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## GAS CHROMATOGRAPHIC EVALUATION OF THE ORGANIC COMPONENTS PRESENT IN THE ATMOSPHERE AT TRACE LEVELS WITH THE AID OF CARBOPACK B FOR PRE-CONCENTRATION OF THE SAMPLE\*

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### SUMMARY

Enrichment on traps packed with Carbopack B adsorbent is proposed as a suitable method for the evaluation of organic compounds present at parts per  $10^9$ – $10^{12}$  levels in atmospheric samples. The technique has been applied to the determination of organics, dispersed in a suburban atmosphere, dissolved in rainwater or volatilized from the particulate matter emitted from an industrial emission and a diesel engine exhaust.

A comparison between the collection efficiency of Carbopack B and Tenax GC in the sampling of  $C_6$ – $C_{10}$  hydrocarbons is also presented. The results obtained with both simulated and natural atmospheres indicate that Carbopack B is more efficient and does not give rise to sampling artifacts in the presence of oxidants and acidic pollutants, which are shown instead to cause decomposition of the Tenax GC polymeric matrix. The chemical inertness of Carbopack B also permits the determination of organic compounds in anthropogenic emissions, where large amounts of  $NO_2$ , water and strong acids are present.

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### INTRODUCTION

Often the determination of certain organic species, released into or formed in the atmosphere, cannot be performed by direct injection of the sample into a chromatographic column, because the concentration levels that need to be measured are far below the detection limits of the instrumental devices currently available. In order to accumulate sufficient material to be sensed by the detector without changing drastically the chromatographic performance of the analytical column, several enrichment techniques, capable of separating as efficiently as possible the species of interest from the bulk of the dispersion medium, have been developed and tested by environmental chemists. Among these techniques, those based on traps, packed with adsorbing ma-

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materials that permit the specific retention of the organics dispersed in air and rainwater or volatilized from the particulate matter accumulated on the filter, have enjoyed increasing success, specifically because they are simple to use in field measurements, are fairly efficient and do not require sophisticated and expensive equipment. However, the high enrichment factors required for the determination of components present at parts per  $10^9$ – $10^{12}$  (ppb–ppt) levels, combined with the need to maintain the composition of the sample to be analysed, restrict the selection of the solid materials to adsorbents characterized by chemical inertness toward the oxidizing and acidic agents present in environmental samples. Additional restrictions in the choice of adsorbents must be accepted when short sampling times are required for measuring daily trends as, in this event, thermal desorption is the only way to achieve sufficient sensitivity. Among the adsorbents suitable for the enrichment of organic pollutants, Tenax GC<sup>1–3</sup>, porous polymers<sup>4,5</sup> and, to a lesser extent, graphitized carbon blacks (GCB) with different surface areas<sup>6,7</sup> have been applied to the enrichment of atmospheric samples, as they provide excellent recoveries for hydrocarbons, coupled with satisfactory adsorption capacities. Undoubtedly the largest number of results have been obtained on Tenax GC traps, as they require relatively low temperatures for the thermal desorption of vapours and provide better recoveries of polar compounds. However, the convenience of enriching atmospheric samples on Tenax GC traps has been questioned by some workers<sup>8–11</sup>, who have found that this material can be a source of serious interferences when strong oxidants and inorganic pollutants commonly found in the atmosphere and industrial emission come into contact with the polymer. Experiments carried out with gas streams simulating polluted atmospheres have clearly shown that, in the presence of ozone, water, SO<sub>2</sub> and NO<sub>2</sub>, Tenax GC undergoes chemical decomposition, giving rise to substantial amounts of organic compounds that can simulate the presence of pollutants in the sample.

