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Review

Carbon sorbents and their utilization for the preconcentration of organic pollutants in environmental samples

Eva Matisová*, Svetlana Škrabáková

*Department of Analytical Chemistry, Faculty of Chemical Technology, Slovak Technical University, Radlinského 9,
812 37 Bratislava, Slovak Republic*

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Abstract

This review deals with carbon sorbents and their utilisation to trace analysis of organic pollutants in environmental samples. The first sections are devoted to the general characteristics of various kinds of carbon sorbents, carbon formation, the structure of carbon, their classification and characterisation (activated charcoal, graphitized carbon black, carbon molecular sieves and porous carbon). Information is given on the development of carbonaceous adsorbents, their characteristics and properties, development of various preconcentration techniques, off-line or on-line combination with the analytical measuring system (GC and HPLC), and the application of carbon sorbents to the enrichment of analytes is evaluated. The main use of carbon materials as a preconcentration/preseparation step has been in the sampling and trapping of volatile organic compounds (VOCs) from air and water matrices. An other field of application is the trapping of semi-volatile and non-volatile compounds and/or their separation into subclasses. According to the characteristics of the sampled components, carbon sorbents have been utilised in single-bed or multi-bed arrangement (combination of various carbon sorbents or combinations of carbon sorbents with other non-carbonaceous materials) to achieve quantitative trapping of trace components from environmental samples, followed by their desorption for subsequent identification and quantitation. Various achievements and problems, particularly in multicomponent-mixture analysis, are discussed. The physico-chemical properties of recently developed carbon adsorbents are superior compared to those of the "traditional" sorbent materials. Over the recent years much attention has been paid to the application of carbon sorbents for the on-site automated analysis and monitoring of trace pollutants.

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* Corresponding author.

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1. Introduction

Most of the analyses that have to be performed with respect to the control of organic pollutants in the environment, can not be done without the application of preconcentration and sample pretreatment techniques. Samples are very often not compatible with direct injection onto the chromatographic system, analysed components are usually present in matrices incompatible with the gas and/or liquid chromatographic system (soil, sediments), or the concentration of the analytes is lower than the detection limit. Thus, it is necessary to perform sample preparation steps prior to analysis. This mainly consists of preconcentration of the analytes, isolation of the analytes from the matrix and removal of interfering compounds. Nowadays also materials with selective sorption properties are being utilized to a large extent for this purpose. Besides to broad spectrum sorbents, much attention is given to tailored sorbents, which allow the optimal solution of a particular separation problem. Carbonaceous sorbents, the matrix of which mainly consists of carbon,

belong to the group of materials of interest. The main advantage of the carbon sorbents is their high chemical inertness and thermal stability. In contrast to sorbents with a SiO₂ matrix (silica gel, porous glass) their use is not limited by pH and compared with organic polymer sorbents they withstand much higher temperatures. Sorbents with a carbon matrix may also serve as carriers for various functional groups.

In the following sections we present an overview on carbon sorbents and their application to the preconcentration of organic pollutants from environmental samples and their subsequent analysis, particularly of volatile organic compounds by gas chromatography. Preconcentration with carbon sorbents is applicable also to other separation techniques, mainly in the analysis of semivolatile and non-volatile compounds by HPLC.

2. Carbon formation

In principle four consecutive stages may be distinguished in the formation of carbons from

naturally occurring or synthetic precursors: homogenization, carbonization, volatilization of inorganic impurities, and graphitization [1,2].

The term “homogenization” covers all operations which lead to an improved ordering of the structure of any solid or liquid carbonaceous starting material. It usually consists of a thermal treatment of the starting material at 450–700°C in an inert atmosphere. It is well known that the degree of structural order of the carbon precursor essentially determines the extent to which the penultimate material is converted into a graphitic or an amorphous carbon, which represent the two limiting cases.

Carbonization covers a number of processes including coking, charring and reaction with oxidising gases such as oxygen, carbon dioxide and water vapour. It is carried out between 700 and 1200°C. Carbonization increases the percentage of carbon content and introduces pores. The products so formed are termed active carbons and possess a high adsorptive capacity. Carbonization also covers processes whereby a gaseous hydrocarbon is pyrolysed between 1000 and 1700°C to yield dense non-porous layers of pyrolytic carbon [3].

Active carbons may still contain inorganic impurities such as sulphur and silica depending upon their origin. These can be removed by volatilization at 1200–1700°C. This process leaves a large number of defect sites in the structure and causes a disordering of the mutual arrangement of layers. Microscopic holes may even be formed within the particles.

Graphitization covers the subsequent heat-treatment in an inert atmosphere at 1700–3000°C. Such heat treatment brings about densification with concurrent removal of structural defects, and forms a three-dimensionally ordered graphitic structure. The degree of graphitization of any carbon brought about by high temperature treatment depends strongly on its initial structure. Thus treatment of some active carbons at a temperature as low as 1200°C can greatly reduce or even completely eliminate the porosity of the material, whereas some glassy carbons may not convert to graphite even on heating to 3000°C.

3. Structure of carbon

Many varieties of carbon are produced industrially on a large scale [4]. The most important of these are: electrographite (for industrial electrodes), nuclear graphite (as a moderator in nuclear reactors), active carbons or charcoals (for adsorption of vapours, extraction of organics from water, decolourising), carbon blacks (fillers in rubber), graphitized carbons, and carbon fibres.

The term “graphitized carbon” generally means that a particular carbon has been heated to a temperature in the region of 3000°C in a graphitizing furnace. In crystallographic terms, the degree of graphitization of such a carbon may fall within wide limits, supposedly “graphitized” carbons ranging from almost amorphous materials to perfect three-dimensional crystalline graphites. There are, in fact, three distinct forms of carbon to which the term “graphitized” can reasonably be applied and which have well-defined crystal structures. The Bernal structure of perfect three-dimensional graphite [5] (Fig. 1) consists of layers of carbon atoms, organized in a hexagonal array and ordered ABABAB... This form of graphite is termed hexagonal graphite. A rarer form of three-dimensional graphite, the Lipson–Stokes form, also exists, but here the layers are ordered ABCABC... This is termed rhombohedral graphite [6]. In both crystalline forms the layer spacing is 3.35 Å and the atomic spacing within the layers is 1.42 Å. Perfect graphite is rarely formed synthetically from amorphous solid carbon, since the bonding between the carbon atoms within the graphitic planes is extremely strong, while the interlayer bonding is weak. Thus graphitization tends to develop by the formation of graphitic sheets which are initially randomly oriented. The reorganization of these sheets into ordered three-dimensional graphite requires such a high activation energy that formation of three-dimensional crystalline graphite is generally impossible below 3000°C. Thus, most synthetic carbons, when heated to about 3000°C, assume the two-dimensional graphite (Warren structure, Fig. 1) in which graphitic sheets are randomly oriented

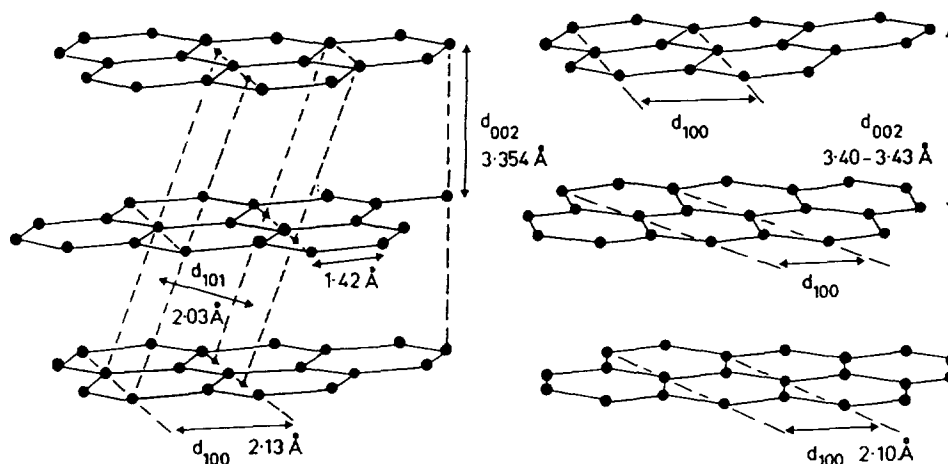


Fig. 1. Atomic structures of graphites. Left: Bernal structure of perfect 3-dimensional graphite with ABAB layer registration. Right: Warren structure of two-dimensional turbostratic graphite with no layer registration. (Reproduced from Ref. [4]).

relative to one another. In two-dimensional graphites the layer spacing is slightly greater than in three-dimensional graphites at 3.40–3.43 Å, and the atomic spacing within the layers is slightly less. Two-dimensional graphites are often said to have a turbostratic structure [7].

While three-dimensional graphites rarely arise from heating of amorphous solid carbons, they can nevertheless arise by high temperature pyrolytic deposition from organic vapours in the gas phase [8]. Presumably, properly oriented layers are laid down in the first place, and no reorganization is required.

4. Types of carbon sorbents

Various kinds of carbon sorbent are available that may be utilized for the enrichment of analytes:

- activated carbon
- molecular sieves
- graphitized carbon black
- porous carbon.

They differ in their physico-chemical characteristics, such as pore size and shape, surface area, size, volume of pores, functionality of surface, and chemical inertness. Kinetic and thermodynamic properties of carbon sorbents (breakthrough volumes, adsorption isotherms,

equation of state, intermolecular interaction mechanisms occurring at the adsorbate/carbon sorbent interface) strongly influence the preconcentration and/or prepreparation step. The extent to which these often conflicting characteristics can be achieved will be dependent upon:

- type of starting material
- procedure chosen for preparation of the product
- conditions under which it is used.

The development of carbon sorbents suitable for the enrichment of analytes has generally paralleled the development of chromatographic sorbents. Active carbon adsorbents have long been an obvious choice for the studies in classical liquid chromatography [9]. With the advent of gas chromatography attention turned to graphitized thermal carbon blacks (GTCB) [10], which were found to be suitable nonpolar adsorbents either for gas–solid chromatography [11] or, when coated with a small percentage of liquid phase as a “tailing reducer”, for gas–liquid/solid chromatography [12–14], and to novel active carbons, prepared e.g. by the reduction of polytetrafluoroethylene by lithium amalgam [15,16].

Interest in preparation of the novel carbonaceous adsorbents has recently increased because of the theoretical non-polar character of these materials for HPLC, their applicability over a wide pH range, and the better defined surface prop-

erties in comparison to activated carbon. This is connected with the development of porous carbon packings [1,17] and porous glassy carbon [4,18].

4.1. Activated carbon

Activated carbons have been used since the time of the ancient Egyptians, when charcoals were employed for medicinal purposes. Industrial applications originated in the late 18th century, when it was discovered that activated carbons could adsorb gases and remove colour bodies from solution. A stimulus to industrial production was the development of protective gas masks after the introduction of chemical weapons. Activated carbons are now used extensively in diverse applications [19]: potable and waste water treatment; respirators; solvent recovery from process streams; air and gas purification; prevention of gasoline vapour emissions from automobiles. More specialized applications, sometimes involving the addition of impregnants, can be found in catalysis, medicine, military gas masks and gold recovery.

Commercial sources for activated carbons include biomass materials: wood, coconut shell and fruit pits; and fossilized plant matter: peats, lignites and all ranks of coal; or synthetic polymers [20]. Adsorbent carbons are usually produced by a two-step process of carbonization and then activation by partial gasification. The highly porous structure produced during activation provides the extensive surface area of an activated carbon on which its usefulness as an adsorbent depends.

Problems in using carbon for analytical work are related to the large variations in the physical and chemical properties of the different sources of carbon, the greater difficulty in obtaining low background contamination levels compared to other sorbents, and the fact that many organic compounds are adsorbed so strongly that desorption is only accomplished in very low yields. Activated carbon has a very complex surface structure containing a wide range of functional groups including phenolic, carboxylic, carbonylic, aldehydic, etheric, peroxidic, quinone

and lactone groups [21]. The principal binding mechanisms include hydrophobic interactions, charge-transfer complexation, hydrogen bonding, cation exchange and another specific interactions. The surface of such carbons possesses a high sorption capacity, but it is very heterogeneous. Low recovery of many organic solutes is often associated with the strength of multiple binding interactions, which provide an efficient adsorption mechanism accompanied by inefficient solvent elution, leading to a low overall recovery. Irreversible adsorption can occur in some cases as well as catalytic transformations to different products.

4.2. Molecular sieves

Carbon molecular sieves are formed by the controlled pyrolysis of suitable polymeric materials (e.g. polyvinylchloride) or petroleum pitch materials at temperatures usually above 400°C. They have a highly porous structure with almost uniform micropores [22,23]. They are comprised of very small crystallites crosslinked to yield a disordered cavity–aperture structure.

Carbon molecular sieves are microporous and have a high surface area, with a very pronounced retention of organic compounds, but they can be very easily contaminated by impurities from air. The structure, the purity of the starting polymer material and the technology used for carbonization dictate the particle size and the distribution and size of the pores of the final product. The presence of polymer impurities substantially decreases the homogeneity of the porous structure.

4.3. Graphitized carbon black (GCB)

GCBs as adsorbent for GC were studied in the sixties by Kiselev and his coworkers [10], as well as Horvath [24] and Guichon and coworkers [25].

