Translated from *Uspekhi Khimii*, 52 1225-1246 (1983) U.D.C. 543.544

Use of Porous Polymer Sorbents for Concentrating Traces of Organic Compounds from Gases or Liquids

L.D.Glazunova, L.I.Panina, and K.I.Sakodynskii

The advantages and disadvantages of the adsorption method of concentrating organic trace impurities of various types from air or from liquids are discussed. The main types of sorbent currently used are examined, and their adsorption characteristics are compared, with special emphasis on porous polymer sorbents. The special features of these polymers when used as concentrators are stressed, and interrelationships are established between the characteristics of the sorbents and their effectiveness in the sorption of different classes of organic compounds, and between their adsorption capacity (or percentage extraction) and the concentration conditions. Problems in the storage of samples concentrated on polymer sorbents are discussed. Some examples of the practical use of polymer sorbents for concentrating organic trace impurities from air or from liquid media are given. 106 references.

CONTENTS

I. Introduction 693
II. Main methods of concentrating trace impurities of organic compounds 693
III. Choice of sorbent for preparing concentrator columns 694
IV. Porous polymer sorbents in the adsorption method of concentrating trace impurities 695
V. The use of porous polymer sorbents in solving concentration problems 697

I. INTRODUCTION

The analysis of air contamined by industrial and by domestic waste products and the analysis of natural waters and effluents are among the most important problems in the wide-ranging efforts now being devoted to the protection of the environment. Information on the relative amounts of trace impurities (especially in the case of toxic substances) is needed both in theoretical studies and in the control of industrial practices. Chromatography is now the main method of impurity analysis for air and water[1,2]: its most important advantages are its high selectivity and the wide choice of sorbents and of separation conditions, which make the method ideally suitable for monitoring the composition of the environment.

Because of the relatively low concentration of organic impurities in air, water, and biological fluids most of the chromatographic methods used for impurity detection rely on a preliminary concentration stage. The main steps in the determination of trace impurities† in air and in water are the same: 1) collecting and storing the sample, 2) concentrating the components, and 3) chromatographic analysis. However, depending on whether the sample is air or water, the stages differ in a number of important aspects, discussed (for example) in Refs.1–5.

II. MAIN METHODS OF CONCENTRATING TRACE IMPURITIES OF ORGANIC COMPOUNDS

The following methods have been used for the pre-concentration of organic trace impurities in air: liquid extraction, freezing, chemical trapping of the components, and adsorption of the impurities by sorbents. In the case of water samples additional methods are available, including thermal methods (based on changes in solubility on heating), vacuum and thermo-vacuum methods (based on gas evolution at reduced pressure), and studies of the equilibrium vapour phase.

The extraction method requires high-purity extracting agents and offers only a moderate sensitivity. Liquid–liquid extraction is usually organised as a cyclic process. It is applicable mainly to samples with relatively high concentrations of impurities and relatively low volumes, since large-volume samples make the method excessively laborious. The most commonly used extractants are methylene chloride, chloroform, hexane, and carbon disulphide. The efficiency and speed of the extraction depend on the distribution coefficient of the substance between water and the organic solvent, and on the area of contact between the two phases. The cyclic process is not very effective even when the distribution coefficient is relatively high, and a continuous (or multi-stage) extraction process is now recommended for effective extraction[6]. The main shortcoming of the extraction method is the need to introduce a new solvent, which complicates the subsequent gas-chromatographic analysis. The scrubbing of gas samples with organic solvents has the same disadvantages as liquid–liquid extraction.

When freezing is used as a method of concentrating impurities it is difficult to avoid the incorporation of the wanted impurity in the growing ice crystals. Furthermore, the presence of large amounts of salts in the samples introduces additional complications in the freezing method.

Chemical trapping of the components has only a limited application. The use of thermal and thermo-vacuum methods is difficult in the presence of mechanically entrained contaminants and of surface-active compounds. Decomposition and hydrolysis of the components during desorption (by raising the temperature) must also be guarded against.

Organic compounds dissolved in water are often determined by analysing the equilibrium vapour phase[7,8]. The method involves heating the liquid sample in a closed vessel and studying the composition of the vapour phase in thermodynamic equilibrium with the liquid. Several variants have been described. In the simplest, the equilibrium vapour phase is sampled with a hypodermic syringe, from which the sample is transferred directly to the chromatograph[9]. However, if the organic compound is present in trace amounts in the water, direct sampling of the vapour is seldom adequate, because of the limitations imposed by the sensitivity of the chromatographic detector.

† The trace impurity range corresponds to concentrations between 10^{-1} and 10^{-7} % by volume or weight.

In a method recently proposed[10] for extracting organic impurities from water 5–10 ml samples are forced in air pressure through a special column (called the concentrator) consisting of a glass tube with capillary contructions, which assists the transfer of the impurity to the vapour phase, from which it is injected into the chromatograph by a stream of air. The main shortcomings of this method is its limited application (to high-boiling substances).

The most promising of the methods of concentrating trace impurities listed above is the adsorption method, in which a column packed with a porous sorbent is used as the concentrator. The experimental procedure is the following: a known volume of gas or liquid is passed through a column 2–4 mm in diamter and 2–5 (or up to 50) cm long, packed with the sorbent, under controlled flow-rate and temperature conditions. The organic compounds present in the air (or water) sample are retained and accumulated in the column: the concentrator column acts as a chromatographic column operated at room temperature or below, and the sample of air or water acts as the mobile phase.

The adsorbed substances are recovered from the concentrator by extraction with an organic solvent, or by thermo-desorption. Both these methods are widely used in practice, though the extraction variant causes dilution of the sample with a corresponding loss of analytical sensitivity. The thermo-desorption method is therefore preferred for compounds stable at high temperatures, as it is both simpler and less time-consuming. The choice of the desorption method assumes thermal stability of the sorbent: it should be possible to desorb the impurity completely and without decomposition of any component of the mixture at a temperature chosen according to the boiling points and chemical nature of the components. The thermo-desorption method can form the basis of a simple and fully automated system for concentrating trace impurities from air[11].

However, even in the thermo-desorption method the detection limit may be affected by the spreading of the chromatographic bands of the impurity components being transferred to the analytical column. Therefore, in order to increase the analytical sensitivity, we must optimise the transfer of the concentrated impurities to the analytical column. One way of doing this is to insert an additional trap cooled in liquid nitrogen (capillary loop) after the concentrator; this makes the injection of the concentrated sample even more compact[11–13]. An alternative method is to raise the temperature of thermo-desorption of the impurities, but of course this method makes even more stringent demands on the thermal stability of the chosen sorbent. The desorbed impurities are analysed gas-chromatographically in analytical columns (packed, or capillary). The chromatograph is combined with a mass-spectrometric detector to identify the peaks resolved by the analysis.

Interesting results have been obtained by combining the analysis of the equilibrium vapour phase and the adsorption method. It is found in practice that the sensitivity of the analysis is substantially increased by concentrating the substances present in the vapour phase on columns packed with sorbent. Thus a modification[14] of a system previously described[10] (by inserting a Polisorb-1 column to remove the impurities from the vapour phase) has enabled alcohols, ketones, aldehydes, and esters to be detected in the effluent waters of hydrolysis and alcohol production plant.

One of the variants of the combined method (analysis of the equilibrium vapour and pre-concentration by adsorption) is to examine the vapour over the heated liquid sample swept by a stream of inert gas[15,16] into an adsorption concentrator. Another variant (the gas-phase extraction method[17,18]) relies on bubbling an inert gas through the water sample at a known rate (usually 40–80 ml min^{-1}). The organic impurities pass into the gas phase and are thus gradually removed from the water. The distillation time is 1–3 h, depending on the flow rate of the gas and on the volume and temperature of the sample vessel, controlled by a regulator between room temperature and 70–80 °C. The dynamical nature of this method ensures a high level of extraction at room temperature for substances boiling below 150 °C. If additional concentration of the impurities is needed a water-cooled condenser (to remove the water entrained by the gas flow) and a concentrator filled with adsorbent are inserted into the gas outlet stream[6].

III. CHOICE OF SORBENT FOR PREPARING CONCENTRATOR COLUMNS

The choice of sorbent for the concentrator column depends mainly on the nature of the compound for analysis, and is determined by the intermolecular interactions in the sorbent–sorbate system (as in any other chromatographic process).

The sorbent should have an adequate capacity for the given substance. The adsorption should be reversible, i.e. without chemical changes. Furthermore the sorbent should be thermally stable and its affinity for water should be low (especially for the analysis of solutions and moist gases). If the capacity of the sorbent is insufficient for all the components of the mixture several sorbents can be used instead of a single sorbent[19,20], and placed in the same concentrator.

