Journal of Chromatography, 165 (1979) 167–206
Chromatographic Reviews

CHREV. 119

EXTRACTION OF TRACE AMOUNTS OF ORGANIC COMPOUNDS FROM WATER WITH POROUS ORGANIC POLYMERS

M. DRESSLER
Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, 611 42 Brno (Czechoslovakia)
(Received February 11th, 1979)

CONTENTS

1. INTRODUCTION

The determination of organic contaminants in water is fundamental to the solution of environmental protection problems. As waters are usually contaminated with a large number of compounds (*e.g.*, petroleum products), separation methods, particularly gas chromatography, are advantageous in analytical determinations, and a preferred arrangement is then combination of this separation method with the identification method, mass spectrometry. Samples of water of various origin can be subjected to chromatographic analysis in two basic procedures, either by direct injection of the polluted water or by concentration of the contaminants in the water prior to the analysis proper.

The method involving the direct injection of contaminated water into the gas chromatograph is subject to difficulties associated with the presence of water in the chromatograph, which in many instances makes the application of this method impossible. Its sensitivity is generally low (usually *ca.* 1 mg/l), although in some instances determinations down to 0.1 μg/l have been reported[1] (injection of up to 100 μl of water into a pre-column packed with diglycerol, which makes the retention time of water very long in comparison with those of the contaminants). Problems connected with direct injection, associated with the large volumes of water injected into the gas chromatograph, can be partly eliminated by a modification of the direct injection method, which uses water vapour as a carrier gas, by steam–solid chromatography[2]. The sensitivity of this procedure reaches[3] 10 μg/l in certain instances.

Relatively high concentrations of organic pollutants in water, which can be determined by using the direct injection method, are usually encountered only in certain emergency situations, and in most instances it is trace concentrations of compounds that must be determined. The investigation of water contamination with such low concentrations of compounds is a complex problem which can only be solved by using a concentration step prior to the determination proper. Extraction with a liquid, the headspace method and extraction with a sorbent are commonly used. Problems with liquid extraction are associated with the purity of the extraction agent, different quantitative and qualitative extraction efficiencies of various compounds with various extraction agents and a poor sensitivity (0.1 mg/l). The headspace technique, *i.e.*, analysis of the gaseous fraction that is in contact with and/or in equilibrium with water using stripping with an inert gas and subsequent concentration by freezing or adsorption on sorbents, is a fairly widespread and sensitive method (*e.g.*, refs. 4–6). Concentrations down to 10^{-12} g/l can be determined. A disadvantage of the method is its limitation to volatile substances.

Activated carbon (*e.g.*, refs. 7 and 8) and particularly porous organic polymers have recently been used for concentration from water by direct extraction with solid sorbents. The utilization of activated carbon for this type of concentration of trace compounds in water has been known for a number of years, and has been elaborated in detail and standardised [carbon chloroform extract (CCE) and carbon alcohol extract (CAE) methods]. The advantage of activated carbon is its high adsorption capacity, which permits the use of a small amount of sorbent for the extraction and a high thermal stability of the material, up to 700°. The basic requirement imposed on the concentration method is, however, that the identities and relative amounts of contaminants must not be affected by the concentration procedure. In this respect

the situation is not always advantageous[9–11] with activated carbon. Carbon does not adsorb completely all of the organic compounds dissolved in water, the desorption from the activated carbon is not always total and the compounds that are desorbed are not always identical with those which were extracted from water.

Considering the above problems associated with the use of activated carbon, the application of porous organic polymers, particularly non-polar polymers, as sorbents capable of concentrating water contaminants by the solid sorbent extraction method has been studied in detail.

2. PRINCIPLE OF THE METHOD

Extraction of trace amounts of organic compounds from water with a porous polymer is a method in which adsorption on a solid substance (porous polymer) is used in order to isolate compounds dissolved in water. Whereas liquid extraction is based on the distribution of the dissolved compounds between the extraction liquid and the water, with the partition coefficient being shifted in favour of the extraction liquid, sorbent extraction is based on the distribution of the dissolved compounds between the solid sorbent and water. In this instance, provided that the sorbent has been selected correctly, the partition coefficient is shifted even more towards the sorbent than in liquid extraction. Hence the principle is analogous to that of liquid extraction, the differences lying in the extraction materials used and in the resulting effect, the enrichment factor.

The basic factors that make the use of organic porous polymers advantageous for the extraction of trace concentrations of organic compounds from water are as follows:

(1) the partition coefficients of compounds in a polymer–water system tend to infinity if the polymer is selected correctly for the types of contaminants present;

(2) adsorption of water itself on the polymer is minimal;

(3) the "wettability" of the polymer with water makes possible the satisfactory transport of the substances towards the polymer surface;

(4) the polymer surface is inert.

Examples of the partition coefficients for porous polymer–liquid systems are given in Table 1. The sorbent used is a styrene–divinylbenzene copolymer, Porapak Q. In this instance[12], the extraction of hydrocarbons from water is obviously highly efficient, the separation coefficient being infinite.

TABLE 1

PARTITION COEFFICIENTS IN PORAPAK Q–LIQUID SYSTEM[12]

Liquid	*Partition coefficient*			
	o-Xylene	*Naphthalene*	*Benzene*	*Toluene*
Cyclohexane	1.43	0.98	—	—
Acetone	1.43	1.93	—	—
Isopropanol	1.75	—	—	—
Methanol	2.73	—	—	—
Water	∞	∞	∞	∞

In general, hydrophobic molecules are attracted from aqueous solutions by the hydrophobic surface of the sorbent and hydrophilic molecules, in contrast, by the hydrophilic surface. Hydrophobic non-polar sorbents can thus be used to concentrate hydrophobic compounds with the adsorption capacity of the sorbents increasing with increasing hydrophobicity and decreasing polarity of the compounds (decreasing solubility in water). Adsorption of fatty acids on Amberlite XAD-2 and alkyl benzenesulphonates on SP-1 resin can be cited as examples. From 100 ml of aqueous solution of propionic, butyric and valeric acids, containing 10 g/l of the fatty acid, 0.040, 0.077 and 0.116 g of the acid, respectively, is adsorbed per gram of the resin. The adsorption capacity of the sorbent thus increases as the chain length of the fatty acid increases[13]. A similar situation exists with alkyl benzenesulphonates, where the adsorption capacity increases with increasing length of the alkyl chain[14] [$C_9 = 9.9$, $C_{10} = 15.3$, $C_{11} = 18.4$ and $C_{12} = 19.8$ g/l (concentration of compounds 0.5 g/l)]. With the use of non-polar polymers the adsorption forces are predominantly of the Van der Waals type. Hence by changing the hydrophobic/hydrophilic balance of the adsorbed molecule, the range of its sorption can be changed to advantage. For example, weak acids are adsorbed on Amberlite XAD-2 more strongly in the acid than in the salt form, and they can therefore be easily desorbed after the extraction by elution with sodium hydroxide solution[13].

Capacity factors, k', (mass of the solute sorbed on the resin divided by the mass of the solute present in the void volume of the column) show[15] that Amberlite XAD-8 resin apparently favours aliphatic over aromatic and alicyclic carbon systems. For functional groups, the order of preference is $-CH_3 > -CO_2H > CHO > OH \geqslant -NH_2$. In both instances the order follows an inverse solubility trend. If the logarithm of the aqueous molar solubility, S, is plotted against $\log k'$, a well defined linear relationship exists with a correlation coefficient of 0.9 (significant at less than 0.001). The equation is $\log k' = 1.77 - 0.52 \log S$. This relationship emphasizes that although the absolute retention depends on both the eluent and the sorbent, the interaction between the solute and the solvent decides the selectivity for the resin. By substituting the molar solubility into the regression equation, the capacity factor can be predicted, to a first approximation, for any organic solute from natural waters on the resin. It was found[16] empirically that the amount of sample is related to the resin volume before breakthrough occurs by the equation $6X = k'Y$, where X ml is the volume of sample and Y cm^3 is the bed volume of the concentration column. With this equation and the $\log k'$ *versus* $\log S$ plot, resin to sample ratios can be adjusted for the maximal sorption of the solute of interest. Other non-ionic Amberlite XAD resins (XAD-1, -2, -4 and -7) show similar $\log k'$ *versus* $\log S$ relationships[15].

The adsorption of water on the polymer is very low. An idea of its extent can be gained from gas chromatographic retention data. Usually, water is eluted from the columns packed with porous polymers close to propane (see various sorbents).

Investigations of porous polymers showed that their surfaces are inert. The factors which could, under certain circumstances, affect the inertness of their surfaces are discussed for the corresponding sorbents.

2.1. Extraction

The extraction procedure is as follows (Fig. 1). The water sample is passed,

usually with the aid of a pump, through a concentration column packed with a polymer, where the sorption of organic compounds occurs. The adsorbed compounds are then desorbed from the polymer and analysed chromatographically. The concentration column (Fig. 1) consists (from bottom to top) of a porous septum overlayered with a sorbent, a layer of glass pellets, a layer composed of a mixture of Celite (inert material used in GC as a support for the stationary phase) and silanized glass-wool and a further layer of glass pellets. The weight of the polymer used is usually expressed in grams. The reason for using a two-step concentration column, which contains an inert material in its upper part, *i.e.*, in the part through which water passes first, is that the presence of mineral oils in water at parts per million levels decreases considerably the adsorption of compounds on the sorbent and these compounds remain dissolved in the water (as established[17] for phosphorus-containing pesticides), even after passing through the concentration column. This phenomenon is caused by deactivation of the sorbent and can be eliminated with the aid of the arrangement described above in which the oils are trapped in the first part of the column[17].

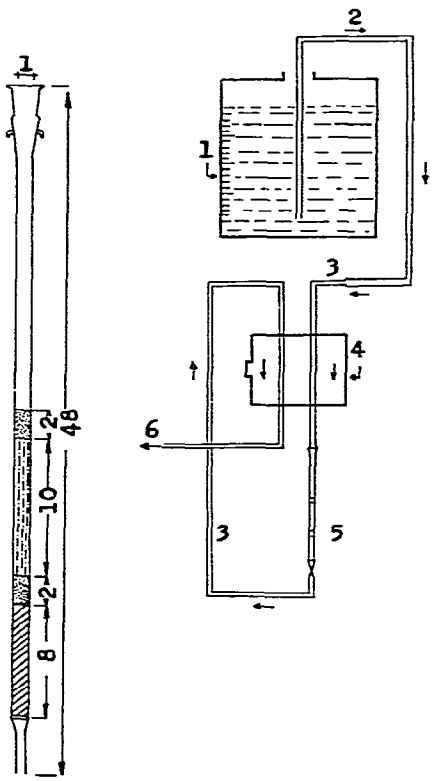

Fig. 1. Equipment for extraction[17]. 1 = Glass container; 2 = glass tubes; 3 = silicone rubber hose; 4 = peristaltic pump; 5 = glass adsorption column; 6 = extracted water discharge. Left: adsorption column (dimensions in centimetres). From bottom to top: Tenax, glass pellets, mixture of Celite and plugs of silanized glass-wool, glass pellets.

In addition to these so-called macro-samplers, a mini-sampler[18,19] has also been described in which the amount of the resin used is *ca.* 80 mg. The arrangement is generally used for small volumes of water. The volume of water treated is about 100 ml (compared with 1–100 l on the macro-scale). The application of the mini-sampler is particularly advantageous if volatile components[18] are to be investigated.

On passing water containing organic compounds through the concentration column, a chromatographic process occurs which proceeds as frontal chromatography because the flow-rate of the water and the concentrations of the compounds in the streaming water are constant. The compounds are extracted from the water by the sorbent according to their partition coefficients for the particular sorbent–water system. If a sorbent is used such that the partition coefficient of the investigated compounds dissolved in water is advantageous towards the sorption, all of the compounds contained in trace concentrations in water are trapped first on the column and the water leaving the column is free of them. After a certain time, after passing a certain volume of the contaminated water, a reverse breakthrough occurs and the water leaving the concentration column again contains organic compounds. From the viewpoint of the maximal concentration effect, the ideal state is reached if the trapping of contaminants on the sorbent is 100%. This depends on a number of factors, particularly the sorbent used, the structure of the compounds under investigation, the composition of the aqueous solution and the original concentrations of the compounds in water. These dependences are illustrated[20] in Fig. 2 for the styrene–divinylbenzene copolymer Synachrom E5. The range of the amounts introduced into the extraction column, where the extraction reaches 100% (with the use of pure solutions of one component only), differs for xylene, quinoline and cresol. For quinoline and creasol it increases with increasing concentration of the solution under investigation. As the concentration of the incoming solution increases, the total adsorption capacity, given by the maximal amount trapped, also increases. For instance, the adsorption capacity is 19 mg for quinoline at a concentration of 20 ppm for the given concentration column, and 341 mg at a concentration of 500 ppm. In the presence of more than one component in the aqueous solution substantial changes occur in the sorption of quinoline and cresol in comparison with pure solutions (Fig. 2C). Mutual interactions occur among the individual components in the adsorbed layer, the extent of these interactions being the higher the greater are the differences in their adsorption forces. The presence of cresol leads to an increased adsorption of quinoline and, *vice versa*, quinoline decreases the sorption of cresol. Xylene does not influence significantly the detailed course of the adsorption of cresol and quinoline; it only increases the equilibrium amount adsorbed, and more distinctly for lower than for higher inlet concentrations[20,21].

2.2. Desorption

Desorption of the compounds from the concentration column can be performed either with a liquid or by heating.

2.2.1. Liquid desorption

Once the extraction is finished, a small volume of liquid, for which the partition coefficient in a given polymer–eluent system is, for the compound being studied,

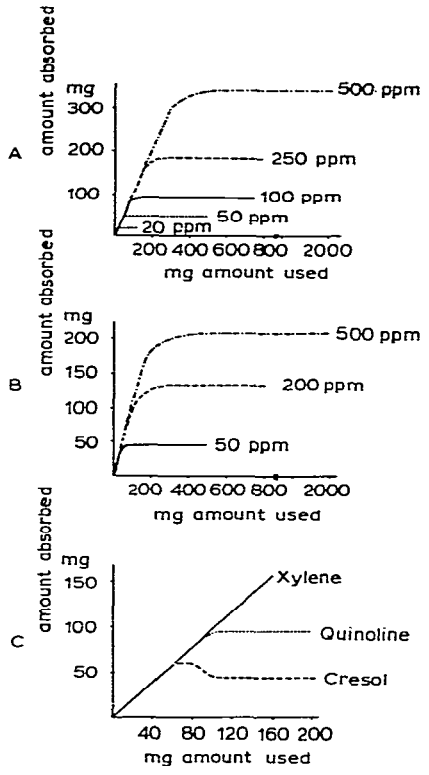

Fig. 2. Dependence of the amount of adsorbed compound on the amount of compound used for the extraction[20]. (A) Quinoline, solution concentrations 20, 50, 100, 250 and 500 ppm; (B) cresol, solution concentrations 50, 200 and 500 ppm; (C) quinoline, cresol and xylene, solution concentrations 50 ppm of each compound.

shifted in favour of the eluent (diethyl ether[22,23], *n*-hexane[24], acetone[12,25], isopropanol[26], methanol[21,27], methyl isobutyl ketone[28], pyridine[18,29]), is allowed to pass through the column. Knowledge and experience from adsorption thin-layer chromatography and liquid chromatography can be used to advantage and the system of eluotropic series[30] can be applied to the selection of the eluent liquid. However, one must take into account that with non-polar polymers a reversible system is involved and the increase in solvent strength will, therefore, have a course that is the reverse of that of a normal eluotropic series. For orientation, a system containing activated carbon can be used where the solvent strength increases in the sequence water < methanol < ethanol < acetone < propanol < diethyl ether < butanol < ethyl acetate < *n*-hexane < benzene. As the liquid passes through the concentration column, a process that is the reverse of the extraction process occurs and the compounds are desorbed from the sorbent. The compounds originally present in the water are now contained in the eluate.