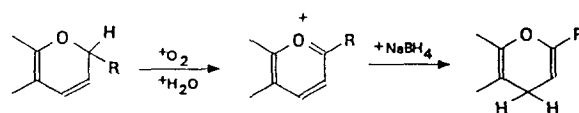
Graphitized carbons are materials with a homogeneous surface and without micropores, they adsorb compounds on their external surfaces based on the molecular size and shape of the adsorbed molecule. GCBs are prepared by

heating ordinary carbon blacks to about 3000°C in an inert gas atmosphere [26–29]. This eliminates volatile, tarry residues and induces the growth of graphite crystallites, particles in which graphite crystals are arranged in the form of polyhedrons. At the same time various functional groups originally present on the carbon black surface are destroyed. The surface of the graphitized carbon blacks is almost completely free of unsaturated bonds, lone electron pairs, free radicals and ions.

The trapping of compounds on GCBs can be explained on the basis of the availability of two types of adsorption sites [27,30]. The vast majority of the surface sites are nonpolar and correspond to a graphite-like array of carbon atoms. These sites show no tendency to interact preferentially with molecules carrying functional groups and dispersive interactions dominate the retention behaviour. Polar adsorption sites are few in number but they can establish specific, strong interactions with polar compounds. Preliminary treatment of the adsorbent may be used to reduce their number. For example, heating to 1000°C in a stream of hydrogen has been used to minimize those active sites associated with the presence of surface oxygen complexes [30–32] while washing with perchloric or phosphoric acid eliminates basic carbonium–oxygen complexes and sulfur present as sulfide [33].

Oxygen complexes with a chromene-like structure may be present as burnt-off residues [34] originating from the heating of carbon blacks. In the presence of water these surface groups are rearranged to form benzopyrylium salts, which are promptly reduced to benzopyrans under mild conditions (see Scheme 1).

Benzopyrylium salts are responsible for binding anions via electrostatic forces [34]. The presence of these positively charged chemical impurities on their surface enables the GCBs to act as both an anion exchanger and a non-specific sorbent. The ion-exchange capacity of non-graphitized carbon black was found to be about twice that of the GCB surface. It seems that carbon blacks are graphitized at very high temperatures at which any surface organic chemical groups should be



Scheme 1.

decomposed. Probably chemical heterogeneities are partially reformed during cooling of the carbonaceous material after the graphitization process [35].

GCBs are composed of loosely aggregated particles of colloidal dimensions. They are hydrophobic. The affinity for water vapour is dependent on the chemical structure of the surface and can be enhanced as a result of oxidation or hydration [36].

4.4. Porous carbon

Porous carbon adsorbents [1,4,17,18,37–39] are materials with a homogeneous hydrophobic surface. They attracted attention because of their stability over a wide pH range and their mechanical stability. They are produced by impregnating a suitable silica gel or another porous template with a phenol–formaldehyde resin mixture, phenol–hexamine mixture, saccharose or another material [18,40,41]. After polymerization within the pores of the template material the polymer is converted to glassy carbon by heating in an inert atmosphere to about 1000°C. The silica template is then removed by alkali to give porous graphitic carbon (PGC). Finally, the material is fired in an inert atmosphere at a high temperature in the range 2000–2800°C to anneal the surface, remove micropores and, depending upon the temperature, produce some degree of graphitization. The particle size, shape, porosity and pore size are determined by the choice of the template material; the surface chemistry is determined by the final heat treatment and any subsequent chemical treatment. It is thus possible in principle to produce PGCs with a range of pore and surface properties tailored to specific requirements [42].

Table 1
Classification of adsorbents

Class	Adsorbent	Surface
Class I	Graphitized carbon black	Graphitic carbon
Class II	Activated silica gel	Oxides of silica gel
Class III	Activated charcoal	–Oxides of amorphous carbon
	Carbon molecular sieves	–Amorphous carbon (weak Class III, can approach Class I)
	Porous polymers	–Organic “plastics” (weak-strong Class III)

5. Classification and characterisation of sorbents

According to the classification scheme of Kiselev [10,43], there are three classes of sorbents (Table 1). Class I adsorbent is an adsorbent which interacts non-specifically with the four groups of adsorbates (groups A, B, C, D), whereas class II and III adsorbents interact both non-specifically (i.e. London forces, van der Waals forces) and specifically (i.e. strong dipole-dipole interactions). Only class I interacts non-specifically with all groups of adsorbates (Table 2).

Examples of the four groups of adsorbates are: group A molecules—*n*-alkanes; group B molecules—aromatic hydrocarbons, chlorinated hydrocarbons; group C molecules—organo-metallic compounds; and group D molecules—primary alcohols, organic acids, organic bases. The classification of some typical adsorbents assists in determining the adsorbate/adsorbent interactions occurring between the two surfaces.

Kinetic and thermodynamic properties of the solid surface could be characterized by the dynamic gas–solid chromatographic (GSC) technique [43–45]. The physico-chemical measure-

Table 2
Classification of adsorbates

Group	Molecules	Adsorbents	
		Class I	Class II and III
A	–Spherically symmetrical shells – σ -bonds	Nonspecific interaction Dispersion forces	
B	–Electron density concentrated on bonds/links – π -bonds	Nonspecific	Nonspecific
C	–(+)-Charge on peripheral links	interaction	+
D	–Concentrated electron densities –(+)-Charge on peripheral links		specific interaction

ments by GSC could be used to obtain the breakthrough volumes, the adsorption isotherms, equation of state, to interpret the mechanism of intermolecular interactions [28,46,47], to study the heterogeneity of the surface [48]. Another physico-chemical characterization of carbons can be performed through particle size analysis, shape determination via electron microscopy, diffuse reflectance FT-IR spectroscopy and IR-PBDS (photothermal beam deflection spectroscopy) [40,49–53], optical microscopy, X-ray microscopy for resolving inorganic impurities in carbon black, transmission electron microscopy for particle/aggregate size and shape distributional information [54], scanning tunnelling microscopy [55], surface area measurements, high-resolution thermogravimetry to obtain information on total porosity, adsorption capacity of porous solids and detection of the active sites present on the carbon surface [56].

Evaluation of the sorbent characteristics and the suitability of a sorbent to trap organic compounds is usually focused on calculation of the specific retention volumes, adsorption coefficients, and equilibrium sorption capacities [43].

The specific retention volume, or breakthrough volume, is the calculated volume of a mobile phase passing through an adsorbent bed that causes a “challenge slug” of adsorbate molecules to migrate from the front of the adsorbent bed to the back of the bed. The challenge slug is introduced via a typical gas and/or liquid chromatographic technique and is detected after it migrates through the adsorbent bed, via a suitable detector. The elution volume is divided by the weight of the adsorbent bed to obtain the specific retention volume, expressed in cm^3/g . This specific retention volume value can be used in constructing an adsorbent tube that possesses known breakthrough characteristics for known adsorbent bed weights.

6. Application of carbon sorbents

For the solution of analytical problems in trace analysis, particularly in the analysis of multi-component mixtures, various preconcentration

and/or pre-separation steps have been utilised dependent on the sample matrix. The application of carbon materials for these purposes is related with the development of sorbents with (a) physicochemical properties, and (b) adsorption-desorption properties which provide effective sample enrichment. Carbon sorbents have been applied in various enrichment techniques, particularly in solid-phase extraction (SPE), the purge-and-trap technique and head-space analysis.

In environmental samples the target of the qualitative and quantitative analysis may be the complete multicomponent trace analysis in various matrices, or only the analysis of individual trace component(s). The whole preconcentration/pre-separation procedure differs accordingly. The need for enrichment of trace analytes generally depends on a combination of:

- the volume injected for the analysis,
- the nature and concentration of the compounds analysed,
- the nature of the sample matrix,
- the minimum detectable amount characteristic for the selected sample introduction, separation and detection system.

6.1. Choice of the proper sorbent

The use of different carbons (single bed) depends strongly on the applications, but also on the techniques used. Depending on gases, volatile, semi-volatile or non-volatile compounds, both the sorbents and the techniques differ. Different techniques do not require the same characteristics of the carbons.

At present commercially available types of carbon sorbents are active charcoal, graphitized carbon black, molecular sieves and porous carbon. Their specific surface areas range from 5 to $1200 \text{ m}^2/\text{g}$. The main types of carbon sorbents used for preconcentration of organic compounds and their further determination predominantly by GC and/or HPLC are listed in Table 3.

The general physico-chemical characteristics which are taken into account for the choice of an adsorbent are functionality, particle size and

Table 3
Carbon sorbents for pre-concentration of organic compounds

Type	Name	Particle size (mesh)	Porosity (nm)	Surface area (m ² /g)	Producer	
Activated charcoal			1.8–2.2	500–1200		
Molecular sieve	Carbosieve B		1–1.2	1174	King's Lynn, Norfolk	
	Carbosieve S-III	60/80	1.3	1000	Supelco, Inc.	
	Carbosieve S-II	60/80	3.9	1000	Supelco, Inc.	
	Carboxen 1000	60/80	7	1200	Supelco, Inc.	
	Carboxen 1001	60/80		500	Supelco, Inc.	
	Carboxen 1002	60/80		1100	Supelco, Inc.	
	Carboxen 563	20/45		510	Supelco, Inc.	
	Carboxen 564	20/45		400	Supelco, Inc.	
	Carboxen 569	20/45		485	Supelco, Inc.	
	Purasieve	20/40		1070	Union Carbide,	
	Sphero carb	60/80	1.5	1200	Analabs, Inc. (Norwalk, CT, USA)	
	Sortophase					
		Carbosphere	80/100			
		Saran Carbon				Alltech, Assoc.
	Ambersorb					
Porous carbon	Carb I			1200	Polymers	
	Carb II			400	Institute SAS	
	Hypercarb			150–200	Shandon, Runcorn,	
	TSK-Gel Carbon			150–200		
	500					
Graphitized carbon black	Carbopack F	60/80		5	Supelco, Inc.	
	Carbotrap F	20/40		5	Supelco, Inc.	
	Carbograph 3			6–7	Alltech, Assoc.	
	Carbopack C	60/80		12	Supelco, Inc.	
	Carbotrap C	20/40		12	Supelco, Inc.	
	Carbograph 2			10–12	Alltech, Assoc.	
	Carbopack B	60/80		100	Supelco, Inc.	
	Carbotrap B	20/40		100	Supelco, Inc.	
	Carbograph 1			80–100	Alltech, Assoc.	
	Graphtrap			80–100	Alltech, Assoc.	
	Graphtrap 5				Alltech, Assoc.	
	Graphon, Spheron			80–100		

shape, surface area, pore size, and chemical inertness.

Functionality plays the main role in the choice of a sorbent for various organic compounds. It is an expression of the affinity of the sorbent for various organic compounds. The classification of some typical adsorbents (section 5) assists in determining the adsorbate/adsorbent interactions occurring between the two surfaces, the

graphitized carbon blacks, or graphitized carbons, behaving as class I adsorbents. The carbon molecular sieves, or amorphous carbons, behave as weak class III adsorbents and may approach a class I classification. Activated charcoal, due to the carbon oxides present on the adsorbent (amorphous carbon) surface, is classified as a class III adsorbent. Chemical inertness is a very important parameter, as the quality of the sor-

bent surface influences the recovery and the reproducibility of the accumulation procedure.

Particle size and shape influence the hydrodynamic conditions in the bed of a sorbent, and are related to the value of the surface area. Smaller particles have a larger surface area, and columns packed with these particles yield a higher performance.

Sorbents having a higher surface area per mass unit have a higher number of active accumulation sites. The surface area can be increased by a porous structure of the sorbent. The factor of pore size is inversely proportional to the surface area. The pores should be as small as possible for effective accumulation, but the size of the analyte molecules should not hinder the penetration of the molecules into the pores.

6.2. Preconcentration of air contaminants

The use of gas–solid chromatographic techniques for the characterisation of the kinetic and thermodynamic properties of carbon sorbents provides insight into the adsorbent characteristics [26,57]. A small gas chromatographic column is an effective tool for determining the interactions occurring between contaminants and adsorbent (adsorbate/adsorbent interactions). Using such a column to evaluate adsorbent/adsorbate interactions allows for quick and effective extraction of data that can be applied to the reconstruction of a sampling tube with known sampling parameters. These interactions in the low coverage (Henry's law) region, provide information such as adsorbent surface homogeneity, adsorbate specific retention volume (i.e. analyte breakthrough), and adsorbent capacity for the chosen adsorbate. The choice of water as adsorbate also provides valuable information about the hydrophobic surface properties of the adsorbent, since high humidity sampling conditions can affect the validity of air sampling data.

Specific retention volumes and/or breakthrough volumes (BTVs) which relate to the adsorbent capacity have been studied by several authors [26,43,45,57,58] for a number of carbon sorbents. This specific retention volume value

can be used in constructing an adsorbent tube that possesses known breakthrough characteristics for known adsorbent bed weights. Specific retention volume data can be utilised to obtain the adsorption coefficient, which is a measure of the equilibrium distribution of the introduced adsorbate between the gas and solid phases. Similarly, the equilibrium sorption capacity can be extracted from the specific retention volume data. Equilibrium sorption capacity data are a measure of the adsorbent's capacity for the adsorbate.

The specific retention volume data obtained for the non-specific graphitized carbon black adsorbents (Carbotrap B, Carbotrap C, Carbopack F) [43] and the group A (*n*-alkanes), group B (aromatic and chlorinated hydrocarbons), and group D (oxygenated compounds) adsorbates illustrate the typical interactions occurring between an adsorbate molecule and the surface of a graphitic carbon. The higher surface area of graphitic carbon and the increase in the molecular length results in an increase in the surface-to-surface interactions. This increase is noted as a progressive increase in the specific retention volumes (tested with C₄–C₁₄ alkanes). A similar trends is found for group B and D molecules; the molecular size and shape of the adsorbate molecules lend themselves to predictable retention data.