The sorbents most commonly used for concentrating trace impurities include activated carbon, graphitised thermal black, molecular sieves (including carbon-based sieves), various grades of silica gel and aluminium oxide, sorbents for gas–liquid chromatography[3,21], and porous polymer sorbents.

Activated carbon has a high adsorption capacity, which allows this sorbent to be used in small amounts, and it is also thermally stable. However, it holds the trace impurities very strongly, making them difficult to desorb. Thus the use of carbon may lead to incomplete recovery of the impurities (due to the irreversibility of the adsorption) accompanied by the appearance of spurious peaks (due to impurities already present in the carbon)[22]. Effective removal of low-molecular-weight compounds (for example, ethylene and methylene chlorides) requires strong cooling of the concentrator, which is not always convenient[4]. Furthermore activated carbon reacts with several organic compounds (especially with sulphur compounds). Desorption from carbon usually requires extraction with organic solvents. Transfer of the concentrated substances to the analytical column can be achieved also by thermo-desorption, but often the temperature required is unacceptably high because of the very fine porous structure of carbon.

The use of carbon molecular sieves and graphitised blacks (Carbopaks, Carbochroms, Carbosieves, Spherocarbs) for concentrating traces of organic compounds is limited by the irreversible sorption of many compounds on these sorbents and by the high reactivity of the sorbents. Their main disadvantage, as with the activated carbons, is the need to use organic solvents for the desorption of the concentrated impurities (causing dilution of the sample and loss of analytical sensitivity) or alternatively to use elevated desorption temperatures (causing decomposition of the organic compounds).

Silica gels are used for concentrating hydrocarbons with a C_3 or higher carbon skeleton, as well as organic compounds of other classes. The adsorbed substances are usually

desorbed by extraction of (very unusually) by thermodesorption. Among the shortcomings of silica gel as an adsorbent for concentrating trace impurities we should list incomplete recovery of volatile hydrocarbons, adsorption of water vapour from the air sample for analysis, and a tendency towards irreversible sorption of easily polymerisable unsaturated compounds and of compounds chemically reactive towards silica gel (for example, organic bases).

The sorbents used in gas–liquid chromatography (i.e. carriers coated with a stationary phase) are unsatisfactory in the following respects[23]: 1) possible reaction between the compound and the stationary phase (for example, Dexsil-300 and alkalis), and 2) contamination of the sample for analysis by impurities from the liquid phase.

IV. POROUS POLYMER SORBENTS IN THE ADSORPTION METHOD OF CONCENTRATING TRACE IMPURITIES

The porous polymer sorbents Porapak Q, P, N, Tenax GC, Chromosorb (100 series), Amberlite XAD, Polisorb 1, 10, etc. are now widely used for concentrating impurities from air and water. They offer a high adsorption capacity towards many organic substances and a rapid concentration of the impurities, shortening the analysis time of an air sample (say) to 10–20 s.[24] They have a low sorption capacity for water, which is often present in analytical samples (especially in the analysis of the equilibrium vapour phase), and they are chemically inert and thermally stable. Concentration on porous polymer sorbents can be combined with direct thermal desorption (instead of liquid extraction) to transfer the impurity from the concentrator to the gas chromatograph. This offers an enhanced analytical sensitivity and avoids possible interference by the solvent. The concentration of trace organic impurities on porous polymer sorbents is now widely used in analytical practice including impurity analysis in environment protection studies, in industrial hygiene, and in biochemistry and medicine[15,25–30].

1. Main Characteristics of the Sorbent

The sorbents most commonly used for concentrating trace impurities are listed in Table 1. In most cases the sorbent surface is hydrophobic, but XAD-7, XAD-8, the Spherons, and Amberlyst A-26 are hydrophilic. Dressler has pointed out[5] that hydrophobic non-polar sorbents are more effective for concentrating non-polar compounds, whereas for polar compounds hydrophilic adsorbents should be used: the adsorption capacity of the hydrophobic sorbents increases as the polarity of the compound decreases. The particle size of the polymer sorbents used at present is 25–50 or 35–60 mesh. However. an increased sorption capacity can be achieved[6] by using a smaller fraction (80–100 mesh) of the sorbent particles.

The fairly wide choice of types of synthetic polymer sorbent (differing in structure and in surface-chemical properties) which can be combined within the same concentrator explains the successful use of these materials for concentrating organic trace impurities of different classes, with boiling points covering a wide range. Dynamical enrichment on porous polymer sorbents is subject to the following limitations: 1) incomplete adsorption of molecules of low molecular weight, and 2) the appearance of spurious peaks during desorption, due to impurities in the initial polymer. The first of these shortcomings can seriously limit the application of the method, but it can be overcome by an appropriate choice of polymer sorbent. The influence of the second factor can be lessened by a thorough preliminary purification of the sorbent. Hence the purification procedures applied to the sorbents are among the most important aspects of the practical application of porous polymer sorbents to the concentration of trace impurities.

Table 1. Polymer sorbents for concentrating trace impurities[5,94].

Sorbent	Composition of polymer	S_{sp}	d, Å	t, °C
Amberlite XAD-1	copolymer of styrene and divinylbenzene	100	200	250
Amberlite XAD-2	ditto	290—330	85—90	250
Amberlite XAD-4	"	750	50	250
Amberlite XAD-7	copolymer of methyl methacrylate and divinylbenzene	450	80	150
Amberlite XAD-8	ditto	140	250	150
Amberlyst A-26	anion exchange resin containing trimethylamino groups	25—30	—	—
Ostion SP-1	Copolymer of styrene and divinylbenzene	350	86	250
Polisorb-1	ditto	200—250	130	250
Polisorb-10	polyvinylbenzene	300—350	—	250
Polisorbazol	copolymer of *N*-vinyl-3(5)methylpyrazole and ethylene glycol dimethacrylate	300—400	100	280
Polisorbimid-1	copolymer of pyromellitic dianhydride and diaminodiphenyl ether	40—60	1000	450
PFKh	polyphenylquinoxaline	30—50	1600	300
Porapak N	copolymer of styrene, divinylbenzene, and vinylpyrrolidone	500—550	75	200
Porapak P	copolymer of styrene and divinylbenzene	100—200	—	250
Porapak Q	copolymer of ethylvinylbenzene and divinylbenzene	630—840	75	250
Sinachrom	copolymer of styrene and divinylbenzene	520—620	45	250
Spheron MD 30/70	copolymer of methyl methacrylate and divinylbenzene	320	—	230
Spheron SE	copolymer of styrene and ethylene dimethacrylate	70	—	280
Tenax GC	poly(2,6-diphenylphenylene oxide)	19—30	1400	350—375
Chromosorb-102	copolymer of styrene and divinylbenzene	300—400	85—95	250
Chromosorb-105	copolymer of the polyaromatic type	600—700	—	200
Chromosorb-106	cross-linked polystyrene	700—800	—	250

Symbols. S_{sp} is the specific surface, d is the average pore diameter, t is the upper limit of the working temperature range.

2. Preparation of Sorbents for Concentrating Impurities

Preliminary purification of the sorbents removes the main impurities and improves the reproducibility of the analytical results. The polymer sorbents can be prepared in a form suitable for the experiment by the following methods: conditioning in a stream of oxygen-free carrier gas at high temperature (e.g. for Porapak, heat treatment at 225–250 °C in a stream of carrier gas for 12–24 h is recommended[5]), degassing at high temperature in a vacuum, or extraction with organic solvents. The latter method is used most often with sorbents of the Amberlite type, used for concentrating impurities in water. Thus Junk and co-workers[31] recommend the following pre-treatment of Amberlite XAD-2 and XAD-4: wash the sorbent particles several times with water or 0.1 *N* NaOH solution, decant them from methanol, and extract them in a Soxhlet apparatus with methanol, acetonitrile, and diethyl ether (8 h in each solvent). After this pre-treatment the sorbent is stored in a glass vessel under methanol. The

concentrator trap is prepared by filling the column with the purified sorbent (added as a suspension in methanol) and washing the packed layer several times with distilled water.