The volume of the eluent required for the total desorption is usually tens of millilitres (*e.g.*, the optimal procedure elaborated[22] for the styrene–divinylbenzene copolymer Amberlite XAD-2 requires 25 ml). Gas chromatography is most often

used for the subsequent determination of the contaminants and thus only a part of this volume can be used for the analysis. This means that only *ca.* 0.01–0.1 % of the total amount of the compounds that were trapped by the sorbent can be used for the determination itself. This situation is, of course, unfavourable from the viewpoint of the sensitivity of the method. Therefore, the extract is concentrated[22] by evaporating the eluent to a volume of 1 ml. However, even this volume is still too large to be injected into the gas chromatograph and, therefore, even in this instance only a portion, *ca.* 0.1–1 %, of the total amount desorbed is used for the analysis itself. The advantage of this procedure is, however, that several analyses can be carried out from a single extract. On the other hand, a risk of losses, particularly of compounds with lower boiling points, is introduced if concentration of the eluate is performed by evaporation of the eluent.

The difficulties associated with the concentration of the extract with large volumes of the eluent are eliminated by using a mini-sampler method (see Section 2.1.) when 1–2 ml[18] or 50–100 μl[19] of the eluent agent are sufficient for the desorption.

The presence of the eluent liquid in the solution used for the gas chromatographic analysis is another problem brought about by liquid desorption. A peak due to the eluent is present in the chromatogram and, as the eluent is in excess, its peak may overlap some peaks of the compounds extracted from the water. In some instances the peak of the eluent can be eliminated by using an abstraction pre-column. For instance, pyridine was used for desorption by Chriswell and co-workers[18,29]. The peak of this solvent can be removed selectively on a pre-column packed with copper(II) chloride. However, the method suffers from two drawbacks: amines, if present, are also removed together with pyridine and compounds which are not eluted in the course of the analysis at the temperatures at which the pre-column can be used efficiently cannot be determined.

The arrangement in which liquid chromatography[31–34] is used for determination is an interesting variant of liquid desorption. A diagram of this arrangement is shown in Fig. 3. In this instance[31] the concentration column is situated before the analytical column of the liquid chromatograph. During the extraction water passes through the concentration column while the analytical column is disconnected.

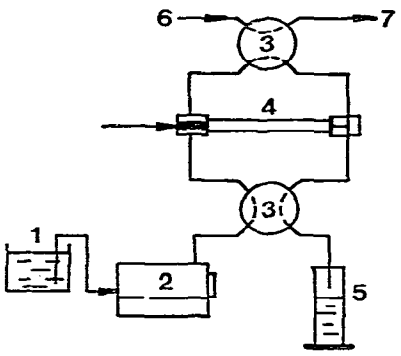

Fig. 3. Diagram of arrangement using liquid chromatography[31]. 1 = Glass container; 2 = pump; 3 = four-way stopcock; 4 = concentration column; 5 = waste; 6 = joint with the pump of the liquid chromatograph; 7 = joint with the analytical column of the liquid chromatograph.

When the extraction is completed, the concentration column is connected to the analytical column and to the inlet of the carrier liquid. The compounds adsorbed are now desorbed from the concentration column by the eluent directly into the chromatographic column. The carrier liquid is thus used as an eluent, and a gradient or heating of the concentration column can also be applied at the same time.

2.2.2. Thermal desorption

In thermal desorption the concentration column is situated before the analytical column of the gas chromatograph and is heated to an appropriate temperature during the desorption. The desorption process is similar to that of headspace analysis. As a consequence of the action of heat, desorption of the compounds occurs and these are then transported by the carrier gas into the chromatographic column. The increase in temperature during the desorption to a required value (measured directly in the polymer bed) proceeds for a certain period of time (up to several minutes) and differs for various polymers[35]. Hence it is important that the desorption time is sufficiently long for the given polymer that all of the compounds concentrated on the column are totally desorbed. In order to eliminate the peak broadening that occurs with this method of "injection" into the chromatographic column, the first portions of the chromatographic columns are usually cooled (*e.g.*, refs. 6, 32, 36 and 37) and only after finishing the "injection" are they heated to the temperature required for the analysis. The use of temperature programming has also been described for thermal desorption using the same polymeric sorbent for both the concentration and analytical columns[38].

The temperature used for the desorption must be such that all of the compounds contained in the sorbent are transferred from it into the gaseous phase within a reasonable time. One of the drawbacks of activated carbon is that the temperature required for desorption is so high that many substances decompose.

The maximal desorption temperature is determined by the maximal temperature at which the chromatographic background of the sorbent applied is acceptable from the analytical viewpoint. Fig. 4 shows gas chromatograms obtained by flash heating of Tenax and Amberlite XAD-2 to 400° and 275°, respectively. The chromatographic background of polymers of the Amberlite type is large and complex, whereas chromatographic analysis of Tenax heated to the temperature higher by 125° gives a small number and small amounts of volatile products[32]. On comparing Chromosorb 102, 105 and 106, Chromosorb 102 was found[39] to be the least suitable as its chromatographic background is large (obviously caused by thermal or oxidative decomposition). Reactions with oxygen, similar to those occurring with Chromosorb 102, also appeared[40] with Porapak Q.

The total amount of the extracted compounds is analysed following desorption of this type. Hence lower concentrations (by 2–3 orders of magnitude) of the compounds can be found in water than in the case of liquid desorption, but the extracted sample is consumed completely in the analysis.

3. REQUIREMENTS REGARDING THE MATERIAL USED

The purity of all of the chemicals that are used and the procedure for the preparation of the solutions for the analyses are of fundamental importance for the

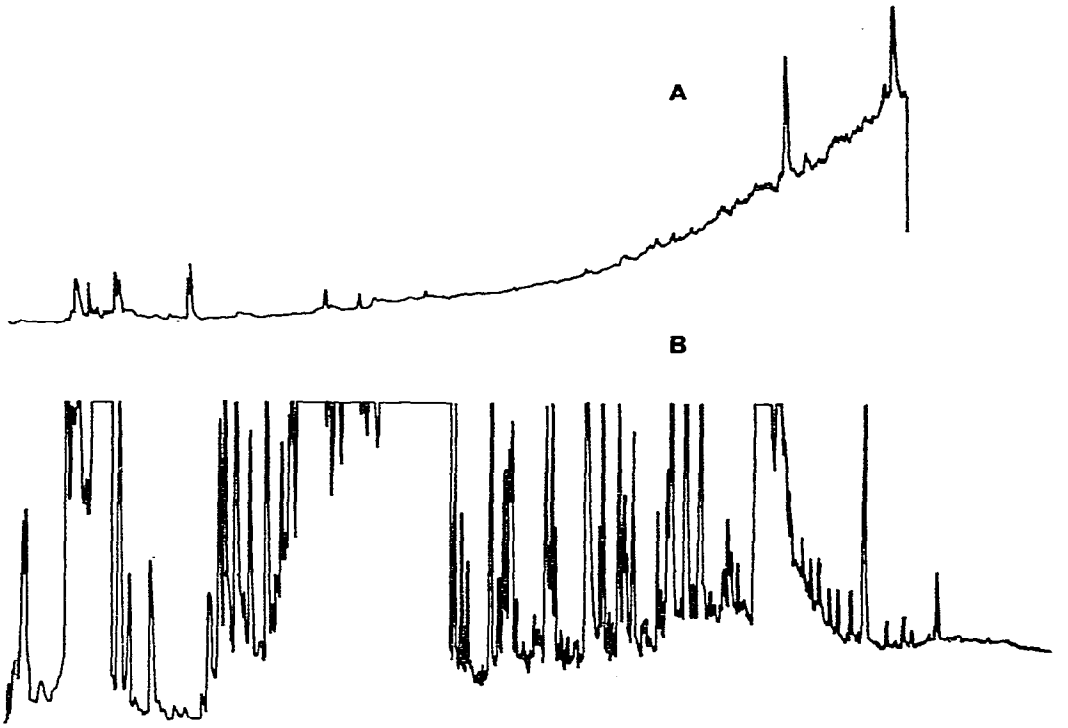

Fig. 4. Polymer blanks[32]. (A) Tenax, 400°; (B) Amberlite XAD-2, 275°.

determination of trace concentrations of substances in water. Particular attention must therefore be devoted to these problems even if the method of extraction with a polymer is applied.

3.1. "Pure" water

Water completely free from organic substances in detectable concentrations must be available for the preparation of model and calibration solutions and for blank experiments. Distilled water is usually not suitable for these purposes and must, therefore, be further treated. If only volatile compounds are present, boiling of water in a pure atmosphere is sufficient. In order to treat water that contains substances with higher boiling points, desorption pre-columns are used in which the distilled water passes through the sorbent packed in these columns and dissolved substances are adsorbed. Porapak Q[33], Amberlite XAD-2 and activated carbon[22,41], permanently bound phases (Bondapak)[33] and Tenax[42] are used as adsorption materials. "Pure" water obtained in this manner should not be stored for longer than 3 days[33].

Chriswell[43] described a procedure called spray vaporization, which leads to a significant reduction in the concentration of most gas chromatographable organic compounds. The technique consists in the atomization of water into a high-velocity gas stream (Fig. 5). A very fine mist of water is created which hits the glass surface, where it condenses and falls into a reservoir. This arrangement produces 600 ml of water per hour.

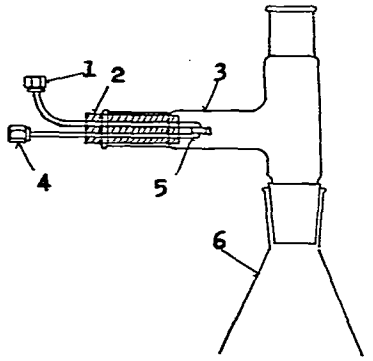

Fig. 5. Spray vaporization device[43]. 1 = Water inlet; 2 = PTFE stopper; 3 = connecting tube; 4 = air inlet; 5 = spray head from throat sprayer; 6 = reservoir.

3.2. *Solvents*

Essentially no solvent may be considered pure[44] for trace analysis and they must therefore be purified prior to use. For instance, acetone is purified by distillation[11] in a glass apparatus[45], *n*-hexane by distillation after sulphonation of aromatic impurities and nitration[45,46], and methanol by distillation[47].

3.3. *Standards*

Considering that the amount of standards added to solutions in quantitative analytical techniques should be comparable to the contents of impurities, a purity of 99% is sufficient even for the trace analysis. Compared with the demands on the purity of standards, the demands on the purity of water, glass and other facilities are much more stringent.

3.4. *Inorganic compounds*

The procedures for the determination of trace concentrations of organic compounds in water sometimes involve the use of inorganic compounds in order that the residues of water in the eluent after the desorption may be eliminated on the one hand, and as an addition to the solutions in order that the volatility of the substances may be increased on the other. These materials can act as a source of impurities and their purification prior to use is advantageous. For example, sodium sulphate, which is most often used for these purposes, is heated in a muffle furnace for 2 h in order to remove[22] the residues of organic compounds.

3.5. *Materials used for water treatment*

Strict demands on the conditions must be followed during the storage of "pure" water, calibration mixtures and water samples and during the analysis itself. Glass vessels must be used for these purposes. Rubber and synthetic materials, with the exception of Teflon[24,47], must not be used[44]. Water that had come into contact with plastic material was found[33,42] to contain compounds originating from these materials (*e.g.*, phthalates; *cf.*, Fig. 8). Junk *et al.*[41] investigated the contamination of "pure" water due to its passage through a synthetic polymer tube. The concentrations of organic contaminants were in the range 1–5000 ppb, depending on the type

of polymer and flow-rate of water through the tube. The contaminants consist of a very complex mixture of substances, some of which are toxic (*e.g.*, butyl chloroacetate). They originate from plasticizers and other additives contained in the polymers and from impurities in the starting materials which become trapped during the polymerization process.

In order to purify glass materials, mostly washing with detergents, rinsing with "pure" water and several-fold washing with methanol[22] or multiple washing with distilled water, acetone and *n*-hexane with glass drying at 130° after each wash are used[24]. Some workers[48] do not recommend washing with organic solvents and use only several-fold washing with tap water.

Sorption of trace amounts of dissolved compounds on the walls of the vessels can occur[17] and hence the quantitative results can be distorted. The adsorption of insecticides on glass and glass-wool from aqueous solutions at parts per billion concentrations was investigated, for instance, in such a manner that water was pumped through an empty glass column and the column was then washed with an eluent (10% of diethyl ether in *n*-hexane). The extent of adsorption was up to 32% for *p,p'*-DDE (Table 2). Similarly, the use of glass-wool during the extractions can also represent a source of impurities. Schwartz[49] found that the amount of organic matter on glass-wool that was extractable with pentane and dichloromethane can be up to 0.5 mg/g. The most efficient means of eliminating the impurities was treatment of the glass-wool for a few minutes with hydrogen chloride followed by continuous extraction in a Soxhlet extractor with dichloromethane for 24 h.

TABLE 2

SORPTION OF INSECTICIDES ON GLASS AND GLASS-WOOL [46]

Insecticide	*Concentration (ppb)*	*Amount adsorbed (%)*
α-BHC	1	1
Lindane	1	2
β-BHC	1	0
Aldrin	1	21
p,p'-DDE	2	32
Dieldrin	1	7
Endrin	10	0
o,p'-DDT	10	29
p,p'-DDE	10	12
p,p'-DDT	10	16

3.6. Model solutions

The solubility of some organic compounds, *e.g.*, alkanes, is low and the preparation of their model solutions in water therefore requires particular attention. Their preparation by dissolving the compounds directly in water results in large errors. Their preparation from solutions of the substances in organic solvents proved to be advantageous[5,22]. The solution is first prepared at a concentration such that after dissolution in water the required concentration is obtained and this solution is mixed only with water. It is not recommended to add more than 20 μl of the solution per litre of water[5]. Methanol[42,44], diethyl ether[22] and acetone[5,11,17,48] are used as solvents. A disadvantage of this procedure appears, of course, if contaminants

at concentrations below the parts per million level are to be analysed by gas chromatography, as the peak of the solvent utilized can overlap the peaks of the contaminants themselves.

Tateda *et al.*[19] verified the assumption that the addition of an organic solvent might solubilize the organic solutes. They found that 10% and 20% of methanol and 5% and 10% of acetone have little effect on many compounds tested (concentrations of 100 and 10 ppb). The only compound that showed a remarkable effect was methyl palmitate. More soluble compounds, such as hexanol, benzene and benzaldehyde, however, show an inverse effect in that their recovery is substantially lower.

With more volatile non-polar compounds a considerable proportion of these compounds occurs over the liquid, which, *e.g.*, in the case of hydrocarbons, can be up to 80%. It is therefore necessary to take into consideration the fact that, in contrast to polar compounds, calibration systems are used. After the transfer of such a calibration system, this system is no longer usable. Hence the most suitable means of storage is in a perfectly leak-proof vessel that does not contain any gaseous phase.

4. APPLICATIONS

4.1. Amberlite

The manufacturer of Amberlite sorbents is Rohm & Haas, Philadelphia, Pa., U.S.A.

4.1.1. XAD-2

Amberlite XAD-2[13] is a styrene–divinylbenzene copolymer of hydrophobic character. The average pore diameter is 85–90 Å and the specific surface area is 290–330 m^2/g (dry polymer). The grain size of common commercially available material is 20–50 mesh.