Experts monitoring volatiles and airborne contaminants in various sampling modes must decide which adsorbent will provide the best adsorption/desorption efficiencies for the adsorbates of interest. Carbon molecular sieves are used to trap the more volatile C₅ and smaller compounds. With carbon molecular sieves the diameter of the micropores and the percentage of micropores present are directly responsible for variations in specific retention volume, adsorption coefficient, and equilibrium sorption capacity data. In a systematic study by Betz et al. [57] nine molecular sieves and activated charcoal were evaluated to determine their interactions with four adsorbates—water, ethane, vinylchloride, and dichloromethane. The data obtained from this evaluation reveal trends in both the adsorbent working range and the adsorbents

hydrophobic properties. First the breakthrough volumes for the adsorbate dichloromethane (the adsorbate with the largest molecular size) provide the order of the adsorption strength of the molecular sieves and charcoal tested. The ordering shows that Carbosieve S-III and Carboxen-569 (commercially available Carbosieve and Carboxen types of sieves, Supelco, Bellefonte, PA, USA) followed by activated charcoal, possess the highest affinity for dichloromethane.

Water adsorption is important during sampling under high humidity conditions in the workplace, when competition for the adsorbent surface is occurring between the chosen adsorbate and water. Carboxen-569 and Carboxen-564 possess the smallest breakthrough volumes for water. The hydrophobic properties are a function of the pyrolysis temperature used to prepare these sieves and of the subsequent non-specific surface interactions. The hydrophobic properties of these sieves are, therefore, a function of the tailorability of the carbon molecular sieves. In comparison, the largest water breakthrough volume value is noted for activated charcoal. This greater water/adsorbent interaction for charcoal is a function of the polar functional groups such as carbonyl and carboxyl groups present on the adsorbent surface and the presence of metallic and ionic salt impurities in the adsorbent. This provides insight into the differences between a weak class III adsorbent such as Carboxen-569 and a strong class III adsorbent such as activated charcoal [43].

It was also found that microporous carbon molecular sieves (a polymer-based Carbosieve B and others tested) are potential adsorbents for diffusive sampling of hydrocarbons with more than four carbon atoms [59]. Hydrocarbons with more than seven carbon atoms have extremely high specific retention volumes (20°C) which show that diffusive sampling may not be suitable for these sorbents.

6.2.1. Sampling

Sorbents with a large specific surface area have been utilised for the sampling of very volatile organic compounds, such as dichloromethane and vinylchloride; sorbents with a small surface

area are convenient for semi-volatile compounds. Adsorptive sampling of organic pollutants in industrialised and remote areas (emission and immission measurements) on non-polar polymers and carbon adsorption traps has been widely used in single-bed and multi-bed cartridge arrangements. This largely solves the problem of moisture affecting the chromatography compared to canister sampling [60].

Preconcentration tubes containing sorbent, which are the most efficient and cheapest samplers, are widely used in the sampling of industrial atmospheres and ambient air. These are most frequently glass tubes (cartridges) containing about 100–300 mg of solid sorbent in the primary section and 50 mg in the rear (control) section, separated by an inert plug (e.g. silanized glass wool, carbon wool, etc.). Trapped components are desorbed from individual sections separately with a convenient solvent, in the case of activated charcoal most frequently with CS₂ [61,62]. The sorbent in the rear section is often placed in a separate tube when recovery is effected through thermal desorption or in order to detect the migration of the concentrated analyte during storage [63]. Besides the utilisation of “the standard robust” adsorption traps, there is a tendency in recent years to develop miniaturised sorbent traps, particularly for in situ monitoring and on-line automated systems.

6.2.2. Sorption from the gaseous phase—desorption into liquid phase

There are general requirements with regard to the solvents used for liquid desorption, to obtain high desorption yields, high purity and with respect to the injector used with capillary GC (splitless, on-column) giving good peaks shapes.

6.2.2.1. Activated charcoal—“classical” sampling bed

Adsorption by means of activated charcoal is the most widely employed sampling method for volatile airborne pollutants in the field of industrial hygiene, both by active and passive sampling devices. Carbon disulphide is recommended for solvent desorption because of its good properties, low gas chromatographic re-

tention time and very low response on a flame ionization detector (FID). Working with CS₂, however, poses some health problems because of its high toxicity.

Standard Practice for Sampling Atmospheres to Collect Organic Vapours (Activated Charcoal Tube Adsorption method) [62] covers a method for determining the presence of up to 100 certain organic vapours, particularly hydrocarbons, halogenated hydrocarbons and oxygenated compounds (alcohols, ethers, esters). The range of boiling points of compounds commonly collected from air on activated charcoal is from -28°C (dichlorodifluoromethane) to 259°C (naphthalene). A relative humidity higher than 60% can reduce the adsorptive capacity of activated charcoal for some chemicals to 50%. The presence of condensed water droplets in the sample tube indicates a suspect sample. The desorption efficiency, dependent on the nature of the analyte, is in most cases over 90% for non-polar and slightly polar compounds. However, the recovery is known to be influenced also by several other thermodynamic and kinetic factors: the amount of analyte, the presence of other adsorbed substances, the humidity of the sampled air, the ratio between the amount of charcoal and the desorbing liquid, the time and the temperature of contact, the particular batch of charcoal, etc. The recovery of polar compounds from activated charcoal may be incomplete, therefore in some cases binary solvent mixtures were recommended, such as CS₂-water, or with polar organic solvents, e.g. 2-propanol, methanol, 2-butanol, dimethylformamid [62,63].

Precision and bias in this type of analytical procedure are dependent upon the precision and bias of the analytical procedure for each solvent analyte of concern and the precision and bias of the sampling process [64]. When the errors involving determination of desorption efficiency, sampling, analysis (GC), and pump calibration are combined, the state-of-the-art indicated a relative precision of ± 15% at the 95% confidence level for most solvent vapours.

Charcoal is a sorbent adsorbing most organic and inorganic pollutants. Permanent gases (O₂, N₂, H₂, CO) and CH₄, however, are not ad-

sorbed on charcoal. Ethylene, formaldehyde, and other gases with a boiling point between -100 and 0°C, are only partially adsorbed, whereas gases with boiling points above 0°C are readily adsorbed [63]. Mercury vapour is effectively adsorbed by charcoal, but water vapour only slightly, although moisture reduces the sorption of other substances by charcoal. The physical properties of this popular adsorbent depend to the great extent on its source and subsequent treatment. Charcoal is an excellent sorbent for numerous compounds, but their desorption is often difficult.

With the application of activated charcoal series of problems are encountered, as it is not possible to prepare absolutely identical batches of active charcoal, adsorption is dependent on the size of the carbon particles, micropores, the time of contact with analyte, carbon does not adsorb all organic components and recovery in some cases is small. Activated charcoal obtained from coconut shells is considered to be an almost all-purpose sorbent. The adsorption capacity is an exclusive function of the micropore structure. The best grades of charcoal used for adsorption of air contaminants have a specific surface of ca. 1000 m²/g with 70–75% of the surface area containing pores smaller than 2 nm in diameter [63]. On the surface of activated charcoal reactions may occur (isomerisation, hydrolysis—the large carbon surface functions as catalysator), and therefore the desorbed compounds are not always identical with the original analyte.

The on-column injection of charcoal extracts has some advantages for this type of analysis [65]. One is that discrimination effects can be reduced if the technique is handled correctly, particularly with multi-component mixtures. Another advantage is, of course, the increased sensitivity over that of the split technique and/or combination of larger injection volumes. However, also with the split injection regime for emission measurements sufficiently low determination limits could be obtained (e.g. 30-l sample volume and split ratio 1:50, benzene 6.7 μg/m³ [66]; acrylonitrile 15 μg/m³ [67]). An example of a chromatogram of the analysis of benzene emission measurement is given in Fig. 2.

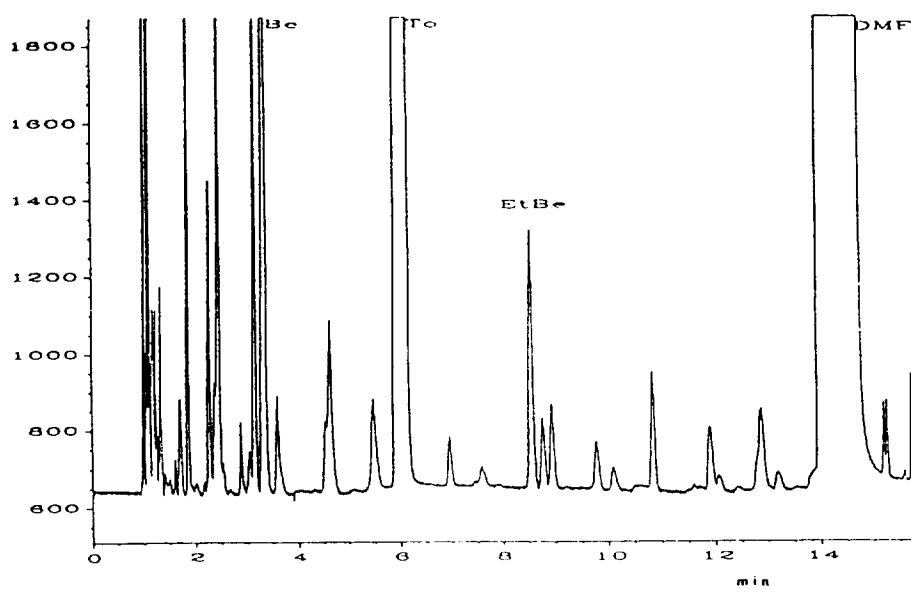


Fig. 2. Chromatogram of analysis of benzene emission measurement; (fused-silica capillary column SP-Nucol, Supelco); sampling on activated charcoal; DMF desorption: split injection (1:50). FID: Peaks: Be = benzene, To = toluene, EtBe = ethylbenzene, DMF = dimethylformamid. (Reproduced from Ref. [66]).

Sampling on pre-treated charcoal tubes allows control of some airborne contaminants, e.g. methylbromide in concentrations ranging from a few mg/m^3 (about 1 ppm) to $1 \text{ g}/\text{m}^3$ (250 ppm) after liquid desorption and FID-GC analysis [68]. The use of electron-capture detection (ECD) slightly reduces the detection limit. Charcoal must be pre-treated in order to reduce the chemical reaction of CH_3Br with the support and improve the recovery. For high hygrometer levels or low concentrations, the trapping capacity of treated charcoal is reduced. However by using 900-mg charcoal tubes, a minimum sampling of about 10 l is possible without breakthrough. Samples must be kept refrigerated and analysed within 14 days. Sampling with eight different porous polymers (including Tenax GC and TA, Chromosorbs) and three mineral molecular sieves showed that the trapping capacity of those sorbents was poor. The unsatisfactory results of thermal desorption from pre-treated charcoal were found to be due to reactions between the pollutants, the support and the atmospheric water.

6.2.2.2. Activated charcoal–miniaturised sampling bed

An other approach in the development of methods for the preconcentration of analytes is the use of a miniaturised bed of adsorbent combined with off-line liquid desorption, where the high sorption capacity of charcoal has been utilised; the main advantage of this technique is the increased sensitivity of the method and vice versa the decreased limit of quantitation—via the decreased overall volume of solvent used for the extraction. An other advantage is the lower material consumption which leads to less expensive analysis. A disadvantage is the handling of small volumes and the possible introduction of significant errors in quantitation, which however may be reduced by application of internal standards.

A charcoal preconcentration technique was developed for the enrichment of volatile organic compounds from multiliter volumes of air (1–100 l) [69,70]. The method preconcentrates analytes on a 5-mg charcoal trap in a glass tube ($65 \times 6 \text{ mm O.D.} \times 2 \text{ mm I.D.}$); the charcoal bed is

typically 2–3 mm long (Paxton Scientific Glass, Lowland, OH, USA). Analytes are desorbed from the charcoal with a small volume of solvent (several tens of μl) and analysed by HRCGC. Laboratory and field tests have been performed to evaluate method precision, analyte breakthrough, and compound recovery from the charcoal. Tests verified that the sampling/analytical system is free from artefact formation under clean to moderately polluted conditions, but further tests are required for areas with a high concentration of hydrocarbons, NO_x , and oxidants. The method was developed for alkylnitrates and halocarbons and allows measurement of $\geq \text{C}_3$ alkylnitrates and C_1 – C_2 halocarbons at concentrations in the pptv range. Most halocarbons and alkylnitrates showed good recoveries of analytes spiked into the gas stream ranging from 200–1000 pg per compound (a 600-pg spike corresponds to atmospheric concentrations of about 3–6 pptv depending on the compound in 20-l sample). Experiments indicate loss of 30–40% of most analytes over a 48-h period storage at room temperature. Freezing the sample tube improved recovery of the analytes. The samples stored frozen remained reasonably intact for at least 1 month. Despite of the small quantity of charcoal used in the trap, the retention of halocarbons and alkylnitrates from multiliter volumes of air was generally excellent (high relative humidity, air temperature ~ 28 – 30°C). As traps are repeatedly used and reused, collection efficiency may be lost. Prior to sampling traps are precleaned with solvents. No heat treatment of the charcoal is necessary. Over a concentration range from ~ 0.05 to 10 pptv, the average error of alkylnitrate measurement was estimated at $\pm (0.1 \pm 8\%)$ pptv; for halocarbons $\pm (0.1 \pm 5\%)$ pptv.