Lower levels of detection of organic impurities in drinking water have been achieved[32] by adopting a method of purification of the XAD-2 resin which includes successive washings with methanol, diethyl ether, and water. It is stressed that this preliminary purification prevents the formation of decomposition products of the sorbent in contact with water, such as alkanes from $n\text{-}C_{10}H_{22}$ to $n\text{-}C_{24}H_{50}$.[32]

When Tenax GC is used as the sorbent in gas chromatography a conditioning treatment in nitrogen (1 h at room temperature and 1 h at 350 °C) is recommended[33]. Tenax samples for packing concentrator columns have been conditioned at 350 °C for 30 min [34] or for 3 h, followed by 12 h at 200 °C.[35]

3. Sorption Capacity of Porous Polymer Sorbents

The most important factor in the successful application of trace impurity concentration processes is an adequate sorption capacity of the sorbent at the concentration temperature. The sorption capacity for each sorbate (g g^{-1} of sorbent) can be determined from measurements of the sorption front[36]:

$$\alpha = \frac{(t - t_M) F}{W_s} \cdot c$$

where α is the dynamical adsorption capacity for the given sorbate (g g^{-1}), t is the time needed to saturate the sorbent to break-through of the sorbate (s), t_M is the retention time of the gas which is not sorbed (s), W_S is the mass of sorbent (g), F is the flow rate of the carrier gas ($cm^3\ s^{-1}$), c is the concentration of sorbate in the carrier gas (g cm^{-3}), and $(t - t_M)F/W_S$ is the volume of carrier gas containing sorbate at concentration c needed to saturate 1 g of sorbent at the chosen concentrator temperature (293 K).

Comparative studies of the adsorption capacity of several polymer sorbents (Tenax, Porapak P and Q, Amberlite XAD, and Chromosorb 101 and 102) towards volatile organic compounds have been reported[15,20,37,38]: alcohols, ketones, organic acids, nitrogen and chlorine compounds, saturated and aromatic hydrocarbons. The capacity of a sorbent for a given compound was shown to be determined by the nature of the sorbate as well as by that of the sorbent. On the whole, polar compounds are sorbed more effectively by polar polymer sorbents, for example XAD-7 and XAD-8 Amberlites. In non-polar polymer sorbents (e.g. Porapak P, XAD-1, XAD-2, etc.) the adsorption increases with the molecular weight of the sorbate and with decreasing polarity of its molecules.

If the chemical nature of the sorbent is kept constant the adsorption capacity is determined by structural characteristics (specific surface area and porosity). Experimental data on the adsorption capacity for volatile organic compounds have led to the classification of the porous polymer sorbents in the following sequence[37].

$$\text{Tenax} \cong \text{XAD-1} < \text{Porapak P} \ll \text{XAD-2} < \text{Porapak Q} < \text{XAD-7} < \text{XAD-4}$$

For Tenax and the XAD-7 and XAD-4 Amberlites[38] the lowest adsorption capacity is observed with cyclohexane, methanol, and ethanol. The concentrator properties of XAD-7 are the most favourable of this group of three sorbents[38], but nevertheless most of the recent work on the concentration of volatile organic compounds (especially from air) has been done with Tenax because of its exceptionally high thermal stability.

The capacity of a sorbent towards a given compound determines the break-through volume, i.e. the volume of gas or liquid which passes through the sorbent before the appearance of the substance of interest. The break-through volume is treated by many workers as synonymous with the retention volume V_R. However, in general the break-through volume can be smaller than the retention volume because of the correction for the concentration conditions[39].

The break-through volume for the polymer sorbent Tenax has been determined[39] by passing a stream of gas containing the impurity through a trap packed with the sorbent and connecting the outlet to a flame-ionisation detector (direct measurement); it has also been calculated theoretically[40] from the retention volumes and the number of theoretical plates in gas-chromatographic measurements (indirect measurement).

The dependence of the break-through volume on the basic concentration conditions (flow rate of the mobile phase, concentrator temperature, concentration of the impurity and of water vapour in the gas stream) has been investigated. The break-through volume in Tenax was found to be strongly dependent on the velocity of the mobile phase. Thus for a stainless steel concentrator (75 mm × 4.5 mm) containing 0.13 g of Tenax which had been pre-heated at 250 °C for 16 h the optimum flow velocity was 50 ml min^{-1}. The impurity concentration and the temperature also have an effect on the break-through volume. To a first approximation V_R increases two-fold for a decrease in temperature of 10 K. The break-through volume in Tenax is almost independent of the water content of the air sample. This is confirmed by measurements[41] of the specific retention volumes of several model compounds (methanol, ethanol, propanol, ethyl acetate, acetone, and benzene) on Tenax in a carrier gas saturated with water vapour. The difference between retentions in the presence and in the absence of water vapour was shown to be ±10%.

Thus Brown and Purnell conclude[39] that a flow rate of the mobile phase of 500–600 ml min^{-1}, a concentration of the impurity vapour of 100 ppm, a concentrator temperature of 20 °C, and a relative humidity of 95% the break-through volume in Tenax is not less than 50% of the measured retention volume of each compound. Hence they recommend determining the retention volume of the organic compounds experimentally at 20 °C and taking 50% of this quantity as the safe volume for a number of stated assumptions (i.e. the volume of contaminated air which can be passed through the adsorbent before break-through). Other workers[42] take the safe volume as 1/3 of the measured retention volume.

The capacity of the packed column is calculated from the parameter V_R at the concentrator temperature (usually room temperature or below). Since V_R is often determined gas-chromatographically at higher temperatures, linear extrapolation of the retention volumes to room temperature[20] is needed. The possibility and the validity of this extrapolation for polymer sorbents have been examined[43] by using $CHCl_3$, CCl_4, and CH_3CCl_3 as sorbates. The retention volumes determined gas-chromatographically at room temperature were compared with those obtained by extrapolation, and in this way the sorption capacity of the column (filled with polymer sorbent) extrapolated from measured retention volumes was shown to differ somewhat from the true value. The discrepancy is different in different systems, and is a characteristic of the particular system. For example, the capacity of Porapak Q columns for all these halogen compounds is higher than the extrapolated value. Nevertheless the extrapolation of V_R to room temperature is often used in practice because of the simplicity of the calculation.

4. Percentage Extraction of the Compounds for Analysis

The parameter which most accurately characterises the ability of a sorbent to adsorb a compound during the concentration stage and to desorb it during treatment with solvents or when heated to a suitable temperature is the percentage extraction, defined as the ratio of the quantity of substance found in the model sample of air or water after concentration to the quantity of the same substance originally present in the sample (expressed as a percentage). At least two effects can cause low percentage extraction: 1) incomplete adsorption, when a substantial proportion of the trace impurity is lost in the stream of mobile phase, and 2) strong adsorption, when the substance is incompletely desorbed by heating the concentrator. When porous polymer sorbents are used to concentrate the trace impurities from water or air the percentage extraction of organic substances is relatively high. Thus for Amberlite XAD-2 and XAD-7 used in concentrating water samples the percentage extraction of most of the common organic substances (including aliphatic and aromatic hydrocarbons, ketones, ethers, organic acids, phenols, nitrogen and halogen compounds, pesticides, and herbicides) is 75–100%, [5] and in the concentration of impurities from air on Tenax the percentage extraction for hexane, light petroleum, biphenyl, acetone, diphenylamine, and *o*-cresol is 90% with a standard deviation of 5%. [44]

It has also been shown[45–49] that the percentage extraction depends on the particle size of the sorbent, on the concentration of the components in the sample, on the flow rate of carrier gas through the layer of sorbent, on the size of the column, and (in the case of water analysis) on the pH of the sample, on the polarity of the eluent, and on the presence of electrolytes. For example, when a finer fraction of XAD-2 Amberlite (85–120 instead of 60–80 mesh) was used for concentrating chlorinated insecticides a higher percentage extraction was obtained[47]. It has been pointed out[46] that the percentage extraction can often be improved by using a 60 mm × 10 mm column instead of a 30 mm × 10 mm column, while the adsorption of herbicides on XAD-2 Amberlite is relatively unaffected by changes in flow rate from 2 to 10 ml min^{-1}. A flow rate of the water sample of 5 ml min^{-1} was found to be the optimum, but increasing the flow rate still further (from 10 to 32 ml min^{-1}) lowered the percentage extraction. It was also shown[46] that the percentage extraction of organic acids and phenols is related to the dissociation of these compounds and therefore depends on the pH of the solution. In an acid medium the percentage extraction of acids and phenols is markedly higher, and acidification of these samples to pH 2 with HCl is recommended.

5. Permissible Storage of the Concentrated Impurities in the Concentrator

Trace impurities from air or water can be concentrated in the field and stored in the concentrator (trap) until they can be taken to the laboratory for analysis. The use of polymer sorbents in concentrators helps to overcome the difficulties presented by the lengthy storage of concentrated compounds. A possible reason is the relative inertness of the surface of these sorbents, which ensures that the composition of the sorbed organic compounds remains constant, as shown by an analytical study[12,50] of a series of volatile compounds concentrated on Tenax. It has also been shown[50] that the percentage extraction of substances from the concentrator is unaffected by one week's storage of the concentrator at 0.4 or at 20 °C. Goldberg and Sandler[12] mention that a previously conditioned Texan column retained its good adsorption properties throughout the investigation (several weeks), and no spurious peaks were noted in the chromatograms. Keeping the concentrator (containing the concentrated impurities) for 90 days gave a chromatogram indistinguishable from that obtained by carrying out the concentration and the desorption on the same day.