Junk and co-workers[22,41] recommend the following procedure for the treatment of the sorbent. Fine copolymer particles are decanted in methanol several times and the residual polymer is extracted in a Soxhlet extractor for 8 h each with methanol, acetonitrile and diethyl ether. The purified sorbent is stored in a glass vessel under methanol. This purification procedure proved to be more suitable than degassing at 225° and 10^{-7} torr or than thermal desorption in an inert gas at 200°. To prepare the concentration packing, the purified resin is added to a column as a methanol slurry until a bed of polymer *ca.* 6 cm high is obtained. Methanol is allowed to drain until its level reaches the top of the polymer bed. The polymer is then washed three times with 20 ml of "pure" water. The flow of water is stopped each time the sorbent surface is reached.

The extraction proper is performed at a water flow-rate of 30–50 ml/min. After most of the sample has passed through the column and the water level is at the top of the sorbent, the walls of the reservoir from which the water was taken are washed twice with 20 ml of "pure" water. The second 20 ml of this "pure" water are allowed to drain through the adsorption column completely. The desorption is carried out by eluting 20 ml of diethyl ether, which is allowed to be sucked into the column and to be in contact with the polymer for 10 min. Then it is drained off and an additional 5 ml of diethyl ether are added and allowed to run off. The residue of water (0.5–2 ml) in the eluate is frozen out by immersing into liquid nitrogen for 10

sec. The eluate is concentrated to 1 ml. Immediately after the elution methanol is added to the sorbent. It is allowed to pass through the column and the polymer is stored under a further 15 ml of methanol.

The polymer can be dried to such an extent in prolonged contact with air that on repeated wetting with water total hydration cannot be obtained. In this instance the manufacturer recommends[13] the following procedure in order to ensure the proper functioning of the polymer as a concentration medium. The polymer is placed in a column and methanol is added in such an amount that its level is above the polymer. The column is allowed to stand for 15 min and then the methanol is displaced by an ascending stream of water. After removing air bubbles, the column is washed with *ca.* 20 bed volumes of water in a descending manner with, and always in such a way that the bed does not become dry.

The manufacturer washes the material prior to delivery with a solution containing 5% of sodium chloride and 1% of sodium carbonate in order to control the growth of bacteria and moulds. The commercial hydrated polymer must therefore be washed with water prior to use.

The basic parameter that is used if the sorbents are employed for concentrating compounds in water is the so-called "recovery", which is defined as the amount of the compound determined in a model solution after completing the concentration procedure compared with the amount originally present in the model solution. Hence it characterizes the ability of the sorbent to trap the compounds from solution and to release them during the adsorption process. Table 3 shows these characteristics for Amberlite XAD-2. The concentrations of the various types of compounds were in the range 10–100 ppb, and those of pesticides in the ppt range*.

Partially dissociated organic molecules are adsorbed weakly[22]. The percentage of these compounds adsorbed by the polymer is less for very dilute solutions where the dissociation is more complete (*e.g.*, 44% of 1-naphthol is adsorbed at concentrations up to 50 ppb, whereas none is adsorbed at a concentration of 2 ppb). The recovery of organic acids and phenols is also associated with dissociation and is dependent on pH. In acidic media the recovery increases and an aqueous solution of these compounds must be acidified prior to the extraction. Octanoic acid, the recovery for which is 22% prior to and 91% after the addition of hydrochloric acid, can serve as an example[22] (compare with Table 4).

Many acidic compounds were found to be desorbed with aqueous solutions of bases (*e.g.*, 0.05 *M* sodium hydroxide solution) without washing out the neutral compounds. The elution of some substituted phenols is, however, slow or incomplete. Basic compounds (with the exception of indole) are only eluted with an acid (1.0 *M* hydrochloric acid). Hence a pre-separation[22,23] can be accomplished in the column; acidic and basic fractions can be washed (with 0.05 *M* sodium hydroxide solution and subsequently with 1 *M* hydrochloric acid) prior to the elution of the neutral fractions with diethyl ether.

Ionic inorganic compounds and also strongly ionic organic compounds (benzenesulphonic, *p*-toluenesulphonic and 4-naphtholsulphonic acids) are not adsorbed[23]. Weakly ionic organic compounds (carboxylic acids, phenols and amines),

* Throughout the article, the American billion (10^9) and trillion (10^{12}) are meant.

TABLE 3

OVERALL RECOVERY OF THE METHOD FOR THE USE OF AMBERLITE XAD-2[22]

Compounds tested	*Recovery (%)*	*Compounds tested*	*Recovery (%)*
Alcohols		*Alkylbenzenes*	
Hexanol	93	Ethylbenzene	81
2-Ethylhexanol	99	Cumene	93
2-Octanol	100	*p*-Cymene	92
Decanol	91	*Halogen compounds*	
Dodecanol	93	Benzyl chloride	88
Benzyl alcohol	91	Chlorobenzene	95
Cinnamyl alcohol	85	Iodobenzene	81
2-Phenoxyethanol	102	*o*-Dichlorobenzene	88
Aldehydes and ketones		*m*-Dichlorobenzene	93
2,6-Dimethyl-4-heptanone	93	1,2,4,5-Tetrachlorobenzene	74
2-Undecanone	88	α-*o*-Dichlorotoluene	96
Acetophenone	92	*m*-Chlorotoluene	80
Benzophenone	93	2,4-Dichlorotoluene	71
Benzil	97	1,2,4-Trichlorobenzene	99
Benzaldehyde	101	*Nitrogen compounds*	
Salicylaldehyde	100	Hexadecylamine	94
Esters		Nitrobenzene	91
Benzyl acetate	100	Indole	89
Dimethoxyethyl phthalate	94	*o*-Nitrotoluene	80
Dimethyl phthalate	91	N-Methylaniline	84
Diethyl phthalate	92	Benzothiazole	100
Dibutyl phthalate	99	Quinoline	84
Di-2-ethylhexyl phthalate	88	Isoquinoline	83
Diethyl fumarate	86	Benzonitrile	88
Dibutyl fumarate	92	Benzoxazole	92
Di-2-ethylhexyl fumarate	84	*Ethers*	
Diethyl malonate	103	Dihexyl ether	75
Methyl benzoate	101	Dibenzyl ether	99
Methyl decanoate	95	Anisole	87
Methyl octanoate	98	2-Methoxynaphthalene	97
Methyl palmitate	70	Diphenyl ether	91
Methyl salicylate	96	*Pesticides and herbicides**	
Methyl methacrylate	35	Atrazine	83
Polynuclear aromatics		Lindane	95
Naphthalene	98	Aldrin	47
2-Methylnaphthalene	95	Dieldrin	93
1-Methylnaphthalene	87	DDT	96
Biphenyl	101	DDE	81
Fluorene	84		
Anthracene	83		
Acenaphthene	92		
Tetrahydronaphthalene	62		

* Concentrations, with the exception of atrazine, were 20 ppt.

depending on pH, either are or are not adsorbed, which can again create conditions suitable for pre-separation on the column[23]. The polymer has a lower concentration efficiency for low-molecular-weight aliphatic compounds than for aromatic compounds. With increasing molecular weight in a homologous series the efficiency also increases[23]. The recoveries for some other compounds are shown in Table 5.

TABLE 4

INFLUENCE OF THE pH OF THE SOLUTION ON RECOVERY[22]

Compounds	*Recovery (%)*	
	Distilled water	*+5 ml of HCl*
Acids		
Octanoic acid	22	108
Decanoic acid	8	80
Palmitic acid	32	101
Oleic acid	32	100
Benzoic acid	7	107
Phenols		
Phenol	41	40
o-Cresol	62	73
3,5-Xylenol	71	79
o-Chlorophenol	70	96
p-Chlorophenol	75	95
2,4,6-Trichlorophenol	72	99
1-Naphthol	43	91

Junk *et al.*[22] investigated the influence of different operating conditions on the recovery. The use of a finer grain size (150 mesh), a change in concentration (from tens of ppb to tens of ppm), a change in the flow-rate through the column and the addition of up to 50 g of sodium chloride per litre produced no significant change. On studying the concentration of sterols in waste waters, it was found[50], however, that the operating conditions do have an influence. A finer grain size (60–120 mesh) increases the recovery, whereas an increase in the flow-rate (3–7 ml/min),

TABLE 5

RECOVERIES WITH THE APPLICATION OF AMBERLITE XAD-2[23]

Compound	*Concentration (ppm)*	*Recovery (%)*
Methyl isobutyl ketone	100	100
n-Hexanol	200	85
Ethyl butyrate	100	100
Naphthalene	0.05	100
Benzenesulphonic acid	3.0	31
p-Toluenesulphonic acid	9.0	23
Benzoic acid	1.0	23
Benzenesulphonic acid (pH 3.2)	1.0	100
Phenylenediamine	0.9	98
2-Hydroxy-3-naphthoic acid	0.6	39
Phenol	0.4	45
Phenol*	0.4	86
2,4-Dimethylphenol	0.4	100
p-Nitrophenol	0.2	100
2-Methylphenol	0.3	100
4,6-Dinitro-2-aminophenol	0.4	43
Aniline*	4.0	100
o-Cresol	0.3	100

* Sorbent used: XAD-7.

the addition of sodium chloride (1–5 g/l) and acidification of the solution impair the recovery. A decrease in recovery resulting from an increase in the flow-rate through the concentration column was also found for naphthalene and *o*-cresol[51] and for humic and fulvic acids[52].

The recovery of neutral compounds was studied[22] when, having extracted water, the column was washed with a further 100 l of "pure" water of pH 8. Desorption by elution with diethyl ether was then carried out. At a concentration of 10 ppb, a slight decrease in recovery occurs within the limits of experimental error with compounds that are only slightly soluble in water in comparison with extraction in which an additional 100 l of water was not used. The decrease is, however, considerable (from 91 to 63 %) for more soluble compounds (*e.g.*, dimethyl phthalate).

Polychlorobiphenyls were analysed[53] in waters from the northern part of the Atlantic Ocean, 20–60 l being pumped through the concentration column at a flow-rate of 250 ml/min. A 300-ml volume of boiling acetonitrile was used to elute the compounds from the column. The acetonitrile was then diluted with 1 l of distilled water and the mixture was extracted with *n*-hexane and concentrated. The concentrations found were $3.5 \cdot 10^{-8}$ g/l in surface water and $1 \cdot 10^{-8}$ g/l in water from a depth of 200 m. A comparison of the results obtained by analysing waters filtered prior to extraction through a 0.3-μm glass filter or glass-wool with those obtained for unfiltered waters showed that the results are *ca.* 10 % lower if filtration is applied.

The analysis of marine water for contamination with pesticides and hydrocarbons has also been described[47]. The recovery of model compounds at concentrations of 1 ppb was about 80 % for pesticides, except for lindane (25 %). Prior to the extraction with a sorbent, the water was filtered through a glass filter. Not only the compounds trapped on the adsorption column but also the material trapped on the filter were analysed. The results showed that the compounds are partially adsorbed on solid particles contained in the water. When determining the compounds in water that contains also solid particles, it is therefore necessary for the material trapped on the filter during the filtration to be analysed.

Organic substances contained in waste waters prior to and after chlorination were studied by Glaze *et al.*[54]. Chlorinated compounds that had been absent in the original sample were found to be produced by the chlorination. During the storage of tap water containing chlorine and/or bromine, an increase in the amounts of halogen compounds (chloroform, bromodichloromethane, dibromochloromethane, bromoform) occurs, which is caused by the reaction of halogens with organic matter still contained in the water[55]. The addition of a small amount of ascorbic acid stabilizes the concentration. For the concentration of such compounds an acetylated resin proved to be efficient.

Halogenated hydrocarbons can be determined at the micrograms per litre level[56] (in the case of compounds of higher molecular weight, *e.g.*, hexadecyl and dodecyl chloride, the recovery is, however, poor).

The manufacturer[13] gave examples of applications of the polymer to anionic (sodium alkylbenzene sulphonate), non-ionic (Triton X-100) and cationic [dimethylbenzylalkyl (C_{22}–C_{24})-ammonium chloride] detergents.

The dependence of the adsorption of herbicides (2,4-di- and 2,4,5-trichlorophenoxyacetic acids) at concentrations of 25 and 500 ppb on pH and water flow-rate through the column was studied[25] and compared with the results obtained for

dieldrin. As the pH increases, the adsorption of acids decreases and, in order to achieve the quantitative adsorption, the pH must acquire a value of 2. For dieldrin the course is the reverse and the pH must be at least 6. The adsorption remains constant on changing the flow-rate within the range from *ca.* 2 to 10 ml/min, then it decreases; the recommended flow-rate is 5 ml/min. A recovery of 100% was found for the concentrations under study, a column with dimensions of 60 × 10 mm and elution with acetone; the recovery was lower with a shorter column (30 mm).

The contents of pesticides (atrazine, DDE and dieldrin) were studied[57] in waters from Iowa, U.S.A. The concentrations in various types of water were high (units to thousands of ng/l). Surface waters of all major watersheds were found to have contamination levels that fluctuated with the season of the year. Contamination of waters was highest after the agricultural application of pesticides in early spring as heavy rains cause appreciable erosion. As for as the underground aquifer lies within an alluvial plain of the contaminated river, pesticides are also present in ground water. Natural percolation leads to a slight decrease in the contamination. If the well system lies outside the alluvial plain, the concentration of these compounds is maximally 0.5 ng/l. This is also the only case when the drinking water does not contain any pesticides.

Chlorinated pesticides were investigated in drinking water[24] and river water[58] from Ottawa, Canada (the highest concentrations found were 17 ppt for α-BHC), and in model solutions, together with polychlorinated biphenyls (recovery 96% and 83%, respectively, at 0.01–0.1 ppb levels)[59].

Phosphorus insecticides were investigated in well and spring water[60] (ethyl and methyl parathion) and in model solutions[61,62] (fenitrothion and its degradation products fenitrooxon and aminofenitrothion). The recovery was 90–100%.

Adsorption equilibria[52] were measured for humic acid. The standard enthalpy of adsorption is −5.4 kJ/mole, the standard free energy is −36.4 kJ/mole (at 21°) and the standard entropy is 103 J/mole·°K (at 21°). The adsorption of humic and fulvic acids decreases, in the pH range 1.5–3.5, with decreasing acidity of the solution; the optimal pH value (considering the risk of denaturation) is 2.2. The maximal recovery was achieved by using 0.2 *M* sodium hydroxide solution 40 ml of which elutes *ca.* 95% of the acids. Slightly greater recoveries (98%) can be obtained if the eluent is allowed to stand in the concentration column overnight. A similar efficiency was also obtained in studies of humic substances in the water of the Sargasso Sea[63].

4.1.2. XAD-4

Amberlite XAD-4 is a hydrophobic styrene–divinylbenzene copolymer with a specific surface area of 750 m^2/g and an average pore diameter of 50 Å[64]. The preparation of the column is similar to the procedure described for Amberlite XAD-2.

Musty and Nickless[46] described a procedure for the analysis of chlorinated insecticides and polychlorinated biphenyls. The flow-rate of model solutions through the column is 8 ml/min, the polymer is dried with air and the insecticides are eluted with 50 ml of *n*-hexane–diethyl ether. The eluate is concentrated to a volume of 5 ml.