The extremely high capacity of charcoal was also utilized for retaining VOCs in air or head-space gas (e.g. food) in miniaturised charcoal coated open tubular traps (COT)–glass capillary pieces some 5 cm in length and with an internal diameter approximately corresponding to the capillary separation column coated with a layer of fine charcoal particles [71–73]. Due to their small size, these traps are well suited to capillary GC; such traps placed in the GC injector can be

extracted with ca. 2 μl of solvent [74,75]. Alternatively thermal desorption is possible at capillary GC gas flow-rates, and minimised dilution of the traps with carrier gas results in sharp peaks, even for volatile components; no cold-trapping or refocusing is necessary (e.g. 20 ml of gas can be sucked through this trap in 20 s). Detection limits in 20 ml of air or head-space gas sucked through the trap by a syringe were found to be for benzene 1–3 $\mu\text{g}/\text{m}^3$ and 0.05 $\mu\text{g}/\text{m}^3$ for chlorinated compounds. The total weight of activated charcoal particles (10–18 μm) was 0.05–0.1 mg. This technique was shown to be convenient for the analysis of compounds with boiling points in the range 90– 235°C [76]. The capacity of COT for highly volatile compounds can be improved by increasing the length of the trap up to 1 m [77–79] or utilising traps with a thick film of crosslinked methylsilicones [80], where highly volatiles are, however, not effectively retained. Decomposition of thermally labile compounds during the desorption from a COT presents a problem.

6.2.2.3. Porous carbon

With the advanced technology of carbon adsorption traps, specially tailored porous carbon materials suitable for the preconcentration of various organic groups have been tested. The preparation of porous carbon is based on the pyrolysis of organic precursors (saccharose) in the matrix of silica gel. This and a similar kind of sorbent were found to be convenient materials for the enrichment of VOCs (hydrocarbons, halocarbons) [81–84] in simulated and real air samples at various concentration levels. By studying recovery data with liquid (and thermal) desorption also of polar compounds–alcohols, aldehydes, ketones [84]–significantly lower recovery data than 100% indicate the presence of residual polar groups on the sorbent, which is in agreement with an FT-IR spectroscopy study of this type of sorbents [40].

6.2.3. Sorption from the gaseous phase–desorption into supercritical fluid

Supercritical fluid extraction (SFE) of organic adsorbents represents a powerful alternative to traditional methods of sample preparation. SFE

exhibits densities similar to those of a liquid, yet with solvent diffusivities and viscosities closer to those of a gas; these properties facilitate mass transfer of solutes resulting in rapid and efficient extractions at relatively mild conditions, thus minimising chemical changes. Determination of volatile and semi-volatile mutagens in air using solid adsorbents and SFE (CO₂) has been described [85]. Solid adsorbents, activated charcoal, Carbosieve S-III and XAD-4 (styrene-divinylbenzene copolymer) were compared in their trapping efficiencies for dichloromethane (DCH), ethylene dibromide (EDB), 4-nitro-biphenyl, 2-nitrofluorene, fluoranthene. Extraction of different spikes of compounds from adsorbents resulted in >90% recovery of EDB and 60–92% recovery of the aromatics. For more volatile compounds (such as DCH) alternative techniques are necessary to quantitatively recover extracted analytes using SFE due to their volatilisation in the expanding CO₂ stream.

6.2.4. Sorption from the gaseous phase—desorption into gaseous phase

An interesting alternative to the use of a solvent is desorption with a carrier gas at elevated temperature, followed by on-line introduction of the desorbed analytes onto the gas chromatographic column. This technique requires a compromise between the demands of desorption and those of injection of the sample. In fact, while complete desorption would be favoured by the use of a large amount of carrier gas, for a good chromatographic separation it is mandatory to introduce the analytes onto the column in the form of a narrow band. One can overcome this difficulty by a large amount of carrier gas for the desorption and by concentrating the analytes either on the top of the GC column held at sub-ambient temperature or in an intermediate device, which in turn can be a cold trap or a smaller desorption tube. In the last years ballistic heating of the trap has been applied with cryogenic refocusing of the volatile analytes on the top of the capillary GC column and/or in combination with a thick film of stationary phase in a capillary column. Thermal desorption has the advantage over solvent desorption of greater sensitivity and the absence of

a solvent peak which could potentially mask analyte peaks.

An inherent limitation of the thermal desorption methods is that they do not allow a repetition of the analysis. They are, therefore, not very suitable if complete qualitative information on the pollutants present in the sampled air is not available beforehand and if the order of magnitude of their concentration is not known at least approximately. For these reasons, the thermal desorption methods have been primarily employed for the determination of pollutants, the presence of which could be anticipated.

With thermodesorption reasonably low blanks are required. The problem of low blanks is particularly important for sampling very low ppt–ppb concentrations of organic compounds in ambient air from remote areas. Tenax TA or GC, which has been the most frequently used adsorbent for C₅–C₁₅ substances in air, is difficult to clean. Blanks of a few ppt which are stable for weeks, are essential for sampling in remote areas since transport of the non-exposed and exposed solid adsorbent tubes to the laboratory can be very time-consuming. It has been shown that sufficiently low blanks of carbon materials (Carbotrap) could be maintained for a storage period of at least one week [86]. However, this required a careful selection of suitable sealing and tube material. Sampled VOCs (on GCBs in multi-bed arrangement and/or in combination with carbon molecular sieves) stored in a sealed glass container were found to be stable for more than two months [87–91].

6.2.4.1. Single-bed sorbents

Thermal desorption of analytes from activated charcoal is problematic, particularly due to the slow desorption of analytes and the high catalytic activity in comparison with polymeric sorbents. The necessary desorption temperature is so high that many compounds decompose. In spite of that several methods have been published of thermal desorption of pollutants from activated charcoal, e.g. microwave heating of the sorbent up to 700°C, which is convenient for stable analytes [92], heating the adsorbent and sucking the released pollutants into an evacuated gas sampling bulb [93,94], and others. It was found

that the gram size of a given charcoal does not influence the desorption properties, that the maximum temperature needed for complete desorption is independent of the loading and that the members of a homologous series (*n*-alkanes) obey some regularities [95]. Accumulation of thermally desorbed analytes in a reservoir allows repeated GC analysis of sample aliquots [96]. The desorption yields and especially their reproducibility compare favourably with literature data for the standard solvent technique. Even strongly polar analytes can be desorbed satisfactorily, although the yields and their reproducibility are not as good, probably because of decomposition processes. For more polar compounds, the variation of recovery with concentration is significant and should be taken into account if accurate results are required. Application of graphitized sorbents reduces many problems of thermal desorption.

6.2.4.1.1. *Comparison of graphitized carbons with porous polymers* Porous polymers, introduced into analytical practice more than 20 years ago are used no less extensively than activated charcoal. They are relatively inert, hydrophobic and normally have large surface areas. Most porous polymers poorly retain volatile compounds, water and solvent vapour, but this is turned into an advantage if a sample is collected in an atmosphere with a high content of water and solvent vapour [63]. Porous polymers such as Tenax GC, Porapak, Chromosorbs, XAD resins and polyurethane foam are most successfully used to trap toxic agents of high molecular mass and non-volatile substances such as pesticides. Many of the limitations associated with the application of porous polymers are the result of their batch-to-batch variations. Various applications of polymer sorbents, in particular those used for the concentration of toxic substances from air, have been considered in reviews [63]. Certain disadvantages of these sorbents create a number of problems: (1) displacement of the more volatile compounds especially by CO₂; (2) irreversible adsorption of some compounds, e.g., amines and glycols; (3) oxidation, hydrolysis and polymerization of the sample; (4) contamination of the sorbent due to chemical reactions in the

presence of reactive gases and vapour, e.g., oxides of nitrogen and sulphur, inorganic acids; (5) formation of new compounds arising from reactions and thermal desorption; (6) limited retention capacity; (7) thermal instability; and (8) limitations of sampling volume, rate and time.

Tenax GC, a polymer based on 2,6-diphenyl-*p*-phenylene oxide commercially available with a specific surface area of 19–30 m²/g, is preferred in the last years by many analytical chemists for the preconcentration of volatile and non-volatile organic pollutants from atmospheric and water samples because of its high thermal limit (350–400°C), which facilitates thermal desorption.

Owing to its high thermal stability and its ability to trap compounds of various molecular masses and polarity, Tenax is used more often than other sorbents for the recovery of pollutants from environmental samples, particularly air and water. However, it should be born in mind that Tenax, while efficiently trapping non-polar high-molecular-mass compounds, is less efficient with respect to volatile polar compounds, such as alcohols, ketones, ethers and chloro-hydrocarbons [63]. The convenience of enriching atmospheric samples on Tenax GC has been questioned and it was found that this material may be a serious source of interferences, when strong oxidants and inorganic pollutants commonly found in the atmosphere and in industrial emissions come into contact with the polymer. In the presence of ozone, water, SO₂, and NO₂ Tenax GC undergoes chemical decomposition, giving rise to substantial amounts of organic compounds that can simulate the presence of pollutants in the sample [87,97–99].

Because of the problems encountered with the use of Tenax, particularly in ultra-trace analysis, one started to look for the application of very inert sorbents. A comparison between the collection efficiency of Carbo-pack B (graphitized carbon black material, which is a relatively pure form of carbon [100]) and Tenax GC in the sampling of C₆–C₁₀ hydrocarbons from both simulated and real atmospheres [87], indicates that Carbo-pack B is the more efficient sorbent (Fig. 3); it does not give rise to sampling ar-

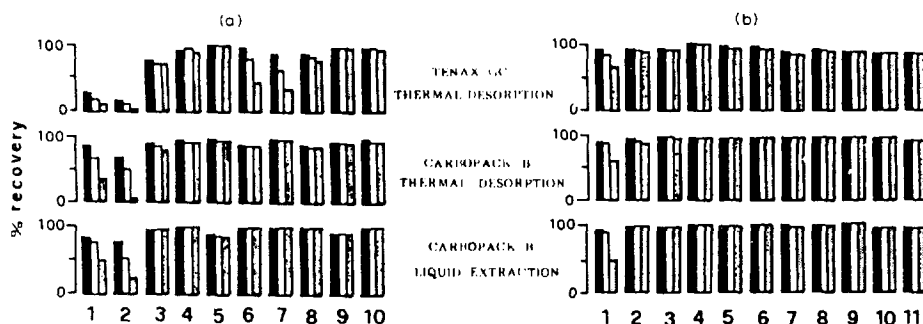


Fig. 3. Percentage of test compounds recovered from Carbopack B and Tenax GC when 2 (closed bars), 5 (open bars) and 10 l (shaded bars) of air were passed through the adsorption traps. (a) Olefins and monoterpenes: 1 = 1-hexene; 2 = bicycloheptadiene; 3 = 1-heptene; 4 = vinylcyclohexene; 5 = 1-octene; 6 = *cis,cis*-octadiene; 7 = α -pinene; 8 = carene; 9 = α -terpinene; 10 = limonene. (b) Benzene and alkylbenzenes: 1 = benzene; 2 = toluene; 3 = ethylbenzene; 4 = *o*-xylene; 5 = *m*-xylene; 6 = *p*-xylene; 7 = 1,3,5-trimethylbenzene; 8 = *n*-butylbenzene; 9 = 1,3-diethylbenzene; 10 = 1,3,4,5-tetramethylbenzene; 11 = 1,2,3,4-tetramethylbenzene. (Reproduced from Ref. [87]).

tefacts in the presence of oxidants and acidic pollutants, which are shown to cause decomposition of the Tenax GC polymeric matrix. Enrichment on Carbopack B adsorbent traps was proposed as a suitable method for the evaluation of organic compounds present at ppm–ppt levels in atmospheric samples. The technique has been applied to the determination of organics dispersed in a suburban atmosphere, dissolved in rain water or volatilized from particulate matter emitted from an industrial emission and diesel engine exhaust. With regard to the adsorption efficiencies of Tenax GC and Carbopack B, it was clearly shown, that the latter is a material better suited for the enrichment of low-boiling compounds and particularly of natural hydrocarbons (e.g. α -pinene, carene). In the presence of 500 ppb of ozone in simulated air samples serious decomposition of the polymeric matrix of Tenax GC was observed and a substantial amount of interfering compounds was detected by GC–MS analysis. The major decomposition products arising from the oxidation of the polymeric matrix were found to be acetophenone and benzaldehyde (Fig. 4). The presence of these compounds is in complete agreement with the results presented by other authors [101], but there is some contradiction with regard to the presence of water, which is according to Kröst et al. [101] equally important in producing de-

composition of the polymer. According to Ciccioli et al. [87] water was always present during sample collection at 50% relative humidity, but the production of benzaldehyde, phenol, and benzophenone was observed when ozone was added to the mixture. It is likely that water becomes effective when other pollutants (such as NO_2 and SO_2) are added to the air stream. The study on Tenax decomposition was also performed in a real atmosphere (ozone conc. < 100–200 ppb) and the formation of artefacts was confirmed. From experiments it follows that ozone is likely to be the main cause of decomposition of the Tenax GC adsorbent and traps packed with Tenax GC can lead to erroneous results in the evaluation of organics in air. The possibility of sampling artefacts is also increased by the fact that in the atmosphere free acids (e.g. HNO_2 , HNO_3 , H_2SO_4) can be observed concurrently with high levels of ozone. It must be also recollected that benzaldehyde is an extremely important compound in the photochemical pollution cycle, as it is one of the main products of the reaction of alkylbenzene hydrocarbons with OH radicals.

