K. Dettmer · W. Engewald

# Adsorbent materials commonly used in air analysis for adsorptive enrichment and thermal desorption of volatile organic compounds

**Abstract** A review is given dealing with commonly used adsorbent materials in ambient air analysis of volatile organic compounds (VOCs). The adsorbents covered in the paper are selected in consideration of their compatibility with thermal desorption. Initially, we discuss the requirements that an adsorbent should fulfill, and useful parameters for the selection and evaluation of an appropriate material. Then, the most important materials are presented considering their properties, advantages, and drawbacks. A few applications are given, but a complete review of sampling techniques and applications dealing with adsorptive enrichment and thermal desorption is beyond the scope of this paper.

**Keywords** Adsorptive enrichment · Thermal desorption · Adsorbents · Air analysis

## Introduction

Volatile organic compounds (VOCs) are an important class of airborne contaminants. Due to the well-known toxicity of several compounds, such as benzene or 1,3-butadiene, they can pose a serious hazard to human health and the environment. In the presence of $NO_x$, VOCs can act as precursors for the formation of photo-oxidants in the troposphere whereby the contribution of single species greatly varies [1, 2, 3].

Owing to the importance of individual constituents a single component analysis is preferred instead of a sum determination of VOCs. This commonly requires a separation technique. The method of choice is gas chromatography.

Because of the complexity, heterogeneity, and occurrence of many analytes at ppt($v$)-ppb($v$) levels, air belongs to the most complicated matrices to analyze. The crucial point in air analysis is the sampling step. It has to fulfill the following requirements:

- The sample taken should be representative.
- Qualitative and quantitative adulterations of the sample composition should be avoided.
- The sampling procedure should be as simple as possible to enable field sampling.

The analysis of VOCs in ambient atmospheres at trace levels normally requires a pre-concentration step to achieve the detection limits of commonly applied analytical techniques. The pre-concentration step is often combined with the sampling step. A widely used sampling technique is adsorptive enrichment on solid adsorbents. The desorption of the analytes could be either done by solvent or thermal desorption. The latter enables a complete and solvent-free transfer of all analytes into the gas chromatographic system.

There are a number of different adsorbents commercially available, and the user is very often faced with the difficulty of selecting an appropriate adsorbent from the great variety of materials on the market. The adsorbent used for adsorptive enrichment in combination with thermal desorption should generally meet the following criteria to guarantee an accurate determination of VOCs:

- Complete enrichment of the analytes of interest.
  The specific surface area and the porous structure gives a rough indication of the adsorption strength of a material. A more closer characterization of the adsorption strength is given by the specific breakthrough volume (BTV) of model compounds.
- Complete and fast desorption of the analytes.
- Homogenous and inert surface to avoid artifact formation, irreversible adsorption, and catalytic effects during sampling, storage of the loaded adsorbent tubes, and desorption.
  The homogeneity of a material can be assessed using the elemental composition of the material (see Table 1). Furthermore, the characterization of trace impurities could be advantageous (see Table 2).

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- Low affinity to water to avoid displacement and hydrolysis reactions and to minimize disturbances of the gas chromatographic analysis, for example, damage of the stationary phase or retention time shift.

  The hydrophobicity of an adsorbent can be characterized by the specific retention volume of water.

- Low adsorption capacity for other inorganic constituents of air, for example, nitrogen oxide, sulfur dioxide, carbon dioxide, or ozone.
- High inertness against reactive species such as ozone.
- High mechanical and thermal stability.
- Multiple usability.

## The specific breakthrough volume

The term specific breakthrough volume is defined as the volume of gas that causes a compound to migrate through an adsorbent bed of one gram at a specific temperature [4]. Because adsorption is an exothermic process, the sampling temperature has to be considered carefully. The breakthrough volume enables the estimation of the maximum sampling volume that ensures a quantitative sampling of a compound using a certain adsorbent mass at a specific sampling temperature. It is, therefore, an important parameter if active sampling is applied. The specific breakthrough volume can be calculated on the basis of adsorption isotherms [5, 6]. But usually it is determined experimentally using two practical approaches; the frontal technique and the elution technique. A defined amount of adsorbent is filled in an adsorbent tube for both methods. The packed tube is placed into a GC-oven and attached to the injector and detector.

If the elution technique is applied a model substance is injected (as a pulse) onto the adsorbent bed, and the elu-



**Fig. 1** Chromatographic techniques used for the determination of the specific breakthrough/retention volume

tion chromatogram at a defined temperature is recorded (see Fig. 1) [4, 7]. This method is based on the assumption that the analyte is present at infinite dilution and the breakthrough is only caused by a migration of the analyte through the adsorbent bed similar to gas-solid chromatography using packed columns.

In the frontal chromatographic mode, a gas containing the model substance is led continuously through the adsorbent bed at a defined temperature, and a frontal chromatogram is recorded (Fig. 1) [8]. In this case, the breakthrough can be caused by a migration of analytes and by a capacity overload at high analyte concentrations. It is likely that the breakthrough is caused by a capacity overload (all "adsorption sites" are occupied) especially for strongly adsorbed compounds.

The chromatograms obtained in these experiments provide different values to quantify the breakthrough behavior of the compound. The "real" breakthrough volume is calculated using the reduced breakthrough time, that is, peak starting time in the elution technique or the time that marks an increase of the baseline in the frontal chromatogram. The peak starting time is defined as the intersection between the baseline and the tangent of the rising edge of the peak. The 5% criteria can also be used to mark the breakthrough of a substance [9].

Instead of the specific breakthrough volume, the specific retention volume is very often calculated using the reduced retention time (elution technique) or the point of inflection (frontal technique).

These values are taken for the calculation of the specific breakthrough or retention volume according equation 2 and 3 in Fig. 2. The temperature and pressure-corrected gas flow is obtained according equation 1 in Fig. 2.

The specific retention volumes are normally determined at higher temperatures than used for sampling. The linear dependence of the logarithm of the specific retention volume on the reciprocal value of the absolute temperature allows the calculation of the specific retention volume at a certain (lower) temperature after linear regression.

