The use of solid sorbents for direct accumulation of organic compounds from water matrices : a review of solid-phase extraction techniques

Critical Review

The Use of Solid Sorbents for Direct Accumulation of Organic Compounds from Water Matrices – A Review of Solid-Phase Extraction Techniques

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Key Words:

Solid-phase extraction
Sorption and desorption processes
Sorbents

Summary

The main principles of solid-phase extraction techniques are reviewed in this paper. Various solid sorbents can be used as a suitable trap for direct accumulation of organic compounds from aqueous solutions. The trapped analytes can be desorbed by elution with suitably chosen liquid phases. These preconcentration procedures can be considered as low performance liquid chromatography and the efficiency of the procedure can thus be related to the retention characteristics of the preconcentration column. The main sorbents used for trace enrichment purposes are also reviewed. Besides, the concise methodology, sample storage, and automation are discussed. The advantages of solid phase extraction as compared to liquid-liquid extraction are given as well as some drawbacks of this method.

1 Introduction

The identification and quantification of organic compounds in water matrices are necessary for solving various environmental or biological problems. The accuracy and precision of any analysis of an environmental or biological sample are dependent upon both sample preparation and instrumental performance. Although the former can be omitted in some cases (on direct injection of the water sample into a gas chromatograph), it is usually the most laborious and less reliable part of the whole procedure. Aqueous sample preparation is necessary to minimize matrix interferences, and to lower detection limits.

At present, various preconcentration methods are being used, based on various physico-chemical principles. Among them, extraction with liquids, head-space analyses, stripping analyses, and extraction with sorbents are commonly used. Head-space analysis, *i.e.* the analysis of the gaseous fraction which is in contact and in equilibrium with the water sample, is an excellent and sensitive procedure for the analysis of volatile compounds. A disadvantage is that, with decreasing volatility of the analyte, the recovery of the head-space method usually decreases. Liquid-liquid extraction (LLE) is still often preferred as a sample preparation technique. This method uses the partitioning of the analyte between the aqueous sample and anorganic water immiscible solvent according to *Nernst*'s law. The selectivity of LLE depends on the choice of the solvent, and on the nature of the water matrix (pH, ionic strength, *etc.*). Disadvantages of LLE methods are emulsion formation, different extraction efficiencies for various compounds with various extracting agents, and low sensitivity. The sensitivity of LLE methods can be increased by removing part of the extracting solvent by heat or by a stream of an inert gas. This step, however, can lead to losses of analytes, and safety hazards involved in handling toxic and inflammable solvents are not negligible. Frequently, the whole LLE procedure is tedious, time consuming and costly

An alternative to solvent extraction is the recovery of organic compounds by direct contact of the aqueous sample with a sorbent. Volatile compounds can also be transferred from the aqueous sample to a sorbent bed by a stream of inert gas. Desorption of accumulated organic compounds can be carried out by elution with a suitable solvent or solvent mixture, or by increasing temperature (thermal desorption). It is advantageous to use these procedures in conjunction with separation methods (off-line or on-line), in combination with proper identification methods. Such complex methods are an appropriate tool for analyzing aqueous samples of various origins.

In the past twenty years the use of sorbents for preconcentration purposes developed very widely, and is still of growing interest. In this report, all the possibilities that can be provided by sorbent extraction technologies are reviewed.

One of the physico-chemical properties of solid matter is the presence of active sites in its surface structure. These sites can interact with molecules of compounds present in the phase that is in contact with the solid surface. The so-called sorption properties depend on

many factors, among which the surface structure of the solid matter (porosity, surface area) and its chemical composition are the most important.

Thermodynamically, the sorption processes can be described by various types of isotherms (Langmuir, Freundlich, BET). For diluted solutions, where a linear behavior of sorption processes can be expected, it is possible to use a sorbent for the quantitative isolation of one or more organic compounds from the original neighboring phase. After changing the conditions, the trapped compounds can be released into another phase. The ratio of the former and latter phase volumes gives the preconcentration factor. In the majority of cases, the composition of the latter phase is simpler than that of the original phase. Thus, the possible interferences are smaller.

The first successful attempts to characterize organic components present in water, by means of sorption onto carbon columns and desorption with organic solvents, were reported in the fifties [1]. In the following years the utilization of activated carbon for these purposes spread rapidly, leading to the extensive use of carbon for both analytical and water treatment purposes. While the use of granulated active carbon for drinking-water purification is of great interest nowadays, carbon as an analytical medium for preconcentrations was mostly replaced in the early seventies by macroreticular polymer resins. These resins are, at present, together with bonded silicas, the most widely utilized sorbents for analytical purposes [2]. Procedures for the enrichment of organic trace compounds on suitable sorbents, in order to isolate and preconcentrate them prior to their separation and detection by means of a suitable chromatographic technique, have been reviewed in the past ten years by several authors. *Junk* [2] and *Dressler* [3] described the use of polymer sorbents for the accumulation of organic compounds from water. *Frei et al.* [4, 5] reviewed sorbent preconcentration techniques with respect to on-line precolumn technologies. *McDowall et al.* [6] surveyed liquid-solid sample preparation in drug analysis, and *Svoboda* [7] reviewed the use of sorbents for the preconcentration of pesticides. A description of solid phase extraction technologies can also be found in the literature available from Analytichem International Inc. [8, 9] and J. T. Baker Chemical Co. [10-12].

The number of literature citations, concerning the use of sorbents for preconcentration purposes, is growing rapidly. In many studies the accumulation of organic compounds from water matrices is only a small part of the total research effort. Only few authors pay attention to the study of factors affecting sorption and desorption processes during the preconcentration procedure. However, it is obvious that only the knowledge of the critical parameters and their optimization can secure the efficiency and the reproducibility of the entire preconcentration process.

Methods using sorbents for aqueous sample preparation can be classified according to various criteria. With respect to the methodology used, and the characteristics of the sorption and desorption processes, these methods can be divided into four groups:

1.1 Sorption from the Gaseous Phase – Desorption into the Gaseous Phase

Organic compounds are stripped from a water matrix by means of a stream of inert gas, and transported into a column packed with a suitable sorbent. The sorbent traps the stripped organic compounds. After heating the column, the trapped compounds are desorbed into a stream of inert gas, and transported into the analyzer (mostly a gas chromatograph). The so-called purge-and-trap method according to *Bellar at al.* [13] is based on this principle.

1.2 Sorption from the Gaseous Phase – Desorption into the Liquid Phase

Stripping and trapping of organic compounds is similar to the previous procedure, but desorption is performed by elution with proper organic solvents or solvent mixtures. Carbon is mostly used as a sorbent and carbon disulfide as an eluent. The original closed-loop-stripping analysis, proposed by *Grob* [14], has been modified in various ways, *e.g.* the open stripping modification [15].

1.3 Sorption from the Liquid Phase – Desorption into the Gaseous Phase

Organic compounds are accumulated directly from a water matrix into a (metal) column packed with sorbent. After removal of water, the analytes are thermally desorbed into a stream of an inert gas and carried into the gas chromatograph. The sorbent used in this case (as well as in case 1.1), must be thermally inert at high temperatures to provide low blank runs. For these purposes polymer sorbents are used, among which Tenax-GC is considered the most suitable.

1.4 Sorption from the Liquid Phase – Desorption into the Liquid Phase

This group includes all procedures in which organic analytes are directly accumulated from water, and subsequently eluted with a proper liquid phase. Static, batchwise operations are not widely spread, and have been virtually replaced by dynamic column applications. These procedures are often called solid-phase extraction (SPE), liquid-solid adsorption (LSA), liquid-solid extraction (LSE), or sorbent extraction. In this review, the commonest name solid-phase extraction will be used. SPE can be considered as low performance liquid chromatography, applied in two extreme situations: maximum and minimum retention during extraction and desorption, respectively. This can be realized with two extreme mobile phases (*e.g.* "pure" water and "pure" organic solvent). The range of compounds isolated is not restricted only to undissociated ones with low molecular weight, but can be extended to molecules of acidic or basic natures or with high molecular weight (*e.g.* humic acids). The interactions used can vary from dispersive to covalent. Off-line procedures can be converted into an on-line approach, known as multidimensional chromatography/column switching (MD/CS), which incorporates microprocessor controlled switching of precolumns, samples, eluents, flush solvents, analytical chromatographic columns, *etc.* Because of many possible variations, SPE has been developing in a highly dynamic manner.

1.5 Scope of Review

The scope of this review is to describe the processes for direct accumulation of organic compounds from aqueous media (*i.e.*, cases 1.4 and, in part, 1.3), and desorption of the accumulated analytes by elution with an appropriate liquid phase (*i.e.* cases 1.4 and, in part, 1.2). This means that the processes in the liquid phase-solid phase system will be discussed. Furthermore, the methodology of SPE, the sorbents used, and automation will be surveyed. The processes in gaseous phase-solid phase systems, characteristic for trapping stripped organics from a stream of inert gas and their thermal desorption, are concerned with the processes of sampling of gas samples and, thus, are beyond the scope of this review.

2 Sorption and Desorption Processes in the Liquid Phase–Sorbent System

2.1 Sorption from Water

Sorption from water is essentially a dynamic process in a heterogeneous system, in which the transport of particles (molecules or ions of organic compounds) from one phase into the other is carried out. This process proceeds by a decrease in free energy until it reaches the minimum value, *i.e.* equilibrium. In view of the material balance, the organic matter originally dissolved in water is partitioned between the sorbent and the water according to the partial distribution coefficients. There is an analogy between this process and solvent extraction, governed by *Nernst*'s law. There are differences in the extraction medium used, and often in the resulting effect: the distribution coefficient for a proper sorbent is much higher than that with solvent extraction. In the thermodynamic view of the adsorption process, two mechanisms are involved, *viz.* surface adsorption and interaction of solutes with water.

The nature of the latter mechanism depends on the type of organic solute. For hydrophobic solutes *Frank* and *Evans* [16] suggested that a non-polar organic molecule is solubilized in water, because of the orientation of many layers of water molecules around the organic molecule. In this way, the water becomes more ordered in a partial crystalline form, and the entropy of the water decreases. When the organic molecules are adsorbed on the sorbent, oriented water molecules are dispersed, the order of the water system decreases and its entropy increases. This usually leads to negative changes in free energy, and makes the whole process spontaneous and favorable [2]

For ionic solutes, theories of electrolytes and acids and bases can be applied, using such parameters as pH or ionic strength. The mechanism of surface adsorption is governed by the character of interactions between solutes and active sites of the surface. Different interaction mechanisms with their corresponding energies are given in **Table 1**. From this table it might be concluded that the most suitable interaction for the solid-phase extraction procedure is that with the highest energy, *i.e.* the covalent interaction. However, one should realize that the higher the energy released in the retention process, the more difficult the elution of analytes will be, because of the energy required for breaking the covalent bond.

