered during use of activated carbon in SPE resulting from its heterogeneous nature hampered an extensive and successful development of applications of carbon filter method. Disadvantages, such as irreversible adsorption or chemical modification on activated carbon surfaces and low recoveries for certain groups of compounds, have resulted in gradual replacement of the carbon adsorption method by techniques using other types of sorbents. Nevertheless, the importance of activated carbon in SPE development was that this was the material which initiated the interest of analysts in the use of solid-phase for trace enrichment of organic analytes from aqueous matrices. It must be also mentioned that despite the loss of interest in its use in the field of water analysis, classical active carbon remained very popular in water treatment technologies [14].

The renaissance of the carbon materials in SPE applications came later after new carbonaceous materials appeared having homogeneous structure and hence improved physico-chemical properties. These applications will be discussed in following chapters.

3. The age of search for the most appropriate material

This age of a wide development of off-line SPE procedures examining new types of sorbents in an attempt to find the best SPE material started in the late 1960s and lasted until the early 1980s. Naturally, new SPE materials are being developed until now and it seems to be a never-ending story, however, the present efforts are aimed mostly at finding an optimum material for a particular application rather than an universal sorbent suitable for every purpose.

In the 1960s it had become clear that the heterogeneous nature of carbon used in the initial SPE experiments was a limiting factor to the wider utilization of this sample handling procedure. Carbon did not adsorb many organic compounds dissolved in water, the desorption from carbon was not always complete and the compounds desorbed were not

always identical to those originally extracted from water [2]. Thus, the efforts of analysts were focussed to finding a more homogeneous solid adsorbents to replace the active carbon successfully. This effort can be considered as a dominant activity in the evolution of the SPE in the late 1960s and in the 1970s. The decisive driving force that stimulated an increased interest of environmental analysts in SPE at that time was the introduction of polymer materials and, later on, bonded silicas.

In the mid-1960s, Rohm and Haas Company introduced a cross-linked polystyrene resin, Amberlite XAD-1. The resin was in form of beads (20–50 mesh), each of which was a conglomerate of a large number of microbeads. Riley and Taylor [15] were the first who reported the use of polymer materials for the preconcentration of organic compounds from water samples. Their adsorption studies were carried out with 1 cm diameter columns, which had been packed to a depth of 7 cm with Amberlite XAD-1 resin. Before use, the resin columns were washed with distilled water and ethanol. Seawater samples (1 l) spiked with appropriate amounts of analytes were allowed to percolate through the columns at a rate of ca. 5 ml/min. After washing, the columns were eluted with successive 10 ml aliquots of an appropriate eluent (ethanol, diluted nitric acid, diluted potassium hydroxide). The eluates were analyzed by different methods (photometry, fluorimetry, GLC, ^{14}C counting). The study was focussed not only on pollutants but also on carbohydrates, amino acids and humic acids. The series of Amberlite polymeric resins started to attract the attention of other analysts in the early 1970s. Apart from XAD-1, other styrene–divinylbenzene Amberlites (XAD-2, XAD-4) and ethylene–dimethacrylate resins (XAD-7 and XAD-8) were also introduced. Burnham et al. [16] developed a method for extracting trace organic contaminants from potable water using XAD-2 and XAD-7. The resins were able to extract weak organic acids and bases and neutral organic compounds quantitatively from water solutions at ppb levels. In other work polychlorinated biphenyls (PCBs) were analyzed in seawater using a combined SPE–liquid–liquid extraction (LLE) approach with XAD-2 [17]. Apart from Amberlite resins, the first experimental studies also employed other polymeric materials for preconcentration purposes. Gesser et al. [18] used porous polyurethane foam for sorption of PCBs from water followed by solvent elution and analysis by GC. Mieure and Dietrich [19] extracted organic compounds from water with a column packed with Chromosorb 102. After sampling, the column was then attached to the head of a GC analytical column and organic compounds were thermally desorbed by the flow of the carrier gas.

In 1974 Junk et al. published an extensive study of preconcentration methodology using XAD-2 resin [20]. In this study the organic impurities were isolated from water by sorption on a small column of a macroreticular resin and eluted by diethyl ether. The eluate was concentrated by evaporation and the organics were separated and determined by gas chromatography. Studies on a large number of model compounds added to water in the 10–100 ppb range (20 ppt for pesticides) demonstrated that this method was accurate and reliable. This study stimulated the interest of water analysts in the use of styrene–divinylbenzene materials and during the following decade the extensive recovery tests published by other authors [21–23] as well as the selective tests focussed to, e.g., nitro compounds [24], organosulphur compounds [25], humic substances [26], nonionic detergents [27] or alkyl/triaryl phosphates [28], confirmed the advantages of polymers. In addition to styrene–divinylbenzene resins, other polymeric materials also attracted the attention of analysts. Ethylene–dimethacrylate copolymers from the Amberlite series (XAD-7, XAD-8) have already been mentioned. Higher polarity of acrylates improved the recovery of more polar compounds so that they were suitable for preconcentration of fulvic acids [26] or phenol [16], however, a comparative study by Thurman et al. [29] also showed a high affinity of acrylates to aliphatic compounds. Separon and Spheron acrylate copolymers manufactured in the former Czechoslovakia were also found to be suitable for preconcentration of toluene, *m*-cresol, prometryne [30], phenoxycarboxylic acids and *s*-triazines [31]. Next to Amberlites the copolymers from other manufacturers were also applied to SPE procedures in water analysis such as Porapaks [32] and Chromosorbs [19,33]. Although Tenax (2,6-diphenyl-*p*-phenylene oxide) was predominantly used as trap packing in purge-and-trap applications, the extensive studies of Pankow et al. [34–36]

confirmed this sorbent to be suitable for direct accumulation of organics from water followed by thermal desorption into a GC system. However, classical SPE applications using Tenax were also published by Leoni et al. [37,38]. Many other polymers were tested in seventies for the recovery of various organic compounds from water. The applications using polyurethanes (as open-pore polyurethane [39] and polyurethane foam [40,41]), polypropylene [42], polytetrafluoroethylene [43] or ion-exchange resins [44], can be given as examples of the search for the most appropriate SPE material.

The number of papers dealing with SPE applications using polymer resins published in the 1970s and the early 1980s is high. Tens of papers are cited in review of the use of XAD resins [5], hundreds of references can be found in the overview published by Junk [4]. The analytical future for macroreticular resins seemed to be perspective, but the standardization of analytical procedures employing resins was adversely affected by their major drawback – the necessity of removal of artifact compounds such as naphthalene, styrene, hydrocarbons and phthalates. Although successful resin cleaning schemes had been developed [4,45], too many aspects of the resin standardization that had to be considered prior to its analytical use stimulated the testing and employment of other types of SPE materials.