The possibility of lengthy storage of concentrated impurities without change in qualitative or quantitative composition has been reported[51] also for polyurethane sorbents and sorbents of the Amberlite type

V. THE USE OF POROUS POLYMER SORBENTS IN SOLVING CONCENTRATION PROBLEMS

1. Concentration on Tenax

Tenax is the porous polymer sorbent most widely used for concentrating trace impurities[24,28,35,52–63]#. Its main advantages over all other similar sorbents are a high thermal stability (up to 375 °C) and a low "noise" level during thermo-desorption.

The sorption capacity of Tenax towards organic compounds of different types has been shown[50,64] to be high: an important attribute in the analysis of biological fluids, perfumes, and atmospheric pollution. Furthermore the sorption of test substances on a Tenax fore-column was found to be unaffected by the presence of water vapour. Losses of trace impurities during concentration from the 10^{-6}–10^{-9} g ml^{-1} level, and the consequent errors in the quantitative determination, were shown[64] to be due in many cases to the irreversibility of the adsorption on Tenax, and to depend on the composition of the mixture and on the concentration conditions. The sensitivity of the determination of trace impurities can be improved by blocking the Tenax active centres. Thus a preliminary injection into the column of a few microlites of octan-1-ol produces a large increase in the peak area (and a corresponding lowering of the detection threshold) for tributylamine, 2-ethylphenol, butyrophenone, etc. [64]

Bunch and Pellizzari[65] examined the possibility of chemical changes in unsaturated compounds (but-2-ene and cyclohexene) during concentration on a Tenax surface in the presence of traces of Br_2 and Cl_2 in the air sample. They showed that under these conditions the sorbent surface can induce reactions leading to the formation of halogenated hydrocarbons. These reactions can be suppressed by inserting a filter of glass wool soaked in sodium thiosulphate in the gas stream before the concentrator. However, in general the Tenax surface is acceptably inert, giving concentration without significant changes in chemical composition[52–63].

The retention volumes of many organic substances on a Tenax column have been determined[66] at 100–200 °C and extrapolated to 25 °C. The conclusion was that Tenax can be used most successfully for concentrating compounds containing more than seven carbon atoms. For lighter molecules the carbon adsorbent Ambersorb XE-340 is recommended[66], though Porapak sorbents are also usable[20].

The sorption characteristics of Tenax and Carbopak in the concentration of trace impurities of different classes from air contaminated with industrial effluent gases[52] has been published. Carbopak B, a graphitised thermal black with a specific surface of 90 m^2 g^{-1}, can be used at practically any

Tenax is a linear polymer of 2,6-diphenylphenylene oxide with a molecular weight of (0.5–1.0) × 10^6, a specific surface of 19–30 m^2 g^{-1}, and an average pore diameter of 1400 Å.

temperature. When compared in terms of the percentage extraction of a series of organic compounds the adsorption characteristics of Tenax and Carbopak B are generally similar, but sorption properties specific to each adsorbent can also be detected. Thus benzene and n-hexane are fully retained by Carbopak B, but they pass through Tenax (in which their percentage extraction is 35 and 20% respectively). Similar effects are observed for the alkanes from n-pentane to iso-octane. Acetone is most effectively retained by Tenax, but butanol and diethylamine should be concentrated on Carbopak B. On average, for all the classes of organic compounds so far examined, the percentage extraction is 83% on Carbopak B and 75% on Tenax. The use of Carbopak B for the absorption of the C_4–C_5 hydrocarbons and of Tenax for organic compounds with a greater number of carbon atoms has been recommended[52].

A concentrator trap containing 2 cm^3 of Tenax of 30–60 mesh particle size has been used[15] to extract impurities for air and water in the analysis of perfumes and biological fluids. The compounds held on Tenax were desorbed at 300 °C, and the sorbent was regenerated at 375 °C. Gas-chromatographic analyses were carried out on a capillary column.

Columns 15 cm long and 1 cm in diameter containing 2.5 g of Tenax (60–80 mesh) have been used[44] to concentrate trace impurities from air. A 5 litre sample was passed through the concentrator at 0.5 cm^3 min^{-1} and 20 °C. The concentrated substances were transferred to traps (stainless steel tubes of 1.6 mm inside diameter) cooled in liquid nitrogen. Desorption from the trap involved heating the tubes to 300 °C. The percentage extraction of individual organic compounds from model mixtures was ~90% on average.

A preliminary concentration of the trace impurities was used to analyse the volatile components in the cabin of the orbital station Skylab-4 at various times during the mission[11]. More than 300 components were detected gas-volumetrically, and 107 0f these were identified on a mass spectrometer (Freons, siloxanes, hydrocarbons, benzene derivatives, and other compounds with molecular weights between 60 and 500). The concentration was carried out in a Pyrex tube (50 mm × 10 mm) filled with Tenax (60–80 mesh). The procedure included thermo-desorption, transfer of the sample by a gas stream to a trap cooled in liquid nitrogen, and temperature-programmed gas chromatographic analysis.

An analysis[67] of cigarette smoke in air relied on a preliminary concentration in a column (115 mm × 5 mm) packed with Tenax (60–80 mesh) and Carbopak BHT, followed by thermo-desorption at 270 °C into a capillary column coated with OV-101 (25 or 55 m × 0.35 mm). The smoke was found to contain a very wide range of compounds, from low-boiling gases to almost involatile polymers and other high-molecular-weight compounds. The main constituents of smoke are aliphatic and substituted aromatic hydrocarbons.

A special study of concentration problems in the analysis of complex mixtures of organic compounds in water at and below the 1 ppm level has been described[12]. The method included direct injection into the system of a 100 μlitre sample of the water, removal of the water in a condenser at 0 °C, concentration of the trace impurities in a small fore-column (2 cm × 1 mm) cooled in solid CO_2 and filled with Tenax (35 to 60 mesh), and gas-chromatographic analysis of the impurities in a capillary column with a flame-ionisation detector. The method gave very good reproducibility (mean standard deviation 5–6%). Only 4 min were needed for the preparation of the sample for analysis.

A recent review[68] is devoted to the apparatus for extracting trace impurities from water or air and to the methods of concentration on Tenax. The following systems are discussed in detail: hexachlorobutadiene in air (at the 20 ppb level), glycol esters in water (500 ppb), chlorobenzenes in water (3–8 ppb), chlorobenzenes in methylene chloride (100 ppb), and phenols and soluble aromatic compounds in water (300 ppb).

An interesting method of analysis for complex mixtures containing low-boiling gases, water, and organic compounds has been described[69]. It relies on the reversibility of the adsorption of the vast majority of organic compounds on Tenax, whereas water and the light gases pass through the column without being sorbed. A short fore-column containing 0.3 g of Tenax, placed in front of the main column, is used to sorb all the organic compounds from the mixture, while water and the gases pass into the analytical column filled with Chromosorb 101 or Porapak QS. After elution of the water and gases the organic compounds are thermally desorbed from the Tenax into a second analytical column filled with 10% XE-60 on Chromosorb WHP. A system of valves allows the two parts of the analysis to be carried out with a single sample injector and a single detector.

2. Concentration on the Porapak, Chromosorb, and Spheron Types of Porous Polymer Sorbent

Porous polymer sorbents other than Tenax has been used[5,38] for concentrating trace impurities from air, water, and organic liquids. Chromosorb-105 was used[70] to concentrate trace impurities from the equilibrium vapour phase of organic liquids, from air, or from water. Volatile compounds from juices, biological fluids, wine, and brandy were concentrated, analysed on a capillary column, and identified mass-spectrometrically. The preliminary activation of the concentrator filled with Chromosorb-105 consisted in heating the tube at 225 °C for 12–24 h in a nitrogen stream (10 ml min^{-1}).

In the determination of trifluorochloromethane, chloroform, and other chlorinated compounds in air from Michigan the samples were pre-concentrated[71] on Porapak N, and sulphur compounds in town gas from Nogai (Japan) were pre-concentrated[72] on Porapak Q.

A method of determining benzene and trace amounts of 1,2-dibromoethane and 1,2-dichloroethane simultaneously in town air contaminated with motor-car exhaust gases (Stockholm) or in garage atmospheres has been described[73]. It is stressed that the sorption capacity of Porapak towards these compounds is greater than that of Tenax or Chromosorb-105.