Table 1

Energy of the interactions used by SPE [17].

Interaction	Energy (kJ/mol)
Dispersive	5– 20
Dipole – induced dipole	8– 25
Dipole – dipole	25– 40
Hydrogen bonding	25– 40
Ionic	250–1050
Covalent	670–3360

Thus, the choice of the proper sorbent must be a compromise between retention and elution. In practice, this choice is based on considering the nature of the compounds to be isolated and the nature of the solvated solid phase (bonded phase, respectively). The "like adsorbs like" principle can often be used successfully. In addition to the preferred process of interaction between the compound of interest and the active site on the solid phase, competitive processes may also exist. These processes can include secondary interactions between the compound of interest and the solid phase, the interactions between the components of the sample matrix and the solid phase, and the interactions between the compound of interest and the components of the sample matrix. The whole system of possible interactions is drawn schematically in **Figure 1**.

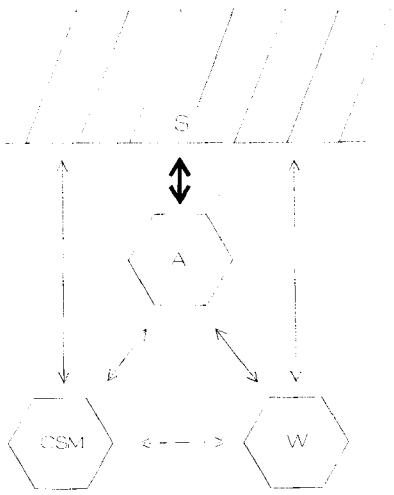

Figure 1

Scheme of the interactions in the system solid phase – water sample matrix.
S = solid phase, A = analyte, CSM = sample matrix constituents, W = water.

An example of secondary interactions between the compounds of interest and the solid phase is given by the retention of an ionogenic aromatic compound on a polystyrene-type ion-exchanger. Besides the prevailing ion exchange mechanism, there are also π-π interactions, causing additional retention. The affinity of residual silanol groups on chemically bonded silicas for amines is another known example [17]. The interactions between the components of the sample matrix and the solid phase concern the question of selectivity. If the concentrations of competitive components are low, the compounds can play significant undesirable roles as possible interfering.

High concentrations of other constitutents of the sample matrix, even though they do not affect the resulting chromatographic resolution, can cause overloading of the sorbent bed. Accordingly, if a specific compound is to be determined, the selectivity of the sorbent to be used should be emphasized. On the other hand, for screening purposes, *i.e.* identification of a broad spectrum of compounds, the retention should be taken into account. For samples with a high content of competitive organic compounds a sufficient amount of sorbent or, alternatively, selective sorbents should be used.

Other competitive processes are the interactions between the compound of interest and the components of the sample matrix. Here, phenomena like adsorption of analytes on sediments or dissolved particles or drug protein binding may affect the total efficiency of the preconcentration. Preconcentration of pesticides on Tenax-GC [18] can serve as a practical example: when a standard mixture of pesticides was added to non-filtered surface water containing suspended solids, the recoveries of substances such as DDT and Malathion were much lower than when filtered or distilled water was used. Effects of dissolved and suspended organic carbon on the efficiency of the adsorption of the solutes were studied by *Carter* and *Suffet* [19]. If the dissolved and suspended organic carbon both sorb an analyte in the same manner, they proposed eq. (1) for the calculation of the fraction of solute sorbed:

$$f_s = 10^{-6} K C_{tot} / (10^{-6} K C_{tot} + 1) \qquad (1)$$

where K is the sorption constant in g/ml for the organic carbon, and C_{tot} is the concentration of total (dissolved +

suspended) organic carbon (mg/l). The percent error that would result if f_s is not captured on the sorbent bed would be $-100\ f_s$. From eq. (1), for known values of C_{tot} and K, the percent error value can be calculated. For ground and surface waters typified by C_{tot} values below 10 mg/l, the error will be usually small for all but the most hydrophobic analytes [polycyclic aromatic hydrocarbons (PAH's), chlorinated pesticides]. It may be pointed out, however, that very large C_{tot} values are possible in some waste waters. The use of sorbent beds to preconcentrate analytes in such matrices will probably be ill-advised in most cases [20]. Generally, it can be summarized that high efficiency of adsorption can be achieved if the analyte-sorbent interaction is strong, the analyte-water and sorbent-water interactions are weak, and all other interactions shown in Figure 1 are negligible. Otherwise, the equilibrium in the system can be shifted undesirably.

An inevitable condition for effective adsorption is perfect mutual contact between the solid and the liquid phases. Since more than 99% of the surface area of polymer sorbents is the internal area of the pores, the need for the penetration of liquid phase into the pores is obvious. Complete permeation of the water into all of the pores of the hydrophobic polymer is usually assured by wetting the polymer first with an organic water-miscible solvent, which is then replaced by water. Prewetting of chemically bonded silicas causes opening of the hydrocarbon chains of the stationary phase, thus increasing its surface area. Omitting the prewetting step can lead to less effective adsorption of analytes. A decrease in the efficiency of adsorption was also observed if the wetting solvent was replaced by too large a volume of water [6]. Organic solvents commonly used as prewetting media are methanol, acetonitrile, and acetone. For sorbent amounts up to 1 g, the volume of solvent used usually varies from 2 to 10 ml. The volume of replacing water is approximately equal [17, 21-26]. Application of the prewetting step is always recommended, although results are available where activation of an octadecyl silica column by 15 ml of methanol had no influence on the accumulation of Bunker-C oil from seawater [27]. The adsorption efficiency can be increased by weakening the analyte-water interactions. For non-dissociated molecules, this can be theoretically carried out by increasing the ionic strength of the aqueous sample. This phenomenon, the so-called salting-out effect, is performed in practice by adding a certain amount of an indifferent electrolyte (NaCl, KCl) to the original aqueous sample. Studies on the influence of salting-out effects on the recovery of the preconcentration step are available in the literature, mostly for chemically bonded silicas. It was demonstrated that cyclohexyl silica sorbents provided more than 90% recovery of phenol at NaCl concentrations between 20% and 25% (*w/v*), while the recovery of phenol without addition of NaCl was only 37% [25]. A similar effect was observed, with cyclohexyl silica sorbents, on the recovery of *p*-chloroaniline. The addition of 30 g of NaCl to 100 ml of the water sample increased the recovery from 32% to 102% [21].

In another report [26], the positive effect of the addition of NaCl to water samples on the recovery of phenol from cyclohexyl silica was accompanied by a negative effect on the recovery of neutral compounds. The positive salting-out effect on adsorptions on octadecyl silica was observed for some herbicides [28] and pyrazone [29]. *Thurman et al.* [30] showed that with increasing ionic strength, the capacity factor for hydrophobic organic solutes in the water - Amberlite XAD-8 system increases. However, the addition of NaCl up to 50 g/l showed no significant effect on the sorption of a wide spectrum of organic compounds on Amberlite XAD-2 [31]. Summarizing these results, it can be stated that the increase of the ionic strength can often have contradictory effects. That means that application of the salting-out effect should be studied individually for every particular case. If the uptake of analyte molecules onto a sorbent surface is performed in a dynamic column, system parameters analogous to those used in frontal elution chromatography can be applied for the description of the processes in the preconcentration column. To obtain an effective accumulation of an analyte, two parameters should be considered, *i.e.* capacity and retention. Both parameters should be optimized, to prevent a breakthrough of the analyte during loading of a sample onto the extraction column. When the concentration of analytes in the sample is too high, a localized saturation of the stationary phase at the head of the column can result in overloading of the chromatographic support. Deformation of the Gaussian elution curve, and its shifting to smaller retention volumes, are the result of this phenomenon. The capacity of a solid phase extraction column depends on the amount of active sites on the solid support. This amount depends on the type of the stationary phase and the bed volume of the column. For sorption of complex mixtures, deviations from linear isotherm behavior are expected to be observed whenever the total surface concentration of all adsorbed species approaches a monolayer [32]. In this case, a quantitative description of the mass overload for a given column and eluting conditions is very complicated. The problem of overload characterization has been studied by several authors [32-35]. They all used operational definitions for the description of overloading. Thus, column overloading has been suggested to occur when the plate number, peak width, or capacity factor decreases by 10%.

The concept most frequently used for the characterization of the upper limit of linear chromatographic conditions is that of linear capacity [35]. Sorbent capacity under linear chromatographic conditions, C_{slin}, is given by:

$$C_{slin} = \frac{V_m}{M} \cdot k \cdot C_m \qquad (2)$$

where V_m is the volume of the mobile phase in the column, M is the mass of the packing material in the column, k is the capacity factor, and C_m is the solute concentration in the mobile phase. According to this concept, high solute concentration is the main reason for sorbent overloading. However, is has been experimentally observed that the capacity factor of a solute must be taken into account as well [35]. Since, most of the time, various chromatographic columns exhibit comparable V_m/M ratios (ranging between a factor of 1 and 2), the effect of this ratio is negligible in comparison to k and C_m, which can each range over several orders of magnitude. According to the sorption studies of *Bitteur* and *Rosset* [35], the chromatographic behavior of the Partisil ODS-3 bonded silica and the PRP-1 styrene-divinyl benzene copolymer is linear, provided that the sample exhibits a $k \cdot C_m$ value lower than 10^{-2} *M*. *Pietrzyk* and *Stodola* [34] observed that mass overloading occurred for sample concentrations over about 0.23% *w/w* for a 8.0 mm i.d. preparative column, and 0.25% *w/w* for a 20.5 mm i.d. column, when using samples with k values less than 2.