An increased analytical use of bonded phases was stimulated by the fast development of HPLC in the 1970s and chemically bonded silicas are still the most popular HPLC packings nowadays. It took some time while the analysts realized that adjustment of eluting strength to two extreme conditions (pure water–pure solvent) might convert separation on a reversed-phase to a total accumulation and subsequent release of analytes. May et al. [46] and Little and Fallick [47] seem to be the first who reported the applicability of bonded phases to the accumulation of organic compounds from water in middle of the 1970s. The commercial availability of a wide choice of well standardized and relatively stable (if high pH values were avoided) bonded phases resulted in the extensive use of these materials in SPE procedures in both water analysis and clinical analysis of biofluids. This use had been stimulated after the commercial SPE cartridges packed with bonded silica had appeared in the market. Later on, the development of on-line applications remarkably strengthened the position of bonded silicas in SPE. With respect to the type of the bonded phases, octadecyl-bonded silica had become the most popular phase although also SPE procedures employing silicas with other alkyl- or aryl- groups (C_2, C_4, C_8, C_{22}, cyclohexyl, diol, cyanopropyl, phenyl, diphenyl or phenetyl) were published. The initial published applications of bonded phases were focussed mainly on hydrocarbons [46–50], but owing to good results that had been obtained, the tests were also focussed later on pesticides [51–53], phthalates [54], phenols and chlorophenols [54–56], N-heterocycles [55] or tributyltin chloride [57]. The wide spectrum of compounds that could be accumulated using bonded silicas initiated comparative studies on standard liquid–liquid extraction methods. Chladek and Marano [54] compared the SPE procedure with the standard US Environmental Protection Agency (EPA) method No. 625, and they obtained the average recovery with silica about 20% higher than that of standard method.

Along with the development of polymer materials and bonded phases, a new generation of carbon sorbents appeared in the 1970s and 1980s. Due to controlled technology of the preparation of the carbonaceous materials, their properties were more reproducible and their structure more homogeneous than those of the classical active carbon. The advantage over the other SPE materials was an increased affinity to more polar analytes and selective behavior to some groups of compounds. The sorption properties of the carbonaceous molecular sieve were compared to those of XAD-4 resin [21]. Even though the average recoveries on both sorbents were comparable, the advantage of carbonaceous support was higher retention of low-molecular-mass polar compounds. Bacaloni et al. [58] tested nine eluents to desorb organochlorinated pesticides from graphitized carbon black. They reported hexane–diethyl ether (50:50) to be the most efficient desorbing medium. The recoveries of other groups of compounds showed that using this mixture pesticides could be completely separated from polycyclic aromatic hydrocarbons (PAHs) and, partially, also from PCBs. Golkiewicz et al. [59] compared the retention on pyromodified silica to that on bonded phases. The results they obtained for polar solutes containing

polarizable substituents like chlorine, nitro or phenyl groups on pyrocarbon sorbents, were much better than those obtained using bonded phases. A high affinity of pyromodified silica to chlorophenols was demonstrated by the same group [60]. Moreover, the last two mentioned references employed pyromodified silica in an on-line SPE–HPLC system, and they also demonstrated growing capabilities of this alternative configuration.

During the search for the best SPE material it became apparent that there did not exist any universal sorbent suitable and optimum for all purposes. Each material was found advantageous for certain applications but the drawbacks were reported when used with other compounds, matrices or techniques. Therefore, the aims to find the best material slowly turned into the efforts to find the optimum solution for a particular problem. Simultaneously, the major attention of analysts was being gradually shifted to technological issues.

4. The age of technical developments

Introduction of new materials was a great incentive for fast development of the standard SPE methodology. The typical SPE sequence included sorbent cleaning (if necessary), activation of the sorbent (wetting), conditioning (removal of the excess of the activation solvent), application of the sample, removal of interferences (clean-up) and water, elution of sorbed analytes and, if desired, column regeneration. The theoretical considerations on processes occurring in the SPE column focussed on capacity [29], mass overloading [61] or breakthrough properties [34,62], and they created a sound scientific background for the efficient use of SPE cartridges. Introduction of commercially made cartridges eliminated the need for laborious preparation of laboratory-made columns, and the use of cartridges such as Sep-Pak or Bond-Elut in connection with vacuum manifolds speeded up the tedious sample handling procedures in environmental laboratories. However, some technical problems such as undesired dilution and possibility of sample contamination still remained. Therefore, the idea appeared to substitute the off-line sequence of analyte elution, eluate processing and the transport of the eluate aliquot into the analytical system with direct on-line elution (desorption) of analytes from the sorbent into the chromatographic column. In the simpler on-line approach the analytes were preconcentrated directly on the top of an analytical column. This approach was used primarily in HPLC methods. In this technique conditions were chosen so that during the preconcentration step the analytes were strongly retained at the top of the analytical column as the water sample was forced through. Subsequently, the retained analytes were chromatographed using isocratic or gradient elution. This approach was reported for the first time by Little and Fallick [47] and also later used by other authors [63,64]. Despite its apparent advantages this approach caused problems in the analysis of complex matrices and/or heavily contaminated samples when the performance of the analytical column deteriorated rapidly. In addition, the high back-pressure of long analytical columns did not enable the use of high pumping speeds to reduce the time of sample handling step. A simple solution to these problems was to use a separate small precolumn for the preconcentration, which, similar to HPLC guard columns, could be replaced as often as needed at remarkably lower costs. This so called on-line precolumn technology was introduced in the 1970s [46,65,66] and it originated from the two-dimensional column liquid chromatography that had been successfully applied earlier to pharmaceutical analysis [67]. The major innovations in the on-line approach were reported in the 1980s and early 1990s and they have already been well reviewed [3,7–9].