The influence of changing the polarity of the eluent on the recovery of above chloro compounds (by changing the percentage of diethyl ether in *n*-hexane) was

studied[46]. The best recovery was achieved with 10% of diethyl ether in *n*-hexane. The recovery with 2 g of the polymer was always greater than with 1 g. The use of a polymer with a smaller grain size (85–120 mesh instead of 60–80 mesh) improved the recovery of some insecticides, but the recovery was lower for aldrin, dieldrin and BHC. An increase in the flow-rate of water from 8 to 32 ml/min resulted in a decrease in the recovery of most insecticides. Lindane can be introduced into the column (2 g of the polymer) in an amount up to 30 mg without the appearance of penetration.

The results of a study on the application of this polymer to the concentration of herbicide derivatives of phenoxyalkanecarboxylic acids[25,65] are similar to those obtained with Amberlite XAD-2. The sorption decreases[25] with increasing pH of the solution and with increasing flow-rate.

The resin has been applied[66] to the determination of ionic dialkyl phosphates and thiophosphates. As these compounds must be methylated prior to their GC analysis, inorganic phosphates must first be eliminated.

The resin was also used to determine insecticides and biphenyls in river waters[67]. Samples were taken in silanized glass bottles, then filtered (a high content of suspended particles) through Whatman 541 filter-paper within 24 h. The concentrations found ranged from units to tens of ng/l.

Amberlite XAD-4 proved to be[68] an excellent adsorbent for polyethoxylated compounds (with the exception of polyethylene glycols with molecular weights below 300), including high flow-rates of water through the concentration column (50–100 ml/min).

Adsorption of phenols was measured[64] as a function of the concentration of electrolytes present and 13% of sodium chloride was found to increase the sorption.

Thruston[69] used mixtures of XAD-4 and XAD-8 resins for the extraction of organic compounds from drinking water followed by high-performance liquid chromatographic separation using a linear solvent gradient. Compounds are separated into several polarity ranges, which are subsequently analysed and identified by a GC–MS system. Liquid chromatography improves the quality of the mass spectra by eliminating the co-elution of compounds or the background (*cf.*, Fig. 6).

Amberlite XAD-4 has adsorption properties similar[22,25] to those of XAD-2 and they can therefore be interchanged[22]. The recoveries of various types of compounds are presented in Table 6.

4.1.3. XAD-7

Amberlite XAD-7 has a hydrophilic structure[70]; it is based on a methacrylate polymer[51]. The specific surface area is 450 m^2/g, the mean pore diameter 80 Å, the grain size 20–50 mesh and thermal stability extends up to 150°[70].

In a similar manner to other types of Amberlite, this polymer also is treated by the manufacturer in order to confer resistance against bacteria and moulds and it must therefore be washed with water before use. After the preparation of the column, as with other types of Amberlite, the column is washed with distilled water, methanol, isopropanol (or acetone) and again with water[70].

Adsorption isotherms were measured[70] for fatty acids, phenol and *m*-chlorophenol. The adsorption increases with increasing length of the chain and with decreasing solubility of the acids in water. It is greater for *m*-chlorophenol than for

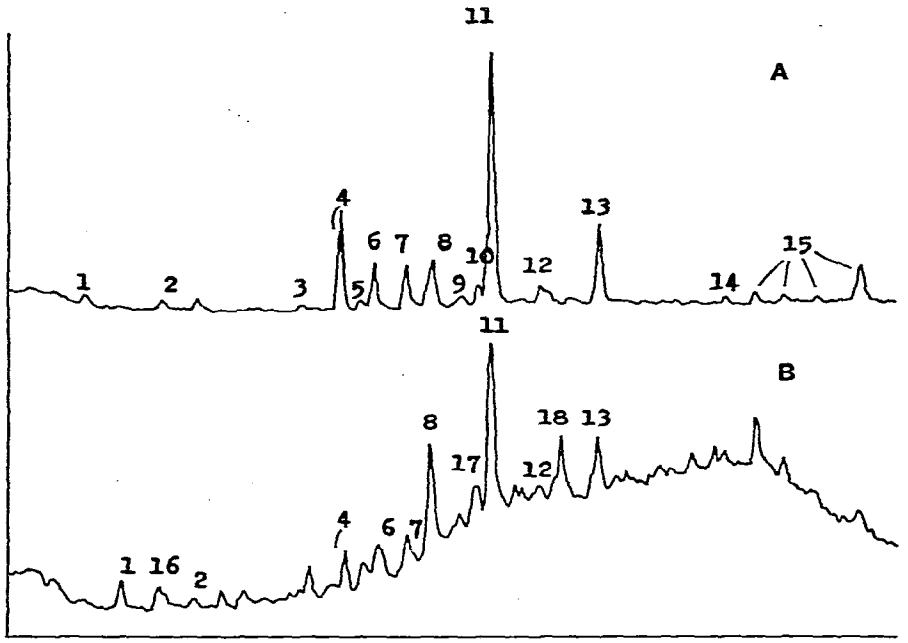

Fig. 6. Gas chromatogram of tap water[69]. (A) First fraction obtained from LC; (B) extract from the sorbent. 1 = Hexachloroethane; 2 = naphthalene; 3 = biphenyl; 4 = pentachloro hydrocarbon; 5 = methylbiphenyl; 6 = dibenzofuran; 7 = fluorene; 8 = hydrocarbon; 9 = methylfluorene; 10 = dibenzothiophene; 11 = phenanthrene; 12 = methylphenanthrene; 13 = fluoranthene; 14 = chrysene; 15 = hydrocarbons; 16 = toluonitrile; 17 = 9-fluorenone; 18 = anthraquinone.

phenol. Phenol was eluted with methanol or sodium hydroxide solution, acids with methanol or methanolic sodium hydroxide solution[52].

Fritz and Willis[71] studied the dependence of the partition coefficients of *o*-, *m*- and *p*-nitrophenols and phenol on the pH of the solution. The partition coefficients decrease as the pH increases for all of the compounds at low pH. This effect is due to the decrease in the concentration of the portion of the phenols in molecular form having a high partition coefficient in aqueous solution. A decrease in recovery with the increasing pH of the solution was also observed[51] for *o*-cresol. The recovery decreases[51] with increasing flow-rate through the column for phenol and *o*-cresol (20–200 ml/min).

The polymer is influenced chemically by the action of a solution of sodium hydroxide (0.05 *M* in 60% methanol), its ester group being partially hydrolysed[71]. Hence no eluent can be used that contains a mixture of a strong base and an anhydrous solvent. Proceeding from a strong base to an anhydrous solvent, water must be used between them.

Burnham *et al.*[23] also mention the use of Amberlite XAD-7 (*cf.*, Table 5) for extractions of phenol and aniline.

4.1.4. XAD-8

Amberlite XAD-8 is[16] a methyl methacrylate resin with an average pore diameter of 250 Å and a specific surface area of 140 m^2/g.

TABLE 6

RECOVERY OF MODEL ORGANIC COMPOUNDS FROM XAD-4 AT 2–10 ppb LEVELS[19]

Compounds tested	*Recovery (%)*	*Compounds tested*	*Recovery (%)*
Alcohols		*Phenols**	
1-Hexanol	95	*o*-Cresol	64
1-Octanol	103	3,5-Dimethylphenol	88
1-Decanol	93	2,4,6-Trimethylphenol	93
Cinnamyl alcohol	93	2-Naphthol	105
Esters		*Chloro compounds*	
Diethyl malonate	91	Chlorobenzene	85
Methyl decanoate	95	*o*-Dichlorobenzene	91
Methyl palmitate	35	1,2,4-Trichlorobenzene	87
Diethyl phthalate	99	*p*-Chlorotoluene	86
Dibutyl phthalate	96	Benzyl chloride	93
Ketones and aldehydes		*Acids (acidified)* [22]	
2-Nonanone	93	Octanoic acid	108
2-Undecanone	105	Decanoic acid	90
Acetophenone	96	Palmitic acid	101
Benzophenone	98	Oleic acid	100
Benzaldehyde	92	Benzoic acid	107
Alkylbenzenes		*Phenols*[22]	
Benzene	65	Phenol	40
Toluene	70	*o*-Cresol	73
Ethylbenzene	73	3,5-Xylenol	79
p-Cymene	80	*o*-Chlorophenol	96
Polynuclear aromatics		*p*-Chlorophenol	95
Naphthalene	83	2,4,6-Trichlorophenol	99
Biphenyl	87	1-Naphtnol	91

* The water was acidified by adding 5 ml of concentrated HCl prior to adding the organic solute.

The resin as supplied contains significant amounts of impurities, primarily as unpolymerized monomers. It must be purified by washing with 0.1 *N* sodium hydroxide solution and sequential extraction with methanol, acetonitrile and diethyl ether in a Soxhlet extractor. It is then washed with deionized water until free of organic solvent and placed in a concentration column as a resin slurry[16].

The extent of sorption on the resin depending on the character and the structure of the compound is discussed in Section 2. The mean free energy of adsorption at 20° is[15] 646 cal/mole per carbon atom for the aromatic system. Even though the difference in the free energy of various compounds is small, the capacity factor, k' (*cf.*, p. 170) changes from 30 to 90 to 270 for butanol, pentanol and hexanol, respectively. During concentration from 1 l of water by using 6 g of the resin this corresponds to differences in the sorption of the solutes from 10 to 50 to 95%, respectively.

XAD-8 resin appears to be an advantageous material for the concentration of low-molecular-weight organic solutes and natural organic polyelectrolytes, particularly humic and fulvic acids[16,72].

4.1.5. XAD-1

Amberlite XAD-1 is a styrene–divinylbenzene copolymer with a specific surface area of 100 m^2/g and a mean pore diameter 200 Å[73].

Sorption by this polymer (Table 7) was investigated[74] on model solutions prepared by dissolving the corresponding compounds in 1 l of marine water. In the pH range 2–9 and at concentrations of 2–5 ppb no adsorption of sugars, amino acids, proteins and phenols (phenol, resorcinol) occurred. Inorganic cations and anions also were not sorbed.

TABLE 7

RECOVERIES WITH THE APPLICATION OF AMBERLITE XAD-1[74]

Compound	*Concentration (μg/l)*	*Optimal pH*	*Eluent*	*Recovery (%)*
Enanthic acid	5.0	2.0	2 *N* ammonia solution	100
Heptadecanoic acid	5.0	2.0	1 *N* alcoholic KOH	100
4-Ketoglutaric acid	0.5	7.6	Ethanol	100
Cholesterol	10.0	2.0	Ethanol	100
Pregnenalone	1.0	2.0	Ethanol	100
Pyridostygmine	1.0	5.0	2 *N* HNO_3	35
Vitamin B_{12}	2.0	7.6	Ethanol	100
Vitamin B_2	2.5	2.0	Ethanol	100
Detergents				
Teepol	300	2.0	Ethanol	100
Hyamin-2389	5000	2.0	Ethanol	100
Triton X-100	5000	2.0	Ethanol	100
Nonidet P80	1000	2.0	Ethanol	100
Insecticides				
Lindane	1.0	2.0	Ethanol	100
DDT	1.0	2.0	Ethanol	100
Endrin	10.0	2.0	Ethanol	75
Malathion	10.0	2.0	Ethanol	100
Dyestuffs				
Rhodamine B	200	7.6	Ethanol	100
Methylene blue	100	7.6	2 *N* HNO_3	100
Humic acids		2.0	0.2 *N* KOH	100

4.2. Ostion SP-1

This polymer was developed by the Research Institute of Synthetic Resins and Lacquers, Pardubice, Czechoslovakia. Its properties are similar to those of Amberlite XAD-2. The specific surface area is 350 m^2/g and the mean pore diameter is[75] 86 Å.

For model compounds (phenol, nitrophenol) the adsorption and desorption isotherms[76] were determined in a static arrangement. The amount adsorbed depends, as with Amberlite XAD-2, on the original concentrations of the substances in water and decreases as the operating temperature increases. The results obtained suggest that physical adsorption occurs. Similar results of comparative studies were also obtained in a dynamic arrangement for ε-caprolactam[77] and for detergents (alkylbenzenesulphonates)[14].

The preparation of an adsorption column containing Ostion SP-1 is analogous to the preparation of Amberlite columns[75].

4.3. Porapak

The manufacturer of polymers of this type is Waters Assoc., Framingham, Mass., U.S.A.

4.3.1. Porapak Q

Porapak Q is an ethylvinylbenzene–divinylbenzene copolymer with a specific surface area[78,79] of 630–840 m^2/g and a mean micropore volume (up to 500 Å) of 74.8 Å. It is recommended that a temperature of 250–300° should not be exceeded[80]. The main products of its pyrolysis at temperatures of 300° and above are ethylvinylbenzene, *m*- and *p*-diethylbenzene, *m*- and *p*-divinylbenzene and styrene. Reaction with nitrogen dioxide leads[81] to the production of water and nitric oxide and to the nitration of aromatic rings of the polymer. Water elutes between ethane and propane. A certain amount of water (a few per cent) can be adsorbed[82] irreversibly up to temperatures of *ca.* 200°. The polymer reacts with oxygen at *ca.* 200° with the production of carboxylic compounds on the polymer surface and with subsequent depolymerization and oxidation[40]. The oxidative degradation is usually reported[83] as a drawback of Porapak Q in comparison with Tenax.

A concentration effect was investigated[12] for solutions of hydrocarbons in water, using as examples benzene, toluene, naphthalene and *o*-xylene. The partition coefficients and the course of the sorption with time were measured in a static arrangement. The time course shows that following the dispersion of *o*-xylene in water the hydrocarbon is adsorbed almost immediately. The dissolved hydrocarbon is adsorbed more slowly; however, the establishment of equilibrium does not exceed 4 min. The partition coefficient is infinite for all of the compounds investigated at 25° (*cf.*, Table 1). The course of the isotherms is linear up to a Porapak coverage of 12–25% by weight.

The concentration effect of the material was verified[12] on waste waters from styrene production (Fig. 7). In a static arrangement, 100–1000 ml of water were extracted by 0.5 g of Porapak (250–325 mesh), first wetted with acetone, for 0.5 h. The polymer was placed in a thin glass tube, to which a filter plate was melted and the excess of water was removed with pressurized air or sucked off. Then acetone was added dropwise into the column from a burette. The first millilitre of the eluate contained 95–99% of the total amount of the hydrocarbons originally dissolved in the water (from the viewpoint of trace analysis the desorption can be considered to be quantitative). Even after a 50-fold repeated application of the resin no deterioration of the sorption properties was observed. In a dynamic arrangement, a glass tube, 3 mm in diameter, to which a glass frit was melted, was packed with 0.5 g of Porapak. The polymer column was wetted with *ca.* 3 ml of acetone and the water under analysis was sucked through for 10–30 min. The residues of water were sucked off. Acetone was used for the elution. The volume of the treated water was 1 l. The lower part of Fig. 7 shows the chromatogram of a sample that was injected directly. The upper part shows the chromatogram of water after purification containing more than 100 times lower concentrations of hydrocarbons, using the concentration step. The enrichment ratio is obviously 4–5 orders of magnitude.