Both methods for the determination of specific retention volumes possess some advantages and drawbacks. In general, the frontal technique is a better simulation of the real sampling procedure. But the production of a test atmosphere steadily spiked with a model substance could be demanding. Bertoni et al. compared the performance of both methods and obtained good agreements for low boiling compounds. Greater discrepancies in the BTV values were achieved for higher boiling analytes whereby the elution technique supplied higher values [10]. Similar experiences were reported by Mastrogiacomo et al. [11].

The breakthrough behavior of a compound is influenced by different parameters. Studies using the frontal technique with analyte concentrations at ppm($v$)-level showed that the breakthrough volume decreases with increasing analyte concentration indicating that the capacity of the material is exhausted. The adsorption sites are saturated more rapidly [9, 10]. Peters and Bakkeren demonstrated that for dichloromethane on Tenax GR, the breakthrough volume is independent from the analyte amount
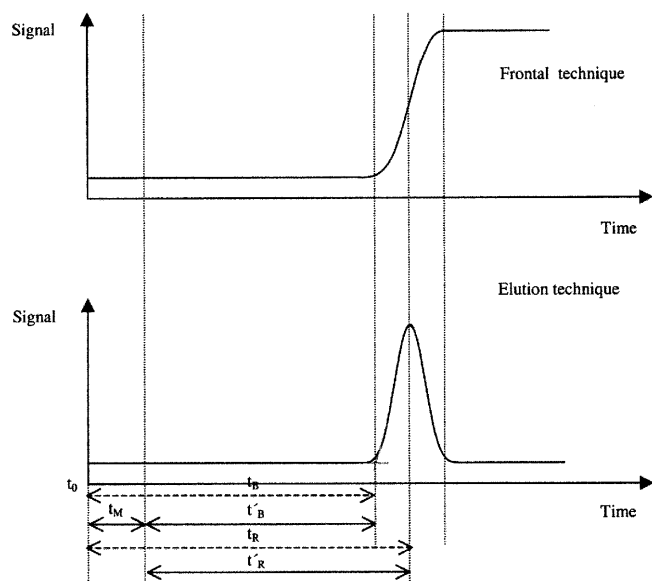
**Fig. 2** Calculation of the specific breakthrough/retention volume

$$F_c = F_a \frac{T_c}{T_a} * \frac{3}{2} \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}$$

Specific breakthrough volume:

$$V_{g(B)}^\theta = \frac{t'_B}{m_A} * F_a \frac{T_c}{T_a} * \frac{3}{2} \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}$$

Specific retention volume:

$$V_g = \frac{t'_R}{m_A} * F_a \frac{T_c}{T_a} * \frac{3}{2} \frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1}$$

| | |
|---|---|
| $V_{g(B)}^\theta$ | specific breakthrough volume |
| $V_g^\theta$ | specific retention volume |
| $t'_B$ | reduced breakthrough time: $t'_B = t_B - t_M$ |
| $t'_R$ | reduced retention time: $t'_R = t_R - t_M$ |
| $t_B$ | breakthrough time |
| $t_R$ | retention time |
| $t_M$ | hold-up time |
| $F_c$ | column gas flow |
| $F_a$ | measured gas flow at the end of the column |
| $T_a$ | temperature at the end of the column |
| $T_c$ | column temperature |
| $p_i$ | column head pressure |
| $p_0$ | pressure at the end of the column |
| $m_A$ | adsorbent mass |

at low concentration. (3–20 µg L$^{-1}$) It is dominated by the migration of the analyte through the adsorbent bed [12].

Furthermore, the presence of other compounds can decrease the breakthrough volume [10]. Peters and Bakkeren have also shown that analytes with a low affinity for the adsorbent can be displaced by molecules with a higher affinity [12]. A high sample humidity can likewise influence the breakthrough behavior if the adsorbent retains noticeable amounts of water [13]. A further important parameter is the sampling flow. It must allow a sufficient time for the interactions between analyte and adsorbent surface. Sampling $C_5$–$C_8$ hydrocarbons on Tenax TA and Anasorb CMS, Baya and Siskos have demonstrated that the breakthrough volume is independent from the sampling flow within the tested range of 50–500 mL min$^{-1}$ [14]. These many factors influencing the breakthrough volume cannot be simulated entirely in the laboratory. It is, therefore, recommended to reduce tabulated or measured data of specific retention or breakthrough volumes by at least one-third to ensure a quantitative sampling [9].

## Adsorbents

There are a huge number of adsorbent materials which can be used for the trace analysis of volatile organic compounds. A rough classification might be based on three categories: inorganic materials, carbon based adsorbents, and organic polymers. Polydimethylsiloxane, a new type of sorbent, is an exception since enrichment is based on an absorption process. A number of important adsorbent materials are characterized in Table 1. Furthermore, the results of the element analysis of selected carbon adsorbents using X-ray fluorescence analysis are shown in Table 2.

Inorganic materials such as silica gel, zeolithes, or alumina are of minor importance because of the often higher hydrophilicity of these materials [9, 15] and are therefore not discussed further.

### Carbon adsorbents

Carbon adsorbent materials could be sub-classified into activated carbon, carbon molecular sieves and graphitized carbon blacks. Recently, porous carbon was introduced as a new adsorbent material produced by pyrolysis of saccharose and cellulose impregnated on silica gel as a support material which is removed after pyrolysis [16, 17, 18].

### *Activated carbon*

Activated carbon is made out of carbon-containing biological materials, such as wood or coconut shells, synthetic polymers or lignite. The production of activated carbon usually comprises two parts: carbonization of the starting material and activation, which could be done successively or at once. The carbonization includes the thermal decomposition of the starting material at temperatures of 500–1200 °C, elimination of volatile components and formation of a primary pore structure. These pores could be blocked by non-volatile pyrolysis products, which makes an activation essentially leading to the formation of the final pore structure especially of micro-pores. Thus, the carbonization process is commonly followed by physical activation that entails a treatment of the material with water vapor and/or carbon dioxide at 700–1000 °C [19, 20]. For chemical activation, the carbonization procedure (500–900 °C) of the starting material is done in the presence of dehydration agents (zinc chloride, magnesium chloride, phosphoric acid), which are washed out afterwards [20].