The theoretical considerations of the on-line SPE–HPLC approach were studied extensively in the past and Frei and Brinkman, along with their co-workers, made the fundamental contribution to the development of the on-line SPE applications. For the assessment of the breakthrough capacity they employed the relationship between the capacity factor, k', and the volume fraction of organic modifier Φ in reversed-phase HPLC which had been studied by Schoenmaakers et al. [68]. Due to linear relationship between $\ln k'$ and Φ in the lower Φ range, the capacity factor of a solute in pure water could easily be determined by measuring $\ln k'$ at two or more mobile phase compositions and graphical extrapolation to $\Phi=0$ [59,60,69,70]. Goewie et al. [71]

studied the influence of precolumn design on the efficiency of liquid chromatographic separation systems which involved the use of an on-line trace enrichment step. They recommended the use of precolumns having an internal diameter of 2–4.6 mm and a length of 2–10 mm. These precolumns allowed sampling flow-rates of up to at least 10 ml/min at a back pressure of 1–10 MPa. Within this range, the precolumn geometry did not appear to be critical in the on-line trace enrichment of either strongly retained or more weakly retained analytes. Since high retention during sampling had to be combined with negligible retention during desorption in order to minimize additional column band broadening during elution, they recommended the use of the same material in the analytical column and precolumn. Similar results as to the precolumn geometry and optimal sample volume assessment were reported by Nondek and Chvalovsky [72,73]. The possibilities and practical applicability of the determination and prediction of solute capacity factors for the use in SPE was studied later also by Bitteur and Rosset [74] and Jandera and Kubat [75].

The rule that the precolumn packing should be identical to that in the analytical column or in case that two different sorbents are used, the retention of the analyte in the precolumn should be lower than that in the analytical column could be easily kept for preconcentration of nonpolar compounds. However, this became more critical in the trace enrichment of polar compounds, when a sorbent having stronger interactions to these analytes, than a conventional C_{18} material, should have been used in the precolumn. For such applications PRP_1 – a newly emerging type of spherical styrene–divinylbenzene copolymer – was found to be an excellent medium. Comparative study of PRP1 and XAD-2 done by Lee and Kindsvater [76] had shown that the quantitative chromatographic characteristics of both sorbents were identical. PRP1 had a higher surface area and it retained organic compounds even better than Amberlite XAD-2. These characteristics and the spherical shape of the reversed-phase resin microparticles made PRP1 very suitable for on-line SPE–HPLC applications. Zygmunt et al. [69] described the use of PRP1 for determination of chloro- and amino-aromatics in industrial wastewaters. Tested polymers showed interesting characteristics to preconcentrate the majority of pollutants studied. Retention experiments performed by Bitteur and Rosset [77] showed that PRP1 was better suited for trace enrichment purposes than octadecyl-bonded silica material. Similarly positive results were achieved also with the other type of polymeric material, PLRP-S, which was proved to be a good compromise between sufficient retention and limited additional band broadening [78]. It was also found to be suitable for preconcentration of a wide range of pesticides [79]. However, the experiments with on-line SPE–HPLC were not limited only to bonded phases and styrene–divinylbenzene copolymers. To achieve better retention or more selective trace enrichment, precolumns were packed with pyrocarbon sorbents [60], cation-exchanger [80] or metal loaded sorbent [81] and in most of the cases promising results were reported.

Another possibility on how to adjust the on-line SPE–HPLC system to be fit for purpose was a multicolumn design. The basic on-line system could be converted to a more sophisticated one by incorporation of additional valves, precolumns and/or LC pumps. Such systems usually employed two or more precolumns with different sorbents connected in series. Subra et al. [82] preconcentrated organic pollutants using C_{18} and polymeric precolumns in series connected to a C_{18} analytical column. Nonpolar compounds were extracted by the first precolumn whereas the moderately and relatively polar compounds were recovered from both precolumns. The ratio of amounts preconcentrated on C_{18} and polymer (PRP1) precolumns and variations of this ratio with the sample volume served as a useful information for the identification of solutes. Nielen et al. [80] used for preconcentration and fractionation of organic pollutants in industrial effluents three precolumns in series (C_{18}, PRP1 and cation-exchanger) and eluted all precolumns separately. Brouwer et al. [83] connected two polymer (PLRP-S) precolumns in series and the outlet of each precolumn was on-line directed to a separate PLRP-S analytical column. While the first precolumn was operated in the reversed-phase mode, the trace enrichment in the second precolumn was based on an ion-pairing mechanism. This enabled preconcentration of acidic and basic compounds within one analysis. The same authors developed a similar

system with one HPLC analytical column. In this system they used specially designed holders packed with membrane extraction discs as precolumns [84]. The advantage of this type of precolumn packing was that its amount was easily adjustable in accordance with the needs of a particular application. A two-precolumn system was also found advantageous for the removal of interferences [85]. Except of the use of different materials and/or multiple precolumns, the other possibility of selective on-line sample handling was specific adjustment of preconcentration conditions. Thus, aromatic sulphonic acids could be satisfactorily enriched as ion-pairs [86].

Although on-line SPE is predominantly suitable for HPLC applications, coupling of a SPE precolumn to GC was also proved to be a promising approach. The major obstacle in this approach was to avoid water from the sample entering the GC column. The first successful use of on-line SPE–GC is usually ascribed to Noroozian et al. [53]. They modified six-port switching valve to incorporate an internal microcolumn packed with C_8-bonded silica onto which chlorinated pesticides and PCBs could be adsorbed from aqueous samples. After sorption, the precolumn was dried by helium purge and vacuum, and analytes were eluted with hexane directly to a GC column using retention gap. Although this was the first real attempt to apply on-line SPE–GC in water analysis, fourteen years earlier Mieure and Dietrich [19], as already mentioned above, had sampled aqueous streams directly with 80–100 mesh Chromosorb 102 packed in 4 in.$\times\frac{1}{4}$in. columns. After sorption they attached the column at the head of the analytical GC column and started the carrier flow and temperature program to obtain the GC separation. Nevertheless, the real development of LC–GC and SPE–GC applications started at the end of the 1980s and growing interest in this approach can be seen in a number of references presented in related reviews [87,88].

5. Present status – the modern age of solid-phase extraction

The present status in SPE (i.e., with respect to the length of SPE history, under ‘‘present’’ one can understand the last decade) can be characterized as a boom situation. Many decades of research effort resulted in wide acceptance of this sample handling technique and also in a growing interest of both analysts and manufacturers. With certain exaggeration it can be stated that four decades of know-how are being heavily exploited in the 1990s.