According to a study by Ciccioli et al. [87] the chemical inertness of Carbopack B permits the determination of organic compounds in anthropogenic emissions, where large amounts of NO_x , water, ozone and strong acids are present.

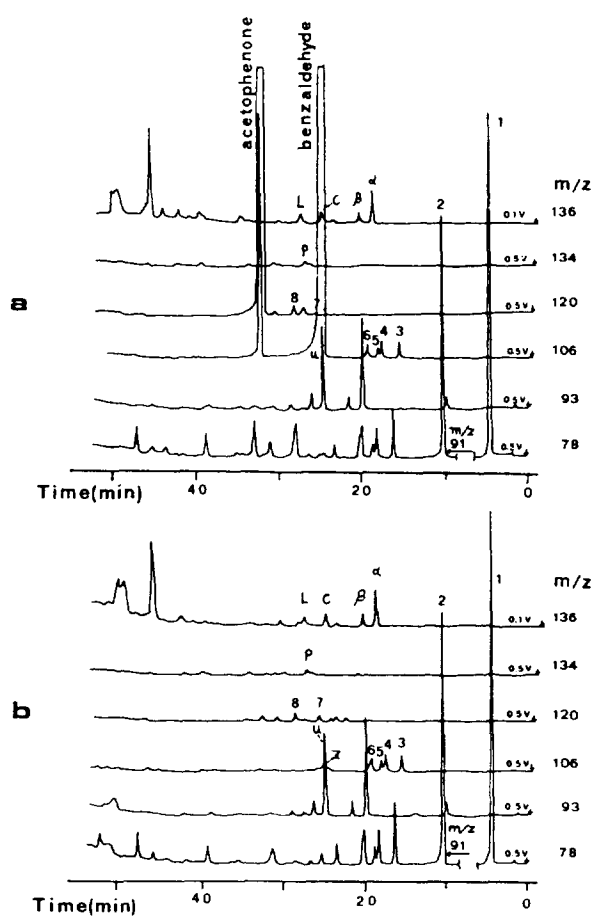


Fig. 4. Selected-ion chromatographic profiles obtained by analysing 10 l of an air sample collected at noon in a pine forest. (a) Tenax GC; (b) Carbo-pack B. Peaks: 1 = Benzene; 2 = toluene; 3 = ethylbenzene; 4 = *m*-xylene; 5 = *p*-xylene; 6 = *o*-xylene; 7 = 2-ethyltoluene; 8 = 1,2,4-trimethylbenzene; α = α -pinene; β = β -pinene; c = carene; L = limonene; p = *p*-cymene; u = unknown; z = benzaldehyde. The individual concentrations of compounds ranged between 0.09 and 0.004 ppb. (Reproduced from Ref. [87]).

Comparison of Tenax TA (a further development of Tenax GC, which is stable up to 280°C and produces less artefacts than Tenax GC) and Carbotrap B [102] for sampling and analysis of volatile organic compounds in air on the bases of recovery data shows (desorption temperature of Tenax 260°C, Carbotrap 320°C), that many VOCs (toluene, *n*-alkanes C₇–C₁₃, styrene, aniline, dimethylformamide, phenol, butylacetate) with boiling points up to 270°C and occur-

ring in trace amounts could be desorbed quantitatively from Tenax TA, but not from Carbotrap; α -pinenes and aldehydes (acrolein, hexanal) show some reactivity on Carbotrap. For very volatile compounds and various polar VOCs, substantial losses, most probably due to breakthrough, were observed. With aldehydes similar results were obtained by other authors [103], who found a stronger decomposition of the aldehydes at a desorption temperature of 300°C. When desorbing α -pinene from Carbotrap, additional peaks were found [102]; GC-MS investigation suggests that rearrangement to other terpenes had taken place; the recoveries of polar compounds, such as acetic acids, isopropanol and 1,2-ethanediol, were unsatisfactory on both sorbents. With Tenax TA a decrease in capacity for volatile compounds was observed when using the same Tenax tubes more than five times; the adsorptive properties of Carbotrap do not change even after being used 30 times. On Tenax TA benzaldehyde and acetophenone were found in small quantities—due to sorbent decomposition. According to results presented by Supelco [104] for Carbotrap, recovery of 1-butanol and 2-ethoxyethylacetate and other compounds is virtually complete both by liquid desorption (CS₂) and thermodesorption.

The applicability of stainless steel canister and solid adsorbent sampling (Tenax TA and Carbotrap) was studied for very low concentration (> 15 ppt) of compounds \geq C₆ in ambient air samples from remote areas (Arctic) [86]. Different cleaning methods were tested to get sufficiently low blank values for the solid adsorbent Tenax TA and Carbotrap. It was shown that sufficiently low blanks could be obtained for a storage period of at least 1 week. Both sampling techniques were suitable for very low ppt concentrations of benzene and toluene, but their application is complementary. The maximal sampling volume for Tenax tube was 10 l, for Carbotrap 60 l.

6.2.4.2. Multi-bed sorbents

A number of adsorbent materials have shown utility for trapping organics and for desorption particularly by thermal techniques [105]. How-

ever, none of these materials can individually fully accommodate a complete range of organic volatilities or polarities, and thus they must be used in combination with each other. It is apparent from published results, that no single sorbent material is practical for collecting all solutes. In some instances this is because the sorbents do not retain low-molecular-mass materials (Carbotrap C); in other cases it is because the analytes are too strongly retained to be easily desorbed of the heavier solvents (activated charcoal).

Given the lack of a universal sorbent, the best approach to the problem was to construct tubes containing several different materials to attain the desired collection and desorption characteristics, the so-called multi-bed sorbents, where the principle of sequential trapping is taking place [57,106–109]. The scheme of a multi-bed adsorbent tube is given in Fig. 5. The materials would ideally have the ability to stand up to repeated use and heating without changing their characteristics and should additionally give a low background on a chromatogram. It is also desirable that they would have a low affinity for water. The adsorption layers are arranged in such a way that compounds with the lowest molecular mass go through the initial layer(s) and are trapped on the last layer. The initial layer(s) protect the next layer(s) from compounds which could be adsorbed irreversibly. It is important that the flow during sample collection enters the sorbent tube at the least active layer and leaves through the most tenacious layer. Each layer of adsorbent material protects the succeeding more active layer. The direction of the flow during desorption is the reverse of that during sample collection. Consequently,

when the tube is heated to desorb the sample, the heat energy required for volatilisation is kept to a minimum, since each molecular mass range is trapped on an appropriate sorbent material from which it is easily released.

Trapping material selections are based on the collection efficiency, the ability to retain a particular class of analytes, and on the desorption efficiency, i.e. the ability to quickly release the trapped compounds. In recent years various combinations of carbonaceous and non-carbonaceous sorbents for trapping organic pollutants from air and other environmental samples (water and soil) were tested.

Supelco produces several combinations of carbon sorbents in multi-bed adsorbent tubes (Table 4), which should be effective for trapping volatile and semi-volatile organic compounds with a broad range in boiling points. Thus one tube would be sufficient instead of several traps for special or multitask applications. Adsorbents of the Carbotrap type comprise various arrangements of several layers of graphitized carbon black with a specific surface area in the range of 5–100 m²/g, carbon molecular sieves with a specific surface area of 400–1200 m²/g and glass beads. In many applications these traps are used to refocus the analytes after thermal desorption without the need of cryofocusing. The sample is transferred from a sampling 4-mm I.D. tube into a tube with a narrower diameter before desorption onto the GC column. Using a low flow-rate during the transfer step provides for less deeply adsorbed components. Also, the narrower inside diameter provides for a greater linear velocity across the tube when desorbing at the same flow-rate. This technique is certainly effective and less costly than the cryogenic technique. Using a 2-mm I.D. tube to desorb the sample onto the GC column, as opposed to a 4-mm I.D. tube, quadruples the linear velocity with which the desorption flow passes through the tube. Direct sampling with the narrower I.D. tube would lead to a decrease of the sampling tube volume by a factor of 4, giving only 1/4 of the amount of adsorbent in the tube. Challenging that smaller amount of adsorbent with four times the linear velocity, at identical sampling flow-

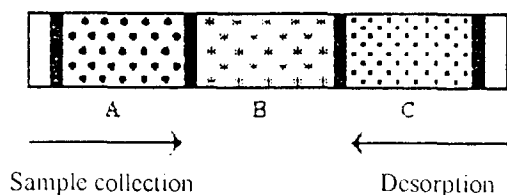


Fig. 5. Multi-bed adsorption tube scheme: A,B,C = different adsorbents with various specific surface area (A = small; B = middle; C = large).

Table 4
Multi-bed sorbents commercially available from Supelco

Name	Adsorbents	Use
Carbotrap 150	70/80 glass beads (200 mg)/ 20/40 Carbotrap C (425mg)	Large molecules (PCBs, alkylbenzenes) in air, aqueous samples, suspensions of solid materials
Carbotrap 200	70/80 glass beads (80 mg)/ 20/40 Carbotrap B (200 mg)/ 60/80 Carbosieve S-III (350 mg)	C ₂ –C ₁₄ compounds in air
Carbotrap 201	60/80 Carbotrap B (11.5 mg)/ 60/80 Carboxen 1000 (12.5 mg)	Focus very volatile, semi-volatile compounds
Carbotrap 300	20/40 Carbotrap C (300 mg)/ 20/40 Carbotrap B (200 mg)/ 60/80 Carbosieve S-III (125 mg)	C ₂ and heavier compounds in air
Carbotrap 301	60/80 Carbopack C (12 mg)/ 60/80 Carbopack B (7 mg)/ 60/80 Carboxen 1000 (8 mg)	Focus volatile, semi-volatile compounds
Carbotrap 302	60/80 Carbopack C (125 mg)/ 60/80 Carbopack B (150 mg)/ 60/80 Carboxen 1001 (200 mg)	Volatile compounds in aqueous samples
Carbotrap 370	60/80 Carbopack F (40 mg)/ 60/80 Carbopack C (50 mg)/ 60/80 Carbopack B (20 mg)	C ₅ –C ₃₀ compounds thermally extracted from solid samples; focus semi-volatile compounds
Carbotrap 400	20/40 Carbotrap F (150 mg)/ 20/40 Carbotrap C (150 mg)/ 20/40 Carbotrap B (125 mg)/ 20/40 Carboxen 569 (125mg)	C ₂ and heavier compounds in aqueous samples, soils
VOCARB 3000	Carbopack B/Carboxen 1000/ Carboxen 1001/	VOCs from water
VOCARB 4000	Carbopack C/Carbopack B/ Carboxen 1000/Carboxen 1001	Alcohols, ketones, polar oxygenated compounds, VOCs from water
CONCAWE	Chromosorb 106 (200 mg)/ activated charcoal (300 mg)	C ₁ –C ₄ from air
BTEXTRAP	Carbopack C/Carbopack B	Benzene, toluene, xylenes from water, soil

rate, would increase sample breakthrough by at least 8-fold.

Various applications of multi-bed sorbents (combinations of carbonaceous and non-carbonaceous sorbents) for sampling of organic compounds in air are summarised in Table 5. It was shown in scientific and commercial literature that combination of carbon sorbents allows the sampling of a large variety of compounds differ-

ing in polarity (non-polar/polar compounds) and volatility (C₂–C₁₅) at various concentration levels (ng–mg/m³). From the listed papers in Table 5 the most important are considered to be the papers of Bishop and Valis [105] and Ciccioli et al. [88,90].