The content of Halothane (2-chloro-2-bromo-1,1,1-trifluoroethane), an anaesthetic compound present in the air of surgical buildings at the 0.01 ppm level, has been measured[74] by preliminary concentration on Porapak Q and P.

The volatile flavouring agents in brewery products have been concentrated[75] by passing the distillate obtained from beer through an Amberlite column at 25 °C. Other workers[76] used XAD-2 to extract phenols and other compounds which interfere with the chromatographic separation of nucleotides from plant extracts (potato tubers, tomatoes, nuts). The conditions which favour the sorption of phenols on XAD-2 while suppressing the sorption of nucleotides, and those which give preferential sorption of nucleotides, were investigated. An attempt was made to correlate the electronic structure of the nucleotides with their affinity for XAD.

XAD-2 Amberlite has been used also to extract steroids from bile[77], urine[78,79], and milk[80], and morphine[81] and hexachlorophene compounds[82] from urine.

Spheron SE has been used for concentrating aromatic hydrocarbons, phenols, and pesticides from river waters of northern Bohemia[83].

Table 2. Determination of the trace impurities of organic compounds using porous polymer sorbents.

No.	Compound to be determined	Sorbent	Concentration conditions	Conditions and method of extraction	Chromatographic separation conditions	c_{min}	References
1	Amines (b.p. up to 300 °C) from air	Tenax	Glass column, 15 cm × 0.5 cm, air flow rate 1.3 litre h^{-1}	thermo-desorption at 250 °C	glass column, 2 m × 2 mm, filled with 8% Silar 10C on Chromosorb WHP, flame ionisation detector	1 ppb	[28]
2	Aromatic hydrocarbons, alcohols, chlorinated compounds, ketones from town or country air	Tenax	110 mm × 8 mm column, sample volume 3–30 litre, flow rate 100–300 ml min^{-1}	thermo-desorption	capillary column, flame ionisation or electron capture detector	–	[66]
3	Alkanes up to C_{18}, unsaturated and aromatic hydrocarbons, alcohols and ketones in industrial atmospheres	Tenax, Carbopak B	9 cm column with 0.28 g of Tenax and 0.45 g of Carbopak B, flow rate 30 ml min^{-1}	thermo-desorption	combined chromatograph and mass spectrometer	1 ppb	[52]
4	Ethylene from air	Porapak S	copper tube 10 cm × 6 mm containing 0.4 g of sorbent and cooled to −95 °C	concentrator heated rapidly to 100 °C and immersed in boiling water	3 m column filled with Porapak R, 40 °C, flame ionisation detector	0.01–0.1 ppb	[26]
5	Trichlorofluoromethane, chloroform, CCl_4, trichloroethylene, perchloroethylene from air	Porapak N	10 cm × 5 mm stainless steel column, sample volume 0.3–3 litre, flow rate 30–150 ml min^{-1}	thermo-desorption at 200 °C for 15 min	2 m column filled with 20% DC-200 on WAWDMCS Chromosorb, programmed temperature (from −40 to 140 °C, 16 K min^{-1}), electron capture detector	30–130 ppt	[71]
6	1,2-Dibromoethane, 1,2-dichloroethane, benzene from town air	Porapak Q, Chromosorb 105, Tenax	200 mm × 1.8 mm column, sample volume 3 litre, flow rate 50–100 ml min^{-1}	thermo-desorption at 175 °C, 3 min	2 m × 1.8 mm column filled with 6% poly-(*m*-phenyl ether) on Tenax	10–200 ppb	[73]
7	Carbonyl sulphide, CS_2, thiophene, tetrahydrothiophene from natural gas domestic supply	Porapak Q	31 cm × 4 mm column cooled in liquid O_2, sample volume 0.05–0.1 litre	heating from −183 to 100 °C, thermo-desorption at 100 °C	3 m × 3 mm column with Porapak Q 140 °C, flame photometer detector	0.7 ppm	[72]
8	Hydrocarbons, polynuclear aromatic compounds, dibenzofuran, etc., from mains water	XAD-2, –4, –7, –8, and mixtures	40 mm column, flow rate 80 ml min^{-1}	elution with acetone–methylene chloride mixture	analysis on SE-30, SP-2100, or Carbowax 20 M, flame-ionisation detector	1 ng $litre^{-1}$	[22]
9	Fenitrothion from water	XAD-2	10 cm column, sample volume 1 litre	elution with diethyl ether or acetone	column filled with 3% OV-101 on Cromosorb W, 190 °C	50 ppb	[51]
10	Acid food dyes from water	XAD-2	30 cm × 0.5 cm column	elution with methanol	analysis by the TLC method on XAD-2 plates	100 ng ml^{-1}	[86]
11	Fenitrothion and its decomposition products in water from areas treated with insecticides	XAD-2	10 cm × 1.9 cm column, sample volume 1 litre, flow rate 50 ml min^{-1}	elution with ethyl acetate	1.8 m × 4 mm column filled with 4% OV-101 and 6% OV-210 on Chromosorb WAW	10–30 ppb	[88]
12	Carbamate insecticides from water	XAD-2	35 cm × 1.5 cm column, sample volume 1 litre, flow rate 20 ml min^{-1}	elution with ethyl acetate	75 cm × 4 mm column with 3% Carbowax 20 M on Chromosorb WHP	0.01–1 ppm	[101]
13	Pesticides from river water	XAD-2	60 g of sorbent added to 20 litre of water and stirred for 8 h	sorbent stirred with 200 ml of toluene and ethylacetate (1 : 3) for 10 h	analysis by gas chromatography	0.3 ng $litre^{-1}$	[102]
14	Fenitrothion from water	XAD-4	30 cm × 1.9 cm column, sample volume 1 litre	elution with a solvent	analysis by TLC	50 μg $litre^{-1}$	[89]
15	Alcohols, ethers, ketones, aldehydes, alkylbenzenes, phenols, etc. in drinking water and in effluents	XAD-4	25 mm × 1.2–1.8 mm column, sample volume 50–100 μlitre, flow rate 0.8–1.2 ml min^{-1}	elution with 100 μlitre of acetone or acetone–CS_2 mixture	1.8 cm × 3 mm Tenax column	2–10 ppb	[92]
16	*p*-Nitrophenol-glucuronic acid from water	XAD-4	column with 10 g of sorbent flow rate 6 ml min^{-1}	elution with a water–acetone mixture (1 : 1)	analysis by TLC method	–	[103]
17	Fenitrothion and its decomposition products	XAD-7	flow rate 113 ml min^{-1}	elution with ethyl acetate	analysis by TLC method	50 ppb	[90]
18	Organo-chloro and organophosphorus pesticides	Tenax	48 cm × 1 cm column	elution with diethyl ether	gas-chromatographic analysis with electron capture detector	1 ppb	[85]
19	Toluene, *m*-cresol, phenol, pesticides in water	Spheron SE	40 mm × 5 mm column	elution with mixed solvents	120 cm × 3 mm column with Chromosorb-102, 200 °C	10–30 ppm	[83]

Table 2 (continued).

	Compound to be determined	Sorbent	Concentration conditions	Conditions and method of extraction	Chromatographic separation conditions	c_{min}	References
20	Phenol, *p*-nitrophenol, *p*-nitroaniline frow water	Styrene–divinyl-benzene–acrylonitrile	20 cm × 0.5 cm column flow rate 40 ml h^{-1}	elution with acetone	gas chromatographic analysis	—	[91]
21	Volatile metabolic products of micro-organisms	Tenax	–	thermo-desorption	2 m × 3 mm column with 5% Carbowax on Gas-chrome Z	–	[30]
22	Impurities from technical styrene monomer	Tenax	100 mm × 8 mm column	thermo-desorption at 290 °C for 15 min in a stream of helium, 20 ml min^{-1}	100 m × 0.5 mm capillary column, from 60 to 150 °C	–	[56]
23	Benzene and toluene from pentane	Tenax	100 mm × 1 mm column, cooled in water	thermo-desorption at 240 °C	50 m × 1 mm capillary column coated with PEG 20	10^{-5}–10^{-7} vol.%	[104]
24	Phenols from plant extracts	XAD-2	22.5 cm × 1.5 cm column	elution with methanol	–	–	[76]
25	Volatile flavouring agents from beer	XAD-2	60 mm × 7 mm column	elution with diethyl ether	2.8 m × 4 mm column with 10% Carbowax 20M on Chromosorb WAWDMCS, 50–200 °C, 3 K min^{-1}, flame ionisation or flame photometric detector	ppb–ppm	[75]
26	Volatile compounds from juices, wine, brandy, and biological fluids	Chromo-sorb-105	–	thermo-desorption	analysis on a capillary column	–	[70]

Notes. Two types of concentration unit have been recommended[105]: the mass of impurity in unit mass of sample (mass/mass) and the volume of impurity in unit volume of sample (volume/volume). Mass concentration units: 1×10^{-4} % ≡ 1 ppm, 1×10^{-7} % ≡ 1 ppb, and 1×10^{-10} % ≡ 1 ppt. Volume concentration units: 1×10^{-4} % ≡ 1 ppm, 1×10^{-7} % ≡ 1 ppb, 1×10^{-10} % ≡ 1 ppt. The choice of mass or volume units depends on the measurement method and on the practical use made of the results. Concentrations calculated from gas-chromatographic measurements have the dimensions of g ml^{-1}. They can be converted into ppm by using the formula[106] 1 ppm = 1 g $ml^{-1} \times 10^{-6}$ RT/pM, where R is the gas constant, cm^3 atm K^{-1} $mole^{-1}$, T is the temperature, K, p is the pressure, atm, and M is the molecular weight of the compound being analysed.