In principle, all classical types of SPE materials are in current use and their new modifications have improved SPE properties. New carbon materials have become interesting SPE media because of their specific properties and high stability. Their potential in on-line applications is promising, especially for preconcentration of polar compounds as it was shown, e.g., with porous graphitic carbon (PGC) [71]. PGC is characterized by a highly homogeneous and ordered structure and shows a reversed-phase behavior. Owing to its crystalline structure made of large graphitic sheets held together by weak Van der Waals forces, it is often presented as a more retentive reversed-phase sorbent than octadecyl-bonded silica. But the retention mechanism was shown to be very different from that observed on octadecyl-bonded silicas and styrene–divinylbenzene copolymers. Compounds are retained by both hydrophobic and electronic interactions, so that non-polar analytes, but also very polar and water-soluble analytes, were shown to be retained in water [89]. In the off-line applications employing carbon materials, DiCorcia and co-workers developed several sophisticated procedures suitable for the screening and determination of pesticides in water. They extracted phenoxyacetic acid herbicides from water using miniaturized cartridge containing graphitized carbon black (GCB) in the top side and silica based strong anion exchanger in the lower side [90]. After the percolation of the water sample through this cartridge, the anion exchanger was activated by sodium acetate solution. Sorbed analytes were then transferred from GCB to anion exchanger by a methylene chloride–methanol solvent mixture basified with sodium hydroxide. After washing, herbicides were desorbed from the anion exchanger with a water–methanol mixture containing trifluoroacetic acid and potassium chloride. A similar procedure with a cation exchanger was applied to chloroanilines [91]. Di Corcia and Marchetti [92] also presented an off-line approach to monitoring of a large group of pesticides in ground

and river water. The method incorporated a fractionation of analytes into basic/neutral and acidic compounds, which was based on two different interaction mechanisms of graphitized carbon black. Processing of large volumes of water (0.5–2 l) and evaporation of eluates led to detection limits lower than 0.1 μg/l for most of the pesticides in this case.

Styrene–divinylbenzene (PS–DVB) copolymers, owing to their high retention and good compatibility with C_{18} analytical columns, have been successfully used in screening methods for determination of a wide variety of priority pollutants [79,93]. As a result of these efforts, PLRP-S is employed as the preconcentration medium in the fully automated SAMOS-LC (on-line SPE–HPLC) system that is commercially available and in routine use in many river basins [94]. However, at present, PS–DVB sorbents are not the only polymer materials suitable for SPE. In recent years, chemically modified resins containing different polar functional groups (acetyl, hydroxymethyl, benzoyl or *o*-carboxybenzoyl), have been developed and used in the SPE of polar compounds from environmental waters. These modified resins have excellent hydrophilicity and they also give higher recoveries than their unmodified analogues [95]. This has been attributed to an increase in surface polarity which enables the aqueous sample to make better contact with the resin surface. They have also been compared with other SPE materials such as PLRP-S and GCB in preconcentration of pesticides and phenolic compounds, and they yielded higher breakthrough volumes for the most polar compounds than the latter sorbents [96–98]. In the last few years, several new highly crosslinked polymers such as Envi-Chrom P, LiChrolut EN or Isolute EN have become available. These sorbents have a higher degree of crosslinking and so have an open structure (high porosity material), which increases their specific surface area and allows greater π–π interactions between analytes and sorbent. This increases the breakthrough volumes of analytes. The use of chemically modified resins as well as highly crosslinked polymers for SPE of polar organic micropollutants from environmental water has recently been reviewed by Masque et al. [95].

Despite all the new types of polymer and carbon materials, octadecyl-bonded silica is still the most used sorbent for off-line procedures [9,99]. Similarly, in on-line applications its perfect compatibility with the bonded-phase packing in the analytical column makes C_{18} the material of choice for all who prefer not to spend much time with method development. Due to their non-specificity, C_{18} cartridges tend to hold up anything that has a hydrophobic character. And if we also include good reproducibility in retention and very seldom irreversible adsorption of analytes, it is obvious that it is suitable material for simple on-line as well as off-line applications. However, bonded phases also enable sophisticated approaches. Geerdink et al. [100] tested a combination of three eluting solvents with a conventional and non-endcapped C_{18} cartridge for the separation of triazines and their degradation products from each other and/or from humic and fulvic acids. Slobodnik et al. [101] used silica with bonded octadecyl and hydroxyl groups for the preconcentration of carbamate pesticides. The presence of hydroxyl groups enabled sufficient trapping of very polar carbamates but, on the other hand, good compatibility of Bondesil C_{18}–OH precolumn with C_{18} packing material in the analytical column suppressed additional band broadening even if larger precolumns were used.

Contrary to the development of classical types of SPE materials, the typical situation in the 1990s is the rapid development of new types of materials. Probably the most important phenomenon is the introduction of membrane extraction disks. They have been developed by 3M at the end of the 1980s and were first reported by Hagen et al. [102]. The disks are in fact membranes consisting of a fibrillated PTFE matrix in which sorbents such as, e.g., bonded silicas, polymers or ion exchangers are enmeshed. Due to the internal structure of disks, a high flow-rate of water sample can be achieved and reducing of the recovery due to channeling is avoided. The easy manipulation with disks makes them suitable for quick testing methods but also more complex approaches have been published. Disks have been successfully used as precolumn packing in on-line SPE–HPLC systems [84]. In the off-line approach, the membrane disk is a versatile preconcentration medium suitable for both GC and LC. The eluate from the disk can be injected into a GC system and, if necessary, derivatization of analytes can be performed prior to the injection [103]. For screening of

a wide range of pesticides, the eluate can be analyzed by both GC and LC systems simultaneously [104]. As an alternative approach, trapped analytes can be eluted from the disk also via supercritical fluid elution [105].

Another novel approach in SPE is the extraction with sorbents based on immunoaffinity employing analyte–antibody interactions. In this approach antibodies produced against a target compound are immobilized on a solid phase to obtain an immunosorbent which can be used as a classical SPE material. The first immunosorbents were used for the pretreatment of biological samples [106]. Because of unavoidable cross-reactivity of antibodies against small molecules, antibodies are also able to trap compounds from the same structural family as the one of the antigen. By coupling the antibody cartridge with HPLC, selective extraction and a quantitative analysis of a specific group of compounds can be achieved. Promising immunosorbent applications in analysis of pesticides [107,108] and PAHs [109] in water were demonstrated by the Hennion's group.

The other possibility of how to reach a very selective affinity of SPE materials towards target substances is the use of molecularly imprinted polymers (MIPs). Molecular imprinting is a technique by which highly selective binding matrices can be prepared using a chosen target molecule as a template in a casting procedure. MIPs were used as stationary phases in molecular imprinting chromatography and since they had been found to exert antibody-like affinities to specific analytes, they were successfully used for selective extraction [110]. In an on-line configuration, MIPs could be used for a selective preconcentration of atrazine herbicides from water containing 20 ppm of humic acids. The use of suitably tailored MIPs reduced the influence of the matrix on the resulting chromatogram, thus, enabling high sample enrichment factors [111].