An alternative approach to the problem of calculating the approximate capacity of

various sorbents was demonstrated by *Werkhoven-Goewie et al.* [36]. Assuming the accessible surface area of the sorbents to be equal to that determined by nitrogen (BET) adsorption, and assuming the sorbed solute molecules to lie flat on the sorbent surface, the loading capacity of various stationary phases was determined for pentachlorophenol as a model compound. For most of the stationary phases studied, the calculated loading capacity varied between 1 to 15 % *w/w*, approximately. Although in practical environmental, pharmaceutical, biological, and food analyses the total concentration of both the analyte and possible interferences should be considered, it is rather unlikely that in these cases (where the concentrations typically are in the µg to ng per ml level) breakthrough will occur due to overloading of the column [11,12,17]. This breakthrough is, in the majority of situations, a function of the mobility of the analytes in the solid phase extraction column, which is usually expressed as a capacity factor *k*. If the aqueous solution of an analyte, at the concentration of C_o, is pumped through the column and the effluent is monitored on-line continuously, a curve is obtained which is known as a frontal analysis chromatogram or a breakthrough curve (**Figure 2**). The derivative

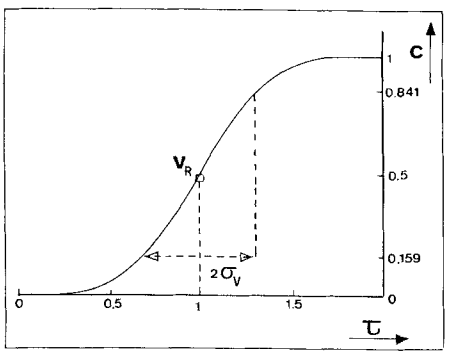

Figure 2

The breakthrough curve of a SPE column. $c = C/C_o$, and $\tau = t/t_R$, where C and C_o are the solute concentrations in the effluent and in the sample (*i.e.* the influent), respectively, t and t_R are the time and the retention time of the solute, respectively. (V_R = the retention volume of the solute, and σ_V = the elution band broadening.)

of a breakthrough curve is a Gaussian-shaped curve, similar to those known in chromatographic elution analyses. The retention volume, V_R, of an analyte can be read from the breakthrough curve as indicated in Figure 2. For the proper choice of the total sample plus flushing volume, to prevent losses of accumulated analytes, the actual value of the breakthrough volume should be known. This breakthrough volume can be defined in many ways, but a reasonable definition is [36]:

$$V_B = V_R - 2\,\sigma_V \qquad (3)$$

where σ_V is the band broadening as depicted graphically in Figure 2, or determined analytically from the relationship:

$$\sigma_V = \frac{V_o}{N^{1/2}}(1 + k_{H_2O}) \qquad (4)$$

where N is the number of theoretical plates generated by the solid phase extraction column, V_o is the void volume of this column, and k_{H_2O} is the capacity factor in pure water. While V_o and N are parameters characterizing the solid phase extraction column, k_{H_2O} characterizes the mobility of a given analyte in this column. The simplest method for obtaining k_{H_2O} values is by frontal analyses in pure water. As many k_{H_2O} values are hardly accessible experimentally, because of the excessive retention of the solutes in totally aqueous eluents, a less time-consuming but reliable method has to be employed to estimate them. To predict k_{H_2O} values, various relationship have been studied. These studies covered the relationship between the logarithm of k_{H_2O} and the logarithm of the aqueous molar solubility [30,98], the logarithm of k_{H_2O} and the logarithm of the octanol-water partition coefficient [37], and the logarithm of k_{H_2O} and the volume fraction of organic modifiers [36,38-41], respectively. In the majority of cases, satisfactory correlations can be obtained.

Generally, to find the breakthrough volume of a sampling column, an equation describing the level of breakthrough as a function of volume or time is needed. Having such an equation, it is possible to find the volume that will give a breakthrough level. The breakthrough level is often defined as the ratio of the outlet-to-inlet concentration, or as the fraction of the total mass of an analyte which has passed out of the column. *Lövkvist* and *Jönssen* [42] have compared several alternative equations for breakthrough curves, and have developed a realistic model for the breakthrough properties of short columns. They have proposed the following breakthrough function:

$$b = \frac{\tau-1}{\tau}\Phi\left[N^{1/2}\frac{\tau-1}{\tau^{1/2}}\right] + \frac{\tau+1}{\tau}\exp(2N)\times\Phi\left[N^{1/2}\frac{\tau+1}{\tau^{1/2}}\right] \qquad (5)$$

where $\tau = t/t_R$, with t = time, and t_R = retention time of the analyte, and the function $\Phi(x) = 0.5\ \mathrm{erf}\,(-x^2/x^{1/2})$. The breakthrough volume can be calculated numerically from the following expression:

$$V_B = V_R\left[(1-b)^2 + \frac{a_1}{N} + \frac{a_2}{N^2}\right]^{-1/2} \qquad (6)$$

where b is calculated from eq. (5), and the parameters a_1, a_2 are complicated functions of b. Their numerical values have been tabulated [42]. The results of this study suggest that columns with very low numbers of theoretical plates can have significant sampling capacity.

In addition to these general theoretical studies, results of studies on the effects of specific factors on the breakthrough volume are available. A decrease of the breakthrough volume for polar compounds has been observed in sorption experiments with nitro compounds on Amberlite XAD-4 [43]. The increase of ionic strengths lowered the breakthrough volume for organic acids on graphitized carbon black [44]. The flow rate of the aqueous sample through the column proved to be another important factor. Generally, increasing a flow rate over a certain critical value resulted in a decrease of the breakthrough volume by 10 % - 80 % [36,44,45]. As an explanation, the decrease of the number of theoretical plates [36], or the occurrence of non-equilibrium processes [44] was proposed. A particular example is the effect of the flow rate on the V_B value for a ACDA-Pt precolumn [46], where the change of the flow rate from 0.5 ml/min to 2 ml/min led to the decrease of the V_B value from 10 ml to 2 ml. This large difference was explained as being caused by slow mass transfer, due to apparently slow complexation kinetics. The linear dependence of the breakthrough volume for organosulfur compounds, in Amberlite XAD-2, on their molar solubility in artificial seawater, as demonstrated by *Przyjazny* [45], corresponds to the relationship between log k_{H_2O} and the logarithm of the solubility mentioned above.

Another approach to understanding sorption processes is the concept of film diffusion, proposed by *Pankow et al.* [47]. According to this concept, the occurrence of breakthrough on Tenax-GC cartridges, provided that the capacity of the bed is not exceeded, reflects the lack of sufficient time for all of the analyte molecules to reach the surface of a particle before exiting the sorbent bed. Prior to the

interaction with the active sites, the analyte molecule has to pass through the diffusion layer, δ. When the transport through this layer is the rate-determining process, the sorption process (onto Tenax-GC particles) is controlled by diffusion through the particle surfaces. Considering this, *Pankow* [47] proposed the following equation for the analyte concentration in the effluent:

$$C_e = C_i \exp\left[-\frac{3D\,(1-p)\,t'}{2\,p\,r\,\delta}\right] \quad (7)$$

where C_i is the influent concentration of the analyte, D is the diffusion coefficient, p is the porosity of the bed, t' is the residence time of the analyte in the bed, and r is the particle radius. Supposing that

$$\delta = \frac{0.0029\,A}{V} \quad (8)$$

where A is the bed cross-sectional area, V is the volume flow rate and

$$t' = \frac{p\,A\,L}{V} \quad (9)$$

where L is the column length, *Pankow et al.* [47] demonstrated that the fraction recovery, given by the equation

$$R = 1 - \frac{C_e}{C_i} \quad (10)$$

can be independent of the volume flow rate, since a large value of V implies a small δ value, and a short residence time, t, as well. Conversely, lower V values increase δ and slow down diffusion. However, an increasing residence time, t, can compensate for this effect, thereby yielding a constant R. This conclusion has not been fully confirmed by experiments with other sorbents [36, 44, 45, 54, 86]. Summarizing, it is possible to conclude that, for every system, there is a critical value of the flow rate. The increase in flow rate over this value leads to the occurrence of non-equilibrium processes and, hence, to a change in retention properties.

2.2 Desorption into Liquid Phases

Desorption is the reverse of sorption. Accordingly, solute-solvent and solvent-sorbent interactions are to be characterized. Description of the column system is partly analogous to elution liquid chromatography. The major challenge is to have the narrowest possible analyte plug in the column with minimal retention, so as to obtain the highest preconcentration factor. For the choice of proper eluting solvents, the values of eluotropic strengths can be used. Solvents used most frequently are methanol [21, 25, 27, 44, 48-54], diethyl ether [18, 31, 53, 55, 56], acetone [43, 55, 57, 58, 59], ethyl acetate [23-25, 57, 60], acetonitrile [22, 25, 26, 61], methylene chloride [26, 29], benzene [44, 55], hexane [55, 62], pentane [55], methyl ethyl ketone [57], tetrahydrofuran [63], and 2-propanol [64]. To obtain effective desorption of dissociated molecules, organic solvents can be modified by addition of an acid, base or buffer solution [21, 22, 24, 65]. In on-line systems, the accumulated analytes are desorbed from the precolumn with the same mobile phase as used in the analytical column [48, 50-52].

A special type of desorption is supercritical fluid extraction [66, 67]. This technique is based on the properties of a solvent at temperatures and pressures above its critical point. Under these conditions, solvents have properties intermediate between those of gas and liquid phases, depending on fluid composition, pressure, and temperature. The density of a supercritical fluid is typically 10^2 to 10^3 times higher than that of a gas. Consequently, molecular interactions increase due to shorter intermolecular distances. However, the diffusion coefficients and viscosity of supercritical fluids, although density dependent, remain more similar to those of gases. These properties give rise to similar solvent strengths as with liquids but with improved mass-transfer properties, providing potentially more rapid extraction rates, and more efficient extractions due to better penetration of the matrix [66]. As phases, carbon dioxide [66, 67], isobutane [66], or carbon dioxide with methanol as modifier [66] can be used.

2.3 Methodology of SPE

A typical SPE sequence includes the following steps: activation of the sorbent (wetting), conditioning (removal of the excess of activation solvent), application of the sample, removal of interferences (clean-up), and water, elution of the sorbed analytes, and column regeneration.

2.3.1 Sorbent Activation

The role of this step is to secure perfect and maximum mutual contact of the liquid and solid phases (hydrophobic sorbents) or, alternatively, recycling of the ion exchanger. This can be performed by flushing the column with approx. 5-10 bed volumes of a proper organic solvent (hydrophobic sorbents) or acid/base solution (ion exchangers).