In their study Bishop and Valis [105] evaluated a number of sorbents (Tenax TA, Carbotrap, Ambersorb XE-340, activated charcoal, Car-

Table 5
Application of multi-bed sorbents for sampling organic compounds in air samples with subsequent GC determination

Multi-bed sorbent	Analysed compounds	Volatility range b.p. (°C)	Sample volume (l)	Detector	Concentration level MLD ^c	Reference
Tenax GC/molecular sieve 5A/Carbosieve S-II	C ₂ -C ₁₀ hydrocarbons	-88-220	1-2	FID	0.7-95.5 ppbC '0.1-0.2 ppbC	110
Carbopack C/Carbosieve S-III	Halocarbons	24.2-174	0.35	ECD	2-200 ppbv	111
	Aromatic hydrocarbons	80-168		FID		
Tenax TA/Carbotrap/Carbosieve S-III	C ₂ -C ₆ alkenes	-104-69	0.1-2	FID/PID	4-3700 µg/m ³	112
Tenax TA/Carbotrap/Carbosieve S-III ^a	C ₂ -C ₈ hydrocarbons	104-142	0.5	FID/MS	9-630 µg/m ³	113
Tenax TA/Ambersorb XE-340/activated charcoal	Non-polar and polar compounds	78-174	1-2	MSD	10-200 µg/m ³ '5 ng	105
Carbotrap C/Carbotrap/Carbosieve S-II	C ₃ -C ₁₄ compounds	-0.5-254	1-2	FID/MSD	0.02-107 µg/m ³	88
Carbotrap C/Carbotrap/Carbosieve S-III	Hydrocarbons Halocarbons Oxygenated compounds				'0.01 µg/m ³	
Carbotrap 200	C ₂ -C ₁ hydrocarbons	-104	0.5-1.2	FID	0.1-1 mg/m ³ '1 µg/m ³	114
Carbotrap 300	C ₂ -C ₁₂ hydrocarbons Hydrocarbons Halocarbons Oxygenated compounds Sulfides	-104-216.2	3-30		1-4330 µg/m ³ '0.5 ng/m ³	115
Carbotrap 400 ^b	Non-polar and polar compounds C ₃ -C ₁₅ Aliphatic and branched hydrocarbons Alkylbenzenes PAH Heterocompounds (O, N, S)	-0.5-448	6	FID/NPD/ MSD		116

^a Vehicle emissions, tobacco smoke.^b Chimney emissions.^c MLD = method detection limit.

bosieve S-III) in single-bed and particularly various multi-bed layer arrangements for their ability to retain and thermally desorb an assortment of solvent vapours. The amounts of analyte vapour recovered from the tubes were quantitated using a GC–MS detection. The method is seen to be precise in its reproducibility of the results and it is sensitive (5 ng of a compound in air sample). Of the tubes tested, the design based on Tenax/Amborsorb/charcoal clearly has the broadest potential for successful sampling of a wide range of solvents at various concentrations and under conditions of high humidity. The tubes based on Carbotrap/Carbosieve may also be used but are limited in their ability to retain low-molecular-mass polar compounds (ethanol having the lowest overall recovery), especially under humid conditions. With regard to storage stability, severe losses of the more volatile polar compounds occur with the studied multi-bed tubes. Whether the losses arise from migration, moisture, long-term effects from coadsorption of multiple compounds, oxidation, or other factors is not certain [117]. Water could cause breakthrough of some of the analytes during transfer and also creates problems with MSD operation [105]. The authors tested two approaches to accomplish water removal; the application of drying tubes such as calcium chloride, anhydrous sodium sulfate, and calcium sulfate placed in front of the sampling tubes and the use of tube conditioning. The drying tubes helped to reduce the level of moisture, but trapped some of the analytes. Application of tube conditioning in conjunction with the use of low sample volumes (1–2 l) should minimize the problem of moisture interferences for both types of traps. The sampling tubes were designed to monitor low levels of atmospheric contaminants, often of an unknown identity.

Ciccioli and co-workers contributed to a large extent to the identification and determination of biogenic and anthropogenic volatile organic compounds in urban, forest areas and remote sites [87–91]. They developed a method for the analysis of multicomponent mixtures of polar and non-polar C_4 – C_{14} hydrocarbons belonging to different classes (over 140 components) involved in photochemical smog formation [88]. The num-

ber and amount of oxygenated compounds in investigated environments highlight the importance of these components to the investigation of the mechanism leading to the formation of photochemical smog. They used multi-bed carbon adsorption traps combined with HRCGC–MS. Two different combinations of carbon adsorbent were tested and used for enrichment of hydrocarbons, halocarbons, aldehydes, alcohols, ketones and aliphatic acids: Carbotrap C/Carbotrap and Carbotrap C/Carbotrap/Carbosieve III. Experiments performed in real atmospheres (air samples with a relative humidity ranging from 40 to 90%) showed that the presence of Carbosieve S-III led to enrichment of water to such an extent that plugging of the fused-silica liner of the commercially available desorption unit was observed when the relative humidity was higher than 50%. Insertion of Nafion dryer, desiccants (sodium carbonate and sodium sulfate), and cryogenic traps at -10°C resulted in severe losses (>50%) of the high boiling alcohols and aldehydes, especially nonanal and decanal and some terpenes. Quantitation was restricted to components with a carbon atom number greater than 4, as a drastic reduction of the adsorption properties of the carbon material was observed when 2-l samples were collected on the trap when the relative humidity was high. Restriction of sampling volume to 500 ml worked well with FID, but the amount of water and carbon dioxide collected by Carbosieve S-III was still large enough to hinder the collection of mass spectra of a large portion of the chromatogram. Identification of the components by GC–MS was possible only when sample enrichment was performed on the traps filled with two types of graphitized carbon black, as these showed little affinity for either water or carbon dioxide. The minimum amounts detectable in 2-l samples are in the order of 0.01 ng/l, which enables the determination of components present at the tenths of pptv level. The difference between the performance of ten traps used for sampling in parallel was small (<10%). The analysis of samples characterized by substantial amounts of polar components was stated to be extremely useful from the methodological point of view, as it showed the capability of carbon traps to retain

and release in a quantitative way very polar organic compounds with a wide range of carbon numbers (Fig. 6) [90]. Sufficiently low blanks were obtained after cleaning and sealing the traps and storing under a prescribed conditions. Sampled VOCs stored in the sealed traps closed in the glass container were found to be stable for more than 2 months.

Analysing air samples with standard robust adsorption traps and evaluating published results, some general problems become apparent, the main problem being humidity affecting the adsorption phenomena and/or the chromatography (GC–MS). Various approaches of selective removal of water [88,105,110,111] from sampled air have been connected with the losses of some components [88,105]. Supelco proposed a combination of GCBs with molecular sieves for monitoring volatile and semi-volatile compounds as they enable sampling in highly humid conditions, e.g. Carbotrap and Carbosieve S-III [115,118]. There is, however, contradictory information in

the literature in this regard, that Carbosieve S-III would lead to enrichment of water [88,105].

The other problem is related to the trapping capabilities of carbons sorbents for the low-molecular-mass compounds. Sampling C_2 saturated and unsaturated hydrocarbons exhibited some limitations [114]. Collection of C_2 hydrocarbons occurred mainly on Carbosieve S-III in the multi-bed adsorbent tube Carbotrap 200 [118]. Compared to the Supelco data significantly lower breakthrough volumes were found for C_2 hydrocarbons on the Carbosieve S-III [114]. For C_1 and C_2 hydrocarbons, canister sampling is still the method of choice unless direct-sampling GCs are available on site.

6.2.4.3. Miniaturized sorbent(s) bed

An other approach in the development of methods for the preconcentration of analytes in air samples is the utilization of miniaturized beds of adsorbents combined on-line with thermodesorption giving the possibility of automated

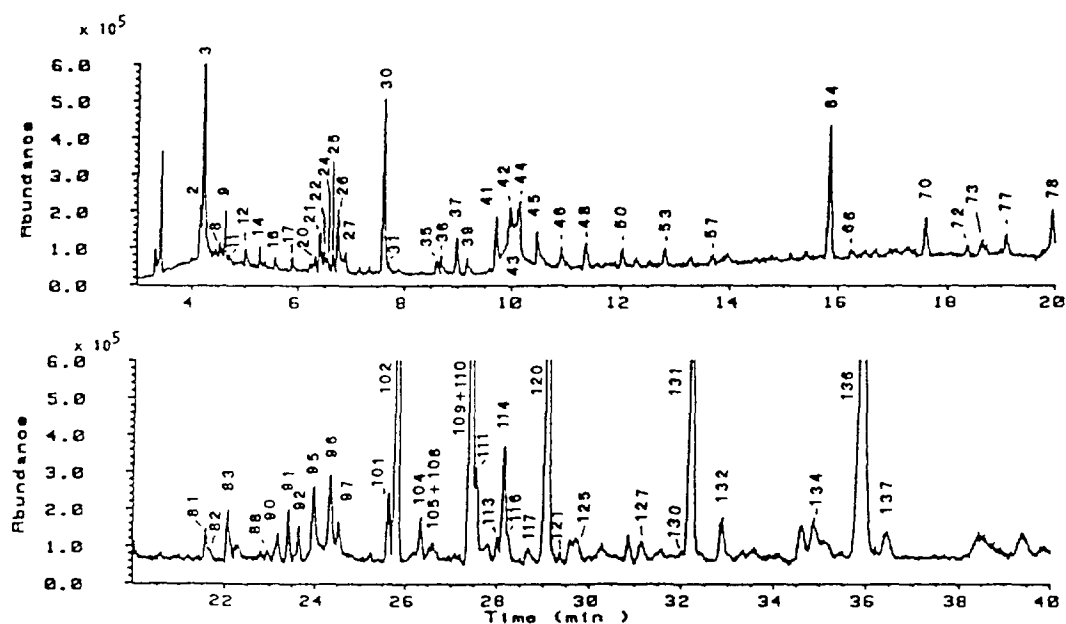


Fig. 6. GC–MS profile of a sample collected in a Northern European pine forest. The trace is the reconstructed chromatogram obtained by using a mass window ranging from m/z 34 to 200. Peaks: 9,21,27,30,46,50,53,97,132,137, alkanes; 8,11,72, alkenes; 41,64,81,83,88,90,105,106,113,121, arenes; 102,104,111,116,120,125,130, monoterpenes; 14,37,42,73, alkyl halides and CFCs; 12,31,36,45,95,96,134, alcohols; 2,16,17,24,39,48,70,91,101,114,131,136, aldehydes; 3,22,26,66,78,92,109,117, ketones; 20, propane, 2-methoxy-2-methyl-; 82, butanoic acid, 3-methyl-; 77, acetic acid, butyl ester; 35,44,57,127, cycloalkanes; 110, phenol. (Reproduced from Ref. [90]).

and continuous monitoring of low-concentration sample streams.

Air samples can be collected at ambient temperature on on-line microtraps [75,119,120], which are made of a few cm long small diameter tubing with a carbon adsorbent (e.g. 0.53-mm I.D. fused-silica capillaries with sorbent held in place with plugs of silanized quartz wool [119]). The sample containing the analyte is introduced onto the analytical column (coated with a thick film of a suitable stationary phase) through the microtrap. The analytes are trapped in the microtrap and can be thermally desorbed by electrical heating. When the heating is rapid enough, the “desorption pulse” serves as an injection for the GC column. Due to the small size and thermal mass of the microtrap, it heats and cools rapidly, and frequent injections can be made as long the GC separation is completed [120]. Automated on-line analysis may be performed even for very volatile compounds (e.g. chlorofluoromethanes) when traps are adopted to have a flow optimum similar to that of the separation capillary without cryogenic peak focusing [119,121,122] (Figs. 7, 8). The precision is comparable to that of other injection devices [120]. The minimum required air sample volume depends upon the noise voltage of the detector, the peak width, the required signal-to-noise ratio, and is inversely proportional to the concentration of the respective analyte and the detector sensitivity [121]; e.g. trichlorofluoromethane has the lowest ambient air concentration of 1.3 pg/ml ($1.3 \mu\text{g}/\text{m}^3$). As the ECD response is high, about 60 μl of air is sufficient for analysis; in contrast about 100 ml of air sample is required for trichloroethene (ambient level at $0.1 \mu\text{g}/\text{m}^3$).

Complete trapping and efficient band-focusing may be achieved at ambient temperature with microtraps packed with suitable sorbents. Two approaches has been evaluated by Frank and Frank [119]: if the boiling points of the analytes are within a range of about 100°C, a single-sorbent trap and direct coupling to the GC column are recommended; for samples containing components with widely different volatilities, a trap composed of two or more segments with complementary affinities and coupling to the

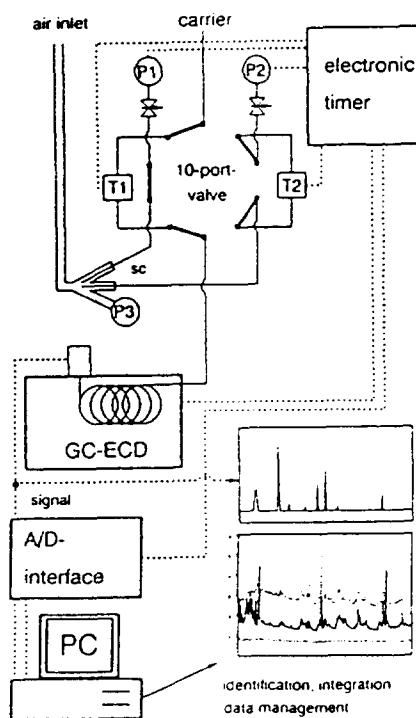


Fig. 7. Schematic presentation of instrumentation for automated sampling and gas chromatographic analysis of volatile trace pollutants in ambient air. Valve position: thermodesorption from trap 1- T1, sample collection on trap 2- T2; P1,P2,P3-membrane pumps. (Reproduced from Ref. [121]).

chromatographic column under carrier gas flow reversion is preferable. Examples of application of carbon sorbents in microtraps are presented in Table 6.

6.3. Preconcentration of water contaminants

The above sections summarise the development and application of single-bed and multi-bed carbon sorbents for the preconcentration of volatile and semi-volatile compounds, particularly in air matrices, and the achievements and problems of enrichment of analytes present in air samples, mainly in mixtures, are discussed. From the point of view of environmental analysis water is one of the other very important matrices. Therefore, the following deals with the problem of organic pollutant enrichment from aqueous solutions.