Both the immunosorbents and MIPs represent a sophisticated approach to development of a tailor-made solid phase for a given application. Further development of these techniques (development of class-specific immunosorbents and optimized MIPs) and commercialization of production of both groups of these highly specific sorbent materials will certainly improve the efficiency of target analyses of complex matrices in the future.

The long-term efforts to find an optimum sorbent and experimental conditions for a given application also continue in the 1990s. Examination of kinetic and retention properties controlling the breakthrough volume seems to be an appropriate way to predict the efficiency of extraction of a compound from water by a sorbent. The prediction of a retention factor in water is still used as an important factor in method development for SPE [112–114]. Based on the evaluation of operational parameters and characterization of a silica-based octadecylsiloxane bonded phase sorbent, Miller and Poole [112] concluded that availability of system coefficients from the relationship between log k' and Φ for reference mobile phases for different sorbents would provide a rational method for selecting the optimum sorbent for a particular application. Moreover, the system coefficients could be used to establish the influence of bonding density and functional group type on sorption properties to establish how many different stationary phases are really needed for SPE, thus avoiding a needless proliferation of new products lacking significant benefits over existing products.

The 1990s have brought also a progress in SPE technology. Even though the basic principles of classical off-line SPE sequence did not change substantially, a high degree of commercialization as well as development of microprocessors, enabled a remarkable increase in sample throughput. Various vacuum manifolds are available allowing processing of up to 96 samples. This enables speeding up the analysis but still some manual labor is required. Full automation of the SPE sequence can be achieved using robotic systems. To speed up SPE method development, SPE plates containing arrays of various sorbent cartridges have been designed. The plates enable a range of suitable sorbents to be screened simultaneously to optimize recovery providing a speedy and economical approach to SPE method development. In on-line applications, coupling of SPE with LC has become a routine method in many laboratories. Commercial systems (OSP-2 or SAMOS–LC using Prospekt) allow problemless transfer of analytes from precolumn into the analytical column with minimized additional band broadening. An increase of the analytical capabilities has been reached by connecting the SPE–HPLC system to MS via a suitable interface. Similarly, on-line coupling of SPE to GC is a promising

approach with good perspectives for the future [88]. An extremely powerful tool can be achieved by combination of the above mentioned on-line systems. This has been demonstrated by Slobodnik et al. [115]. They developed an integrated system combining on-line SPE with LC and GC separation and MS detection. The trace enrichment procedure was automated by a Prospekt cartridge-exchange/solvent-selection/valve-switching unit. After loading of the water sample, the precolumn was eluted on-line in two subsequent runs, first onto the GC–MS system and, next, onto the LC–diode array UV detection (DAD)–MS system using a particle beam interface. With this system GC–MS, LC–DAD UV and LC–MS data of the same water sample could be obtained within 3 h, providing a large amount of structural information on unknown organic compounds present in the sample.

Sometimes, new developments in on-line field reanimate the old ideas. The simultaneous use of the LC column for the trace enrichment and analytical separation was characteristic for the early SPE–LC applications, and this approach was rejected later so as to protect the expensive column from contaminated samples. Nowadays, the improvement of the properties of LC packings stimulated the renaissance of this approach since short columns can provide sufficient separation for reasonably reduced costs. Thus, rapid screening with a single short column for preconcentration and separation can be performed [116].

Another new interesting SPE technique that had been introduced by Pawliszyn and coworkers, almost simultaneously with membrane disks, is solid-phase microextraction (SPME) [117]. SPME, which is usually referred to as a separate sample handling technique and not as a SPE modification, is based on immobilized liquid phase (e.g., polydimethylsiloxane or polyacrylate polymers) as a stationary phase and is used for the direct extraction of organic trace compounds from water by simply dipping the fiber into the aqueous sample. After sorption, the fibre is transferred into the heated injector of the gas chromatograph and exposed for a given period of time, where the organic compounds are thermally desorbed from the polymeric phase. The fibre can be reused many times. SPME is an effective technique for the handling of water samples prior to GC analysis. Its major advantages are the avoiding of organic solvents, simplicity and low operational costs. The combination of SPME and GC was proved to be a rapid and sensitive technique for analysis of different groups of organic pollutants in water. It gave satisfactory results for pesticides [118], nitroaromatics [119], phenols [120] and for volatile organic compounds using both direct extraction from water [121,122] as well as the headspace exposure [123]. The major methodological difference from SPE is that the classical recovery cannot be referred to by SPME as this technique is based on reaching an equilibrium analyte concentrations between two phases. Despite this difference, the precision and reproducibility of SPME methods are similar to other conventional extraction methods. Successful examples of SPME–GC analyses of different compound classes were summarized in the review of Eisert and Levsen [124].

The potential of the solid-phase is not restricted only to the enrichment of the analytes. Green and LePape [125] did observe that XAD-2 macroreticular resin and octadecyl-bonded silica had a preservative effect, which prevented a breakdown of sorbed hydrocarbons by bacteria. Hydrocarbons stored on these solid-phases for periods of up to 100 days in the presence of an oleophilic bacterial population showed no evidence of biological degradation. In contrast, hydrocarbons stored in water samples containing the same bacteria showed pronounced degradation over much shorter storage periods. These authors suggested that the preservative effect resulted from trapping the organic compounds in the adsorbent lattice structure. The pores of XAD-2 or silica gel were smaller than bacteria. Thus, the hydrocarbons were protected from bacterial attack. The stability of 34 selected pesticides extracted from water onto the GCB surface was evaluated under various storage conditions [126]. The best results were obtained by first minimizing the water content into the GCB extraction cartridge by a suitable methanol washing and the freezing the cartridge. Under these conditions and over a storage period of 3 weeks, the stability of pesticides extracted from four river water samples onto the GCB surface was assessed and compared with that in water at 4°C, with and without an inhibitor of biological degradation such as mercuric chloride. Results indicated that storage on the GCB material was a far better preservation procedure than storage in water at 4°C.