Activated carbons are micro-porous carbon materials with a broad pore size distribution and high specific surface areas (800–1500 m$^2$ g$^{-1}$). Their physical and chemical properties are influenced by the starting material and the manufacturing process.

The carbon forms micro-crystallites with a graphite structure. The crystalline zones consist of three to four carbon layers with about twenty to thirty-six rings. The arrangement of these crystallites is irregular and amor-

**Table 1** Characterization of various adsorbent materials commonly used for adsorptive enrichment and thermal desorption in ambient air analysis

| Adsorbent (Provider) | Type | Particle size[a] (mesh) | Sampling range[a] | $T_{max}$[a] (°C) | Density[a] (g mL$^{-1}$) | Pore volume[a] (mL g$^{-1}$) Micro | Pore volume[a] (mL g$^{-1}$) Total | Elemental composition (measured) (mass %) C | H | N | S | O | Cl | Spec. surface area[a] (m² g$^{-1}$) | Spec. surface area measured (m² g$^{-1}$) | $V_g^\theta$ H$_2$O[b] 20 °C (mL g$^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Carbon molecular sieves** | | | | | | | | | | | | | | | | |
| Carboxen 563 (Supelco) | CMS | 20/45 | C2–C5 | >400 | 0.53 | 0.20 | 0.59 | 81.4 | 2.6 | – | 10.6 | 4.7 | 0.1 | 510 | 495 | 778 |
| Carboxen 564 (Supelco) | CMS | 20/45 | C2–C5 | >400 | 0.60 | 0.19 | 0.50 | 88.7 | 0.8 | – | 5.8 | 2.4 | 0.6 | 400 | 460 | 276 |
| Carboxen 569 (Supelco) | CMS | 20/45 | C2–C5 | >400 | 0.58 | 0.07 | 0.39 | 93.7 | 0.3 | – | 4.0 | 1.1 | 0.4 | 485 | 387 | 257 |
| Carboxen 1000 (Supelco) | CMS | 60/80 | C2–C5 | >400 | 0.44 | 0.42 | 0.85 | 91.9 | 0.9 | – | 0.2 | 4.0 | 1.3 | 1200 | 915 | 418 |
| Carboxen 1001 (Supelco) | CMS | 60/80 | C2–C5 | >400 | 0.61 | 0.17 | 0.53 | 93.2 | 0.6 | – | 3.3 | 1.3 | 1.2 | 500 | 420 | 234 |
| Carboxen 1003 (Supelco) | CMS | 40/60 | C2–C5 | >400 | 0.46 | 0.47 | 0.8 | 95.8 | 0.28 | – | 2.41 | 0.92 | 0.61 | 1000 | 1045 | 79 |
| Carbosieve SIII (Supelco) | CMS | 60/80 | C2–C5 | >400 | 0.61 | 0.38 | 0.39 | 95.7 | 0.8 | – | – | 2.0 | 1.1 | 820 | 835 | 378 |
| Carbosphere (Chrompack) | CMS | 60/80 | – | 400 | – | 0.5 | 0.54 | 90.5 | 0.5 | – | 0.1 | 2.1 | 0.2 | 1000 | 1054 | 779 |
| **Graphitized carbon blacks** | | | | | | | | | | | | | | | | |
| Carbotrap F (Supelco) | GCB | 20/40 | >C20 | >400 | 0.66 | – | 0.02 | 99.8 | 0.1 | – | – | – | 0.1 | 5 | 7 | – |
| Carbotrap C (Supelco) | GCB | 20/40 | C12–C20 | >400 | 0.72 | – | 0.02 | 99.7 | 0.1 | – | – | – | 0.2 | 10 | 9 | – |
| Carbotrap (Supelco) | GCB | 20/40 | C5–C12 | >400 | 0.36 | – | 0.58 | 99.9 | 0.1 | – | – | – | – | 100 | 95 | – |
| Carbotrap Y (Supelco) | GCB | 20/40 | C12–C20 | >400 | 0.42 | 0.003 | 0.12 | 99.6 | 0.2 | – | – | – | 0.3 | 25 | 34 | – |
| Carbotrap X (Supelco) | GCB | 20/40 | C3–C5 | >400 | 0.41 | 0.0 | 0.63 | 99.2 | 0.1 | – | 0.1 | – | 0.1 | 250 | 260 | – |
| Carbograph 5 (LARA) | GCB | 20/40 | C3–C5 | >400 | – | – | – | 100 | – | – | – | – | – | 560 | 230 | – |
| **Porous organic polymers** | | | | | | | | | | | | | | | | |
| Chromosorb106 (Supelco) | Styrene-divinyl-benzene-copolymer | 60/80 | Small molecule | 250 | – | 0.09 | 1.33 | 92.1 | 7.8 | – | 0.2 | 0.7 | 0.3 | 750 | 926 | 173 |
| Tenax TA (Supelco) | Poly-(2,6-diphenyl)-p-phenylenoxide | 60/80 | C7–C26 | 350 | 0.25 | 0.002 | 0.05 | 84.5 | 4.4 | – | 0.1 | 6.4 | 0.4 | 35 | 24 | 39 |
| **Miscellaneous** | | | | | | | | | | | | | | | | |
| Tenax GR (Supelco) | 30% Graphit; 70% Tenax | 35/60 | – | 350 | – | 0.002 | 0.05 | 86.9 | 3.6 | – | 0.7 | 5.1 | 0.3 | – | 21 | 92 |
| Activated carbon (Supelco) | Coconut Charcoal | 20/40 | C2–C5 | 220 | 0.44 | 0.5 | 0.54 | 93.7 | 0.9 | – | 0.1 | 3 | 0.2 | 1070 | 1015 | 1454 |

[a]Manufacturer's data. [b]Specific retention volume of water at 20 °C measured using the elution technique (see text). CMS: carbon molecular sieves, GCB: graphitized carbon blacks.