2.3.2 Conditioning

The activation solvent is removed with several ml of water, or a suitable buffer, to obtain a proper environment for the sorption from the water sample. An excessive washing can sometimes produce insufficient wetting of the sorbent, and thus, reduce the recovery [6].

2.3.3 Sample Application

The principles described in section 2.1 should be applied in this case. The volume of the aqueous sample should be chosen in relation to the sorbent used and to the values of the breakthrough volume and the total analyte concentration. *Thurman et al.* [30] have proposed an empirical equation for the calculation of sample volumes that can be applied to a XAD-8 styrene-divinylbenzene resin without breakthrough:

$$V_i = \frac{1}{6}\,k\,V_b \quad (11)$$

where V_i is the volume of the sample, and V_b is the bed volume of the column. Since similar equations should be verified for every type of sorbent used, measurement of the value of the breakthrough volume for the SPE column to be used is generally recommended. This value can be obtained experimentally, or via any of the relationships described in Section 2.1. When a complex sample is to be handled, and accumulation of analytes having a wide range of k values is needed, considerations on the aim of the analysis are a prerequisite. To prevent the loss of less-retained analytes, the sample volume has to be small, but, accordingly, the preconcentration factor will be small, too. To obtain higher preconcentration factors, losses of analytes with low k values are inevitable. To solve this dilemma, several precolumns containing sorbents of various origins with various selectivities and polarities [50] can be used. If one chooses to use one column only, the sample volume has to be chosen as a compromise between total recovery of the analytes and the preconcentration factor.

An alternative strategy for the accumulation of organic compounds from aqueous environments, especially for analytes having low k values, is to overload the cartridge so that the entire packing

material is equilibrated with analyte [22]. After the analyte concentration front has completely passed through a steady-state condition, the analyte may now be eluted with a small amount of solvent. The enrichment factor of this procedure is:

$$F = (1 + k)\frac{V_o}{V_f} \quad (12)$$

where V_f is the final sample volume. A similar approach has been used for the *in-situ* detection of polycyclic hydrocarbons, after their sorption onto an alkylated silica adsorbent [32].

2.3.4 Removal of Interference

The aim of this step is to simplify the original matrix. This can be done by flushing the column after sample application with pure water or water modified with an organic solvent. Ion-exchangers and metal-loaded sorbents can be flushed with an organic solvent which removes the neutral molecules adsorbed onto the skeleton surface while the ions remain captured. For this step, tests should be carried out to verify that no losses of sorbed analytes occur.

2.3.5 Removal of Water

This step can be applied in off-line procedures. Removal of the water simplifies the desorption step; no fractionating or drying of the effluent is needed. Water can be removed by a stream of air (with negative or positive pressures) [23-25, 27, 63], by a stream of nitrogen [62, 68, 69], in a centrifuge [26, 69], or by storing the column some time in a dessicator [70]. Total drying of the column can, however, sometimes lead to a remarkable decrease in recovery [49]. Thus it is recommended, especially for accumulating volatile compounds, that the effect of this step on the total recovery be verified.

2.3.6 Elution of Sorbed Analytes

The principles described in Section 2.2 should be applied in this case. In off-line procedures, the analytes can be eluted with a single solvent or solvent mixtures, or via several eluting steps. In these cases elution is usually performed by flushing the SPE column with the proper mobile phase, using negative (vacuum) or positive (pump, syringe) pressure, or centrifugal force (centrifuge). In on-line procedures, the eluting phase is equal to the mobile phase in the HPLC analytical column.

2.3.7 Regeneration

This is the common way of cutting analysis costs. Hydrophobic sorbents can be regenerated by flushing the column with one or several organic solvents. Ion-exchangers can be regenerated with acid or base solutions. The regeneration of metal-loaded sorbents is accomplished by flushing the column with a solution of the appropriate metal ions. The regeneration procedure must be verified very carefully, to avoid memory effects. It is often recommended that each column be used only once [6]. *Vožnáková et al.* [68] observed hysteresis behavior with some sorbents. This is the phenomenon of an increase in the recovery of an analyte on a regenerated column, which has already been used for preconcentration of the same analyte at a concentration of 2-3 orders of magnitude higher. In this case, when the desorbed amount is higher than the sorbed amount, incorrect results are obtained.

To achieve the highest recovery, the whole SPE procedure or at least the sorption and elution steps should be optimized. A suitable procedure for the development and verification of a SPE method has been suggested by *Wells* and *Michael* [61]. In this procedure, retention is first held constant at known values, then the elution process is optimized. Once the elution is optimized, the variables controlling retention are tested and revised if necessary. Recommended starting conditions are as follows: a sample volume of 200 ml, a sorbent mass of 1.0 g, and a solute concentration of 100 ppb. The factors influencing retention or sample pH, volume, concentration and sorbent mass, and those influencing elution are solvent strength and solvent volume [61].

2.4 Sample Storage

The transport of a water sample from the sampling site to an analytical laboratory, without any changes in its composition, is an important part of the whole analytical procedure.

The proper storage of a sample is a problem, especially if trace concentration levels of organic compounds are to be determined. Changes in concentrations of the sample components can occur, due to interphase transfers from the liquid into the gaseous phase, and due to possible leaks from the gaseous phase out of the sample container. Other changes can occur due to adsorption on the walls of the container [3]. Transfer of groundwater samples from an anaerobic aquefier to an aerobic environment may initiate oxidation or biodegradation of the organic compounds, which may continue during transport. If organic compounds are isolated from groundwater, immediate use of a sorbent will prevent possible sample alteration between the time of sampling and analysis [26]. Moreover, the loss of gaseous phase is minimized and adsorption onto container walls is excluded. Binding of the molecules of the organic compounds to the active sites on the sorbent surface slows down undesirable changes in both quantity and quality. *Green* and *LePape* [71] 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 results from trapping the organic compounds in the adsorbent lattice structure. The pores of XAD-2 or silica gel are smaller than bacteria. Thus, the hydrocarbons are protected from bacterial attack. More examples of the study of effects of the storage period can be found in the literature [3, 72].

3 Adsorbents Used in SPE

3.1 General Characteristics of Adsorbents

The general characteristics which are taken into account for the choice of an adsorbent are functionality, particle size and shape, surface area, pore size, and chemical inertness.

3.1.1 Functionality

This plays the most important role in the choice of a sorbent. It is an expression of the affinity of the sorbent for various organic compounds, which depends on the nature of the functional groups bonded on the sorbent surface and on the whole surface orientation. Affinity can be estimated in both static and dynamic modes, the latter being more useful and reliable because of the dynamic nature of the SPE procedure. More details concerning affinity of the sorbents are discussed in Section 2.2.

3.1.2 Particle Size and Shape

These characteristics influence the hydrodynamic conditions in the column, and are related to the value of the surface area. Smaller particles have a larger surface area, and columns packed with these particles yield higher performance. The pre-columns for on-line trace enrichments are commonly packed with particles with the same diameter as used in the analytical column, *i.e.* 5-10 μm. High performance of such supports is, however, often connected with the high back-pressure and clogging of the pre-column with dirty samples. Therefore, larger particles have to be used, even though a decrease in performance is observed. (It should be realized, however, that the performance of a SPE column does not play such a significant role as the retention properties do, as demonstrated in Section 2.1). In off-line systems, where high-pressure pumps are not often used, particle sizes ranging from 30 to 60 μm are commonly used.

3.1.3 Surface Area

Sorbents having a higher surface area per mass unit have a higher number of active sites and are, therefore, more effective accumulation media. The surface area can be increased by a porous structure of the sorbent, or by the proper spherical orientation of the hydrocarbon chains. From this point of view, it is useful to use porous adsorbents with large surface area [2] and, in the case of chemically bonded phases, to enlarge the area by proper wetting of the stationary phase [6].

3.1.4 Pore Size

This factor is inversely proportional to the surface area. Considering this fact, it might be concluded that the pores should be as small as possible for effective accumulation. However, one should realize that, when the pore diameters become comparable with the molecular diameters, penetration of the molecules into the pores is difficult. Such a situation can occur, *e.g.*, if high-molecular humic substances are accumulated on sorbents with small pore size. In this case a low efficiency is observed. By using a sorbent with a larger pore size, the efficiency of the sorption increases. Such behavior has been practically demonstrated [30, 73-75] with the sorption of humic substances, where a XAD-8 macroreticular resin was more suitable than a XAD-7 macroreticular resin, with a higher surface area. An additional problem may appear whenever large molecules can block the pores and, thus, make them inaccessible even for small molecules. Therefore, XAD-2, having a lower surface area, is often more effective than a XAD-4 polymer for accumulating organic compounds from environmental water samples [2]. Another effect of the pore size is discussed in the section concerning the storage of sorbed compounds.

3.1.5 Chemical Inertness

The change of the quality of the sorbent surface influences the reproducibility of the accumulation procedure. Catalytic properties of the active sites may initiate a change of the original analytes and can, therefore, lead to false identifications. Artefacts, released from the sorbent surface by drastic changes of the conditions, may interfere in subsequent analyses, producing high-level blanks. It is obvious that all these phenomena are undesirable if the required result is to be precise and accurate. To reduce the catalytic properties, the use of homogeneous materials is recommended. To avoid other possibilities of variation, drastic changes of the conditions (*i.e.* pH, pressure, temperature, *etc.*) should not be used and the limits of pH and temperature values should be known. Most of the synthetic polymers are unaffected by extremes in pH, but some acrylates may be hydrolyzed at higher pH values. Extreme pH values, in both acid and base regions, can change the nature of bonded phases; the recommended pH values are between 2 and 8. Another important criterion, especially for thermal desorptions, is the temperature limit that can vary from 150°C to 380°C for various sorbents. From this point of view, Tenax is the best support, having a temperature limit of 380°C and producing low blanks. Generally, it can be concluded that sorbent stability should always be checked to prevent undesirable results.

3.2 Carbon Sorbents

Carbon was the first medium used for the accumulation of organic compounds from water [2]. The first experimental efforts have been substituted gradually by elaboration of various methods (*e.g.* the CCE method [76]). The advantage of activated carbon was high sorption capacity, and high thermal stability. The heterogeneous nature of activated carbons used in these procedures, however, caused problems such as irreversible sorption, affinity for some groups of compounds only, or catalytic activities of the carbon surface [3, 76, 77]. Because of these disadvantages, activated carbon is, nowadays, used mostly in closed-loop-stripping analysis according to *Grob* [14] or its open modifications [15], where the high capacity of activated carbon is the main reason for this choice. Carbon disulfide is commonly used as an eluting solvent in this case [14, 15, 58].