Several of the pesticides considered were completely degraded when stored in water in the presence of $HgCl_2$. Similarly to disposable off-line SPE cartridges, SPE precolumns were also tested as to the analyte storage possibility. The stability of 19 organophosphorous pesticides was investigated using precolumns from the Prospekt (automated on-line SPE) system packed with C_{18} and stored under different conditions [127]. This study demonstrated that many organophosphorous pesticides that showed instability problems in water matrices were stable under disposable SPE precolumns for a period up to 8 months at −20°C. Similar cartridges were also used for the investigation of the stability of different groups of polar pesticides (triazines, phenylureas, carbamates and chlorinated phenols) sorbed onto the polymer sorbent from water [128]. The results showed the stability of most of the tested pesticides stored in the cartridges during 7 weeks at the laboratory temperature or in the refrigerator. Moreover, the compounds that are trapped onto the sorbent are not only preserved but they can also be directly detected using solid-state fluorescence measurements [129].

During the decades of its development, SPE was mostly considered as an experimental technique while standardized applications in water analysis employed usually LLE for sample handling. However, the situation has changed dramatically. At present, SPE has been widely accepted and recognized as a standard tool for the handling of water samples prior to analysis for organic micropollutants. The EPA has approved various methods based on the use of SPE disks or cartridges [130]. As an example method 506: ''Determination of phthalate and adipate esters in drinking water by liquid–liquid extraction or liquid–solid extraction and GC with PID'' can be given. As an alternative to LLE this method allows that a measured volume of sample is extracted with a liquid–solid extraction (LSE) cartridge or disk. The LSE media are eluted with acetonitrile followed by methylene chloride (disk extraction) or with methylene chloride only (cartridge extraction). The eluant is concentrated using a gentle stream of nitrogen gas or clean air to reduce the volume to 1 ml or less. The application of SPE in analysis of organic micropollutants in water can be also found in German DIN standards [131].

6. Conclusions

As can be seen from this historical overview, after five decades of its development SPE has turned from an interesting alternative approach into a powerful standard technique. Experts involved in the field of environmental chromatography often state that sample preparation is the area where the most recent significant advances have been made [132]. Considering the fast progress and many innovations in the SPE field, it may have seemed that, at present, the progress of SPE culminates. However, not only scientists but also the manufacturers claim that the sample preparation area is still in evolution. It is felt that despite the boom in nineties, the SPE developments have not appeared as fast as it was expected and an increase in SPE research is predicted for next few years [133]. Thus, we can only look forward to new sample handling approaches and ideas employing solid-phase in the third millenium.

References

[1] R.E. Majors, LC–GC Int. 4 (2) (1991) 10.
[2] M. Dressler, J. Chromatogr. 165 (1979) 167.
[3] R.W. Frei, U.A.Th. Brinkman, Trends Anal. Chem. 1 (1981) 45.
[4] G.A. Junk, in: I.H. Suffet, M. Malayiandi (Eds.), Organic Pollutants in Water (ACS Symposium Series, No. 214), American Chemical Society, Washington DC, 1987, p. 201.
[5] S.A. Daignault, D.K. Noot, D.T. Williams, P.M. Huck, Wat. Res. 22 (1988) 803.
[6] I. Liška, J. Krupcík, P.A. Leclercq, J. High Resolut. Chromatogr. 12 (1989) 577.
[7] M.C. Hennion, Trends Anal. Chem. 10 (1991) 317.
[8] I. Liška, J. Chromatogr. A 655 (1993) 163.
[9] D. Barceló, M.C. Hennion, in: Trace Determination of Pesticides and Their Degradation Products in Water, Elsevier, Amsterdam, 1997.
[10] H. Braus, F.M. Middleton, G. Walton, Anal. Chem. 23 (1951) 1160.
[11] A.A. Rosen, F.M. Middleton, Anal. Chem. 27 (1955) 790.
[12] A.A. Rosen, F.M. Middleton, Anal. Chem. 31 (1959) 1729.
[13] K.J. Grob, J. Chromatogr. 84 (1973) 255.
[14] I.H. Suffet, M.J. McGuire (Eds.), Activated Carbon Adsorption of Organics from the Aqueous Phase, Vols. 1&2, Ann Arbor Sci. Publ, Ann Arbor, MI, 1980.
[15] J.P. Riley, D. Taylor, Anal. Chim. Acta 46 (1969) 307.
[16] A.K. Burnham, G.V. Calder, J.S. Fritz, G.A. Junk, H.J. Svec, R. Willis, Anal. Chem. 44 (1972) 139.