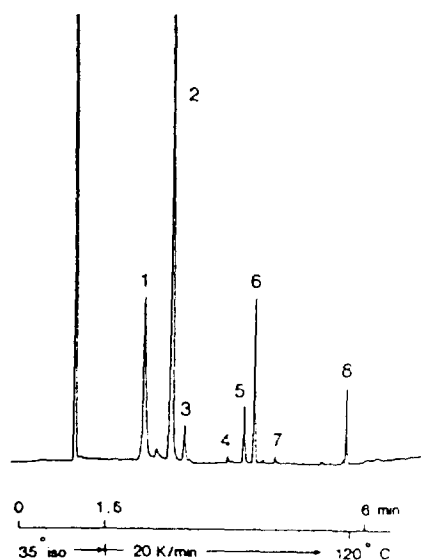


Fig. 8. Gas chromatographic separation of the major C_1 - and C_2 -halocarbons in 40 ml of ambient air on a thick-film ($2\ \mu\text{m}$) capillary coated with crosslinked SE-54 after automated sampling and thermodesorption. Peaks: 1 = CCl_2F_2 ; 2 = CCl_3F ; 3 = $\text{C}_2\text{Cl}_3\text{F}_3$; 4 = CHCl_3 ; 5 = CH_2Cl_2 ; 6 = CCl_4 ; 7 = C_2HCl_3 ; 8 = C_2Cl_4 . The retention time of the peak following CCl_2F_2 corresponds to COCl_2 . (Reproduced from Ref. [121]).

The investigation of the contamination of water with low concentrations of compounds is a complex problem that can only be solved using

isolation and preconcentration procedures prior to the determination. There are many techniques that can be used for the isolation and preconcentration of the considered pollutants from environmental samples (for reviews see Refs. [125–130]). Over the past twenty years carbon materials have been utilised for the analysis of aqueous samples, of volatiles (stripping techniques, purge-and-trap techniques, head-space analysis), but also for semi-volatiles and non-volatiles (dynamic stripping, steam distillation, SPE with liquid desorption).

6.3.1. Sorption from the liquid phase—desorption into liquid phase

In many environmental procedures trace enrichment is still often carried out by means of liquid–liquid extractions; nevertheless, recoveries are low for polar analytes and this technique cannot be applied to hydrophilic compounds, which are more soluble in water than in the usual organic solvents. The solid-phase extraction technique has gained interest as an alternative to the laborious and time-consuming liquid–liquid extraction.

Until recently, various types of activated carbon were the most commonly used sorption media for the preconcentration of pollutants from aqueous phases [126]. Most pollutants

Table 6

Miniaturised bed of sorbents for automated and continuous monitoring of low concentration of volatile trace components in air sample stream; sampling at ambient temperature

Microtrap	Trap dimensions I.D. × length (mm)	Analysed compounds	Volatility range b.p. ($^{\circ}\text{C}$)	Sample amount (ml)	Detector	Concentration level MLD ^a	Reference
Haysed D/Carbosphere	1.2 × 100	C_1 – C_2 halocarbons	–30–147	0.06–100	ECD	0.03–1.3 [$\mu\text{g}/\text{m}^3$]	121
Haysed D/Carbosphere Charcoal/Graphtrap	0.53 × 47	C_1 – C_2 halocarbons	–28–121	60	ECD	0.8–100 [$\mu\text{g}/\text{m}^3$]	122
Carboxen materials ^a 569; 1000	0.5 × 270 (300)	Chlorofluorocarbons	–48.4––9.8	2000	MS	1.5 ppm	124
Carboxen 1000/1003 ^b		Halocarbons	–48.4–28	2000–3000	MS	1 pptv	123
Carbotrap C	0.33 × 65	BTX, hexane	80–135	0.04–40	FID	ppbv–ppmv	120

^a Trapping temperature -40°C .

^b Trapping temperature -50°C .

adsorbed from water on activated carbon are recoverable by liquid extraction. CS_2 is the most frequently used extractant. Some compounds are resistant, particularly at low loading. The adsorption isotherms of organic pollutants are strongly concave with respect to the concentration axis, i.e. extraction efficiency decreases sharply with decreasing loading. The apparent irreversibility of the adsorption of some substances on activated carbon has been a hindrance to its use for the determination of trace pollutants.

The development of new types of sorbents for SPE is growing rapidly [126,128]. Among the sorbents that have been investigated in recent years are the tailored sorbents. They have attracted attention because of their potential for the optimum solution of separation problems. Sorbents with a predominantly carbonaceous matrix should be mentioned in this context. The advantage of these materials are their thermal stability, chemical resistance and stability over a wide pH range. Non-volatile organics require the use of a homogeneous surface, because only these types of surfaces can provide a linear isotherm, and more or less symmetrical adsorption and desorption. If a large volume is required for the analysis, the robustness or the resistance to the pressure of the carbons has to be taken into account. All these requirements are met by GCBs and/or PGCBs, that are non-polar, inert adsorbents with prevailing hydrophobic properties.

Graphitized carbon black cartridges have successfully been applied for SPE of various pollutants such as polynuclear aromatic hydrocarbons (PAHs), chlorinated pesticides, phthalates and herbicides from water [26]. Carbo-pack B, having a nonporous, substantially nonpolar, and homogeneous surface with an area of about $100 \text{ m}^2/\text{g}$, has proved to be a valuable adsorbent for SPE. Cartridges can be easily cleaned and reused without any limitation. The compounds of interest trapped from water are eluted from the cartridge by using the right volume of a suitable solvent (or solvent mixture). Recoveries obtained by spiking Carbo-pack B (at ng level) and the water (at ppt level) with the components of

interest, in general, are very good except for the heavier PAHs. This problem may be solved by using GCBs with a lower surface area. Also Carbo-pack B was successfully utilised by several authors for the preconcentration of non-volatile pesticides [26,131], organochlorine insecticides, triazine, phenoxiacids herbicides and various base-neutral and acidic pesticides [132,133]. For the extraction of phenols [134], chloroanilines [135] and pesticides [133] Carbo-pack B cartridges proved to be more efficient than C_{18} silica [134,135] with higher accuracy [133]. A comparison of pesticides recovery data on both sorbents [133] is presented in Table 7. Di Corcia and Marchetti [133,136] elaborated a multiresidue method for a wide range of pesticides in drinking water using GCB cartridge extraction and liquid chromatographic analysis (Fig. 9). The simple and rapid procedure involves passing up to a 2-l sample through a 250-mg Carbo-pack B cartridge. With respect to chemically bonded silica, an apparent weakness of GCB is that its surface framework is contaminated by few oxygen complexes, having a structure similar to benzopyrylium salts [34]. This apparent weakness is, in fact, an advantage in that acidic analytes can be completely isolated from base-neutral ones by first passing through the sorbent bed a solvent system for elution of the nonacidic compounds and then a suitable basified solvent mixture for desorption of the acidic analytes, which are collected separately. In this way, not only extraction and concentration, but also class fractionation can be achieved simultaneously by a single sorbent cartridge. Compared to the C_{18} cartridge, additional advantages of using a Carbo-pack cartridge are that the extraction procedure is about 7 times shorter, no pH adjustment of the environmental sample is necessary for trapping of the acidic compounds, and one cartridge instead of two suffices to extract base-neutral and acidic pesticides, making the Carbo-pack cartridge more adaptable than the C_{18} one for field use. The detection limit by this method for all 35 pesticides considered was between 0.003 and $0.07 \mu\text{g}/\text{l}$. The European Community (EC) Drinking Water Directive states that individual pesticides must not exceed

Table 7
Comparison of recovery of pesticides (Di Corcia and Marchetti [133]) from drinking water with Carbopack B and C₁₈ cartridges; sampling volume 2 l

Compound	Pesticide class	Recovery (%)	
		Carbopack	C ₁₈
	<i>Base-neutrals</i>		
Oxamyl	Carbamate	89	4
Methomyl	Carbamate	98	3.7
Chloridazon	Phenylpyridazinone	98	18
Metoxuron	Phenylurea	97	64
Bromacil	Uracil	94	53
Monuron	Phenylurea	100	49
Cyanazine	Triazine	96	95
Metribuzin	Triazine	94	60
Carbofuran	Carbamate	98	64
Atrazine	Triazine	97	96
Carbaryl	Carbamate	96	78
Monolinuron	Phenylurea	100	92
Paraoxon	Organophosphate	97	92
Propachlor	Acetanilide	95	92
Propham	Carbamate	98	80
Propanil	Propioanilide	97	97
Linuron	Phenylurea	98	99
Chloroxuron	Phenylurea	95	97
Chloroprotham	Carbamate	97	97
Fenitrothion	Phosphorothioate	95	98
Azinphos ethyl	Phosphorodithioate	98	98
Parthion ethyl	Phosphorothioate	96	97
Coumaphos	Phosphorothioate	98	100
Phoxim	Phosphorothioate	90	90
	<i>Acids</i>		
Bentazon	Benzothiadiazin	97	75
Bromoxynil	Phenol	96	33
Dinitro- <i>o</i> -cresol	Phenol	97	10
2,4-D	Phenoxyacid	93	41
Mecoprop	Phenoxyacid	92	92
2,4,5-T	Phenoxyacid	95	85
2,4-DB	Phenoxyacid	96	100
MCPB	Phenoxyacid	100	99
2,4,5-TP	Phenoxyacid	95	85
Dinoseb	Phenol	96	99
Dinoterb	Phenol	101	96
Grand mean		96	75

Abbreviations: 2,4-D = (2,4-dichlorophenoxy)acetic acid; 2,4,5-T = (2,4,5-trichlorophenoxy)acetic acid; 2,4-DB = (2,4-dichlorophenoxy)butyric acid; 2,4,5-TP = (2,4,5-trichlorophenoxy)propionic acid.

Water was spiked with 0.25–1.5 µg/l of each pesticide; mean values calculated from three determination.

0.1 µg/l in any sample of drinking water. Di Corcia et al. in a recent systematic study [35] devoted to the characterisation of GCB as an

anion exchanger examined the effects of the pH of the aqueous matrix, its ionic strength and the presence of fulvic acids and acidic surfactants on

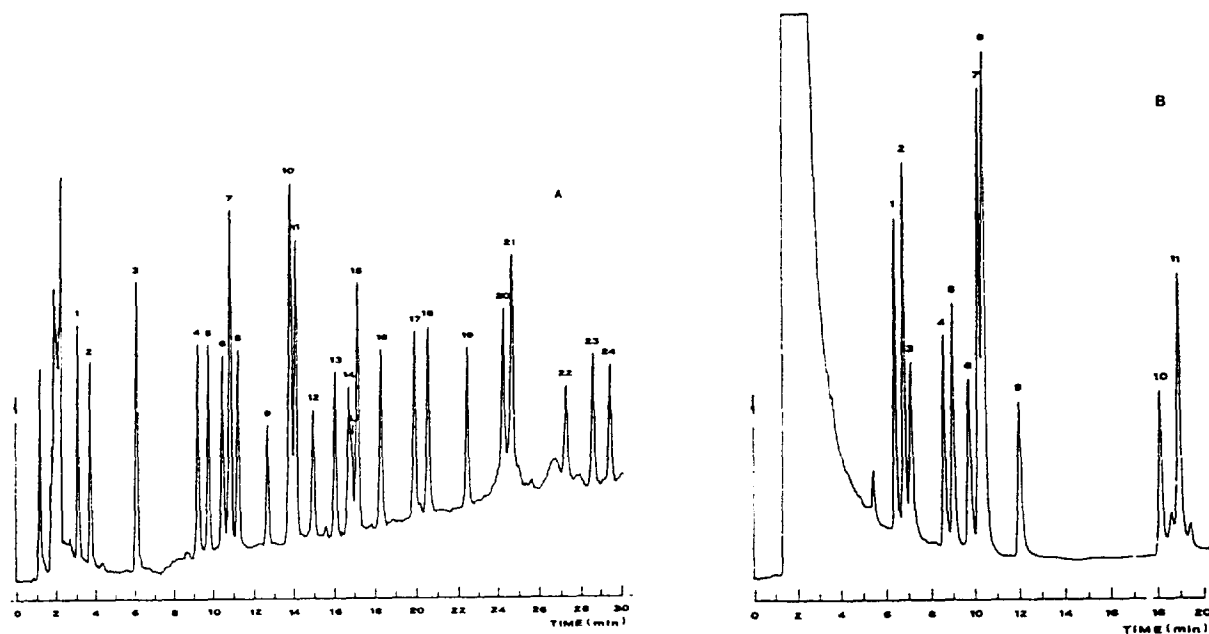


Fig. 9. HPLC chromatograms obtained on sampling the extracts from 2 l of tap water containing 0.4 g/l of sodium sulfite and spiked with base-neutral (A) and acid pesticides (B). Peaks. (A): 1 = oxamyl, 2 = methomyl, 3 = chloridazon, 4 = metoxuron, 5 = bromacil, 6 = monuron, 7 = gyanazine, 8 = metribuzin, 9 = carbofuran, 10 = atrazine, 11 = carbaryl, 12 = monolinuron, 13 = paraoxon, 14 = propachlor, 15 = propham, 16 = propanil, 17 = linuron, 18 = chloroxuron, 19 = chlorpropham, 20 = fenitrothion, 21 = azinphos ethyl, 22 = parathion ethyl, 23 = coumaphos, 24 = phoxim; (B) 1 = bentazone, 2 = bromoxyl, 3 = dinitro-*o*-cresol, 4 = (2,4-dichlorophenoxy)acetic acid, 5 = mecoprop, 6 = (2,4,5-trichlorophenoxy)acetic acid, 7 = MCPB, 8 = (2,4-dichlorophenoxy)butyric acid, 9 = (2,4,5-trichlorophenoxy)propionic acid, 10 = dinoseb, 11 = dinoterb; U = unknown compound contaminating the water specimen. The individual concentrations of the pesticides ranged between 0.125 and 0.750 $\mu\text{g/l}$. (Reproduced from Ref. [133]).

the capability of a GCB cartridge to extract quantitatively sixteen selected acidic model compounds and on their separation from base-neutral species. The possibility of subfractionating co-extracted acidic compounds on the basis of their acid strength by stepwise desorption was also investigated.