**Table 2** X-ray fluorescence analysis of selected carbon adsorbent materials

| Element | Carbotrap X ($\mu g\ g^{-1}$) | Carboxen 569 ($\mu g\ g^{-1}$) | Carboxen 1003 ($\mu g\ g^{-1}$) | Carbosieve SIII ($\mu g\ g^{-1}$) |
|---|---|---|---|---|
| Si | <110 | 443±20 | 696±25 | <130 |
| P | <10 | <93 | <60 | <3 |
| S | 120±10 | 42,610±2100 | 19,050±950 | 84±9 |
| Cl | 33±4 | 74±6 | 40±4 | 24±2 |
| K | 1100±95 | <50 | <50 | <50 |
| Ca | <200 | <292 | <196 | <149 |
| Ti | <33 | <15 | <15 | <15 |
| V | 17±8 | <0.5 | <1 | <5 |
| Cr | <5 | <5 | 96±7 | <5 |
| Mn | <1 | <1 | 11±1 | <1 |
| Fe | <3 | 95±9 | 890±50 | 50±6 |
| Co | <10 | <10 | 25±4 | <10 |
| Ni | <3 | <1.6 | 154±10 | <3.3 |
| Cu | <1.6 | <3.3 | 18±4 | <2.4 |
| Zn | <1.2 | <0.6 | <0.8 | <1.3 |
| Br | <2.6 | <1 | <2.8 | <2.9 |
| Sr | <6.1 | <3.4 | <5.1 | <5.8 |
| Zr | <4.6 | <3.7 | <5.7 | <4.5 |
| Nb | <2.5 | <2.2 | <3 | <3.4 |
| Mo | <9.7 | <8.4 | <13.8 | <11 |
| Cd | <0.1 | <0.1 | <0.1 | <0.1 |
| Sn | <1 | <0.3 | <0.4 | <0.4 |
| I | <1.1 | <1.1 | <1 | <1.2 |
| Ba | <5.9 | <2.4 | <3.3 | <3.4 |
| Pb | <3.3 | <1 | <3 | <4 |
| U | <11.6 | <5.1 | <11 | <13.4 |

phous carbon is deposited among them stabilized by heteroatoms [21]. Activated carbon possesses a chemical heterogeneous surface with mineral admixtures and several functional groups, such as hydroxyl-, carbonyl- and carboxylic-functions [22]. Enrichment is, therefore, caused by non-specific and specific interactions (e.g., hydrogen-bridges). Especially polar analytes, for example alcohols, could be irreversible adsorbed [23]. Owing to those so-called surface oxides, water is more strongly retained on activated carbon than on other carbon adsorbent materials (see Table 1) [24].

Activated carbons are thermally stable materials allowing the application of thermal desorption [25]. But, in the case of polar analytes this energy might be insufficient to break specific interactions and solvent desorption is mostly favored.

Activated carbons are often used for monitoring work place air. They are widely applied as adsorbents in passive samplers [26, 27, 28, 29, 30, 31].

*Carbon molecular sieves*

Carbon molecular sieves are mainly produced by pyrolysis of organic polymers [17]. Common starting materials are poly(vinylidene chloride), poly(vinyl chloride) or cor-

responding copolymers (e.g., Saran). These materials eliminate hydrogen chloride at temperatures of about 180 °C leaving behind the porous carbon backbone [32].

Particle size, pore size, pore distribution and the specific surface area of the final product could be controlled by choosing the starting material and pyrolysis conditions. Accordingly, carbon molecular sieves consist of different proportions of amorphous carbon and layers of condensed aromatic rings, which are orientated in parallel in dependence on the manufacturing process [21]. Impurities of the starting materials reduce the homogeneity of the final product.

Carbon molecular sieves are commercially available as Carboxen, Carbosphere, Carbosieve, or Ambersorb materials. A characterization of some important materials is given in Table 1. The Carbosieve materials are produced from poly(vinylidene chloride), while the Carboxen materials are made out of sulfonated polymers [22].

Carbon molecular sieves are micro-porous adsorbents with a sharp pore size distribution and high specific surface areas. Due to the defined micro-porous structure, carbon molecular sieves can act as molecular sieves – hence their name.

Adsorption is mainly based on non-specific interactions. However, the surface of carbon molecular sieves is not completely chemical homogeneous but there are traces of metals, salts and a low number of functional groups (see Table 1 and Table 2).

Although carbon molecular sieves belong to the non-polar adsorbents they adsorb substantial amounts of water (see Table 1) [33, 34]. This could be explained by surface oxides. Gawlowski et al. propose a condensation of water in the micro-pores. According to this theory, condensation is caused by the strong adsorption field inside the micro-pores, which is a result of the overlapping of dispersion forces originating from the adjacent walls [34].

Carbon molecular sieves are produced as mechanically stable, spherical particles (Fig. 3) with a high temperature stability making them ideal for thermal desorption. Carbon molecular sieves are superior for enrichment of small molecules in the range of $C_2$–$C_5$ [14, 24, 35, 36]. They are
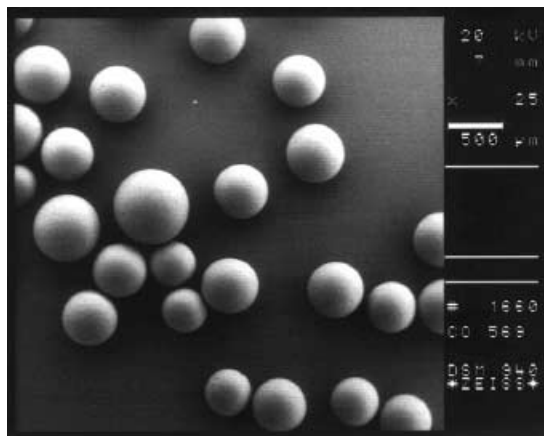


**Fig. 3** Raster electron microscope image of Carboxen 569

often used in combination with weaker adsorbents, which are arranged in front of them to prevent compounds of lower volatility from entering the carbon molecular sieves [37, 38, 39, 40].