A promising way to improve the properties of carbon sorbents is the preparation of carbonaceous supports, with more homogeneous structures than the classical carbons. These developments resulted in the production of various porous carbons, carbonaceous resins, pyromodified silicas or graphitized carbon black supports, as these materials are usually called. These materials have attracted attention because of their potential as completely non-polar sorbents, and because of their stability over a wide pH range [78]. They also show excellent affinity towards specific groups of compounds.

The sorption properties of the carbonaceous molecular sieve were compared to those of XAD-4 resin [58]. The average recovery on carbon was 77 %, and that on XAD-4 was 79 %. Carbon disulfide was found to be the most suitable eluent, even though it did not elute phenols and naphthalene. The advantage of the carbonaceous molecular sieve was the higher retention of low-molecular polar analytes. Considering the recoveries on graphitized carbon black (GCB) [55], its suitability for accumulating chlorinated and organophosphorus pesticides, alcohols, aldehydes, ketones, and nitro compounds was demonstrated. Lower recoveries (30-60%) were achieved for chlorophenols, aromatic hydrocarbons, and PCB's, while GCB is not suitable for the preconcentration of PAH's, esters, and alkanes.

Golkiewicz et al. [40] compared the retention on pyromodified silica and on chemically bonded phases. They showed, for polar solutes, especially those containing highly polarizable substituents like chlorine, nitro, or phenyl groups, that pyrocarbon sorbents are much better suited for preconcentration than bonded phases. Predictions of the capacity factor, as described in Section 2.1, were applied with good results. A good affinity towards polar compounds

was ascribed to the high density of carbon atoms on the surface of the pyro-modified silica, the large entropy effect resulting from solute adsorption, and to the high perpendicular polarizability of the carbon surface which can involve strong permanent dipole-induced dipole interactions [40]. A high affinity of pyro-modified silica towards polar compounds (chlorophenols) was also demonstrated by *Werkhoven-Goewie et al.* [36].

3.3 Polymer Sorbents

Along with bonded silicas, these materials belong to the most widely applied sorbents. Polymers are reported to have been used as an alternative sorbent for trace enrichment, instead of carbon, since the late 1960's. Their homogeneous structure results in a greater reproducibility of the trace enrichment experiments. The most often used types of polymers are shown in **Table 2**.

3.3.1 Styrene-Divinylbenzene Copolymers (ST-DVB)

Styrene-divinylbenzene copolymers are the most popular sorbents for trace enrichment purposes [2]. This group comprises, *e.g.*, Amberlites XAD-1, XAD-2, XAD-4, Chromosorb 102, PRP-1, or Ostion SP-1. Sorbents of this type have the highest efficiency towards non-polar molecules. Their retention increases as the molecular weight increases [79]. Low-molecular aliphatic compounds are sorbed minimally. With increasing polarity of the analytes the retention decreases, and partly dissociated organic compounds are sorbed weakly [31, 43]. After suppression of the ionization, the recovery of the analytes can be enhanced, especially of those with higher molecular weight.

The newer sorbents, if not of analytical grade, have to be purified thoroughly before use to remove the impurities. For purification various procedures can be applied. The most popular are solvent extraction in a Soxhlet appartus or in a shaker, or flushing the column packed with a sorbent with organic solvents. The methodology of a purification procedure can be found, *e.g.*, in a study by *Junk et al.* [31]. The extent of the purification depends on the original quality of the sorbent. The sequences of flushing solvents commonly used are methanol–acetonitrile–ether or methanol–acetone. Purification of macroporous polymers by sonification or thermal means is not recommended, because it causes physical distortions that expose previously inaccessible sources of contamination [2]. Similar distortions can occur if the polymers are harshly handled or ground. Undesirable interferences are often the result of an analyst's activities.

The recoveries of most of the analytes tested on ST-DVB resins were higher than 50% [2]. Extensive recovery tests can be found, *e.g.*, in the studies of *Junk et al.* [31], *Tateda* and *Fritz* [58], *Van Rossum* and *Webb* [77], *Burnham et al.* [79] or *Tabor* and *Loper* [80], where various groups of compounds were tested. In addition, results of recovery tests for some groups of compounds, *e.g.* nitro-compounds [57], organosulfur compounds [45], humic substances [73], non-ionic detergents [81], or trialkyl/aryl phosphates [88], are also available in the literature. To increase the affinity towards polar compounds, a mixture of ST-DVB and acrylate resins can be used [77, 82]. The results of studies of ST-DBV polymers, for accumulating biologically active compounds from water samples, have been reported by several authors

Table 2 Some characteristics of polymer sorbents commonly used for SPE.

Sorbent	Type	Surface area (m^2/g)	Pore size (nm)	Supplier
Porapak Q	EVB-divinylbenzene	500–840	7.5	Waters Assoc.
Porapak R	Vinylpyrrolidine-DVB	450–600	7.6	Waters Assoc.
Porapak S	vinylpyridine-DVB	300–450	7.6	Waters Assoc.
Chromosorb 102	styrene-DVB	300–400	8.5–9.5	Johns-Manville
Chromosorb 105	polyaromates	600–700	40–60	Johns-Manville
Chromosorb 106	polystyrene	700–800	–	Johns-Manville
Chromosorb 107	polymethacrylate	400–500	–	Johns-Manville
Chromosorb T	PTFE	4–7	–	Johns-Manville
Fluoropak 80	PTFE	2–4	–	Fluorocarbon Co.
Amberlite XAD-1	styrene-DVB	100	20	Rohm & Haas
Amberlite XAD-2	styrene-DVB	290–330	8.5–9	Rohm & Haas
Amberlite XAD-4	styrene-DVB	780	5	Rohm & Haas
Amberlite XAD-7	ethylene-dimethacrylate	450	9	Rohm & Haas
Amberlite XAD-8	ethylene-dimethacrylate	140	23.5	Rohm & Haas
Ostion SP-1	styrene-DVB	350	8.5	Lab. Instrum.
Synachrom	styrene-DVB-EVB	520–620	9	Lab. Instrum.
Spheron MD	methycrylate-DVB	320	–	Lab. Instrum.
Spheron SE	methacrylate-styrene	70	–	Lab. Instrum.
Separon HEMA	HEMA-EDMA	20–60	–	Tessek Ltd.
PRP-1	styrene-DVB	–	–	Hamilton
Polypropylene	propylene	1	–	various
Open pore polyurethane	ester	0.6	–	various
Polyurethane foam	amide-ester	0.02	–	various
Tenax-GC	2,6-diphenyl-p-phenyleneoxide	20	72	Appl. Science

EVB = ethylvinylbenzene; DVB = divinylbenzene; PTFE = polytetrafluoroethylene; HEMA = hydroxyethylmethacrylate; EDMA = ethylenedimethacrylate.

[80, 83, 84]. Spherically shaped, 10 μm ST-DVB resin proved to be a suitable support for on-line preconcentrations of pollutants from industrial wash waters [41, 48, 50, 51]. Linear relationships were observed between the logarithm of the capacity factor and the volume fraction of an organic modifier for this resin modification [37, 41]. The preconcentration capabilities of ST-DVB polymers for some groups of compounds were compared with those of methacrylate polymers [45, 77, 79, 87], Porapax R and S [43], activated carbon [58], Chromosorbs 105 and 106 [45], open-pore polyurethane [54], and bonded silicas [35, 37, 50, 85]. The recoveries of XAD-4 were comparable to those on activated carbon. Methacrylates and Porapaks had a higher affinity to polar compounds than ST-DVB resins, but the situation was reversed when non-polar compounds were tested. Chromosorbs were found to be more effective for preconcentration of organosulfur compounds, and open-pore polyurethane was found to be better for the preconcentration of pyrene.

It should, however, be pointed out that these comparative tests aimed to achieve the optimal support for the recovery of specific compounds, while the most common ST-DVB resins serve as a reference material. Generally, taking into account all compounds recovered, ST-DVB resins are the best polymers, as far as the total average recovery is concerned. Comparisons of ST-DVB resins with bonded silicas usually highlighted some advantages of one of them (higher retention on PRP-1 resin that on Partisil ODS-3 C_{18}-silica [37], or, on the other hand, PRP-1 being unsuitable for on-line preconcentrations using gradient elution [41]), or they are regarded as complementary sorbents [41, 85].

3.3.2 Acrylate Polymers

Amberlite XAD-7, Amberlite XAD-8, Chromosorb 107, Separon AE, Separon SE, Spheron SE, Spheron MD, and Separon HEMA are the members of this group most frequently used. Generally, acrylates have similar properties to ST-DVB resins. The most important difference is the higher polarity of acrylates and, hence, the higher affinity for polar compounds as, *e.g. fulvic acids* [73] or phenol [79], as compared to ST-DVB resins. *Thurman et al.* [30] showed that, comparing capacity factors on Amberlite XAD-8, the following functional groups were preferred:

$-CH_3 > -CO_2H > -CHO > -OH > -NH_2$.

For classes of compounds the sequence was as follows:

aliphatic compounds > aromatic compounds > alicyclic compounds.

It is important to point out that the recoveries of a compound using the same sorbent, presented by various authors, can vary considerably. As an example, the recovery of phenol using XAD-7 has been reported as 19% [77] and as 86% [79]. More examples can be found in the literature. The origin of these differences is difficult to trace, since the preconcentration procedures described differ in amount of sample, flow rate, origin of sorbent, *etc.*

Separon and Spheron acrylate copolymers were found to be suitable for preconcentration of toluene, *m*-cresol, and prometryne (Spheron SE) [53], as well as for phenoxycarboxylic acids and *S*-triazines (Separon SE) [68], where the recoveries on acrylate resins were higher than those on Tenax-GC and Porapak Q.