Porapak Q (80–100 mesh) was applied[28] to the concentration of organosilicon compounds. After passing the sample of water through the column, *ca.* 10 ml of methyl isobutyl ketone was eluted. The recovery was 90–95% for substances at con-

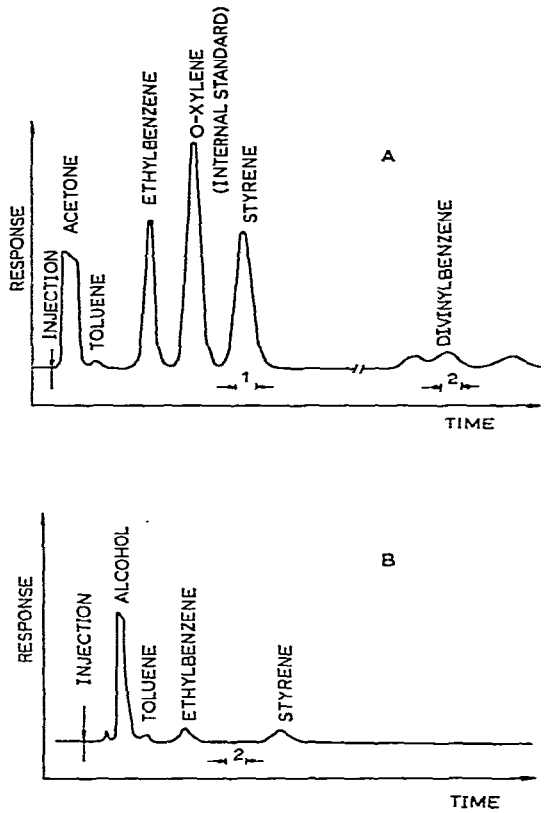

Fig. 7. Chromatograms of waste water from styrene production[12]. (A) Water after purification treatment, using concentration step; (B) original water, direct injection to GC.

centrations from 0.05 (triphenylsilanol) to 1.30 mg (decamethylcyclopentasiloxane) in 100 ml of water.

For halogenated hydrocarbons the recovery is *ca.* 50–80 % and is[56] substantially longer than with Amberlite XAD-2 (p. 183).

A concentration factor of 10^6 was determined[31] for non-ionic detergents of the alkylphenol type.

Niederwieser and Giliberti[84] reported that in order to adsorb indole from aqueous solutions, Porapak must first be washed with acetone, then the acetone must be removed by washing with water and the Porapak must be wet all the time, otherwise the adsorption capacity would decrease considerably. If Porapak is not wetted with acetone first, no sorption will occur.

4.3.2. Porapak N

The efficiency of trapping of silicon compounds was found[28] to be zero in the same arrangement as with Porapak Q.

4.4. Synachrom

Synachrom is a copolymer of styrene, divinylbenzene and ethylvinylbenzene, manufactured by Lachema, Brno, Czechoslovakia. Its characteristics are similar to those of Porapak Q. The specific surface area is 520–620 m^2/g, the average pore diameter is 45 Å and water elutes between ethane and propane[85]. The temperature at which the first loss of weight on the thermogravimetric curve appears is 341°. However, this is not caused by changes in structure due to thermal destruction[86].

The application of the resin to the concentration of substances in water was studied on model compounds by Kubelka and co-workers[20,21,27,87,88]. The results associated with the influence of the original concentration and the composition of the solution on the adsorption capacity and the range where trapping reaches 100% are presented in Section 2.1. Changes in pH from 2 to 7[20] and changes in the flow-rate of water from 80 to 750 ml/h[20,88] were found to have no effect on adsorption for the solutions under study (quinoline, xylene and cresol). The packing of the concentration column was always washed with methanol[27] prior to use.

The desorption (by the elution of methanol at a flow-rate of 75 ml/h) is *ca.* 100% at high concentrations. It is lower for quiniline and xylene in particular, and in some instances it is only 50%, at lower concentrations (20–50 ppm). The amount of quinoline desorbed depends on the pH of the solution used for the sorption. The more acidic is the adsorbed solution, the higher are the desorption yields. During elution with "pure" water the amount adsorbed decreases monotonously with increasing[20] volume of water flowing through the column.

The adsorption on Synachrom is inversely proportional to the solubility of compounds in water. The dependence on other factors is associated with their effects on the solubility. The sorption mechanism is similar to that of activated carbon, *i.e.*, physical sorption[27,88].

4.5. Chromosorb century series

The manufacturer of polymeric sorbents of this type is Johns-Manville, New York, N.Y., U.S.A.

4.5.1. Chromosorb 102

Chromosorb 102 is[89] a hydrophobic, porous styrene–divinylbenzene copolymer with a specific surface area of 300–400 m^2/g, an average pore diameter of 85–95 Å and an upper temperature limit of 250°. It is recommended that conditioning at 250° is carried out overnight. Water is eluted near propane. The resin reacts with oxygen[40] and nitrogen dioxide[81] in a similar manner to Porapak Q.

Chromosorb 102 was applied[38,90] for studying the concentrations of model compounds. A column with dimensions of 4 × 1/8 or 1/4 in. and a flow-rate of 5 ml/min were used. Several tens of microlitres of water were left in the column after the elution. The recovery is shown in Table 8.

4.5.2. Chromosorb 105

Chromosorb 105 is[91] a sorbent of the polyaromatic type and average polarity, with a specific surface area[39] of 600–700 m^2/g and an average pore diameter of 0.04–0.06 μm.

TABLE 8

RECOVERIES WITH THE APPLICATION OF CHROMOSORB 102[38]

Compound	*Concentration (ppm)*	*Recovery (%)*
Methanol	0.79	<5
	6.3	<5
Acetone	0.79	21
	6.3	42
Chloroform	1.5	93
	12.0	85
Benzene	0.88	100
	7.0	100
Pyridine	0.98	46
	7.8	79
Phenol	0.22	25
	1.9	61
Methyl isobutyl ketone	2.7	100
m-Cresol	0.15	75
o-Ethylphenol	0.06	97
p-Ethylphenol	0.35	89

The upper temperature limit is 200°. It is recommended that the column is conditioned in a flow of helium at 225–250° for 12–24 h and then re-filled. After such a conditioning in a stream of nitrogen (free from oxygen), the sorbent becomes stable with an insignificant background[39]. *m*- and *p*-ethylstyrene were determined as the main products of thermal decomposition. After being used, the concentration column is always reconditioned at 150–170° overnight.

Water is eluted near propane. About 50 μl of water remains in the column after the passage of water. Water residues are removed with a stream of nitrogen at 25° for 2 h. The application of this polymer has been reported[39] for mixtures of water with, *e.g.*, liqueurs.

4.5.3. Chromosorb 106

Chromosorb 106 is a non-polar polystyrene copolymer, stable up to 250°[92], with a specific surface area[39] of 700–800 m^2/g.

Chromosorb 106 can be applied instead of Chromosorb 105[39]. Their backgrounds are comparable.

4.6. Tenax

Tenax, (Applied Science Labs., State College, Pa., U.S.A.) is porous poly-(2,6-diphenyl-*p*-phenylene oxide)[93,94] with a specific surface area[95,96] of 19–30 m^2/g. The pore volume[95] is 0.667 cm^3/g and the average pore radius is 720 Å, with 90% of the total pore volume being due to large pores with effective radii from 125 to 75,000 Å. The grain size of the commercial material is 60–80 mesh. Water is eluted near propane.

The manufacturer recommends[97] (for chromatographic purposes) conditioning the sorbent first in a stream of nitrogen at room temperature for 1 h, then increasing the temperature to 350° for a further 1 h. A similar procedure is also followed if

Tenax is applied as a packing for a concentration unit. Tenax is then first heated in a stream of an inert gas to 350° for 30 min[32], or for 3 h with subsequent heating at 200° overnight[42].

The manufacturer reports no loss of organic compounds at temperatures up to 320°. At 350° a slight leak is observed[97]. The influence of high temperature on the separation efficiency was investigated[93]. After 40 h at 425° the separation efficiency is substantially lower than before conditioning. Thermogravimetry showed no substantial weight losses at 400°. At 430° the weight losses are only small (0.3%/h), and they are large (3%/h) at 450°. No changes in adsorption efficiencies were found[96] on repeatedly increasing the temperature to 250°.

The action of nitrogen oxide or nitric acid on Tenax produces 2,6-diphenyl-*p*-quinoline. The degradation does, however, not affect the efficiency or capacity of Tenax[98].

Leoni and co-workers[17,99] studied the possibility of concentrating pesticides and polynuclear hydrocarbons on model samples with the use of mineral waters (free of carbon dioxide) and drinking waters (0.05–0.1 mg/l of free available chlorine) containing *ca.* 0.4 g/l of residues, mainly calcium salts (pH 6.8–7.2). A diagram of the optimal version of the device is shown in Fig. 1. After the passage of 20 l of water (at a flow-rate of 3 l/h) the column was switched off and air was blown through for a few seconds in order to eliminate as much water as possible from the adsorption bed.

Pesticides were eluted with three 10-ml volumes of diethyl ether. The recovery of pesticides was found[99] to be about 90% (for parts per billion concentrations). If free chlorine is present in the water (*e.g.*, in drinking water), the recovery of organophosphorus pesticides from this water falls to zero. This irreversibility is not caused by the reaction of free chlorine with Tenax (and by a subsequent influence on the adsorption capacity) but rather by the oxidation of pesticides. Therefore, if water is analysed for organophosphorus pesticides in the presence of free chlorine, the sample must be neutralized immediately after it has been taken. Acidification of water to pH 1.0 in order to prevent microbial degradation during storage has no harmful effects on pesticides[99].

The influence of the presence of other pollutants on sorption was studied[17]. The presence of detergents (*e.g.*, Arkopal) does not influence the recovery. Mineral oils at the level of 1 ppm, however, decrease the recovery of phosphorus pesticides from the adsorption bed considerably. Phosphorus pesticides remain dissolved in water after the concentration treatment (*cf.*, p. 171).

On analysing surface and marine waters containing solid particles forming suspensions, the recoveries from unfiltered waters were found[17] to be substantially lower (see Table 9) for some pesticides. These substances are adsorbed on the suspended solid particles and the adsorbed fraction cannot be extracted from the water by Tenax. Prior to the analysis proper of such waters, they must first be filtered. Not only the substances extracted by Tenax must then be determined analytically, but also the substances from the suspension that was trapped on the filter.

Polynuclear aromatic hydrocarbons at concentrations of 0.1 ppb were desorbed after extraction with 30 ml of acetone, then the solution was filtered through anhydrous sodium sulphate and concentrated. The recovery[99] was in the range 85–98%.

TABLE 9

INFLUENCE OF THE FILTRATION OF WATER ON RECOVERY[17]

*Compound**	*Recovery (%)*	
	No filtration of water	*Filtration of water prior to addition of the compounds*
Hexachlorobenzene	84.8	83.9
o,p'-DDT	38.0	81.8
p,p'-DDT	47.0	93.1
β-BHC	70.0	73.0
γ-BHC	84.9	92.0
Dieldrin	75.4	92.7
Methyl parathion	82.3	101.0
Malathion	25.0	93.3

* Parts per billion levels.

Tenax was also tested for the determination of organosilicon compounds in the same arrangement as described[28] for Porapak Q. The efficiency of trapping was low (10%) and as with Porapak N it is ascribed to a more polar character of the sorbent.

Versino *et al.*[42] recommended a concentration column packed with 4 g of Tenax mixed with 20% of glass beads (60–80 mesh). This packing makes the flow of water through the bed easier and eliminates cracks in the column bed in the course of the heating during desorption. If cracks occur, preferential routes are created and the water cannot come into contact with the whole bed. After passing water (flow-rate 5–7 ml/min), the column is left in a desiccator with phosphorus pentoxide at 10 mmHg overnight. The recoveries of model compounds at concentrations of 10–30 ppb from a neutral solution were 99, 41, 70, 89, 45 and 89% for benzene, pyridine, *n*-undecane, aniline, phenol and *p*-cresol, respectively. Poor recoveries are thus obtained for compounds that are readely soluble in water (pyridine and phenol). A change in pH towards both the acidic and basic regions does not affect the recovery substantially. In order to improve the recovery of compounds soluble in water, the authors recommend the use of two columns in series.

Fig. 8[42] presents chromatograms (A and B) of mineral waters from two different sources. The volume of water treated was 1 l. The last large peak, belonging to phthalate, is of interest. It is found in both instances and originates from the plastic materials with which the water came into contact during sampling and storage (see Section 3.5). Chromatogram C represents the chromatographic background of Tenax at an applied temperature of 270°.

Fig. 9 B demonstrates[42] the chromatographic analysis of tap water, again with the use of Tenax and 1 l of water. Chromatogram A is obtained for the same water with the addition of 10 ppb of gasoline and 10 ppb of diesel oil and chromatogram C for the water from the lake that is used as the source of the tap water. On comparing the chromatograms, a similarity between the contents of organic impurities in the lake and tap waters can be observed. Both the lake and the tap water contain the compounds present in gasoline.

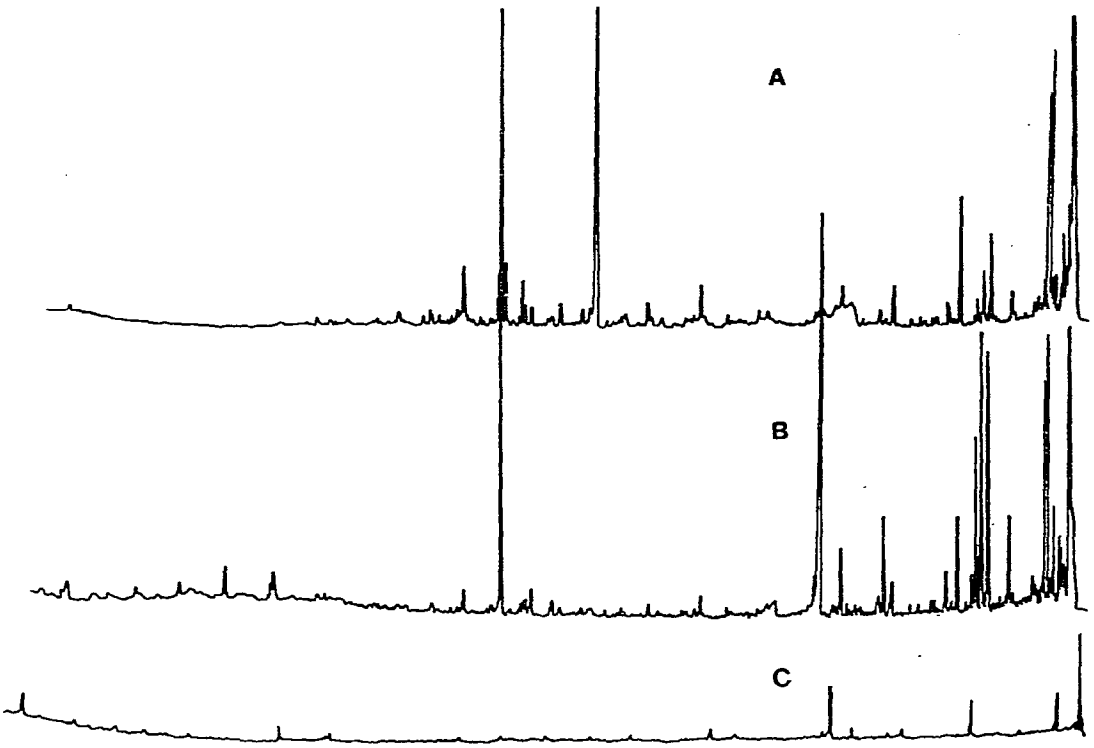

Fig. 8. Profiles of mineral waters[42]. (A) Bottled mineral water from LSCR company; (B) bottled mineral water from SB company; (C) Tenax blank, 270°.

4.7. Spheron

Spherons are materials developed by Laboratory Instruments, Prague, Czechoslovakia.

4.7.1. Spheron MD 30/70

Spheron MD 30/70 is a copolymer of methyl methacrylate with divinylbenzene, with a particle size of 32–40 μm, a specific surface area of 320 m^2/g and with thermal stability up to 230°[100].

After being packed with the sorbent, the concentration column must be washed with methanol–diethyl ether (1:1) and then with distilled water in order to obtain accurate and reproducible results[100].