Coeur et al. reported the decomposition of α-pinene and sabinene on Carboxen 569 [41]. This could be caused by a strong adsorption, which does not allow a complete thermal desorption.

Carbon molecular sieves are not suitable for the sampling of reactive analytes. It has been shown that reactive light hydrocarbons, such as 1,3-butadiene and isoprene, are incompletely recovered from Carboxen 569, Carboxen 1003, and Carbosieve SIII. Losses up to 80% of 1,3-butadiene and isoprene were observed, occurring even immediately after the sampling step. The losses increase with increasing storage time [42]. The losses of 1,3-butadiene on Carbosieve SIII are partly caused by a reaction of the analyte on the surface of the absorbent because the reaction product 4-vinylcyclohexene could be identified. 4-Vinylcyclohexene might be interpreted as the dimerization product of 1,3-butadiene [43].

*Graphitized carbon blacks*

Graphitized carbon blacks are made out of soot in an inert atmosphere at temperatures of about 2700 °C. The soot is usually produced from petroleum or natural gas. Graphitized carbon blacks, which are made out of thermal carbon blacks (pre-treated soot at 3000 °C), are classified as thermal graphitized carbon blacks [44].

Generally, the degree of graphitization is determined by the starting material and the manufacturing process. To remove remaining polar groups from the surface of the adsorbent, the graphitization procedure can be followed by a treatment with hydrogen at 1000 °C [45]. Washing with acids, such as perchloric acid or phosphoric acid, removes basic carbonium complexes and sulfides from the surface [46].

The carbon in graphitized carbon blacks is organized in a hexagonal graphite lattice forming planar layers [47].
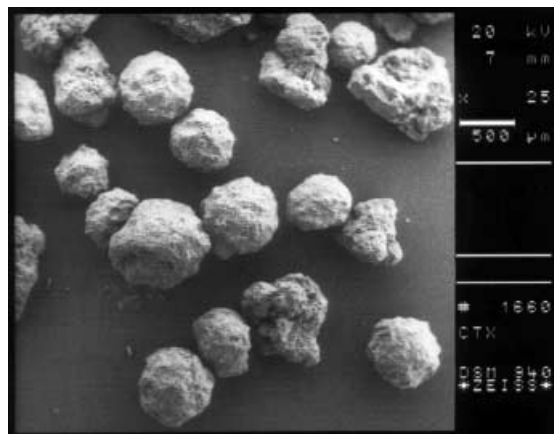


**Fig. 4** Raster electron microscope image of Carbotrap X

The higher the degree of graphitization, the lower the specific surface area of the material, which varies between 5 and 260 m$^2$ g$^{-1}$ for commercial materials.

Graphitized carbon blacks are fine-grained powders which tend to form agglomerates. They are available in different mesh sizes. The irregular particles are of low mechanical stability (see Fig. 4).

Graphitized carbon blacks for analytical purposes are non-polar adsorbents with a physically and chemically homogeneous surface. The carbon content is in the range of 99%. They are characterized by a high hydrophobicity. Enrichment takes place on the basal planes of the graphite crystallites and is caused by non-specific interaction (dispersion, induction). Beside the molecule size, the shape and degree of polarization determine the adsorption strength, for example, *n*-butane has a higher breakthrough volume than *iso*-butane due to the higher number of contacts with the surface [48]. Graphitized carbon blacks are, therefore, used as shape-selective stationary phases in gas-solid chromatography [22, 45, 49, 50].

Although, graphitized carbon blacks are very pure adsorbents, there are indications of traces of polar groups on the surface. Di Corcia et al. identified an oxygen complex with a chromene-like structure that is a burnt-off residue from the production of the material. This surface group is rearranged to a benzpyrylium salt in the presence of water, which enables GCB to act as an anion exchanger in Solid-phase extraction (SPE) [51]. Moreover, Hrouzkova et al. identified traces of metals in Carboback B, Carbotrap and Carbotrap C [52].

A characterization of commonly used graphitized carbon blacks is given in Table 1. Carbotrap Y (*S*: 25 m$^2$ g$^{-1}$) is a new material that is designed to fill the gap between Carbotrap C (*S*: 10 m$^2$ g$^{-1}$) and Carbotrap (*S*: 100 m$^2$ g$^{-1}$). A further quite new material is Carbotrap X. In contrast to the established graphitized carbon blacks, this adsorbent possesses a higher specific surface area of 260 m$^2$ g$^{-1}$. Carbotrap X enables a quantitative sampling of low-boiling, reactive hydrocarbons, such as 1,3-butadiene or isoprene, which could not be determined quantitatively using carbon molecular sieves [42]. Recently, another high-surface area version called Carbograph 5 was introduced, which should have a specific surface area of 560 m$^2$ g$^{-1}$ according to the manufacturer's data. Repeated measurements of the surface area (BET) could not verify this data, but gave a value of 230 m$^2$ g$^{-1}$. Nevertheless, the potential of Carbograph 5 for sampling low molecular weight compounds has been proven [53, 54]. Moreover, Carbograph 5 seems to be promising for the sampling of low boiling carbonyl compounds (e.g. acrolein) [55].