[17] G.R. Harvey, W.G. Steinhauer, J.M. Teal, Science 180 (1973) 643.
[18] H.D. Gesser, A. Chow, F.C. Davis, J.F. Uthe, J. Reinke, Anal. Lett. 4 (1971) 883.
[19] J.P. Mieure, M.W. Dietrich, J. Chromatogr. Sci. 11 (1973) 559.
[20] G.A. Junk, J.J. Richard, M.D. Grieser, D. Witiak, J.L. Witiak, M.D. Arguello, R. Wick, H.J. Svec, J.S. Fritz, G.V. Calder, J. Chromatogr. 99 (1974) 745.
[21] A. Tateda, J.S. Fritz, J. Chromatogr. 152 (1978) 329.
[22] P. Van Rossum, R.G. Webb, J. Chromatogr. 150 (1978) 381.
[23] M.W. Tabor, J.C. Loper, Int. J. Environ. Anal. Chem. 19 (1985) 281.
[24] J.J. Richard, G.A. Junk, Anal. Chem. 58 (1986) 723.
[25] A. Przyjazny, J. Chromatogr. 346 (1985) 61.
[26] G.R. Aiken, E.M. Thurman, R.L. Malcolm, H.F. Walton, Anal. Chem. 51 (1979) 1799.
[27] P. Jones, G. Nickless, J. Chromatogr. 156 (1978) 87.
[28] G.L. LeBel, D.T. Williams, F.M. Benoit, J. Assoc. Off. Anal.Chem. 64 (1981) 991.
[29] E.M. Thurman, R.L. Malcolm, G.R. Aiken, Anal. Chem. 50 (1978) 775.
[30] E. Brízová, M. Popl, J. Coupek, J. Chromatogr. 139 (1977) 15.
[31] Z. Voznáková, M. Popl, M. Kovár, Scientific Papers of the VŠCHT, Prague H19 (1984) 85.
[32] M. Krejcí, M. Roudná, Z. Vavrouch, J. Chromatogr. 91 (1974) 549.
[33] L.D. Butler, F.M. Burke, J. Chromatogr. Sci. 14 (1976) 117.
[34] J.F. Pankow, L.M. Isabelle, T.T. Kristensen, J. Chromatogr. 245 (1982) 31.
[35] J.F. Pankow, L.M. Isabelle, J. Chromatogr. 237 (1982) 25.
[36] J.F. Pankow, M.P. Ligocki, M.E. Rosen, L.M. Isabelle, K.M. Hart, Anal. Chem. 60 (1988) 40.
[37] V. Leoni, G. Puccetti, R.J. Colombo, A.M. D'Ovidio, J. Chromatogr. 125 (1976) 399.
[38] V. Leoni, G. Puccetti, A. Grella, J. Chromatogr. 106 (1975) 119.
[39] J.D. Navratil, R.E. Sievers, H.F. Walton, Anal. Chem. 49 (1977) 2260.
[40] P.R. Musty, G. Nickless, J. Chromatogr. 100 (1974) 83.
[41] D.K. Basu, J. Saxena, Environ. Sci. Technol. 12 (1978) 791.
[42] M.R. Rice, H.S. Gold, Anal. Chem. 56 (1984) 1436.
[43] G.M. Josefson, J.B. Johnston, R. Trubey, Anal. Chem. 56 (1984) 764.
[44] C.D. Chriswell, R.C. Chang, J.S. Fritz, Anal. Chem. 47 (1975) 1325.
[45] E.E. McNeil, R. Otson, W.F. Miles, F.J.M. Rajabalee, J. Chromatogr. 132 (1977) 277.
[46] W.E. May, S.N. Chesler, S.P. Cram, B.H. Gump, H.S. Hertz, D.P. Enagonio, S.M. Dyszel, J. Chromatogr. Sci. 13 (1975) 535.
[47] J.N. Little, G.J. Fallick, J. Chromatogr. 112 (1975) 389.
[48] A.R. Oyler, D.L. Bodenner, K.J. Welch, R.J. Liukkonen, R.M. Carlson, H.L. Kopperman, R. Caple, Anal. Chem. 50 (1978) 837.
[49] K. Ogan, E. Katz, W. Slavin, J. Chromatogr. Sci. 16 (1978) 517.
[50] W.A. Saner, J.R. Jadamec, R.W. Sager, T.J. Kileen, Anal. Chem. 51 (1979) 2180.
[51] J.J. Richard, G.A. Junk, Microchim. Acta 1 (1986) 387.
[52] M.J.M. Wells, J.L. Michael, J. Chromatogr. Sci. 25 (1987) 345.
[53] E. Noroozian, F.A. Maris, M.W.F. Nielen, R.W. Frei, G.J. de Jong, U.A.Th. Brinkman, J. High. Resolut. Chromatogr. 10 (1987) 17.
[54] E. Chladek, R.S. Marano, J. Chromatogr. Sci. 22 (1984) 313.
[55] C.E. Rostad, W.E. Pereira, S.M. Ratcliff, Anal. Chem. 56 (1984) 2856.
[56] S. Fingler, V. Drevenkar, Z. Vasilic, Mikrochim. Acta II (1987) 163.
[57] G.A. Junk, J.J. Richard, Chemosphere 16 (1987) 61.
[58] D. Bacaloni, G. Goretti, A. Lagana, B.M. Petronio, M. Rotatori, Anal. Chem. 52 (1980) 2033.
[59] W. Golkiewicz, C.E. Werkhoven-Goewie, U.A.Th. Brinkman, R.W. Frei, H. Colin, G. Guiochon, J. Chromatogr. Sci. 21 (1983) 27.
[60] C.E. Werkhoven-Goewie, U.A.Th. Brinkman, R.W. Frei, Anal. Chem. 53 (1981) 2072.
[61] D.J. Pietrzyk, J.D. Stodola, Anal. Chem. 53 (1981) 1822.
[62] P. Lovkvist, J.A. Jonsson, Anal. Chem. 59 (1987) 818.
[63] A. Otsuki, J. Chromatogr. 133 (1977) 402.
[64] C.E. Parker, C.A. Haney, J.R. Hass, J. Chromatogr. 237 (1982) 233.
[65] R.W. Frei, Int. J. Environ. Anal. Chem. 5 (1978) 143.
[66] H.P.M. van Vliet, Th.C. Bootsman, R.W. Frei, U.A.Th. Brinkman, J. Chromatogr. 185 (1979) 483.
[67] F. Erni, R.W. Frei, J. Chromatogr. 149 (1978) 561.
[68] P.J. Schoenmakers, H.A.H. Billiet, L. De Galan, J. Chromatogr. 185 (1979) 179.
[69] B. Zygmunt, J. Visser, U.A.Th. Brinkman, R.W. Frei, Int. J. Environ. Anal. Chem. 15 (1983) 263.
[70] V. Coquart, M.C. Hennion, J. Chromatogr. 600 (1992) 195.
[71] C.E. Goewie, M.W.F. Nielen, U.A.Th. Brinkman, R.W. Frei, J. Chromatogr. 301 (1984) 325.
[72] L. Nondek, V. Chválovský, J. Chromatogr. 268 (1983) 395.
[73] L. Nondek, V. Chválovský, J. Chromatogr. 312 (1984) 303.
[74] S. Bitteur, R. Rosset, J. Chromatogr. 394 (1987) 279.
[75] P. Jandera, J. Kubát, J. Chromatogr. 500 (1990) 281.
[76] D.P. Lee, J.H. Kindsvater, Anal. Chem. 52 (1980) 2425.
[77] S. Bitteur, R. Rosset, Chromatographia 23 (1987) 163.
[78] I. Liška, E.R. Brouwer, H. Lingeman, U.A.Th. Brinkman, Chromatographia 37 (1993) 13.
[79] I. Liška, E.R. Brouwer, A.G.L. Osteheimer, H. Lingeman, U.A.Th. Brinkman, R.B. Geerdink, W.H. Mulder, Int. J. Environ. Anal. Chem. 47 (1992) 267.
[80] M.W.F. Nielen, U.A.Th. Brinkman, R.W. Frei, Anal. Chem. 57 (1985) 806.
[81] C.E. Goewie, P. Kwakman, R.W. Frei, U.A.Th. Brinkman, W. Maasfeld, T. Seshadri, A. Kettrup, J. Chromatogr. 284 (1984) 73.
[82] P. Subra, M.C. Hennion, R. Rosset, R.W. Frei, Int. J. Environ. Anal. Chem. 37 (1989) 45.
[83] E.R. Brouwer, I. Liška, R.B. Geerdink, P.C.M. Frintrop, W.H. Mulder, H. Lingeman, U.A.Th. Brinkman, Chromatographia 32 (1991) 445.