3. Extraction of Trace Impurities from Water

The use of polymer sorbents for concentrating trace amounts of organic compounds from water has been widely studied. A review paper[5] stresses the importance of a preliminary concentration, lists the requirements on the solvents used for extraction and on the water samples themselves, and discusses the properties and the applications of porous organic sorbents used for concentrating trace impurities.

In the same review[5] Dressler points out the similarity between the liquid extraction of organic impurities from water and the use of a solid sorbent: in both cases the dissolved impurities distribute themselves between the water and the extractant, whether a liquid solvent or a solid sorbent is used.

However, porous polymers offer a number of advantages over liquid extraction, since the adsorption of water on the polymer sorbent is negligibly small and the distribution coefficients of organic compounds in the polymer sorbent–water system tend towards infinity if the choice of sorbent has been optimised for the organic compound being extracted[5]. Sorbents with similar sorption properties can be used interchangeably in the concentrator. Dressler also notes[5] the superiority of Amberlites of the XAD series for concentrating traces of organic compounds from water (in particular, for the determination of biphenyls and poly-chlorobiphenyls in sea water, of chlorinated pesticides in drinking water, and of detergents, herbicides, insecticides, pesticides, hydrocarbons, and polyethoxy compounds in sewage).

The method of sampling the water and preparing the sample for analysis, and the process used for concentrating the impurities, depend on the concentration and on the chemical nature of the compounds in the water. Hydrocarbons (especially aromatic) are present in very small amounts in surface waters; effluents from the petrochemicals industry contain aromatic amines and phenols, and effluents from large-scale organic production plant contain pesticides and by-products of the paper, food, and pharmaceutical production industry. The permissible concentration of some organochloro pesticides in drinking water is 0.1 mg $litre^{-1}$, and a method of concentrating impurities is essential for effective analytical control.

Leoni and co-workers[84] have obtained up to 90% extraction of trace impurities (pesticides and polycyclic aromatic hydrocarbons) present in water at the 1 ppb level with Tenax. However, the capacity of the polymeric sorbents for given organic impurities depends on the other impurities present in water. In particular, mineral oils cause "deactivation" of Tenax[85], with a corresponding decrease in the percentage extraction of the trace impurities. The results obtained in the extraction of pesticides from water on Tenax were equivalent to those of the liquid extraction method in the case of drinking water and surface waters, especially when the sample was free from suspended matter which tend to adsorb some pesticides in large amounts. For waters containing suspended matter the results were equivalent only if the samples had been previously filtered[84]. The main advantages of the adsorption method (using Tenax GC) over liquid–liquid extraction are the long service life of the

sorbent, the ease of automation of the concentration process, and the avoidance of a solvent, which could complicate the subsequent analysis.

Most workers have used Amberlites of the XAD series to concentrate traces of organic compounds from water (see Table 1). The adsorbed impurities are usually extracted with organic solvents (Table 2).

Junk and co-workers[31] sorbed organic impurities from water on a 10 cm × 0.6 cm column filled with XAD-2 and XAD-4 (20–60 mesh) using the following concentration conditions: volume of sample 1000 ml, rate of flow of sample through the concentrator 30–50 ml min^{-1}. The sorbed compounds were extracted with diethyl ether, and the eluate was concentrated by evaporation and analysed by gas chromatography. The method was applied to a large number of model compounds present in water at the 10–100 ppb level (alcohols, aldehydes, ketones, esters, polynuclear aromatic compounds, pesticides, herbicides), and shown to give reasonably accurate and reproducible results. The conclusion was[31] that polymer sorbents are very effective for extracting neutral organic compounds from water. The sorbent was regenerated with methanol.

The use of Amberlite XAD-2 as a sorbent for extracting water-soluble acid dyes in the presence of triethylammonium bicarbonate has been recommended[86]. It is stressed that XAD-2 can selectively adsorb water-soluble organic compounds as a result of the interaction between the non-polar parts of the molecule and the hydrophobic sorbent surface. The use of XAD-2 for extracting polar compounds is limited by the low (or even negligible) affinity of these compounds for the sorbent.

The use of Amberlites of the XAD series (-1, -2, -4, -7, -8) for concentrating fulvic acid from aqueous solutions has been described[87]. The most effective concentration was achieved with Amberlites XAD-7 and -8, acrylate copolymers having an intermediate polarity and a high sorption capacity. The use of styrene–divinylbenzene copolymers (XAD-1, -2, -4) for concentrating fulvic acid is complicated by the slow adsorption of the acid molecule (diffusion-limited), and by the incomplete regeneration of the sorbent.

Amberlites of the XAD series (-2, -4, -7, -8) have been used also to extract impurities from mains water[22]. 13 Organic impurities were detected, including normal hydrocarbons, polynuclear aromatic compounds, and halogenated hydrocarbons. The most favourable sorption characteristics were obtained with a 1 : 1 mixture of XAD-4 and XAD-8.

Extensive studies have been devoted to the analysis of the organophosphorus insecticide Fenitrothion in spring waters. Some workers[51,88] used XAD-2 for this analysis, and showed that the sorbed insecticide is stable for a long time (up to 5 weeks) in a column filled with this sorbent. This is an important advantage of the adsorption method over the chloroform extraction method. Another useful feature of the method is the possibility of repeated regeneration (up to 20 times) of the sorption columns without loss of efficiency. The main disadvantage of the sorption method using XAD-2 is a fairly long analysis time (25–30 min). Increasing the flow rate of water through the adsorbent causes loss of the compounds being concentrated: the use of XAD-4 (which has a greater sorption capacity than XAD-2) is therefore recommended[89] for concentrating Fenitrothion, since it offers a shorter analysis time by allowing the flow rate of water through the adsorbent to be increased (1 lite of water in 2 min). Volpe and Mallet[90] extracted Fenitrothion and its decomposition products from water with XAD-7 Amberlite, which holds Fenitrothion more firmly than XAD-2 and XAD-4.

Ternary copolymers (styrene–divinylbenzene–acrylonitrile) have been used[91] for extracting phenolic compounds from water. The third component was found to improve the mechanical characteristics of the resin and its adsorption capacity for phenol, *p*-nitrophenol, and *p*-nitroaniline. The swelling of these copolymers in water and in acetone is very slight, and therefore the materials are convenient adsorbents for use under dynamic conditions.

As an alternative to the conventional columns for concentrating trace impurities of organic compounds from water, "mini-columns" containing ~80 mg of sorbents have been proposed[92,93]. Columns 25 mm long and 1.2–1.8 mm in diameter are filled with polymeric or hydrocarbon sorbents, the volume of sample is 50–100 μlitre, the adsorbed impurities (alcohols, esters, ketones, aldehydes, etc.) are extracted from the column with 50–100 μlitre of a suitable organic solvent, and 2 μlitre of the eluate are used in the subsequent gas-chromatographic analysis. This procedure avoids the need to evaporate the eluate to a smaller volume, and thus avoids the losses caused by the evaporation. The main shortcoming of the method is the very small size (~100 μlitre) of the water sample which seriously limits the sensitivity. tivity.

4. Use of Porous Polymer Sorbents Produced in the Soviet Union for Concentrating Trace Impurities

The porous polymer sorbents made in the Soviet Union which have been used for concentrating traces of organic compounds include Polisorb-1, Polisorbimid-1, and a sorbent based on polyphenylquinoxaline.

Polisorb-1 is a porous copolymer of styrene and divinylbenzene[94], similar in chemical nature and in structure to sorbents of the Amberlite (in particular, XAD-2) and Chromosorb-102 type. It can be used as an alternative to these sorbents after appropriate pre-treatment[5].