Graphitized carbon blacks are commonly used in ambient air analysis [56]. Ciccioli et al. used multibed-traps containing Carbotrap C and Carbotrap (also in combination with the carbon molecular sieve Carbosieve SIII) for the analysis of VOCs of anthropogenic and biogenic origin and identified more than 100 individual compounds [57, 58]. McClenny and Colón evaluated multibed traps containing Carbotrap and the carbon molecular sieve Carboxen 1000 for the quantitative VOC analysis according

**Table 3** Characterization of various porous organic polymers

| Adsorbent | Type | Specific surface area (m² g⁻¹) | Max. temperature (°C) |
|---|---|---|---|
| **Tenax** | | | |
| Tenax GC | Poly(2,6-diphenyl-*p*-phenylenoxide) | 19–30 | 450 |
| Tenax TA | Poly(2,6-diphenyl-*p*-phenylenoxide) | 35 | 300 |
| **Chromosorb** | | | |
| Chromosorb 101 | Styrene/divinylbenzene copolymer | <50 | 275 |
| Chromosorb 102 | Styrene/divinylbenzene copolymer | 350 | 250 |
| Chromosorb 103 | Cross-linked polystyrene | 350 | 275 |
| Chromosorb 104 | Acrylnitrile/divinylbenzene copolymer | 100–200 | 250 |
| Chromosorb 105 | Polyaromatic resin | 600–700 | 250 |
| Chromosorb 106 | Styrene/divinylbenzene copolymer | 700–800 | 225 |
| Chromosorb 107 | Polyacrylic ester resin | 400–500 | 225 |
| Chromosorb 108 | Cross-linked acrylic ester | 100–200 | 225 |
| **Porapak** | | | |
| Porapak N | Divinyl benzene/vinyl pyrrolidinone | 250–350 | 190 |
| Porapak P | Styrene/divinyl benzene copolymer | 100–200 | 250 |
| Porapak Q | Ethylvinyl benzene/divinyl benzene | 500–600 | 250 |
| Porapak R | Divinyl benzene/vinyl pyrrolidinone | 450–600 | 250 |
| Porapak S | Divinyl benzene/vinyl pyridine | 300–450 | 250 |
| Porapak T | Ethyleneglycol/dimethacrylate | 250–350 | 190 |
| **Amberlite resins** | | | |
| XAD-2 | Styrene/divinylbenzene copolymer | 300 | 200 |
| XAD-4 | Styrene/divinylbenzene copolymer | 750 | 150 |
| XAD-7 | Polymethacrylic ester resin | 450 | 150 |
| XAD-8 | Polymethacrylic ester resin | 140 | 150 |

the EPA-TO-17 method "determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes" [59]. Due to their high hydrophobicity, graphitized carbon blacks could be used for the sampling of VOCs in extremely humid atmospheres without using additional drying agents [60].

Rothweiler et al. reported the incomplete recovery of α-pinene and of polar analytes (e.g. acrolein and hexanal) from Carbotrap [61]. The authors identified additional peaks in the chromatogram after thermal desorption which refer to rearrangement products of α-pinene. Similar results were obtained by Cao and Hewitt who reported the decomposition of α-pinene and β-pinene after thermal desorption from Carbotrap and the occurrence of decomposition products such as 1,2,3-trimethylbenzene [62].

Porous organic polymers

Porous organic polymers are a large group of adsorbents with different surface areas and polarities. Many of these adsorbents have their origin as stationary phase in packed GC-columns. Porous organic polymers could be sub-classified into three groups: cross-linked linear polymers, homogeneous cross-linked polymers, synthesized from pure monomers and heterogeneous cross-linked polymers, synthesized from a monomer mixture in an inert solvent [63]. A characterization of common porous polymers is given in Table 3 [63, 64].

Due to the controllable manufacturing process, porous polymers are mostly very pure materials. A serious drawback is the limited temperature stability of several adsorbents restricting the application of thermal desorption. Tenax [poly-(2,6-diphenyl-*p*-phenylene oxide)] is the most important material for air analysis among the porous polymers. Nowadays, the high-purity version Tenax TA has replaced Tenax GC due to lower background signals [65]. Moreover, a mixture of Tenax and a graphitized carbon black called Tenax GR is available which should combine the advantages of both materials (see Table 1).

Tenax is a very hydrophobic material which is characterized by a high thermal stability. Due to its low specific surface area (30 m² g⁻¹), it is not suitable for sampling highly volatile organics. Referring to hydrocarbons, it is used for compounds with carbon numbers higher than four [66]. Tenax TA has been utilized for the enrichment of pesticides (atrazine, lindane) [67] and it is in widespread use for sampling terpenes [68, 69]. To reduce breakthrough losses, Tenax could be combined with graphitized carbon blacks [68, 70].