[84] E.R. Brouwer, D.J. van Iperen, I. Liška, H. Lingeman, U.A.Th. Brinkman, Int. J. Environ. Anal. Chem. 47 (1992) 257.
[85] V. Coquart, M.C. Hennion, J. Chromatogr. 553 (1991) 329.
[86] E.R. Brouwer, J. Slobodník, H. Lingeman, U.A.Th. Brinkman, Analusis 20 (1992) 121.
[87] L. Davies, K.E. Markides, M.L. Lee, M.W. Raynor, K.D. Bartle, J. High Resolut. Chromatogr. 12 (1989) 193.
[88] J.J. Vreuls, G.J. de Jong, R.T. Ghijsen, U.A.Th. Brinkman, J. AOAC Int. 77 (1994) 306.
[89] M.C. Hennion, C. Cau-Dit-Coumes, V. Pichon, J. Chromatogr. A 823 (1998) 147.
[90] A. DiCorcia, M. Marchetti, R. Samperi, Anal. Chem. 61 (1989) 1363.
[91] A. DiCorcia, R. Samperi, Anal. Chem. 62 (1990) 1490.
[92] A. DiCorcia, M. Marchetti, Environ. Sci. Technol. 26 (1992) 66.
[93] J. Slobodník, M.G.M. Groenewegen, E.R. Brouwer, H. Lingeman, U.A.Th. Brinkman, J. Chromatogr. 642 (1993) 359.
[94] U.A.Th. Brinkman, H. Lingeman, J. Slobodník, LC·GC Int. 7 (1994) 157.
[95] N. Masqué, R.M. Marcé, F. Borrull, Trends Anal. Chem. 17 (1998) 384.
[96] N. Masqué, M. Galiá, R.M. Marcé, F. Borrull, J. Chromatogr. A 771 (1997) 55.
[97] N. Masqué, M. Galiá, R.M. Marcé, F. Borrull, Analyst 122 (1997) 425.
[98] N. Masqué, E. Pocurull, R.M. Marcé, F. Borrull, Chromatographia 47 (1998) 176.
[99] R.E. Majors, LC·GC Int. 6 (1993) 130.
[100] R.B. Geerdink, A. Attema, W.M.A. Niessen, U.A.Th. Brinkman, LC·GC Int. 11 (1998) 361.
[101] J. Slobodník, S.J.F. Hoekstra-Oussoren, M.E. Jager, M. Honing, B.L.M. van Baar, U.A.Th. Brinkman, Analyst 121 (1996) 1327.
[102] D.F. Hagen, C.G. Markell, G.A. Schmitt, D.D. Blevins, Anal. Chim. Acta 236 (1990) 157.
[103] T.S. Thompson, B.D. Miller, Chemosphere 36 (1998) 2867.
[104] J.S. Salau, R. Alonso, G. Batlló, D. Barceló, Anal. Chim. Acta 293 (1994) 109.
[105] P. Hua-Tang Tang, J.S. Ho, J. High Resolut. Chromatogr. 17 (1994) 509.
[106] A. Farjam, G.J. De Jong, R.W. Frei, U.A.Th. Brinkman, W. Haasnoot, A.R.M. Hamers, R. Schilt, F.A. Huf, J. Chromatogr. 452 (1988) 419.
[107] V. Pichon, L. Chen, M.C. Hennion, R. Daniel, A. Martel, F. Le Goffic, J. Abian, D. Barcelo, Anal. Chem. 67 (1995) 2451.
[108] I. Ferrer, V. Pichon, M.C. Hennion, D. Barcelo, J. Chromatogr. A 777 (1997) 91.
[109] M. Bouzige, V. Pichon, M.C. Hennion, J. Chromatogr. A 823 (1998) 197.
[110] J. Matsui, M. Okada, M. Tsuroka, T. Takeuchi, Anal. Commun. 34 (1997) 85.
[111] B. Bjarnason, L. Chimuka, O. Ramstrom, Anal. Chem. 71 (1999) 2152.
[112] K.G. Miller, C.F. Poole, J. High Resolut. Chromatogr. 17 (1994) 125.
[113] M.L. Larrivee, C.F. Poole, Anal. Chem. 66 (1994) 139.
[114] M.C. Hennion, V. Pichon, Environ. Sci. Technol. 28 (1994) 576A.
[115] J. Slobodník, A.C. Hogenboom, A.J.H. Louter, U.A.Th. Brinkman, J. Chromatogr. A 730 (1996) 353.
[116] K.P. Hupe, M. Riedmann, G. Rozing, Chromatographia 40 (1995) 631.
[117] R.P. Belardi, J. Pawliszyn, Water Pollut. Res. J. Canada 24 (1989) 179.
[118] R. Eisert, K. Levsen, Fresenius J. Anal. Chem. 351 (1995) 555.
[119] J.Y. Horng, S.D. Huang, J. Chromatogr. A 678 (1994) 313.
[120] K.D. Buchholz, J. Pawliszyn, Anal. Chem. 66 (1994) 160.
[121] D.W. Potter, J. Pawliszyn, J. Chromatogr. 625 (1992) 247.
[122] B.D. Page, G. Lacroix, J. Chromatogr. 648 (1993) 199.
[123] Z. Zhang, J. Pawliszyn, Anal. Chem. 65 (1993) 1843.
[124] R. Eisert, K. Levsen, J. Chromatogr. A 733 (1996) 143.
[125] D.R. Green, D. LePape, Anal. Chem. 59 (1987) 699.
[126] C. Crescenzi, A. DiCorcia, M. Madbouly, R. Samperi, Environ. Sci. Technol. 29 (1995) 2185.
[127] S. Lacorté, N. Ehresmann, D. Barceló, Environ. Sci. Technol. 29 (1995) 2834.
[128] I. Liška, K. Bíliková, J. Chromatogr. A 795 (1998) 61.
[129] E.J. Poziomek, D. Eastwood, R.L. Lidberg, G. Gibson, Anal. Lett. 24 (1991) 1913.
[130] Methods for the Determination of Organic Compounds in Drinking Water, Supplement III, EPA/600/R-95/131, US Environmental Protection Agency, August 1995
[131] DIN 38 407, Part 6, 12, 14, Deutsches Institut fur Normung, Berlin, 1993–1995
[132] K. Bartle, LC·GC Int. 10 (1997) 214.
[133] An Interview with . . . , LC–GC Int. 12 (1999) 364.