The adsorption and desorption curves were measured for hydrocarbons and phenols and the capacities of the sorbent were determined. The sorbent capacity depends on the original concentration and the composition of the solution, as with Synachrom (see Section 2.1) and for toluene is *ca.* an order of magnitude greater than for *m*-cresol. The dependence of the adsorption capacities on concentration for original concentrations not exceeding 70 mg/l is linear for toluene and naphthalene. A methanol–diethyl ether mixture is the most suitable solution[100] for liquid desorption.

TABLE 9

INFLUENCE OF THE FILTRATION OF WATER ON RECOVERY[17]

*Compound**	*Recovery (%)*	
	No filtration of water	*Filtration of water prior to addition of the compounds*
Hexachlorobenzene	84.8	83.9
o,p'-DDT	38.0	81.8
p,p'-DDT	47.0	93.1
β-BHC	70.0	73.0
γ-BHC	84.9	92.0
Dieldrin	75.4	92.7
Methyl parathion	82.3	101.0
Malathion	25.0	93.3

* Parts per billion levels.

Tenax was also tested for the determination of organosilicon compounds in the same arrangement as described[28] for Porapak Q. The efficiency of trapping was low (10%) and as with Porapak N it is ascribed to a more polar character of the sorbent.

Versino *et al.*[42] recommended a concentration column packed with 4 g of Tenax mixed with 20% of glass beads (60–80 mesh). This packing makes the flow of water through the bed easier and eliminates cracks in the column bed in the course of the heating during desorption. If cracks occur, preferential routes are created and the water cannot come into contact with the whole bed. After passing water (flow-rate 5–7 ml/min), the column is left in a desiccator with phosphorus pentoxide at 10 mmHg overnight. The recoveries of model compounds at concentrations of 10–30 ppb from a neutral solution were 99, 41, 70, 89, 45 and 89% for benzene, pyridine, *n*-undecane, aniline, phenol and *p*-cresol, respectively. Poor recoveries are thus obtained for compounds that are readely soluble in water (pyridine and phenol). A change in pH towards both the acidic and basic regions does not affect the recovery substantially. In order to improve the recovery of compounds soluble in water, the authors recommend the use of two columns in series.

Fig. 8[42] presents chromatograms (A and B) of mineral waters from two different sources. The volume of water treated was 1 l. The last large peak, belonging to phthalate, is of interest. It is found in both instances and originates from the plastic materials with which the water came into contact during sampling and storage (see Section 3.5). Chromatogram C represents the chromatographic background of Tenax at an applied temperature of 270°.

Fig. 9 B demonstrates[42] the chromatographic analysis of tap water, again with the use of Tenax and 1 l of water. Chromatogram A is obtained for the same water with the addition of 10 ppb of gasoline and 10 ppb of diesel oil and chromatogram C for the water from the lake that is used as the source of the tap water. On comparing the chromatograms, a similarity between the contents of organic impurities in the lake and tap waters can be observed. Both the lake and the tap water contain the compounds present in gasoline.

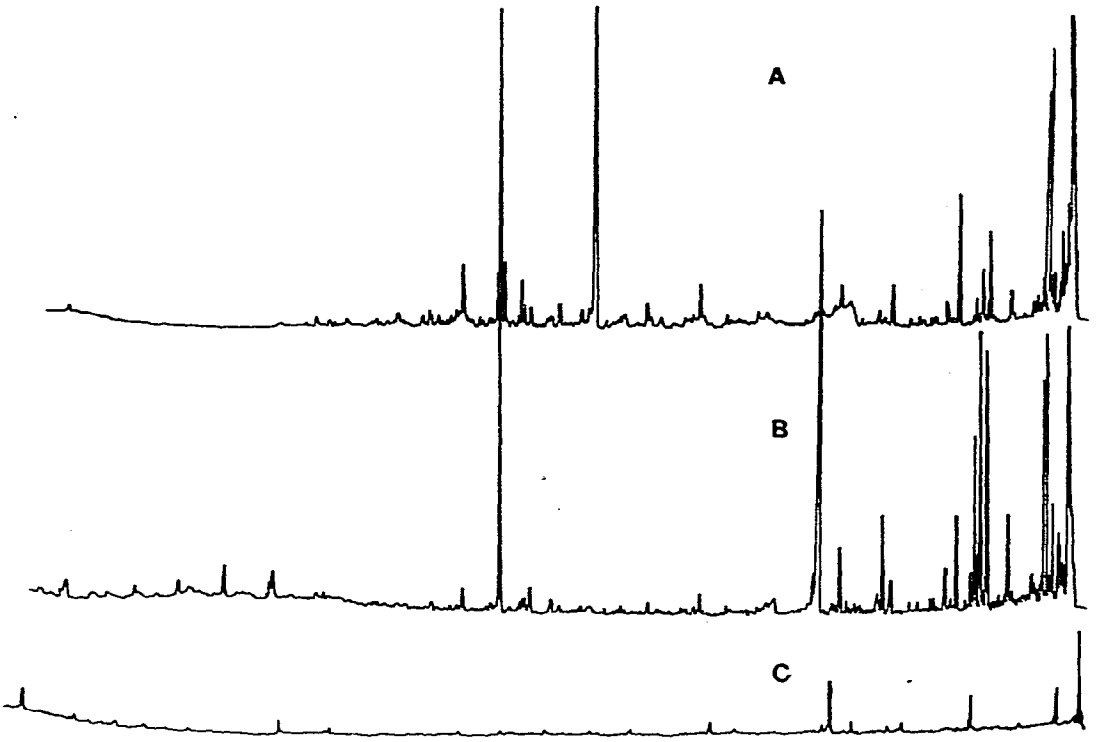

Fig. 8. Profiles of mineral waters[42]. (A) Bottled mineral water from LSCR company; (B) bottled mineral water from SB company; (C) Tenax blank, 270°.

4.7. Spheron

Spherons are materials developed by Laboratory Instruments, Prague, Czechoslovakia.

4.7.1. Spheron MD 30/70

Spheron MD 30/70 is a copolymer of methyl methacrylate with divinylbenzene, with a particle size of 32–40 μm, a specific surface area of 320 m^2/g and with thermal stability up to 230°[100].

After being packed with the sorbent, the concentration column must be washed with methanol–diethyl ether (1:1) and then with distilled water in order to obtain accurate and reproducible results[100].

The adsorption and desorption curves were measured for hydrocarbons and phenols and the capacities of the sorbent were determined. The sorbent capacity depends on the original concentration and the composition of the solution, as with Synachrom (see Section 2.1) and for toluene is *ca.* an order of magnitude greater than for *m*-cresol. The dependence of the adsorption capacities on concentration for original concentrations not exceeding 70 mg/l is linear for toluene and naphthalene. A methanol–diethyl ether mixture is the most suitable solution[100] for liquid desorption.

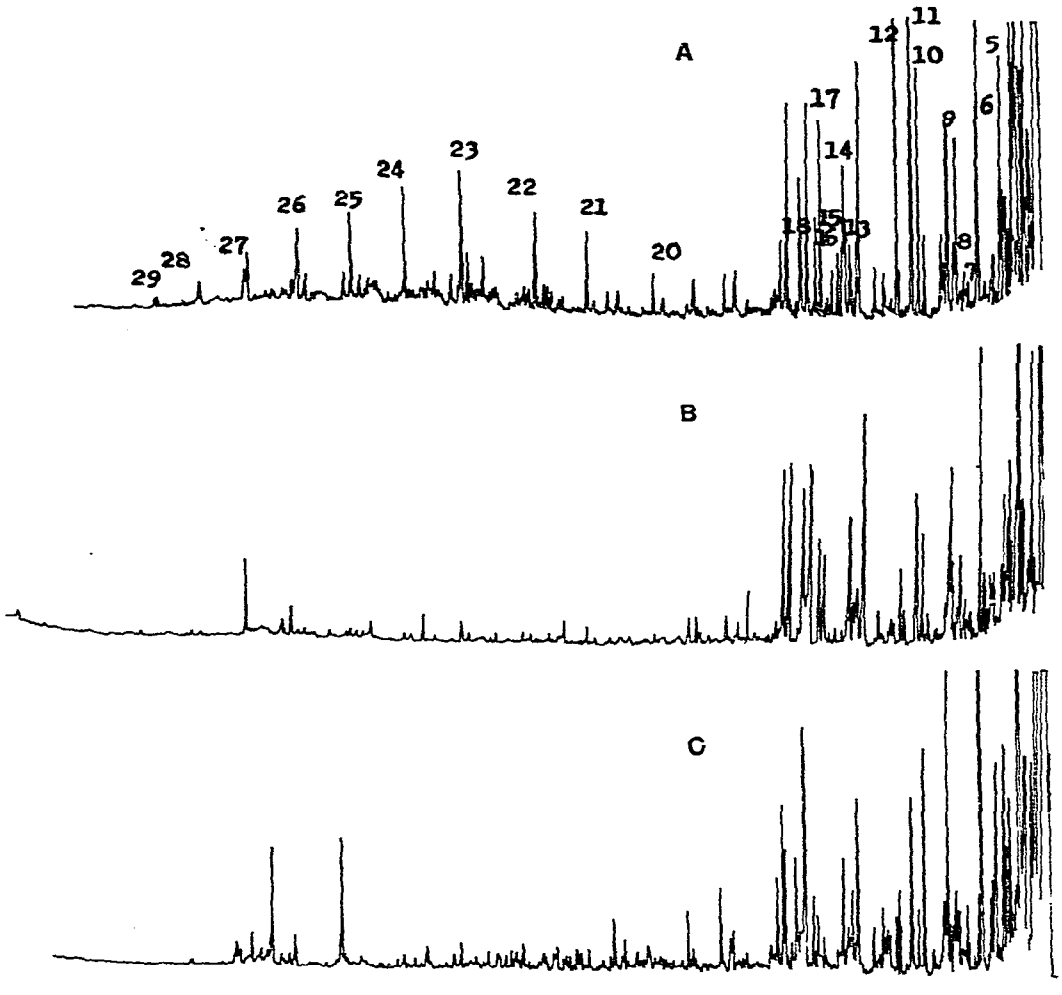

Fig. 9. Profiles of organic compounds in water[42]. (A) Tap water spiked with 10 ppb of gasoline and 10 ppb of diesel oil; (B) tap water; (C) lake water. 5 = *n*-Heptane; 6 = toluene; 7 = octane isomer; 8 = octane isomer; 9 = *n*-octane; 10 = ethylbenzene; 11 = *m*- + *p*-xylene; 12 = *o*-xylene; 13 = *n*-propylbenzene; 14 = methylbenzene; 15 = trimethylbenzene; 16 = trimethylbenzene; 17 = trimethylbenzene; 20 = *n*-dodecane; 21 = *n*-C_{13}; 22 = *n*-C_{14}; 23 = *n*-C_{15}; 24 = *n*-C_{16}; 25 = *n*-C_{17}; 26 = *n*-C_{18}; 27 = *n*-C_{19}; 28 = *n*-C_{20}; 29 = *n*-C_{21}.

4.7.2. Spheron SE

Spheron SE is a copolymer of styrene and ethylene dimethacrylate, with a particle size of 32–40 μm and a surface area of 70 m^2, and is thermally stable up to 280°[101].

Mixtures of the sorbent with an inert non-adsorbing material (crushed silica glass, particle size 50 μm) were used as a concentration packing so that no by-passes occurred in the column.

The adsorption curves were measured for solutions of phenols and hydrocarbons. The sorbent capacity was 150 mg/g for toluene (concentration 30 ppm in

water) and 8.7 or 10.3 mg/g for *m*-cresol (concentration 5.8 or 7.7 ppm, respectively). A methanol–diethyl ether mixture is the most suitable[101] for desorption, as with Spheron MD 30/70.

4.8. Polyurethane

4.8.1. Open-pore polyurethane

Open-pore polyurethane (OPP) consists of agglomerated spherical particles (1–10 μm in diameter) bonded to each other in a rigid, highly permeable structure. It is usually prepared by *in situ* polymerization[102]. OPP is compatible with organic solvents, dilute acids and water[103,104]. Bases, however, appeared to break the OPP–glass column bonds easily[103]. It exhibits weakly base anion-exchange characteristics[103].

An OPP column made of normal glass has a limited life. Passage of large volumes of water breaks the OPP–column bonds in the course of several weeks. The service life can be prolonged by etching the inside of the glass column with hydrofluoric acid prior to the formation of OPP and by decreasing the pH of the water samples[103].

Prior to its utilization, the OPP column is rinsed with *n*-heptane, methanol and deionized distilled water[103].

OPP columns were evaluated[103] for the concentration of polynuclear aromatic hydrocarbons from water. The recovery of model compounds is listed in Table 10. An increase in the flow-rate of water decreases the adsorption.

TABLE 10

RECOVERIES OF POLYAROMATIC HYDROCARBONS WITH THE APPLICATION OF OPEN-PORE POLYURETHANE[103]

Compound	*Flow-rate (l/h)*	*Amount loaded (μg)*	*Recovery (%)*
Benzo(*a*)pyrene	1.8	4	95 ± 6
Biphenyl	0.9–1.5	5–6	98 ± 5
Fluoranthene	0.5–1.0	4–5	77 ± 4
	0.5–1.0	1–2.5	97 ± 3
Naphthalene*	0.1	5	56 ± 3
	0.1–1.0	1–2.5	98 ± 10
Phenanthrene	0.8–1.0	5	58 ± 7
	0.8–1.0	1–2.5	92 ± 9
Pyrene	0.6–0.8	1–4	100 ± 2
	1.2–1.7	4–5	89 ± 3

* Required 10 ml of methanol for quantitative elution; the other compounds required only 5 ml.

4.8.2. Porous polyurethane foam

Porous polyurethane foam was studied as a material for the concentration of chlorinated insecticides and polychlorinated biphenyls[45,67,105] and polynuclear aromatic hydrocarbons (PAHs)[106,107].

A polyurethane plug is first extracted in a Soxhlet extractor for 24 h with acetone[45] or purified by agitation in an *n*-hexane–acetone solution (1:1)[105]. After drying, the polyurethane plug is packed into a glass column (2 cm in diameter) to a

height of 4 cm, acetone is added so that the plug is covered and the plug is pressed with a glass rod in order to expel air. Then the acetone is washed with *ca.* 250 ml of water[45]. In order to remove air and residues of solvent after the purification by agitation, Gesser *et al.*[105] applied 25 ml of ethanol and subsequently 200 ml of distilled water.

Desorption of the amount adsorbed is performed either under static conditions with *n*-hexane in a Soxhlet extractor[108] or by the dynamic procedure by elution with acetone (20–50 ml) and then with *n*-hexane (100 ml)[45,105]. The eluent is finally concentrated to a volume of 5–10 ml.

The adsorption capacity of the polyurethane plug[45] is *ca.* 260 mmole/kg (for methylene blue). The recoveries of various compounds are listed in Table 11. For insecticides it is about 100%. An increase in the flow-rate of water leads to a decrease in the recovery of the adsorbed compounds.