Although Tenax is an excellent adsorbent material it tends to form artifacts, especially benzaldehyde, acetophenone, and higher aldehydes (octanal, nonanal, decanal) [61, 71, 72]. Peters et al. reported alteration by irradiation with sunlight forming artifacts such as acetophenone or benzaldehyde [73]. Further sources of formation of artifacts are the reactions of reactive atmospheric species (e.g. ozone, nitric oxides) with the adsorbent [74, 75].
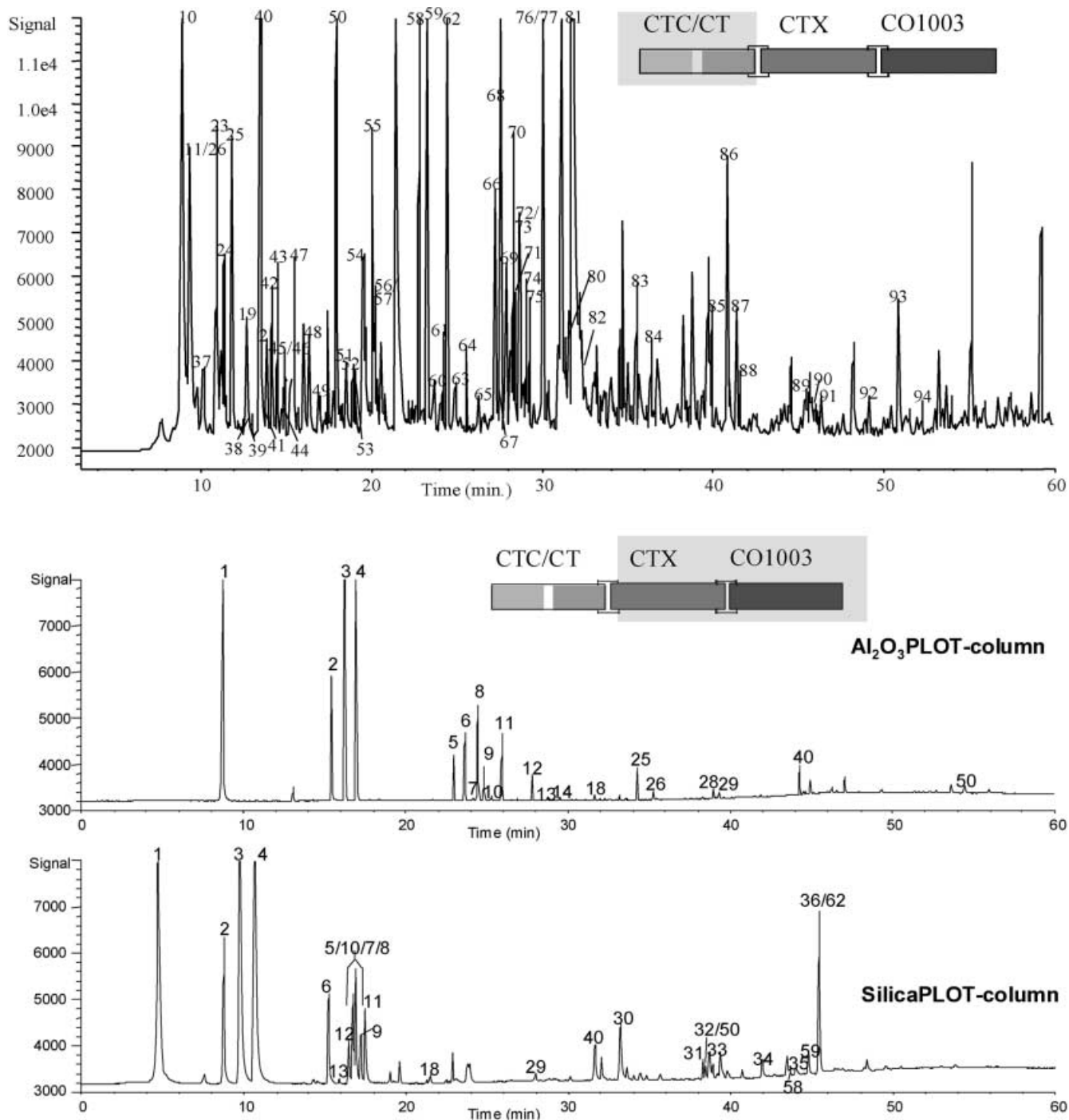
**Fig. 5** Ambient air analysis in the city center of Leipzig (19/02/1998) using four serial coupled adsorbents. Sampling volume: approximately 8 L. *Upper chromatogram*: GC-analysis of medium boiling compounds adsorbed on the multibed trap containing the graphitized carbon blacks Carbotrap C/Carbotrap using a non-polar thick-film column (DB-1, 60 m×0.32 mm I.D. 1 μm film thickness, temperature program: 30 °C (5 min), 3 °C min⁻¹ – 280 °C, carrier gas helium, 3 mL min⁻¹, FID/MSD-detection). *Lower chromatograms*: GC-analysis of low boiling compounds adsorbed on the graphitized carbon black Carbotrap X and the carbon molecular sieve Carboxen 1003 using a dual column technique consisting of an Al₂O₃PLOT –column (30 m×0.32 mm I.D.) and a SilicaPLOT-column (30 m×0.32 mm I.D.). Temperature program: 30 °C (2.5 min), 4 °C min⁻¹ – 200 °C (20 min), carrier gas helium, 6 mL min⁻¹, FID-detection. *Peak numbers* refer to Table 4.

Beside a degradation of Tenax itself, reactive species could lead to a breakdown of reactive compounds adsorbed on the adsorbent surface. Bunch and Pellizzari [76] and Pellizzari and Krost [77] reported the halogenation of olefins (e.g., cyclohexene), the formation of dimethylnitrosamine from dimethylamine in the presence of nitrogen oxides and the reaction of olefins with ozone. The last of these could cause serious analyte losses [73, 78, 79, 80, 81, 82]. Hoffmann observed losses of up to 50% of reactive monoterpenes (limonene, myrcene), as well as sesquiterpenes (e.g., caryophyllene) if ozone is present in the air sampled [83]. These ozone interferences are negligible if carbon adsorbents are used for sampling [84, 68].

**Table 4** Peak identification for Fig. 4

| Peak | Compound | Peak | Compound | Peak | Compound |
|---|---|---|---|---|---|
| 1 | Propane | 33 | Acetonitrile | 65 | Isopropyl benzene |
| 2 | Propene | 34 | Methacrolein | 66 | Benzaldehyde |
| 3 | *i*-Butane | 35 | Butyraldehyde | 67 | α-Pinene |
| 4 | *n*-Butane | 36 | Acetone | 68 | 2-Ethylhexanal |
| 5 | *trans*-2-Butene | 37 | CCl$_2$F-CClF$_2$ | 69 | Propyl benzene |
| 6 | 1-Butene | 38 | 2,4-Dimethylpentane | 70 | 3-Methylethylbenzene |
| 7 | Cyclopentane | 39 | 1,1,1-Trichloroethane | 71 | 4-Methylethylbenzene |
| 8 | *i*-Butene | 40 | Benzene | 72 | Phenol |
| 9 | *cis*-2-Butene | 41 | Tetrachloromethane | 73 | 1,3,5-Trimethylbenzol |
| 10 | *i*-Pentane | 42 | 2-Methylhexane | 74 | 6-Methyl-5-hepten-2-one |
| 11 | *n*-Pentane | 43 | 3-Methylhexane | 75 | 2-Methylethylbenzene |
| 12 | 1,3-Butadiene | 44 | Trichloroethene | 76 | Octanal |
| 13 | Propyne | 45 | 1-Heptene | 77 | 1,2,4-Trimethylbenzene |
| 14 | Cyclopentene | 46 | Isooctane | 78 | *n*-Decane |
| 15 | 2-Methyl-2-butene | 47 | *n*-Heptane | 79 | D-3-Carene |
| 16 | *trans*-2-Pentene | 48 | Methylcyclohexane | 80 | 1,2,3-Trimethylbenzene |
| 17 | 2-Methyl-1-butene | 49 | Ethylcyclopentane | 81 | 2-Ethylhexanol |
| 18 | 1-Pentene | 50 | Toluene | 82 | Limonene |
| 19 | Methyl cyclopentane | 51 | 2-Methylheptane | 83 | Nonanal |
| 20 | *cis*-2-Pentene | 52 | 3-Methylheptane | 84 | *n*-Undecane |
| 21 | Cyclohexane | 53 | Hexanal | 85 | Naphthaline |
| 22 | 2,2-Dimethylbutane | 54 | 1-Octene | 86 | Decanal |
| 23 | 2-Methylpentane | 55 | Butyl acetate | 87 | Benzothiazole |
| 24 | 3-Methylpentane | 56 | Tetrachloroethene | 88 | *n*-Dodecane |
| 25 | *n*-Hexane | 57 | *n*-Octane | 89 | 2-Methylnaphthalene |
| 26 | Isoprene | 58 | Ethylbenzene | 90 | 1-Methylnaphthalene |
| 27 | Butyne | 59 | *m/p*-Xylene | 91 | *n*-Tridecane |
| 28 | Furan | 60 | C9-alkane | 92 | Biphenyl |
| 29 | 1-Hexene | 61 | Styrene | 93 | *n*-Tetradecane |
| 30 | Acetaldehyde | 62 | *o*-Xylene | 94 | Acenaphthylene |
| 31 | Acrolein | 63 | 1-Nonene | | |
| 32 | Propanal | 64 | *n*-Nonane | | |