3.3.3 Tenax-GC

Tenax is poly-(2,6-diphenyl-*p*-phenylene oxide). It is a very popular support for purge-and-trap methods for determining volatile substances [13, 89-92]. Its suitability is a result of its excellent temperature stability (up to 380°C), and virtual absence of volatile by-products. This also makes Tenax a suitable sorbent for adsorption/thermal desorption procedures for accumulating organic compounds directly from water [20, 47, 69, 93]. However, solvent elution of directly accumulated analytes has also been used [18, 94]. The preconcentration efficiency has been found to be highest for non-polar compounds with low solubility in water, such as polychlorinated biphenyls [18], polycyclic aromatics hydrocarbons [93, 94], and chlorinated and organophosphorus pesticides [18, 93, 94], with an average recovery of 70-90%.

Polar compounds (*e.g.* phenol or pyridine) are preconcentrated with lower efficiency [70]. A certain drawback of Tenax is its low capacity of approx. 20 m^2/g, meaning that relatively low analyte concentrations should be treated. *Pankow et al.* [47] showed that the early breakthrough, observed by some workers investigating aqueous sampling with Tenax-GC, was possibly the result of poor transport and not the result of poor retention. Their suggestion was based on the theory of film diffusion (see Section 2.1). They concluded that Tenax-GC would act as a perfect sink for analyte compounds, provided that the analytes are not very soluble in water and that they are present in relatively low concentrations in only slightly contaminated samples. The last two requirements will be met by unpolluted lake, river, and sea water, as well as by rain and snow [47].

3.3.4 Polyurethanes

Open-pore polyurethane and porous polyurethane foam are the most widely used modifications of this polymer type. Open-pore polyurethanes are usually prepared by *in-situ* polymerization. These polymers consist of agglomerated spherical particles (1 to 10 μm in diameter), bonded to each other in a rigid, highly permeable structure. They exhibit weakly basic anion-exchange characteristics [54]. Comparing the open-pore polyurethanes (OPP) with OH/NCO ratios of 1.0 and 2.2, respectively, with XAD-2 resin, it was demonstrated that the retention of pyrene increased in the following sequence:

OPP(OH/NCO = 1.0) < XAD-2 < OPP(OH/NCO = 2.2) [54].

Porous polyurethane foam was studied as a sorbent for the preconcentration of PCB's [95, 96], PAH's [97], and chlorinated insecticides [95] from water samples.

3.3.5 Polypropylene

The polypropylene adsorbent exhibits an affinity for higher compounds in given homologous series [63]. While PAH's and high-molecular phthalates were recovered efficiently, alkanes, ketones, alcohols, and low-molecular phthalates were preconcentrated minimally or not retained at all. The reason was suggested to be the low capacity. This characteristic, however, can be useful in the analysis of some environmental samples which contain a variety of pollutants, and whenever a specific preconcentration is needed.

3.3.6 Polytetrafluoroethylene (PTFE)

This polymer was used for preconcentration of PAH's and xanthines from water [98], and, admixed with XAD, for the preconcentration of hydrocarbons from seawater [99]. *Josefson et al.* [98]

demonstrated that differences in capacity between two different PTFE aggregates were linked to differences in surface morphology, rather than simply to surface area. The capacity of PTFE was inversely related to the solubility of the solute for PAH's. This correlation was worse, however, if the solute was a nitrogen heterocyclic compound. Acetone and methanol were observed to be effective wetting solvents, while the wetting ability of acetonitrile was found to be poor.

3.4 Bonded Silicas

These materials are the most popular supports in reversed-phase liquid chromatography. The first attempts to use them as preconcentration media date to the middle of the 1970's [100]. Nowadays, trace enrichment on bonded silicas is widespread in both the off-line and the on-line modes. This group of sorbents consists of alkyl- or aryl-group substituted silanol bonds to the silica gel support. The character of the sorption and desorption processes within the stationary phase is not exactly known yet. A description of the mechanism of the kinetic processes between stationary phase (plus residual silanol groups) and the components of the mobile phase is beyond the scope of this review. The bonded silica mostly used is that with the octadecyl group [23,29, 46, 49, 61, 64, 72, 100-103]. The reason lies in its large capacity, as compared to other bonded silicas, and in the fact that it is mostly used as a support for analytical columns in HPLC. Compatibility between the precolumn and the analytical column can be secured in this way. Other bonded silicas used for preconcentration of organic compounds from aqueous samples are those with ethyl- [25,101], butyl- [25], octyl- [25,26,62), C_{22}- [36], cyclohexyl- [21,25,26], diol- [25], cyanopropyö- [25], phenyl- [26], diphenyl- [102] and phenetyl [102] groups. These stationary phases were used for the preconcentration of organic compounds ranging from nonpolar to polar, *e.g.* PAH's [25, 26, 100, 103, 104], PCB's [62], phenols and chlorophenols [25, 26, 36], chloranilines [21], oils [27], pesticides [23,61,62], phthalates [25], N-heterocycles [26], and tributyltin chloride [24].

For most of the accumulated compounds, an average recovery between 60% and 80% was achieved. Since bonded silicas can accumulate a wide spectrum of compounds, they can be used as an alternative to standard liquid-liquid extraction methods [25, 26]. *Chladek* and *Marano* [25] compared the SPE procedure with the standard EPA method No. 625. The average recovery obtained with octylsilica was about 20% higher than that obtained by the standard method.

3.5 Ion Exchangers

Ion exchangers can selectively accumulate compounds dissociable in water matrices such as, *e.g.*, phenols, organic acids, barbiturates (anion exchangers), amines or N-heterocycles (cation exchangers). For this purpose, commercially available cation- [48] and anion- [51, 52] exchangers, or those prepared in a laboratory [65,105] were used. Sorption of a basic compound is done at low pH values, and the sorbed ions are subsequently desorbed at high pH values by a mixture of an organic solvent with a suitable buffer [48] or ammonium [65]. Acidic compounds are sorbed at high pH values and desorbed by acid-modified organic solvents. In on-line modes, the analytes are desorbed by the mobile phase used in the analytical column [48, 51, 52].

Nielen et al. [48] observed that the increase in the concentration of the indifferent electrolyte had a negative effect on the retention of 3-amino-4-ethoxyacetanilide on a sulfonic acid-type silica based cation exchanger. This behavior was ascribed to the low capacity of the cation exchanger. To remove the competing ions, precipitation of calcium (II) with oxalic acid, and complexation of iron (III) with EDTA was proposed.

3.6 Metal-Loaded Sorbents

Some organic compounds can form very strong covalent bonds with metal ions. To trap these compounds, the metal ions can be dissolved in an aqueous solution, but a more advantageous approach is to immobilize them on a polymer or silica gel type support. A covalent bond between the internal orbitals of a metal ion and the functional groups of the support can serve for this immobilization. Other orbitals of the metal ion must remain free after its immobilization, to bind the ligands from the mobile phase. Besides accumulated analytes, other competitive ligands and metal ions as well as inorganic ions are usually also present in the aqueous sample. This fact has to be taken into account to establish the sorption conditions properly. The pH must be kept at the optimum value to prevent formation of hydroxides or release of the metal ions from the support. After the analytes have been sorbed, the column can be flushed with organic solvents to remove interference.

Analytes will be eluted by a change of pH value and introduction of a ligand which forms stronger bonds with the metal ions into the system. Another possibility is to flush the analytes out with a solution of a competitive metal ion. The mostly used polymer functional groups are 8-hydroxy-quinoline, thiol and 2-amino-1-cyclopentene-1-dithiocarboxylic acid (ACDA). Metal ions are mercury (II), silver (I), platinum (IV), palladium (II), *etc.*

A Pt (IV) - ACDA stationary phase was used for the analysis of phenylurea type herbicides in the presence of interfering anilines [46]. Anilines were bonded covalently on the precolumn, while the herbicides passed through into the analytical column. The precolumn was regenerated with acetonitrile. *Nielen et al.* [106] used a Hg(II) - 8-hydroxyquinoline stationary phase for the preconcentration of 2-mercaptobenzimidazole. A clean-up was carried out with a water-methanol solution (1:1). The analyte was replaced by cysteine. For the preconcentration of thiols, a Hg(II) - ACDA stationary phase was proposed [17]. Pt(IV) - ACDA and Pt(IV) - thiol phases were found to be suitable for the accumulation of anilines, and an Ag(I) - 8-hydroxyquinoline phase for accumulation of ethynyl type compounds [17].

Generally, it can be said that metal-loaded sorbents are a suitable tool when the selectivity is of prime importance. Unfortunately, they can be used only for classes of compounds which can form covalent bonds with metal ions.

3.7 Other Sorbents

Miscellaneous other sorbents were used for the preconcentration of organic compounds from aqueous samples. *Senin et al.* [59] accumulated butyl acetate on a TSVK-11a type zeolite, and eluted it with acetone. Another report deals with Chromosorb W covered with Carbowax 4000, and *n*-undecane serving for the preconcentration of polychlorinated biphenyls and chlorinated pesticides [107]. This sorbent was prepared by dissolving Carbowax 4000 and *n*-undecane in acetone, followed by the addition of Chromosorb W, mixing of the slurry and drying. For a Carbowax 4000/

C_{11} ratio of 5:50, the average recoveries were about 95%.

Generally, every solid support having an affinity for some organic compounds can serve as a sorbent for preconcentration. Its use for this purpose is, however, in fact determined by the question whether the whole procedure is effective and without excessive demands on labor, time, and costs.

4 Automation

Nowadays, sample preparation is usually the time-determining step in chromatographic analysis. Although the off-line SPE procedure usually shortens the time of sample handling, a certain amount of tedious labor remains. The means for reducing this time-consuming work is to automate the entire procedure as much as possible. At the present time, there is increasing interest in automated sample preparation, interfaced to HPLC or GC instruments via robotics and other on-line devices (even though off-line procedures are still used for GC, in the majority of cases). To resolve complex matrices, an improved separation of these multicomponent mixtures can be very effectively performed by multidimensional chromatography [column switching (MD/CS)] methods. Via MD/CS, the original sample can be fractionated by several subsequent separations, preconcentrated and cleaned up. This method has been used for analyzing samples of various origins [108]. The use of automated precolumn techniques in HPLC, for handling of aqueous samples, has been well reviewed [5, 6, 112], and several companies have introduced on-line devices for SPE (*e.g.* AASP from Varian Assoc., Walnut Creek, CA, USA, Prospekt from Spark Holland, Emmen, NL). Reports on on-line SPE/GC can also be found in literature [62].