TABLE 11

INFLUENCE OF THE FLOW-RATE OF WATER AND NUMBER OF SORPTION UNITS USING POROUS POLYURETHANE FOAM[45] ON THE RECOVERY

Compound	*Concentration (ppb)*	*Recovery (%)*				
		2 units			*4 units*	
		10 ml/min	*30 ml/min*	*250 ml/min*	*250 ml/min*	*100 ml/min*
α-BHC	1	101	95	49	67	91
Lindane	1	101	91	40	62	91
β-BHC	1	101	86	44	60	100
Aldrin	1	99	73	46	82	93
p,p'-DDE	2	106	77	68	97	106
Dieldrin	1	106	77	58	87	100
Endrin	10	100	94	54	80	108
o,p'-DDT	10	113	84	43	62	103
p,p'-DDD	2	102	89	57	86	102
p,p'-DDT	10	114	100	26	46	109
Aroclor 1242	10	69			74	87
Aroclor 1248	10	62			78	99
Aroclor 1254	20	75			76	94
Aroclor 1260	20	42			29	40

The recovery at a higher flow-rate can be increased by including several polyurethane units in series. By applying four plugs of foam at a flow-rate of 100 ml, a 100% recovery is obtained. The recovery of BCB (Aroclor) is worse (40–70%) even at a flow-rate of 10 ml/min (Table 11). For PAHs the recovery is independent of the flow-rate (130–520 ml/min)[106].

A change in pH from 6 to 9 has no influence on the recovery (always 100%); only at pH 5 does the recovery fall slightly[45]. The recovery of PAHs in tap water increases from 62% at pH 3.0 to 76% at pH 10.0[106].

The effect of polyurethane foam coatings on recovery was also studied. A plug of foam[45] coated with DC-200, QF-1, SE-30 or DC-11 always gives poorer results than an uncoated plug, but at 62° an increase of about 4–9% occurs[106].

The procedure was applied to the analysis of chlorinated insecticides and poly-

chlorinated biphenyls in river water[45,67]. The concentrations found were within the range of units and tens of ng/l.

Bedford[109] found, however, that the recovery is *ca.* 50% for polychlorinated biphenyls if small particles are suspended in the water under analysis. He explained this phenomenon by the passage of these particles carrying adsorbed biphenyls through the porous foam. Similar results were obtained[106] for PAHs.

4.9. Ion-exchange resins

This section deals only with the use of macroreticular porous polymers. Amberlyst A-26 (Rohm & Haas, Philadelphia, Pa., U.S.A.) has been applied to the determination of phenols[11]. This polymer is an anion-exchange resin with trimethylamine functional groups[110]. The specific surface area is 25–30 m^2/g and the porosity 27%.

The resin is washed first with 2 *M* sodium hydroxide solution, then with distilled water, 4 *M* hydrochloric acid, distilled water and acetone. This washing is continued until no colouration of the acetone solution is observed. Extraction with acetone is then performed in a Soxhlet extractor[11]. Having been poured into a column, the anion exchanger is converted into the OH form with 20 ml of 0.1 *M* sodium hydroxide solution, the excess of which is removed with 50 ml of distilled water.

Phenols present in alkalinized water are trapped on the polymer in the form of phenolates. Neutral organic compounds, partly adsorbed by the polymer (*e.g.*, naphthalene adsorption is *ca.* 3%), are removed by washing with alkaline methanol. Phenol ions are then converted into the molecular form with hydrochloric acid and eluted with methylene chloride and acetone.

The recovery of phenols (Table 12) is dependent on pH. In general, phenols are trapped by the polymer if the pH is at least 2 pH units higher than the pK_a value of the phenol. All of the phenols under study were trapped at pH 12–12.5.

TABLE 12

RECOVERIES WITH THE APPLICATION OF AMBERLYST A-26[11]

Compound	*Concentration (ppb)*	*Recovery (%)*	*Concentration (ppb)*	*Recovery (%)*
Phenol	500	93	25	95
o-Cresol	300	94	15	90
p-Cresol	800	96	40	80
p-Chlorophenol	900	100	45	95
4-Chloro-3-methylphenol	800	100	40	95
2,4,6-Trichlorophenol	1100	102	55	95
Pentachlorophenol	1700	89	85	80
3,5-Dimethylphenol	700	95	35	90
2-Naphthol	500	95		

Chlorination decreases the recovery of phenols and results in the formation of new chlorinated phenols. In contrast, chlorinated phenols appear to decrease the recovery in the presence of reductive agents which are usually applied in order to eliminate oxidation and chlorination.

5. COMPARISON OF SORBENTS

A direct comparison of various types and/or mixtures of Amberlite XAD resins is given in Table 13. A 1:1 mixture of XAD-4 and XAD-8 is considered to be the most efficient[111] for the first group of compounds. XAD-4 resin is the most efficient[46] for the chlorinated insecticides under study (except aldrin, for which XAD-8 provides a slightly better recovery). Stepan and Smith[51] compared XAD-2 and XAD-7 resins and ascribed the greater sorption of polar substances (phenol, *o*-cresol) on XAD-7 to its higher polarity. A higher recovery of these compounds found here, compared with the data in the first part of Table 13, can be related to the

TABLE 13

COMPARISON OF VARIOUS TYPES OF AMBERLITE

Compound	*Concentration (ppb)*	*Recovery (%) for XAD resin type*										*Reference*
		7	*2/4*	*8*	*2/7*	*2*	*2/8*	*2/4/7/8*	*4*	*4/8*	*12*	
Acenaphthene	50	72	68	20	81	99	85	84	81	81	—	111
2-Benzothiazole		40	80	53	75	74	73	77	82	82	—	
Bis(2-chloroisopropyl) ether		—	74	77	76	76	77	71	80	77	—	
p-Cresol		33	58	47	50	44	49	60	69	68	—	
Dibenzofuran		73	70	95	83	93	86	85	82	84	—	
n-Hexadecane		3	—	—	8	3	18	14	—	11	—	
1-Methylnaphthalene		64	62	80	75	76	82	80	77	79	—	
2-Methylnaphthalene		63	61	77	72	75	80	81	77	77	—	
o-Nitrotoluene		53	75	77	79	82	81	81	83	83	—	
Naphthalene		64	66	78	77	79	81	82	80	80	—	
Phenol		19	30	29	32	14	33	41	38	46	—	
α-Terpineol		36	76	62	77	81	75	75	80	80	—	
sym-Tetrachloroethane		35	58	59	66	61	68	68	72	72	—	
Dehydroabietic acid	100	31	—	85	—	94	—	—	86	—	—	111
Di-2-ethylhexyl phthalate		22	—	13	—	33	—	—	11	—	—	
2-Ethylhexanol		74	—	79	—	85	—	—	91	—	—	
Isophorone		46	—	47	—	76	—	—	86	—	—	
Palmitic acid		12	—	16	—	67	—	—	79	—	—	
Pentachlorophenol		83	—	77	—	84	—	—	84	—	—	
α-BHC	1	—	—	28	—	53	—	—	90	—	9	46
Lindane		—	—	17	—	45	—	—	107	—	10	
β-BHC		—	—	—	—	71	—	—	81	—	32	
Aldrin		—	—	63	—	51	—	—	50	—	25	
Dieldrin		—	—	82	—	61	—	—	107	—	25	
Cumene	10,000	67	—	—	—	67	—	—	—	—	—	51
Ethylbenzene		59	—	—	—	60	—	—	—	—	—	
Naphthalene		93	—	—	—	90	—	—	—	—	—	
n-Hexane		83	—	—	—	82	—	—	—	—	—	
Phenol		45	—	—	—	27	—	—	—	—	—	
Octanoic acid		81	—	—	—	58	—	—	—	—	—	
o-Cresol		67	—	—	—	59	—	—	—	—	—	
Chlorophenol		85	—	—	—	70	—	—	—	—	—	

pH of the solution used. Stepan and Smith[51] used a pH of 5.7, whereas Van Rossum and Webb[111] used distilled water. The recovery using a mixture of XAD-4 and XAD-8 was similar to that with XAD-7 at pH 5.7, however, even with the use of distilled water.

XAD-8 resin is reported[16] to be more suitable than XAD-2 in natural water studies because the pores of XAD-2 have a tendency to become clogged by natural polyelectrolytes. This clogging tends to decrease the capacity of the resin for smaller, lower molecular weight organic solutes. The capacity of XAD-8 is[72] comparable to or, in most instances, greater (*e.g.*, 6-fold for phenols) than that of XAD-2 if it is expressed per unit of the resin surface.

Open-pore polyurethane was compared with Amberlite XAD-2[103] and XAD-4[112] by using the sorption capacity of pyrene and detergent, respectively, and was found to be more suitable. With polyethylated compounds, however, polyurethane foam retained only 46% of the compounds (20% of which were adsorbed irreversibly) whereas XAD-4 resin showed both sorption and desorption of *ca.* 100%[68].

Chriswell *et al.*[113] compared Amberlite XAD-2 resin with Filtrasorb 300 activated carbon. The average recovery for various groups of compounds are listed in Table 14. With the exception of acidic compounds, for which neither of the sorbents is suitable, and alkanes, for which activated carbon is more suitable, the porous polymer is always more suitable. A different recovery is caused by incomplete sorption, which occurs to a greater extent with carbon materials. In total 100 compounds were studied. The recovery was better with XAD resin for 59 compounds and with carbon for 12 compounds. The concentration procedure was identical for both sorbents and was selected as optimal for carbon. The recovery from the polymer is therefore slightly lower than under optimal conditions (see Junk *et al.*[22]).

TABLE 14

COMPARISON OF RECOVERIES WITH AMBERLITE XAD-2 AND ACTIVATED CARBON[113]

Compound type	*Number of investigated compounds*	*Recovery (%)*	
		Resin	*Carbon*
Alkanes	5	5	15
Esters	4	61	49
Alcohols	8	73	47
Phthalate esters	3	82	24
Phenols	10	45	7
Chlorinated alkanes and alkenes	5	43	55
Chlorinated aromatic compounds	13	70	11
Aromatic compounds	7	68	6
Aldehydes and ketones	3	74	4
Amines	13	54	24
Carboxylic acids	11	1	2
Pesticides	4	34	16
Miscellaneous	14	33	11

A comparison of Amberlite XAD-4 with the carbon material Spherocarb (carbon molecular sieve) led to conclusions[19] similar to those obtained for XAD-2 resin. The recovery of some compounds with Spherocarb (some naphthalenes,

phenols, biphenyl) is, as a result of incomplete liquid desorption, very poor. However, Spherocarb has one major advantage over XAD-4, namely the stronger sorption of low-molecular-weight polar organic compounds (*e.g.*, 1-naphthol).

A comparison of the use of Amberlite XAD-4 resin with activated carbon (coconut charcoal) for the determination of polyethoxylated compounds also showed[68] that desorption with ethanol is very poor with carbon.

The adsorption capacity of carbon was compared with those of Amberlite XAD-2[113], Amberlite XAD-4[26,112], Synachrom[27] and open-pore polyurethane[112], and was always found to be lower.

6. STORAGE OF SAMPLES

The transportation of a contaminated water sample from the sampling location to an analytical laboratory and its storage are, in addition to the sampling itself, problems if trace concentrations of organic compounds are to be determined. Changes in the composition of the dissolved compounds can occur during these operations, as a result of transfer of the dissolved compounds from the liquid into the gaseous phase, depending on their partition coefficients and/or leaking of the gaseous phase from the sample container, adsorption on its walls (even if glass material is used; *cf.*, Table 2), and microbial decomposition. Transportation of large volumes of water gives rise to another problem. These difficulties can be solved by extraction with porous polymers executed directly at the sampling location in the field. Contaminants are thus transported to the laboratory concentrated in a small volume of sorbent, and a larger amount of the compounds can therefore be transported in a smaller volume.

The surface of the porous polymers applied in the extraction is inert. Therefore, no changes should occur in samples that are concentrated on such sorbents during their transportation and storage. Zlatkis *et al.*[114] verified this assumption for some volatile compounds from human urine which were adsorbed on Tenax. The samples were stored in the laboratory on the one hand, and transported from the U.S.A. to Germany and back during two weeks on the other. At the same time they investigated the influence of temperature (0°, 4° and room temperature). A comparison of the results showed virtually no differences. Pellizzari *et al.*[96] obtained similar results for the same sorbent that was used for the storage and the transportation through the U.S.A. of some carcinogenic compounds. The recovery of these compounds remains quantitative even after storage for 1 week or transportation. A slight decrease was observed after an additional few weeks. The effect of the period of storage on Amberlite XAD-2 was studied for fenitrothion[61]. This compound is very unstable in water and storage of its samples in water is thus very questionable. The recovery of the compound adsorbed on the polymer remained constant after storage for 5 weeks. Similar results were also obtained[62] for the degradation products of fenitrothion, *i.e.*, fenitrooxon and aminofenitrothion. Storage of polynuclear aromatic hydrocarbons on porous polyurethane foam for 7 days at 4° does not lead to a decrease in recovery. At room temperature the recovery is, however, only 82% of the original value for the same period of storage[106].

Mallet *et al.*[62] compared the results of the analyses of fenitrothion from two localities after forest spraying. The sample (parts per billion concentrations) was

always divided into three 1-l portions. Two 1-l sub-samples were preserved with 50 ml of either chloroform or benzene and analysed at the laboratory within the next few days. The third sub-sample from the first locality was extracted with and eluted from XAD-2 resin in the field. The extract was stored and analysed later at the laboratory. The third sub-sample from the second locality was extracted with XAD-2 resin in the field, immediately capped and returned to the laboratory for analysis 3 days later. The results of the analyses of individual sub-samples were similar and showed that extraction at the sampling location with subsequent analysis after the transportation to the laboratory is applicable with good results.

7. SENSITIVITY OF THE METHOD

The sensitivity of the method, *i.e.*, the minimal detectable concentration of the compounds in water, is determined by the adsorption capacity of the sorbent, the volume of water treated, the sensitivity of the detector used for the final analysis, the type of the compound under study and the desorption procedure.

In order to establish the sensitivity of the method, let us take as an example one of the lowest detection limits, namely that reported by McNeil *et al.*[24] of 0.01 ppt, *i.e.*, $1 \cdot 10^{-11}$ g/l. The experimental data that are important with respect to the sensitivity are as follows: the volume of the water sample treated was 300 l, chlorinated pesticides were the subject of the analysis, a mass spectrometer operated in the specific ion-monitoring mode was used as a detector, liquid desorption was applied with subsequent concentration of the eluate to 0.3 ml and 1 μl of the concentrated sample was injected into the gas chromatograph.

From the detection limit and considering the above experimental conditions, the conclusion can be drawn that $3 \cdot 10^{-9}$ g of the compound under analysis is contained in 0.3 ml of the concentrated eluate at the limiting concentration of $1 \cdot 10^{-11}$ g/l. Thus $1 \cdot 10^{-11}$ g of the substance is injected into the gas chromatograph. It then follows further that:

(1) If the volume of water treated is smaller and the other experimental conditions are kept constant (*i.e.*, detector and desorption procedure) it will be possible to determine higher concentrations of the given compound. An amount of the compound will always be in the eluate that was present in the original total volume of the sample, provided that the recovery is 100%. The maximal volume of the treated sample is then given in practice by the time that can be accepted for the passage of a water sample through the concentration column.

(2) If the detector with a higher sensitivity towards the given compound (*e.g.*, electron-capture detector for halogen compounds) is applied under the original experimental conditions, the detection limit will be shifted towards lower concentrations. Alternatively, if the original detection limit is sufficient, *e.g.*, from the viewpoint of standards, a smaller volume of a water sample can be treated and the time required for the concentration can thus be reduced in proportion to the increase in the sensitivity of the new detector in comparison with the original one.

(3) As already mentioned, in the section dealing with desorption, the concentration effect is impaired during liquid desorption. In the above example, only 1 μl out of the total 300 μl of the eluate is taken for analysis. If it were possible to inject into the chromatograph the total amount of the compound from the concen-

tration column all at once (*e.g.*, on thermal desorption), the detection limit would be reduced in this instance to $3.3 \cdot 10^{-14}$ g/l, *i.e.*, 0.03 ppq. Alternatively, if the same concentration limit were maintained, it would be sufficient to treat 1 l of water.