The key parameter in SPE is the sample volume that can be handled without any breakthrough. In general, C_{18} silicas are convenient for the trace determination of apolar compounds. Nevertheless, the capacity factors of moderately polar analytes are too low with C_{18} silica to allow the handling of a sufficiently large volume. Apolar copolymers cannot be used for on-line preconcentration of more polar compounds, because small-sized precolumns are required [137].

It was shown, that the retention of some polar compounds can be very high using porous graphitic carbon (PGC), available recently as HPLC stationary phase [138]. PGC shows a highly ordered crystalline structure with large bands of delocalized electrons, so that the retention mechanism is a mixture of hydrophobic and electronic interactions and is very different from that observed with C_{18} silicas and apolar copolymers [139,140]. PGC is a reversed-phase sorbent and it is observed that the retention of compounds decreases when the organic content of the mobile phase increases. On-line coupling of SPE to LC has several advantages compared to off-line procedures, particularly there is no risk of loss and contamination as there is no sample manipulation between preconcentration and analysis; more precise and reproducible

quantitative data are expected. The size of the precolumn is an important parameter in the coupling because the profile of concentrated species transferred from the precolumn to the analytical column should ideally be as narrow as possible at the beginning of the separation. Consequently precolumn dimensions should be as small as possible and adapted to those of the analytical column. An on-line technique coupling preconcentration via a precolumn packed with PGC (stainless-steel precolumn 1 cm × 0.46 cm I.D. prepacked with 10–15 μm Hypercarb PGC, Shandon, Runcorn, UK) and LC with a PGC analytical column (Hypercarb PGC, Shandon, UK) was published [137] recently. The system was found to be very efficient for the trace-level determination of some polar and water-soluble organic pollutants from environmental waters (low ppb range). As these analytes are much more retained by PGC than they are by C₁₈ silica, preconcentration on a PGC precolumn cannot be coupled on-line with the widely used and more efficient C₁₈ silica analytical columns, but with a PGC column. Applications were presented for the determination of some organic compounds included in the EC environmental priority pollutant list such as 2-chloro-4-aminophenol, chloroanilines, aminophenols and 2,4,6-trihydroxy-1,3,5-triazine. The influence of the sample matrix was investigated with drinking and river water samples.

6.3.2. Sorption from the gaseous phase–desorption into liquid phase

With regard to the high sorption capacity of activated charcoal this kind of sorbent has been often used in the closed stripping loop according to Grob [141]. For efficient component trapping from the gas phase (after stripping components from the water matrix by a stream of inert gas possibly at elevated temperature) a few mg of sorbent (1.5–5.0 mg) in the form of miniaturised disks is sufficient; off-line liquid desorption is performed by organic solvents, most frequently CS₂ and dichloromethane [142]. This method has the advantage that several portions of eluent, with an overall volume of 8–20 μl, are sufficient to achieve acceptable recoveries [143], where it

is recommended to allow the solvent to go back and forth through the filter. Good recoveries were obtained for hydrocarbons, oxygen-containing compounds and chlorinated pesticides in ppm concentration [144]; at lower concentrations artefact formation was observed. A large number of compounds can be analysed per run, making closed-loop stripping analysis a very cost-effective technique [126].

6.3.3. Sorption from the gaseous phase–desorption into gaseous phase

Several reported purge-and-trap methods rely on the solvent desorption of organics adsorbed onto a charcoal filter bed [145]. However, this method has limitations which must be taken into account. Problems include a strong affinity for water, which is frequently found in head-space vapour samples and which affects the adsorption properties, an excessive surface activity or the presence of large numbers of active sites for polar compounds. Additional problems include masking of highly volatile compounds by the solvent peak.

Application of organic polymeric sorbents as alternative trapping media for head-space volatiles combined with thermodesorption has increased significantly during the eighties. In recent years carbon sorbents have been applied in purge-and-trap techniques in single-bed or in multi-bed arrangement (various carbonaceous sorbent types and/or in combination with other types of sorbents). The unconventional porous carbon sorbent Carb I, prepared by controlled pyrolysis of saccharose in a silica gel matrix, was tested as a suitable material for enrichment of multicomponent mixtures of analytes (particularly hydrocarbons in the gasoline range, Fig. 10.) in the ppm–ppb concentration range from various water matrices by the purge-and-trap method with subsequent liquid desorption and on-column capillary GC analysis [146–148];

Most applications of purge-and-trap systems are combined on-line with thermodesorption and capillary GC. A survey of the used multi-bed applications for trapping volatile and semi-volatile compounds is presented in Table 8. The results of various experiments showed that tem-

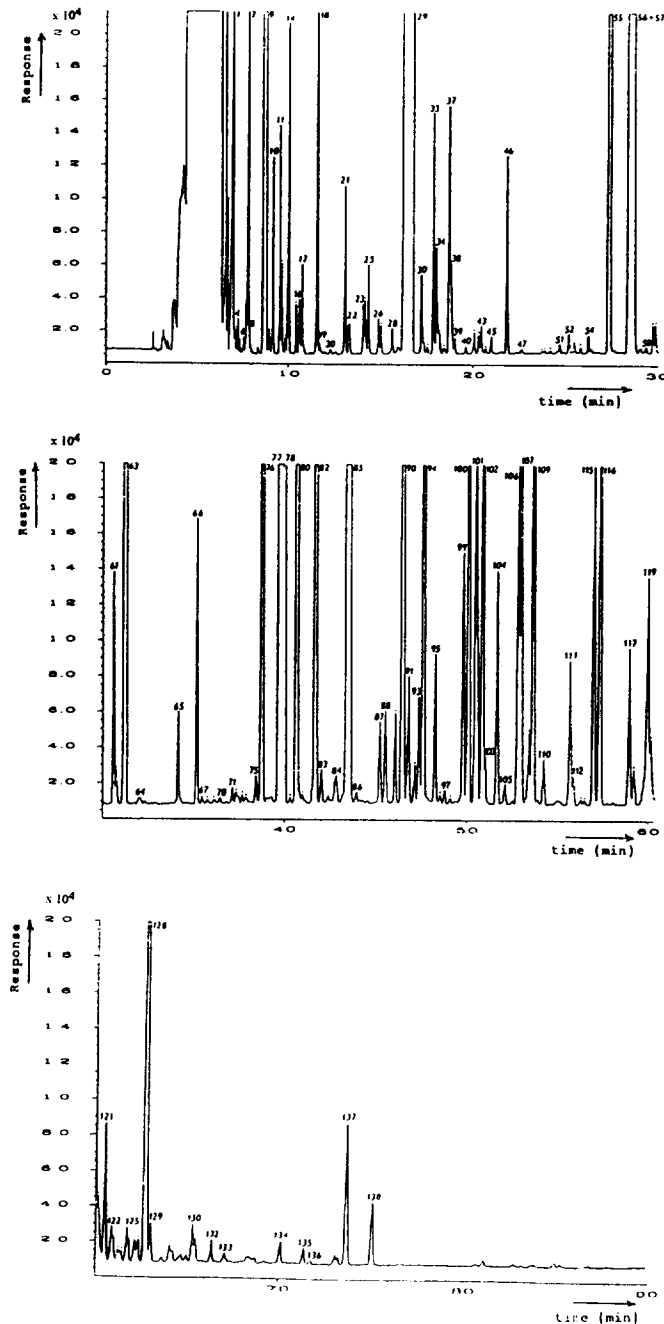


Fig. 10. Chromatogram of the separation of organic compounds (HP-PONA column) stripped from gasoline-contaminated water (30 ml) and trapped on a porous carbon sorbent; CS_2 desorption; on-column injection; flame ionisation detection. Peaks: 1,18,46,65,89,115,119,133, $n\text{C}_6$ – $n\text{C}_{12}$; 2,3,5,6,8,11,12,14,16,19,20,22,24,25,27,31,32,33,34,35,37,38,44,48,50,51,54,58,59,60,61,62,68,70,71,72,75,81,83,84,86,93,95,97,105,110. C_4 – C_{10} branched alkanes; 4,7,10,13,15,16,17,21,22,23,26,28,30,36,39,40,41,42,43,45,47,49,52,53,64,67,68,69,73,74,79,86,95,98. C_4 – C_{10} cycloalkanes; 9,29,55,56,57,63,66,76,77,78,80,82,85,87,88,90,91,92,94,96,99,100,101,102,103,104,106,107,108,109,111,112,113,114,115,116,117,118,119,120,121,122,123,124,125,126,127,128,129,130,131,132,134,135,136,137,138. C_6 – C_{12} aromatics; The individual concentrations of hydrocarbons ranged between 7 ppb–3.5 ppm. (Reproduced from Ref. [146]).

Table 8

Application of sorbents in multi-bed arrangement for trapping volatile and semi-volatile compounds from aqueous samples in purge-and-trap systems with subsequent GC determination

Multi-bed sorbent	Analysed compounds	Volatility range b.p. (°C)	Sample amount (ml)	Detector	Concentration level ($\mu\text{g/l}$) MLD ^b	Reference
Tenax/silica gel/charcoal	Aromatic hydrocarbons	80–217.7	5	ITD	0.2–2; ^b 0.1	149
	Halocarbons	–14–246				
Tenax GC/silica gel/charcoal Carbopack B/Carbosieve S-III	Halocarbons	–29.8–180	5	PID EICD	4; ^b 0.001–0.08 4; ^b 0.5–0.001	150
Carbopack B/Carbosieve S-III	Aromatic hydrocarbons	80–136	5	FID EICD		151
	Halocarbons	–29–180				
Carbopack B/Carbosieve S-III	Aromatic hydrocarbons	80–145	5	MSD	10–100	152
	Aromatic halocarbons	132–180				
Tenax TA/Chromosorb 106/ Spherocarb	C ₄ –C ₂₀ compounds n-Alkanes Branched, unsat. hydrocarbons Aromatic hydrocarbons Organochlorines Oxygenated compounds Sulphides	–4.5–302 35–302 –4.5–104 79–267 40–179 46–179 38–118	1000	ITD,FID	0.005–5	145
Carbotrap 150 ^a	PCB					153
	PAH					154
	Alkybenzenes					
VOCARB 3000	Aromatic hydrocarbons	80–266	5	EICD/PID	5	155
	Halocarbons	–28.9–219				
BTEXTRAP ^a	Aromatic hydrocarbons	80–145	10	PID/FID	18	155
Carbotrap 400	Hydrocarbons	80–266	20	FID	10–100	156
VOCARB 3000 ^a ,4000	Aromatic hydrocarbons	168–217.7	5 25	MS	20–200; ^b 0.05	157
	Halocarbons	–28.9–214				
VOCARB 4000	Oxygenated and polar VOCs	78–127	5	MS	40	158

ITD = ion-trap detector; PID = photo ionisation detector; FID = flame ionization detector; EICD = electrolytic conductivity detector; MSD = mass-selective detector; MS = mass spectrometer.

^a Also solid waste.

^b MLD = method detection limit.

perature, stripping time and purge flow-rates all influence the recovery of organic compounds [145]. It was also shown that there is a dependence of the recovery data on the boiling point

of the analysed compounds, particularly for high boilers, and also on their polarity.

The developed carbonaceous adsorbents (GCBs in combinations with carbon molecular

sieves, e.g. VOCARB 3000, 4000) provide several advantages compared to conventional adsorbents such as Tenax TA/silica gel/charcoal combination used in US EPA methods 502.2, 524.2, 624 and 8260, which are the following: the ability to trap small molecules, to minimise water retention and the possibility to use higher desorption temperatures [157]. The higher thermal stability of these adsorbents also ensures faster, more effective baking (thermal cleaning) of a contaminated trap. Peaks are well resolved with only slight tailing on thick-film columns, without cryogenics. The higher desorption temperature releases the analytes more rapidly, providing a more focused plug and allowing the use of lower column flow-rates [157,159].

A higher temperature can create some disadvantages. Carbonaceous adsorbents can induce thermal and catalytic breakdown of some compounds. Also, because the adsorption is stronger, some of the heavier analytes are more difficult to desorb. For highboilers the Tenax TA/silica gel/charcoal combination provides better recovery. The pores in the carbon molecular sieve also trap carbon dioxide which, when desorbed, might interfere with some early eluting, trace-level compounds [157].

7. Conclusions

The development of carbon sorbents for the preconcentration of analytes utilizes the results of the long-term research and development of stationary phases for HPLC and GSC. Recent developments in the production of thermally modified carbon blacks, carbon molecular sieves and porous carbons for quantitatively trapping of organic components are reflected in their superior performance over "traditional" sorbents such as activated charcoal and porous polymers which tend to lack uniform sorbent characteristics for the adsorption and retention of the different compounds encountered in different environments. The application of such adsorbents has minimized the problems of contamination and artefact formation, and hence they are suitable for the sampling of VOCs in quite

different environments and preconcentration and isolation of semi-volatile and non-volatile compounds from various matrices.

In spite of the broad application of sorbents in trace analysis for several tens of years, the results of tests of new sorbents, synthesis of tailored sorbents, or combination of sorbents with various physico-chemical properties with the aim of special and very broad application, research on the influence of various factors on the efficiency of preconcentration, show that the developments in this field with the aim to obtain an inert sorbent for ultra-trace analysis will continue.

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