Different materials have been employed to remove ozone before entering the sorbent trap to avoid analyte losses, including thiosulfate impregnated sorbent traps [85], potassium-iodide ozone traps [86, 87], polymer materials such as NOXON® (polyphenylene sulfide) [88, 89], or ozone scrubbers based on multi layers of MnO$_2$-coated copper nets [82, 83]. But the application of these oxidant scavengers can also initialize the formation of artifacts as well as the discrimination of reactive analytes [87]. A comprehensive review dealing with different techniques to minimize ozone interferences was performed by Helmig [90].

Apart from degradations caused by oxidants in the atmosphere to be sampled, decomposition processes can take place on the surface of the sorbent. Coeur et al. reported that α-pinene and sabinene were decomposed on Tenax TA [41].

Chromosorb 106 is often used as a porous polymer. Compared to Tenax, it possesses a higher specific surface area but a lower temperature stability. It could replace Tenax for sampling more volatile and polar compounds in workplace air. It has, however, higher blank levels which makes it impractical for trace analysis [35].

Polydimethylsiloxane

A novel sorbent for sampling airborne organics are polydimethylsiloxane particles (PDMS) produced by grinding high-purity silicone tubing [91]. Polydimethylsiloxane is a well-characterized material due to its ubiquitous use as a stationary phase in gas chromatography. In fact, PDMS does not belong to the adsorbents because enrichment is based on absorption of the solutes in the material. As the energy of partitioning is lower than that of adsorption, the analytes could be desorbed at mild temperatures thereby minimizing thermally-induced decomposition. PDMS is an inert material which shows virtually no irreversible adsorption and catalytic reactions [92, 93]. Water is not retained by the siloxane material, but the degradation products of the PDMS can disturb the gas chromatographic analysis although they can easily be identified by a mass selective detector.

Moreover, the retention volume of a species can be calculated on the basis of GC-retention data [91]. A drawback of PDMS is the low breakthrough volume of highly volatile compounds [93], which might be overcome if the equilibrium sampling mode is applied [94]. However, the equilibrium constant is low for highly volatile compounds

and the sampling conditions have to be monitored carefully, for example, extreme temperature variations have to be avoided. A further possibility could be the combination of PDMS with an adsorbent possessing a high adsorbent strength.

Despite the great variety of commercially available adsorbents, a universal adsorbent unfortunately does not exist. As mentioned above, it could be advisable to use more than one adsorbent if analytes in broad volatility range are to be analyzed. In that case the materials are arranged in order of increasing adsorbent strength. They could be placed in one adsorbent tube or in separate tubes that are combined for sampling. Multibed adsorbent tubes are commercially available and contain, for example, the graphitized carbon blacks Carbotrap C and Carbotrap and the carbon molecular sieve Carbosieve SIII. These tubes are designed for sampling compounds in the range of $C_2$–$C_{15}$. However, the separation of these analytes in a conventional one-dimensional gas chromatographic run is difficult or even impossible. The application of multidimensional (comprehensive) gas chromatography seems to be very promising in this context [95]. A further possibility is the careful arrangement of the adsorbents in separated tubes leading to a pre-separation of the analytes in a medium and low boiling fraction which could be analyzed with different chromatographic systems [38]. An example using this technique for ambient air analysis in the city center of Leipzig is given in Fig. 5. Multibed traps containing the two graphitized carbon blacks Carbotrap C and Carbotrap were mounted in front of a Carbotrap X and a Carboxen 1003 tube for sampling. After sampling the medium, boiling analytes retained in the multibed tube were analyzed using a non-polar thick-film column, while the low boiling analytes adsorbed on Carbotrap X/Carboxen 1003 were analyzed using a dual-column technique consisting of an $Al_2O_3$PLOT- and a SilicaPLOT-column. The $Al_2O_3$PLOT-column provides an excellent separation of light hydrocarbons, but more polar analytes, such as carbonyl compounds, are not eluted from this column. These analytes could be separated on the SilicaPLOT-column (see Fig. 5).

## Conclusions

Adsorptive enrichment in combination with thermal desorption and capillary gas chromatography is a well-accepted technique in ambient air analysis. However, the adsorbent used for sampling has to be chosen carefully according the compounds to be sampled. In this context, investigations dealing with the adsorption and desorption behavior of the analytes are still necessary. While the analysis of non-polar compounds such as hydrocarbons is well established, the analysis of more polar compounds by adsorptive enrichment and thermal desorption is still a challenge. The recent introduction of adsorbents with very pure and homogeneous surfaces seems to be promising in extending the application range of the technique. Furthermore, absorption using PDMS instead of adsorption might be advantageous in some cases.

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