(4) Under boundary and optimal experimental conditions, *i.e.*, a very sensitive detector towards the investigated compound (the electron-capture detector for halogen compounds), a very large volume of the water sample (100 l), a desorption procedure such that the total amount of the adsorbed compound can be analysed at once and the capacity of the sorbent such that the sorbent can trap this amount, concentrations up to $1 \cdot 10^{-14}$–$1 \cdot 10^{-15}$ g/l, *i.e.*, 0.01–0.001 ppq, can theoretically be determined.

(5) For heptachlor the maximal permissible level (U.S. Environmental Protection Agency) is[115] 0.0001 mg/l. In order to determine this concentration under experimental conditions identical with those used by McNeil *et al.*[24], 30 ml of water are only sufficient for the treatment at the detection limit reported by them. For thermal desorption 100 μl and with more sensitive detection (electron-capture detector) 1–10 μl of water would be sufficient. Hence even in the case of a very strict standard very small volumes of water are sufficient.

The method is thus obviously advantageous from the viewpoint of both absolute sensitivity and practical application (treatment of a certain volume of water for the investigation of the concentration allowed by the standard).

8. SUMMARY

Determination of organic pollutants in water requires analysis at or below ppb levels. For analysis of such low levels, concentration techniques must be applied. This paper describes a concentration technique based on the sorption of organic compounds on organic porous polymers. The principles of the method, the characteristics and applications of various types of sorbents, the quality requirements for the materials used and the sensitivity of the method are discussed.

REFERENCES

1 T. Fujii, *J. Chromatogr.*, 139 (1977) 297.
2 A. Nonaka, *Advan. Chromatogr.*, 12 (1975) 223.
3 J. Teplý and M. Dressler, *J. Chromatogr.*, in press.
4 J. Novák, J. Žlutický, V. Kubelka and J. Mostecký, *J. Chromatogr.*, 76 (1973) 45.
5 K. Grob, K. Grob, Jr., and G. Grob, *J. Chromatogr.*, 106 (1975) 299.
6 W. Bertsch, E. Anderson and G. Holzer, *J. Chromatogr.*, 112 (1975) 701.
7 A. A. Rosen and E. M. Middleton, *Anal. Chem.*, 31 (1959) 1729.
8 J. W. Eichelberger and J. J. Lichtenberg, *J. Amer. Water Works Ass.*, 63 (1971) 25.
9 O. J. Sproul and D. W. Ryckman, *J. Water Pollut. Contr. Fed.*, 23 (1961) 1188.
10 W. L. Lamar and D. F. Goerlitz, *J. Amer. Water Works Ass.*, 55 (1963) 797.
11 C. D. Chriswell, R. C. Chang and J. S. Fritz, *Anal. Chem.*, 47 (1975) 1325.
12 *Development of the Concentration Method for the Analysis of Low Volatile Lipoid Substances in Waste Waters*, Report, Institute of Analytical Chemistry of Czechoslovak Academy of Sciences, Brno, Czechoslovakia, November 1973.
13 *Technical Bulletin, Amberlite XAD-2*, Rohm & Haas, Philadelphia, Pa., U.S.A.
14 J. Seidl, *Chem. Prům.*, 26 (1976) 94.
15 E. M. Thurman, R. L. Malcolm and G. R. Aiken, *Anal. Chem.*, 50 (1978) 775.

16 R. L. Malcolm, E. M. Thurman and G. R. Aiken, *Proceedings of the 11th Annual Conference on Trace Substances in Environmental Health, Columbia, Missouri, 1977*, pp. 307–314.
17 V. Leoni, G. Pucceti, R. J. Colombo and A. M. Dóvidio, *J. Chromatogr.*, 125 (1976) 399.
18 G. A. Junk, C. D. Chriswell, R. C. Chang, L. D. Kissinger, J. J. Richard, J. S. Fritz and H. J. Svec, *Z. Anal. Chem.*, 282 (1976) 331.
19 A. Tateda and J. S. Fritz, *J. Chromatogr.*, 152 (1978) 329.
20 V. Kubelka, J. Mitera, J. Novák and J. Mostecký, *Collection of the Technical University of Chemical Technology, Prague*, 1976, F-20, p. 85.
21 V. Kubelka, J. Mitera, J. Novák and J. Mostecký, *Chem. Prům.*, 25 (1975) 593.
22 G. A. Junk, J. J. Richard, M. D. Griesser, D. Witiak, J. L. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. Chromatogr.*, 99 (1974) 745.
23 A. K. Burnham, G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec and R. Willis, *Anal. Chem.*, 44 (1972) 139.
24 E. E. McNeil, R. Otson, W. F. Miles and F. J. M. Rajabalee, *J. Chromatogr.*, 132 (1977) 277.
25 V. Niederschulte and K. Ballschmitter, *Z. Anal. Chem.*, 269 (1974) 360.
26 D. C. Kennedy, *Environ. Sci. Technol.*, 7 (1973) 138.
27 I. Viden, V. Kubelka and J. Mostecký, *Z. Anal. Chem.*, 280 (1976) 369.
28 R. M. Cassidy, M. T. Burteau, J. P. Misian and R. W. Ashley, *J. Chromatogr. Sci.*, 14 (1976) 444.
29 C. D. Chriswell, L. D. Kissinger and J. S. Fritz, *Anal. Chem.*, 48 (1976) 1123.
30 R. L. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968, p. 192.
31 M. Krejčí, M. Roudná and Z. Vavrouch, *J. Chromatogr.*, 91 (1974) 549.
32 W. E. May, S. N. Chesler, S. P. Cram, B. H. Gump, H. S. Hertz, D. P. Enagonio and S. M. Dyszel, *J. Chromatogr. Sci.*, 13 (1975) 535.
33 C. G. Creed, *Res./Develop.*, 27, No. 9 (1976) 40.
34 D. Ishii, K. Hibi, K. Assai and M. Nagaya, *J. Chromatogr.*, 152 (1978) 341.
35 E. D. Pellizzari, B. H. Carpenter, J. E. Bunch and E. Sawicki, *Environ. Sci. Technol.*, 9 (1975) 556.
36 W. V. Ligon, Jr., and R. L. Johnson, Jr., *Anal. Chem.*, 48 (1976) 481.
37 A. Zlatkis, A. Lichtenstein and A. Tishbee, *Chromatographia*, 6 (1973) 67.
38 J. P. Mieure and M. W. Dietrich, *J. Chromatogr. Sci.*, 11 (1973) 559.
39 K. E. Murray, *J. Chromatogr.*, 135 (1977) 49.
40 M. G. Neumann and S. Morales, *J. Chromatogr.*, 74 (1972) 332.
41 G. A. Junk, H. J. Svec, R. D. Vick and M. J. Avery, *Environ. Sci. Technol.*, 8 (1974) 1100.
42 B. Versino, H. Knöppel, M. DeGroot, A. Peil, J. Poelman, H. Schauenburg, H. Vissers and F. Geiss, *J. Chromatogr.*, 122 (1976) 373.
43 C. D. Chriswell, *J. Chromatogr.*, 132 (1977) 537.
44 A. K. Burnham, G. V. Calder, J. S. Fritz, G. A. Junk, H. J. Svec and R. Vick, *J. Amer. Water Works Ass.*, 65 (1973) 722.
45 P. R. Musty and G. Nickless, *J. Chromatogr.*, 100 (1974) 83.
46 P. R. Musty and G. Nickless, *J. Chromatogr.*, 89 (1974) 185.
47 C. Osterroht, *J. Chromatogr.*, 101 (1974) 289.
48 K. Grob and F. Zürcher, *J. Chromatogr.*, 117 (1976) 285.
49 D. P. Schwartz, *J. Chromatogr.*, 152 (1978) 514.
50 C. K. Wun, R. W. Walker and W. Litsky, *Water Res.*, 10 (1976) 995.
51 S. F. Stepan and J. F. Smith, *Water Res.*, 11 (1977) 339.
52 R. F. C. Mantoura and J. P. Riley, *Anal. Chim. Acta*, 76 (1975) 97.
53 G. R. Harvey, W. G. Steinhauer and J. M. Teal, *Science*, 180 (1973) 643.
54 W. H. Glaze, J. E. Henderson, J. E. Bell and Van A. Wheeler, *J. Chromatogr. Sci.*, 11 (1973) 580.
55 L. D. Kissinger and J. S. Fritz, *J. Amer. Water Works Ass.*, 68 (1976) 435.
56 W. H. Glaze, G. R. Peyton and R. Rawley, *Environ. Sci. Technol.*, 11 (1977) 685.
57 G. A. Junk, J. J. Richard, H. J. Svec and J. S. Fritz, *J. Amer. Water Works Ass.*, 68 (1976) 218.
58 J. J. Richard and J. S. Fritz, *Talanta*, 21 (1974) 91.
59 J. A. Coburn, I. A. Valdmanis and A. S. Y. Chau, *J. Ass. Offic. Anal. Chem.*, 60 (1977) 224.
60 D. C. Paschal, R. Bicknell and D. Dresback, *Anal. Chem.*, 49 (1977) 1551.
61 K. Berkane, G. E. Caissie and V. N. Mallet, *J. Chromatogr.*, 139 (1977) 386.
62 V. N. Mallet, G. L. Brun, R. N. MacDonald and K. Berkane, *J. Chromatogr.*, 160 (1978) 81.
63 D. M. Stuermer and G. R. Harvey, *Nature (London)*, 250 (1974) 480.
64 *Technical Bulletin, Amberlite XAD-4*, Rohm & Haas, Philadelphia, Pa., U.S.A.

65 S. Mierzwa and S. Witek, *J. Chromatogr.*, 136 (1977) 105.
66 C. G. Daughton, D. G. Crosby, R. L. Garnas and D. P. H. Hsiek, *J. Agr. Food Chem.*, 24 (1976) 236.
67 P. R. Musty and G. Nickless, *J. Chromatogr.*, 120 (1976) 369.
68 P. Jones and G. Nickless, *J. Chromatogr.*, 156 (1978) 87.
69 A. D. Thruston, Jr., *J. Chromatogr. Sci.*, 16 (1978) 254.
70 *Preliminary Technical Notes, Amberlite XAD-7*, Rohm & Haas, Philadelphia, Pa., U.S.A.
71 J. Fritz and R. B. Willis, *J. Chromatogr.*, 79 (1973) 107.
72 E. M. Thurman, G. R. Aiken and R. L. Malcolm, *Proceedings of the 4th Joint Conference on the Sensing of Environmental Pollutants, New Orleans, 1977*, Paper No. 166, American Chemical Society, Washington, D.C., 1978, p. 630.
73 *Amberlite XAD Macroreticular Adsorbents*, Rohm & Haas, Philadelphia, Pa., U.S.A.
74 J. P. Riley and D. Taylor, *Anal. Chim. Acta*, 46 (1969) 307.
75 J. Seidl, *Chem. Prům.*, 25 (1975) 416.
76 J. Seidl and F. Krška, *Chem. Prům.*, 25 (1975) 597.
77 J. Seidl, *Chem. Prům.*, 26 (1976) 30.
78 J. F. Johnson and E. M. Barral II, *J. Chromatogr.*, 31 (1967) 547.
79 O. L. Hollis and W. V. Hayes, *J. Gas Chromatogr.*, 4 (1966) 235.
80 J. Merle d'Aubigne and G. Guiochon, *Chromatographia*, 3 (1970) 153.
81 J. M. Trowell, *J. Chromatogr. Sci.*, 9 (1971) 253.
82 T. A. Gough and C. F. Simpson, *J. Chromatogr.*, 68 (1972) 31.
83 L. S. Frankel and R. F. Blask, *Anal. Chem.*, 48 (1976) 732.
84 A. Niederwieser and P. Giliberti, *J. Chromatogr.*, 61 (1971) 95.
85 O. Dufka, J. Malinský, J. Churáček and K. Komárek, *J. Chromatogr.*, 51 (1970) 111.
86 O. Dufka, J. Malinský and J. Vladyka, *Chem. Prům.*, 21 (1971) 459.
87 V. Kubelka, J. Mitera, J. Novák and J. Mostecký, *Chem. Listy*, 71 (1977) 241.
88 I. Viden, *Detection and Identification of Organic Pollutants in Water, Thesis*, Faculty of Fuel and Water Technology, Technical University of Chemical Technology, Prague, 1975.
89 *Note FF-157B, Chromosorb 102*, Johns-Manville, Denver, Colo., U.S.A.
90 J. P. Mieure and M. W. Dietrich, *26th Annual Summer Symposium on Analytical Chemistry, Oxford, Ohio, 1973.*
91 *Note FF-194A, Chromosorb 105*, Johns-Manville, Denver, Colo., U.S.A.
92 *Note FF-215A, Chromosorb 106 and 107*, Johns-Manville, Denver, Colo., U.S.A.
93 R. van Wijk, *Chimia*, 24 (1970) 254.
94 R. van Wijk, *J. Chromatogr. Sci.*, 8 (1970) 418.
95 K. Sakodynskii, L. Panina and N. Klinskaya, *Chromatographia*, 7 (1974) 339.
96 E. D. Pellizzari, J. E. Bunch, R. E. Berkley and J. McRae, *Anal. Lett.*, 9 (1976) 45.
97 *Technical Bulletin No. 24, Tenax-GC*, Applied Science Labs., State College, Pa., U.S.A.
98 M. B. Neher and P. W. Jones, *Anal. Chem.*, 49 (1977) 512.
99 V. Leoni, G. Pucceti and A. Grella, *J. Chromatogr.*, 106 (1975) 119.
100 E. Břízová, M. Popl and J. Čoupek, *Chem. Prům.*, 27 (1977) 352.
101 E. Břízová, M. Popl and J. Čoupek, *J. Chromatogr.*, 139 (1977) 15.
102 W. D. Ross and R. T. Jefferson, *J. Chromatogr. Sci.*, 8 (1970) 386.
103 J. D. Navratil, R. E. Sievers and H. F. Walton, *Anal. Chem.*, 49 (1977) 2260.
104 T. R. Lynn, D. R. Rushneck and A. R. Cooper, *J. Chromatogr. Sci.*, 12 (1974) 76.
105 H. D. Gesser, A. Chow, F. C. Davis, J. F. Uthe and J. Reinke, *Anal. Lett.*, 4 (1971) 883.
106 J. Saxena, J. Kozuchowski and D. K. Basu, *Environ. Sci. Technol.*, 11 (1977) 682.
107 D. K. Basu and J. Saxena, *Environ. Sci. Technol.*, 12 (1978) 791.
108 H. D. Gesser, A. B. Sparling, A. Chow and C. W. Turner, *J. Amer. Water Works Ass.*, 65 (1973) 220.
109 J. W. Bedford, *Bull. Environ. Contam. Toxicol.*, 12 (1974) 622.
110 R. Kunin, *Amber-Hi-Lites*, No. 78, Rohm & Haas, Philadelphia, Pa., U.S.A., 1963.
111 P. van Rossum and R. G. Webb, *J. Chromatogr.*, 150 (1978) 381.
112 J. D. Navratil and R. E. Sievers, *Int. Lab.*, No. 11/12 (1977) 26.
113 C. D. Chriswell, R. L. Ericson, G. A. Junk, K. W. Lee, J. S. Fritz and H. J. Svec, *J. Amer. Water Works Ass.*, 69 (1977) 669.
114 A. Zlatkis, H. A. Lichtenstein, A. Tishbee, W. Bertsch, F. Shunbo and H. M. Liebich, *J. Chromatogr. Sci.*, 11 (1973) 299.
115 *Interim Primary Drinking Water Standards*, Fed Reg., 4P, Part II, (1975) 11990.