Polisorbimid-1, a polycondensation product of pyromellitic dianhydride and diaminodiphenyl ether, is a thermally stable polymer sorbent (up to 400–450 °C).[94,95] Polisorbimid-1 has been found[96] to retain polar compounds and aromatic hydrocarbons significantly better than Tenax. This sorbent has been used successfully for concentrating traces of oxygen-containing impurities and aromatic hydrocarbons from air. The concentrated impurities were desorbed at 280 °C in a stream of carrier gas, and they were separated and identified gas-chromatographically with a mass spectrometer detector[96].

The sorbent based on polyphenylquinoxaline (PFKh) proposed[97] for the separation and concentration of volatile organic compounds is also thermally stable: its maximum working temperature is 280–300 °C. The gas-chromatographic properties of this sorbent are described in Refs. 98 and 99. The PFKh is pre-conditioned in the concentrator column in a stream of carrier gas by raising its temperature from 100 to 280 °C (in steps of ~50 K) and holding it for 2–3 h at each temperature.

The possibility of using PFKh for concentrating traces of organic compounds from air has been studied in detail[100], and the retention volume was found to be greater than on Tenax for a large number of organic compounds (vinyl chloride, hexene, hept-1-ene, benzene, toluene, ethylbenzene, cumene, pseudocumene, cyclohexanone, and mesitylene) in the effluents from the production and utilisation of structural polymers based on poly(vinyl chloride). For example, at 20 °C the specific retention volume for vinyl chloride on Tenax is 270 ml, as compared with 2250 ml on PFKh. This allows large quantities of the components to be accumulated in the concentrator before break-through, thus increasing the precision of the determination of trace impurities. The impurities are desorbed at 200–280 °C, depending on their chemical nature.

The increasing penetration of these polymer sorbents into analytical practice should hasten the solution of many important problems in the protection of the environment from contamination by toxic trace impurities.

Examples of the determination of traces of organic compounds in gaseous and in liquid media by using porous polymer r sorbents are given in Table 2. The Table also states the conditions used for the concentration, desorption, and gas-chromatographic analysis of the impurities.

---o0o---

This review of published work shows that porous polymer sorbents are now widely used for concentrating trace impurities of organic compounds in gaseous or in liquid media. Their success is due to the great variety of chemical forms and structural characteristics offered by these materials, which allow the choice of the most suitable sorbent for concentrating any given impurity. Another important advantage of polymer sorbents is the associated use of thermo-desorption techniques, which simplify the concentration process and make its automation easier. Polymeric sorbents can be used repeatedly without loss of adsorption efficiency. The continuing expansion of the range of these sorbents, and the penetration of new sorbents into the analytical practice, should result in an increased sensitivity for the determination of trace impurities as well as widening the range of compounds which can be detected.

The use of porous polymer sorbents for concentrating trace impurities will extend the boundaries of gas chromatography as applied to the control of toxic substances in the environment—an essential stage in the fight against the pollution of the atmosphere and hydrosphere of our plant.

REFERENCES

1. S.F.Yavorovskaya and B.I.Anvaer, Zhur.Analit. Khim., 1977, **32**, 2044.
2. Yu.S.Drugov and V.G.Berezkin, Uspekhi Khim., 1979, 48, 1884 [Russ.Chem.Rev., 1979(10)].
3. B.A.Rudenko and G.I.Smirnova, Zhur.Analit.Khim., 1977, **32**, 367.
4. Yu.S.Drugov and V.G.Berezkin, "Gazokhromatograficheskii Analiz Zagryaznennogo Vozdukha" (Gas-chromatographic Analysis of Contaminated Air), Izd. Khimiya, Moscow, 1981.
5. M.Dressler, J.Chromatogr., 1979, **165**, 167.
6. W.Bertsch, E.Anderson, and G.Holzer, J.Chromatogr., 1975, **112**, 701.
7. H.Hohenberg and A.Schmidt, "Gas-chromatographic Analysis of the Equilibrium Vapour Phase" (Translated into Russian), Izd.Mir, Moscow, 1979.
8. J.Drozd and J.Novak, J.Chromatogr., 1979, **165**, 141.
9. Yu.I.Khol'kin, A.M.Bosenko, et al., Gidroliznaya i Lesokhim.Prom., 1972(5), 20.
10. V.E.Stepanenko and Z.M.Golovina, Zhur.Analit.Khim., 1975, **30**, 890.
11. W.Bertsch, A.Zlatkis, and H.J.Schneider, J.Chromatogr., 1974, **99**, 673.
12. E.M.Goldberg and S.Sandler, Chromatographia, 1975, **8**, 331.
13. B.J.Joffe, V.A.Isidorov, and I.G.Zenkevich, J.Chromatogr., 1977, **142**, 787.
14. M.F.Prokop'eva, N.Kh.Tadzhieva, and K.I.Sakodynskii, Symposium, "Analiticheskoe i Preparativnoe Primenenie Khromatografii" (Analytical and Preparative Applications of Chromotography), NIITEKhIM, Moscow, 1980, p.38.
15. A.Zlatkis, H.A.Lichtenstein, and A.Tishbee, Chromatographia, 1973, **6**, 67.
16. A.G.Vitenberg, V.G.Ioffe, and V.M.Borisov, Zhur. Analit.Khim., 1974, **29**, 1795.
17. K.Grob, J.Chromatogr., 1973, **84**, 255.
18. K.Grob and G.Grob, J.Chromatogr., 1974, **90**, 303.
19. J.P.Mieure and M.W.Dietrich, J.Chromatogr.Sci., 1973, **11**, 559.
20. L.D.Butler and M.F.Burke, J.Chromatogr.Sci., 1976, **14**, 117.
21. D.A.M.MacKay and M.M.Hussein, J.Chromatogr., 1979, **176**, 291.
22. P.Van Rossum and R.S.Webb, J.Chromatogr., 1978, **150**, 381.
23. F.Bruner, P.Ciccioli, and F.Di Nardo, J.Chromatogr., 1974, **99**, 661.
24. J.S.Parsons and S.Mitzner, Environ.Sci.Tech., 1975, **9**, 1053.
25. R.Perry and J.D.Twibell, Atmos.Environ., 1973, **7**, 929.
26. J.De Greef, M.de Proff, and G.S.Neff, Analyt.Chem., 1976, **48**, 38.
27. A.Dravnieks, K.Krotoszynski, J.Whitfield, A.O'Donnell, and T.Burgwald, Environ.Sci.Technol., 1971, **5**, 1221.
28. B.E.Bowen, Analyt.Chem., 1976, **48**, 1584.
29. J.D.White and D.P.Schwartz, J.Chromatogr., 1980, **196**, 303.
30. M.Vanhaelen, R.Vanhaelen-Fastre, and J.Greeraerts, J.Chromatogr., 1977, **144**, 108.
31. G.A.Junk, J.J.Richard, M.D.Grieser, D.Witiak, J.L.Witiak, M.D.Arguello, R.Vick, H.J.Svec, J.S.Frits, and G.V.Calder, J.Chromatogr., 1974, **99**, 745.
32. H.A.James, C.P.Stell, and J.Wilson, J.Chromatogr., 1981, **208**, 89.
33. Technical Bulletin No.24, Tenax-GC, Applied Science Labs., State College, Pa., USA; quoted in Ref.5.
34. W.E.May, S.N.Chester, S.P.Gram, B.H.Gump, H.S.Hertz, D.P.Enagonio, and S.M.Dyszel, J.Chromatogr.Sci., 1975, **13**, 535.
35. B.Versino, H.Knöppel, M.de Groot, A.Peil, H.Schauenburg, H.Vissers, and F.Geiss, J.Chromatogr., 1976, **122**, 373.
36. V.Patzelova, M.Wurst, and V.Catska, J.Chromatogr., 1980, 193, 137.
37. R.Sydor and D.J.Pietrzyk, Analyt.Chem., 1978, **50**, 1842.
38. L.Renberg, Analyt.Chem., 1978, **50**, 1836.
39. R.H.Brown and C.J.Purnell, J.Chromatogr., 1979, **178**, 79.
40. F.R.Cropper and S.Kaminsky, Analyt.Chem., 1963, **35**, 735.
41. J.Janàk J.Růžičkowa, and J.Novàk, J.Chromatogr., 1974, **99**, 689.
42. A.Raymond and G.Guiochon, J.Chromatogr.Sci., 1975, **13**, 173.
43. T.Tanaka, J.Chromatogr., 1978, **153**, 7.
44. B.Versino, M.de Groot, and F.Geiss, Chromatographia, 1974, **7**, 302.
45. J.P.Riley and D.Taylor, Analyt.Chim.Acta, 1969, **46**, 307.
46. V.Niederschulte and K.Ballschitter, Z.analyt.Chem., 1974, **269**, 360.
47. P.R.Musty and G.Nickless, J.Chromatogr., 1974, **89**, 185.
48. C.K.Wun, R.W.Walker, and W.Litsky, Water Res., 1976, **10**, 995.