As a support for precolumns used in automated SPE/HPLC, the same sorbent as used in the analytical columns is recommended [17]. Otherwise, additional band broadening can occur. Generally, factors which play an important role for additional band broadening are the geometry of the precolumn and the characteristics of the sorbent in the precolumn. *Goewie et al.* [109] recommended use of 2-10 mm long precolumns with 2-4.6 mm i.d. *Nondek* and *Chvalovsky* [110,111] demonstrated that the optimal volume of the precolumn is related to the volume and plate number of the analytical column and the capacity factor of the analyte to be preconcentrated. If the sorbent in the precolumn is not the same as in the analytical column, a rule of thumb states that the capacity factor of the analyte in the precolumn should be less than or equal to the k value in the analytical column. The incompatibility of the ST-DVB copolymer with bonded silicas can serve as an example [17]. When connected with a proper column, precolumns can be packed with various supports, *e.g.*, ST-DVB copolymers [41, 50], octadecyl bonded silica [50,109], pyrocarbon modified silica [36,40], ion-exchangers [17, 50, 51], and metal-loaded sorbents [17, 46]. Certain drawbacks of the on-line approach are the possibility of memory effects when the precolumn is re-used, and less flexibility with respect to the choice of eluting solvents. While the eluent in on-line systems is equal to the mobile phase used in the analytical column, a wide spectrum of solvents can be used for desorption in off-line SPE. However, the higher speed and the much lower labor requirements make on-line SPE the preferred method for sample preparation.

5 Advantages and Disadvantages of SPE

5.1 Advantages

The advantages can be considered in relation to various other sample handling methods. Since liquid-liquid extraction is the most popular sample preparation technique, it can represent the best choice as reference method for comparison with SPE. This approach has often also been used by other authors [2, 25]. The following advantages are those cited most frequently.

5.1.1 Sampling in the Field

With most preconcentration techniques, large volumes of aqueous samples have to be transported into the laboratory in glass containers. After on-site adsorption of the analytes onto a sorbent bed, it is necessary to transport only small cartridges. This method avoids possible breakage in transit, cuts transport costs significantly, and minimizes the possibility of changes of the sample, as described in the section on sample storage.

5.1.2 Speed and Simplicity

The simplest SPE procedure can be carried out using only a syringe and a SPE cartridge in the off-line mode. More sophisticated system modifications can include pumps, switching valves, centrifuges, vacuum pumps, and other means for more efficient sample preparation and designed to minimize operator's labor. Automation of SPE leads to shortening of the time required for sample handling, since the samples can be processed in parallel.

5.1.3 No Emulsion Formation

Emulsion formation is one of the greatest drawbacks in liquid-liquid extractions. It is often observed during extraction of biological liquids or waste waters. This problem is completely eliminated in SPE.

5.1.4 Safety

This sampling method minimizes the exposure of technicians to possibly hazardous samples. The fire and toxic hazards are also lower when compared to liquid-liquid extractions, since only small amounts of solvent are needed for elution of the analytes.

5.1.5 Low Costs

Besides the savings achieved by transporting only small cartridges, instead of large containers with samples to the analytical laboratory, additional savings are due to less material requirements. While large amounts of organic solvents are needed in liquid-liquid extractions, only a few ml's of solvent are needed at the most, and only a small cartridge containing up to 1 g of sorbent is needed for the SPE procedure. Moreover, the sorbent cartridge can be regenerated and thus re-used. According to *Junk* [2], even if the preconcentration column is used only once, the costs of SPE are 5-10 times less than those of liquid-liquid extraction.

5.1.6 Flexibility

While for liquid-liquid extractions only water-immiscible solvents can be used to elute the analytes from a SPE column, there are almost no limitations in the choice of mobile phase. Moreover, volatile and semivolatile analytes can be desorbed thermally. Considering that, it is obvious that sorbent accumulation provides great flexibility in sample handling. An additional considerable flexibility lies in the wide sorbent choice, ranging from non-polar supports to metal loaded sorbents with covalent interactions.

5.2 Disadvantages

The presence of competitive processes in the water-sorbent system, as described in Section 2.1, is probably the most serious disadvantage of SPE. Overloading of the column, or an early breakthrough due to blocking of the pores, are the undesirable results of the interactions between the sorbent and the components of the sample matrix. The interactions between the components of the sample matrix and the analytes also shift the equilibrium in the system and, thus, lower the recovery. Often, sorption of analytes onto suspended particles in the aqueous sample occurs (see Section 2.1). When these particles are too small, they penetrate through the column along with the sorbed analytes. Larger particles can be captured on the inlet sieve and, thus, the analytes can be desorbed even from these particles using a forward-flush mode. This capture, however, is not totally reliable and additional problems arise from increasing the back-pressure. Another disadvantage which can sometimes be observed is batch-to-batch variation even using the sorbents from one supplier. This variation reduces the reproducibility of the procedure, and hence also confidence in SPE.

6 Conclusions

The increasing number of citations and growing interest of scientists in both on-line and off-line SPE, as well as the expanding range of materials available from the producers, clearly show that the SPE method has become a reliable, useful tool for sample handling. The main reasons are its efficiency and flexibility. Although it is improbable that SPE will ever become the sole universal method that solves all problems in every sampling situation, it has already acquired great popularity. This can be extended by further increasing the reliability of the sorbents, and by attaining a thorough knowledge of the whole complex body of interactions in the water-sorbent system. A continuing increase in the automation of SPE can be expected. The off-line procedures, however, will remain important for field sampling (although partial automation can also be applied in this case). Besides this main line of development special trends will be pursued such as, *e.g* in-column derivatization or *in-situ* detection after sorption of analytes.

References

[1] *A. A. Rosen* and *F. M. Middleton*, Anal. Chem. **31** (1959) 1729.

[2] *G. A. Junk*, in "Organic Pollutants in Water", *I. H. Suffet* and *M. Malayiandi*, eds., ACS Symp. Series No. 214, Washington D.C. (1987) p. 201.

[3] *M. Dressler*, J. Chromatogr. **165** (1979) 167.

[4] *R. W. Frei* and *U. A. Th. Brinkman*, Trends Anal. Chem. **1** (1981) 45.

[5] *R. W. Frei, M. W. F. Nielen*, and *U. A. Th. Brinkman*, Int. J. Environ. Anal. Chem. **23** (1986) 3.

[6] *R. D. McDowall, J. C. Pearce*, and *G. S. Murkitt*, J. Pharm. Biomed. Anal. **4** (1986) 3.

[7] *L. Svoboda*, Chem. Listy **74** (1985) 943.

[8] *K. C. VanHorne*, ed., "Sorbent extraction technology handbook", Analytichem International Inc., Harbor City, CA, 1985.

[9] *Anon.*, "Sample Preparation and Isolation Using Bonded Silicas", Analytichem International Inc., Harbor City, CA (1986).

[10] *Anon.*, "Baker 10 SPE Applications Guide, Vol. 1", J. T. Baker Chemical Co., Phillipsburg, NJ (1982).

[11] *Anon.*, "Baker 10 SPE Applications Guide, Vol. 2", J. T. Baker Chemical Co., Phillipsburg, NJ (1984).

[12] *M. Zief*, "SPE for Sample Preparation", J. T. Baker Chemical Co. Phillipsburg, NJ, undated.

[13] *T. A. Bellar, J. J. Lichtenberg*, and *R. C. Kroner*, J. Am. Water Works Assoc. **66** (1974) 739.

[14] *K. J. Grob*, J. Chromatogr. **84** (1973) 255.

[15] *H. Borén, A. Grimvall, J. Palmborg, R. Sävanhed*, and *B. Wigilius*, J. Chromatogr. **348** (1985) 67.

[16] *H. S. Frank* and *M. W. Evans*, J. Chem. Phys. **13** (1945) 507.

[17] *M. W. F. Nielen*, Thesis, Free University, Amsterdam (1987).

[18] *V. Leoni, G. Puccetti, R. J. Colombo*, and *A. M. D'Ovidio*, J. Chromatogr. **125** (1976) 399.

[19] *C. W. Carter* and *I. H. Suffet*, Environ. Sci. Technol. **16** (1982) 735.

[20] *J. F. Pankow, M. P. Ligocki, M. E. Rosen, L. M. Isabelle*, and *K. M. Hart*, Anal. Chem. **60** (1988) 40.

[21] *K. Thyssen*, J. Chromatogr. **319** (1985) 99

[22] *R. E. Shoup* and *G. S. Mayer*, Anal. Chem. **54** (1982) 1164.

[23] *J. J. Richard* and *G. A. Junk*, Microchim. Acta **1** (1986) 387.

[24] *G. A. Junk* and *J. J. Richard*, Chemosphere **16** (1987) 61.

[25] *E. Chladek* and *R. S. Marano*, J. Chrom. Sci. **22** (1984) 313.

[26] *C. E. Rostad, W. E. Pereira*, and *S. M. Ratcliff*, Anal. Chem. **56** (1984) 2856.

[27] *W. A. Saner, J. R. Jadamec, R. W. Sager*, and *T. J. Kileen*, Anal. Chem. **51** (1979) 2180.

[28] *M. Akerblom*, J. Chromatogr. **319** (1985) 427.

[29] *G. Nyagah*, J. Chrom. Sci. **19** (1981) 500.

[30] *E. M. Thurman, R. L. Malcolm*, and *G. R. Aiken*, Anal. Chem. **50** (1978) 775.

[31] *G. A. Junk, J. J. Richard, M. D. Grieser, D. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz*, and *G. V. Calder*, J. Chromatogr. **99** (1974) 745.

[32] *J. W. Carr* and *J. M. Harris*, Anal. Chem. **60** (1988) 698.

[33] *L. R. Snyder* and *J. J. Kirkland*, "Introduction to Modern Liquid Chromatography", 2nd ed., Wiley, NY (1979).

[34] *D. J. Pietrzyk* and *J. D. Stodola*, Anal. Chem. **53** (1981) 1822.

[35] *S. Bitteur* and *R. Rosset*, Chromatographia **23** (1987) 163.

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

[37] *S. Bitteur* and *R. Rosset*, J. Chromatogr. **394** (1987) 279.

[38] *P. J. Schoenmakers, H. A. H. Billiet*, and *L. De Galan*, J. Chromatogr. **185** (1979) 179.

[39] *P. J. Schoenmakers* and *H. A. H. Billiet*, J. Chromatogr. **205** (1981) 13.

[40] *W. Golkiewicz, C. E. Werkhoven-Goewie, U. A. Th. Brinkman, R. W. Frei, H. Colin*, and *G. Guiochon*, J. Chrom. Sci. **21** (1983) 27.

[41] *B. Zygmunt, J. Visser, U. A. Th. Brinkman*, and *R. W. Frei*, Intern. J. Environ. Anal. Chem. **15** (1983) 263.

[42] *P. Lövkvist* and *J. A. Jönsson*, Anal. Chem. **59** (1987) 818.

[43] *M. P. Maskarinec, D. L. Manning, R. W. Harvey, W. H. Griest*, and *B. A. Romkins*, J. Chromatogr. **302** (1984) 51.

[44] *A. Lagana, G. Goretti, B. M. Petronio*, and *M. Rotatori*, J. Chromatogr. **219** (1981) 263.

[45] *A. Przyjazny*, J. Chromatogr. **346** (1985) 61

[46] *C. E. Goewie, P. Kwakman, R. W. Frei, U. A. Th. Brinkman, W. Maasfeld, T. Seshadri*, and *A. Kettrup*, J. Chromatogr. **284** (1984) 73.

[47] *J. F. Pankow, L. M. Isabelle*, and *T. T. Kristensen*, J. Chromatogr. **245** (1982) 31.

[48] *M. W. F. Nielen, R. W. Frei,* and *U. A. Th. Brinkman,* J. Chromatogr. **317** (1984) 557.

[49] *T. J. Good* and *J. S. Andrews,* J. Chrom. Sci. **19** (1981) 562.

[50] *M. W. F. Nielen, U. A. Th. Brinkman,* and *R. W. Frei,* Anal. Chem. **57** (1985) 806.

[51] *M. W. F. Nielen, G. De Jong, R. W. Frei,* and *U. A. Th. Brinkman,* Int. J. Environ. Anal. Chem. **25** (1986) 37.

[52] *J. De Jong, M. W. F. Nielen, R. W. Frei,* and *U. A. Th. Brinkman,* J. Chromatogr. **381** (1986) 431.

[53] *E. Brízová, M. Popl,* and *J. Coupek,* J. Chromatogr. **139** (1977) 15.

[54] *J. D. Navratil, R. E. Sievers,* and *H. F. Walton,* Anal. Chem. **49** (1977) 2260.

[55] *A. Bacaloni, G. Goretti, A. Lagana, B. M. Petronio,* and *M. Rotatori,* Anal. Chem. **52** (1980) 2033.

[56] *R. Koch, C. Kilz,* and *H. Hermenau,* Acta Hydrochim. Hydrobiol. **8** (1980) 635.

[57] *J. J. Richard* and *G. A. Junk,* Anal. Chem. **58** (1986) 723.

[58] *A. Tateda* and *J. S. Fritz,* J. Chromatogr. **152** (1978) 329.

[59] *N. N. Senin, S. Y. Filipov, N. F. Tolkina, G. A. Smolyaninov, S. A. Volkov,* and *U. S. Kukushkin,* J. Chromatogr. **364** (1986) 315.

[60] *V. N. Mallet, G. L. Brun, R. N. MacDonald,* and *K. Berkane,* J. Chromatogr. **160** (1978) 81.

[61] *M. J. M. Wells* and *J. L. Michael,* J. Chrom. Sci. **25** (1987) 345.

[62] *E. Noroozian, F. A. Maris, M. W. F. Nielen, R. W. Frei, G. De Jong,* and *U. A. Th. Brinkman,* J. High Resol. Chromatogr. Commun. **10** (1987) 17.

[63] *M. R. Rice* and *H. S. Gold,* Anal. Chem. **56** (1984) 1436.

[64] *P. C. Bardalaye* and *W. B. Wheeler,* Intern. J. Environ. Anal. Chem. **25** (1986) 105.

[65] *J. R. Kaczvinsky, K. Saitch,* and *J. S. Fritz,* Anal. Chem. **55** (1983) 1210.

[66] *B. W. Wright, C. W. Wright, R. W. Gale,* and *R. D. Smith,* Anal. Chem. **59** (1987) 38.

[67] *J. H. Raymer, E. D. Pellizzari,* and *S. D. Cooper,* Anal. Chem. **59** (1987) 2069.

[68] *Z. Voznáková, M. Popl,* and *M. Kovár,* Scientific Papers of the VSCHT, Prague, **H 19** (1984) 85.

[69] *J. F. Pankow* and *L. M. Isabelle,* J. Chromatogr. **237** (1982) 25.

[70] *B. Versino, H. Knöppel, M. DeGroot, A. Peil, J. Poelman, H. Schauenburg, H. Vissers,* and *F. Geiss,* J. Chromatogr. **122** (1976) 373.

[71] *D. R. Green* and *D. LePape,* Anal. Chem. **59** (1987) 699.

[72] *H. P. M. Van Vliet, Th. C. Bootsman, R. W Frei,* and *U. A. Th. Brinkman,* J. Chroma togr. **185** (1979) 483.

[73] *G. R. Aiken, E. M. Thurman, R. L. Malcolm,* and *H. F. Walton,* Anal. Chem. **51** (1979) 1799.

[74] *E. M. Thurman* and *R. L. Malcolm,* Environ. Sci. Technol. **15** (1981) 463.

[75] *J. A. Leenheer,* Environ. Sci. Technol. **15** (1981) 578.

[76] *Anon.,* "Standard Methods for the Examination of Water and Wastewater", 13th ed., American Public Health Association, New York, NY (1971) 259.

[77] *P. Van Rossum* and *R. G. Webb,* J. Chromatogr. **150** (1978) 381.

[78] *O. Chiantore, I. Novák,* and *D. Berek,* Anal. Chem. **19** (1988) 638.

[79] *A. K. Burnhem, G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec,* and *R. Willis,* Anal. Chem. **44** (1972) 139.

[80] *M. W. Tabor* and *J. C. Loper,* Intern. J. Environ. Anal. Chem. **19** (1985) 281.

[81] *P. Jones* and *G. Nickless,* J. Chromatogr. **156** (1978) 87.

[82] *A. O. Thurston,* J. Chrom. Sci. **16** (1978) 254.

[83] *J. C. Loper,* Mutation. Res. **76** (1980) 241.

[84] *H. J. Kool, C. F. Van Kreijl, H. J. Van Kranen,* and *E. De Greef,* Chemosphere **10** (1981) 85.

[85] *J. L. Robinson, J. John, A. I. Safa, A. K. Kimberly,* and *P. E. Griffith,* J. Chromatogr. **402** (1987) 201.

[86] *V. Niederschulte* and *K. Ballschmiter,* Z. Anal. Chem. **280** (1976) 369.

[87] *S. F. Stepan* and *J. F. Smith,* Water Res. **11** (1977) 339.

[88] *G. L. LeBel, D. T. Williams,* and *F. M. Benoit,* J. Assoc. Off. Anal. Chem. **64** (1981) 991.

[89] *P. P. K. Kuo, E. S. K. Chian, F. B. De Walle,* and *J. H. Kim,* Anal. Chem. **49** (1977) 1023.

[90] *W. Bertsch, E. Anderson,* and *G. Holzer, J.* Chromatogr. **112** (1976) 701.

[91] *A. Zlatkis, W. Bertsch, H. A. Lichtenstein, A. Tishbee, F. Shunbo, N. M. Liebich, A. M. Coscia,* and *N. Fleischer,* Anal. Chem. **45** (1973) 763.

[92] *J. M. Warner* and *R. K. Beasley,* Anal. Chem. **56** (1984) 1953.

[93] *C. Leuenberger* and *J. F. Pankow,* Anal. Chem. **56** (1984) 2518.

[94] *V. Leoni, G. Puccetti,* and *A. Grella,* J. Chromatogr. **106** (1975) 119.

[95] *P. R. Musty* and *G. Nickless,* J. Chromatogr. **100** (1974) 83.

[96] *H. D. Gesser, A. Chow, F. C. Davis, J. F. Uthe,* and *J. Reinke,* Anal. Lett. **4** (1971) 883.

[97] *D. K. Basu* and *J. Saxena,* Environ. Sci. Technol. **12** (1978) 791.

[98] *G. M. Josefson, J. B. Johnston,* and *R. Trubey,* Anal. Chem. **56** (1984) 764.

[99] *K. A. Burn* and *J. L. Smith,* Aust. J. Mar. Freshwater Res. **31** (1980) 251.

[100] *W. E. May, S. N. Chesler, S. P. Cram, B. H. Gump, H. S. Hertz, D. P. Enagonio,* and *S. M. Dyszel,* J. Chrom. Sci. **13** (1975) 535.

[101] *K. Zech* and *R. Huber,* J. Chromatogr. **353** (1986) 351.

[102] *P. J. Arnold* and *O. V. Stetten,* J. Chromatogr. **353** (1986) 193.

[103] *A. R. Oyler, D. L. Bodenner, K. J. Welch, R. J. Liukkonen, R. M. Carlson, H. L. Kopperman,* and *R. Caple,* Anal. Chem. Chem. **50** (1978) 837.

[104] *K. Ogan, E. Katz,* and *W. Slavin,* J. Chrom. Sci. **16** (1978) 517.

[105] *J. J. Richard, C. D. Chriswell,* and *J. S. Fritz,* J. Chromatogr. **199** (1980) 143.

[106] *M. W. F. Nielen, R. Bleeker, R. W. Frei,* and *U. A. Th. Brinkman,* J. Chromatogr. **358** (1986) 393.

[107] *P. R. Musty* and *G. Nickless,* J. Chromatogr. **120** (1976) 369.

[108] *H. G. Barth, W. E. Barber, C. H. Lochmüller, R. E. Majors,* and *F. E. Regnier,* Anal. Chem. **60** (1988) 387 R.

[109] *C. E. Goewie, M. W. F. Nielen, R. W. Frei,* and *U. A. Th. Brinkman,* J. Chromatogr. **301** (1984) 325.

[110] *L. Nondek* and *V. Chválovsky,* J. Chromatogr. **268** (1983) 395.

[111] *L. Nondek* and *V. Chválovsky,* J. Chromatogr. **312** (1984) 303.

[112] *C. J. Little, D. J. Tompkins, O. Stahel, R. W. Frei,* and *C. E. Werkhoven-Goewie,* J. Chromatogr. **264** (1983) 183.