49. Technical Bulletin, Amberlite XAD-4, Rohm and Haas, Philadelphia, Pa., USA; quoted in Ref.5.
50. E.D.Pellizzari, J.E.Bunch, R.E.Berklay, and J.McRae, Analyt.Letters, 1976, **9**, 45.
51. K.Berkane, G.E.Caissei, and V.N.Mallet, J.Chromatogr., 1977, **139**, 386.
52. P.Ciccioli, G.Bertoni, E.Brancaleoni, R.Fratarcangeli, and F.Bruner, J.Chromatogr., 1976, **126**, 757.
53. A.Zlatkis, H.A.Lichtenstein, and A.Tishbee, Chromatographia, 1975, **8**, 299.
54. E.D.Pellizzari, J.E.Bunch, R.E.Berkley, and J.McRae, Analyt.Chem., 1976, **48**, 803.
55. W.Bertsch, R.C.Chang, and A.Zlatkis, J.Chromatogr. Sci., 1974, **12**, 175.
56. A.Zlatkis, J.W.Anderson, and G.Holzer, J.Chromatogr., 1977, **142**, 127.
57. R.M.Cassidy, M.T.Burtean, J.P.Misian, and R.W.Ashley, J.Chromatogr.Sci., 1976, **14**, 444.
58. H.M.Liebich, W.Bertsch, A.Zlatkis, and H.J.Schneider, Aviat.Space Environ.Med., 1975, **8**, 1002.
59. W.Bertsch, R.C.Chang, A.Zlatkis, H.M.Liebich, and H.J.Schneider, J.Chromatogr., 1974, **99**, 673.
60. J.W.Russell, Environ.Sci.Technol., 1975, **9**, 1175.
61. E.D.Pellizzari, J.E.Bunch, J.T.Bursey, and R.E.Berklay, Analyt.Letters, 1976, **9**, 579.
62. M.E.Fox, Environ.Sci.Technol., 1973, **7**, 838.
63. K.Grob and G.Grob, J.Chromatogr., 1971, **62**, 1.
64. M.Novotny, M.L.Lee, and K.D.Bartle, Chromatographia, 1974, **7**, 333.
65. J.E.Bunch and E.D.Pellizzari, J.Chromatogr., 1979, **186**, 811.
66. G.Holzer, H.Shanfield, A.Zlatkis, W.Bertsch, P.Juarer, H.Mayfield, and H.M.Liebich, J.Chromatogr., 1977, **142**, 755.
67. G.Holzer, J.Oro, and W.Bertsch., J.Chromatogr., 1976, **126**, 771.
68. R.G.Melcher and W.J.Caldecourt, Analyt.Chem., 1980, **52**, 875.
69. G.Marcelin, J.Chromatogr., 1979, **174**, 208.
70. K.E.Murray, J.Chromatogr., 1977, **135**, 49.
71. J.W.Russell and L.A.Shadoff, J.Chromatogr., 1977, **134**, 375.
72. Y.Hoshika and Y.Jida, J.Chromatogr., 1977, **134**, 423.
73. A.Jonsson and S.Berg, J.Chromatogr., 1980, 190, 97.
74. J.Gelbicova-Ruzickova, J.Novàk, and J.Jañàk, J.Chromatogr., 1972, **64**, 15.
75. T.L.Pappard and J.M.F.Douse, J.Chromatogr., 1979, **176**, 444.
76. R.M.Nieman, D.L.Pap, and R.A.Clark, J.Chromatogr., 1978, **161**, 137.
77. M.Matsui, M.Hakozaki, and Y.Kimuyama, J.Chromatogr., 1975, **115**, 625.
78. S.Van der Wal and J.F.K.Huber, J.Chromatogr., 1977, **135**, 305.
79. H.L.Bradlow, Steroids, 1968, **11**, 265.
80. C.R.Brewington, D.P.Schwartz, and M.J.Pallansch, Proc.Soc.Exper.Biol.Med., 1972, **139**, 745.
81. J.M.Fujimoto and V.B.Haarstad, J.Pharmacol.Expt. Therapeut, 1969, **165**, 45.
82. A.J.Gandolfi and D.R.Buhler, J.Agr.Food Chem., 1977, **25**, 21.
83. E.Břizová, M.Popl, and J.Čoupek, J.Chromatogr., 1977, **139**, 15.
84. V.Leoni, G.Puccetti, and A.Grella, J.Chromatogr., 1975, **106**, 119.
85. V.Leoni, G.Puccetti, R.L.Colombo, and A.M.D'Ovidio, J.Chromatogr., 1976, **125**, 399.
86. T.Uematsu, T.Kurita, and A.Humado, J.Chromatogr., 1979, **172**, 327.
87. G.R.Alken, E.M.Thurman, R.L.Malcolm, and H.R.Walton, Analyt.Chem., 1979, **51**, 1799.
88. V.N.Mallet, G.L.Braun, R.N.McDonald, and K.Berkane, J.Chromatogr., 1978, **160**, 81.
89. V.N.Mallet, J.M.Francoeur, and G.Volpe, J.Chromatogr., 1979, **172**, 388.
90. G.Volpe and V.N.Mallet, J.Chromatogr., 1979, **177**, 385.
91. M.Wojaczyńska and B.N.Kolarz, J.Chromatogr., 1980, **196**, 75.
92. A.Tateda and J.S.Fritz, J.Chromatogr., 1978, **152**, 329.
93. G.A.Junk, C.D.Chriswell, R.C.Chang, L.D.Kissinger, J.J.Richard, J.S.Fritz, and H.J.Svee, Z.analyt. Chem., 1976, **282**, 331.
94. K.I.Sakodynskii and L.I.Panina, "Polimernye Sorbenty Dlya Molekulyarnoi Khromatografii" (Polymer Sorbents for Molecular Chromatography), Izd.Nauka, Moscow, 1977.
95. K.I.Sakodynsky, N.S.Klinskaya, and L.I.Panina, Analyt.Chem., 1973, **45**, 1369.
96. V.A.Isidorov, I.G.Zenkevich, and B.V.Ioffe, Dokl. Akad.Nauk SSSR, 1977, **235**, 618.
97. L.D.Glazunova, L.I.Panina, K.I.Sakodynskii, and N.S.Zabel'nikov, Symposium, "Razvitie Metodov Analiticheskoi Khromatografii" (Developments in Analytical Chromatography Methods), NIITEKhIM, Moscow, 1979, p.34.
98. K.I.Sakodynsky, L.D.Glazunova, I.P.Yudina, L.I.Panina, and Yu.A.Yuzhelevsky, J.Chromatogr., 1979, **177**, 181.
99. L.D.Glazunova, N.S.Zabel'nikov, and I.P.Yudina, Symposium, "Tekhnika Khromatograficheskogo Razdeleniya" (Chromatographic Separation Techniques), NIITEKhIM, Moscow, 1980, p.4.
100. V.B.Khabarov, P.A.Direi, V.V.Mal'tsev, L.I.Panina, K.I.Sakodynskii, L.D.Glazunova, and S.B.Makarova, "Tezisy Dokladov Vsesoyuznoi Konferentsii Primenenie Khromatografii v Khimii i Khimicheskoi Promyshlennosti" (Abstract of Papers Presented to the All-Union Conference on the Applications of Chromatography in Chemistry and in the Chemical Industry), Perm, 1981, p.19.
101. K.M.S.Sundaram, S.Y.Szeto, and R.Hindle, J.Chromatogr., 1979, **177**, 29.
102. R.L.Harris, R.J.Huggett, and H.D.Slone, Analyt. Chem., 1980, **52**, 779.
103. J.D.White and D.P.Schwartz, J.Chromatogr., 1980, **196**, 303.
104. V.G.Berezkin, M.N.Budantseva, and E.Dows, J.Chromatogr., 1980, **191**, 309.
105. G.I.Aranovich (Editor), "Spravochnik po Fizikokhimicheskim Metodam Issledovaniya Ob"ektov Okruzhayushchei Sredy" (Handbook on Physicochemical Methods of Studying the Constituents of the Environment), Izd.Sudostroenie, Leningrad, 1979, p.148.
106. J.Novák and V.Vašák, Amer.Ind.Hyg.Ass.J., November–December, 1966, 555.

Karpov Physicochemical Research Institute, Moscow