In this work we have investigated the possibility of using Carbo-pack B, a GCB with a specific surface area of 90 m<sup>2</sup>/g as an alternative material for the collection of air and water samples in which the presence of oxidants and acidic reactants may cause significant decomposition of Tenax GC adsorbents. A comparison of the absorption efficiencies of Tenax GC and Carbo-pack B, measured with selected C<sub>6</sub>–C<sub>10</sub> organic compounds, is presented. The occurrence of sampling artifacts, arising from the polymeric matrix of Tenax GC, is demonstrated and confirmed by field measurements. Three different examples of the practical application of Carbo-pack B traps to real samples are reported: (a) the enrichment of natural and anthropogenic hydrocarbons in suburban atmospheres, where the occurrence of photochemical smog episodes was observed; (b) the pre-concentration of rainwater, collected during a storm; and (c) the determination of polynuclear aromatic hydrocarbons (PAHs), volatilized during the collection of particulate matter, emitted from an industrial plant and a diesel exhaust. The results obtained indicate clearly that, in spite of the relatively high content of reactive pollutants dispersed in such different media, traps filled with Carbo-pack B permit the detection of several pollutants present at ppb–ppt levels, and they are virtually unaffected by the presence of ozone and many other reactive compounds. Field measurements, carried out by using traps packed with Carbo-pack B, showed that an accurate quantitation of hydrocarbons emitted from natural and anthropogenic sources can be achieved, and oxidation products of key importance in photochemical smog events can be detected.

## EXPERIMENTAL

*Solvent, adsorbent materials and reagents*

All solvents used for the liquid extraction of solid samples (benzene, methanol, CS<sub>2</sub>) and for the high-performance liquid chromatographic (HPLC) separation of the soluble organic fraction (CH<sub>2</sub>Cl<sub>2</sub>, *n*-hexane) extracted from the adsorbent and particulate matter were of HPLC grade from Carlo Erba (Milan, Italy). The olefinic standard compounds used for measuring the adsorption efficiency of Tenax GC and Carboxpack B were 1-hexene, bicyclopentadiene, 1-heptene, vinylcyclohexene, 1-octene, *cis,cis*-octadiene,  $\alpha$ -pinene, carene,  $\alpha$ -terpinene and limonene from Carlo Erba and Fluka (Buchs, Switzerland). Benzene, toluene, ethylbenzene, *o*-, *m*- and *p*-xylene, 1,3,5-trimethylbenzene, *n*-butylbenzene, 1,3-diethylbenzene and 1,3,4,5- and 1,2,3,4-tetramethylbenzene, used for measuring the adsorption efficiency of anthropogenic hydrocarbons, were also supplied by Fluka.

Gaseous standard mixtures were prepared by first dissolving suitable amounts of each component in a vial (10 ml) containing a known volume of methanol, and then by aspirating with a gas syringe a known volume of the headspace vapour formed after equilibration of the mixture. The total amount injected into the traps was equivalent to that commonly found in *ca.* 10 l of air when ppb levels of pollutants are present in the sample.

Carboxpack B with a mean particle size between 20 and 40 mesh was supplied by Supelco (Bellefonte, PA, U.S.A.). This material is, basically, a carbon black that has been partially graphitized by heating the particles at *ca.* 2700°C in a reducing atmosphere (nitrogen). Two different procedures were used for cleaning the adsorbent material prior to sampling, and they were selected according to the type of compounds to be enriched. When the traps were used for collecting the volatile components in air, the material was inserted in a glass tube and heated in a small furnace at 350°C for 6 h under a 100 ml/min flow of pure helium. After the cleaning process, the material was transferred into glass tubes, using a 10- $\mu$ m metal screen to maintain the particles within the trap. To prevent contamination, the traps were filled with helium and both ends were closed with metal fittings. A gas-tight connection between the glass tube and the metal fittings was obtained by using Vespal ferrules (Supelco). The traps, protected with aluminium foil, were stored in a tight glass container, filled with an atmosphere of helium, and kept at ambient temperature. When Carboxpack B was used for the enrichment of rain samples or heavy compounds present in industrial emissions, the material was pre-cleaned by Soxhlet extraction with benzene-methanol (4:1) for at least 12 h. The material was then dried under a flow of helium and the solvent residue was removed by subjecting the Carboxpack B to thermal desorption according to the procedure described before.

Tenax GC (60-80 mesh), produced by Enka (The Netherlands) was supplied by Applied Science Labs. (State College, PA, U.S.A.). The material was pre-cleaned under thermal desorption conditions by following the steps adopted for Carboxpack B, except for the temperature of the furnace, which was 280°C.

*Sampling and desorption devices*

Fig. 1a is a schematic diagram of the apparatus used for measuring the trapping efficiency of the two adsorbents investigated. An artificial mixture containing

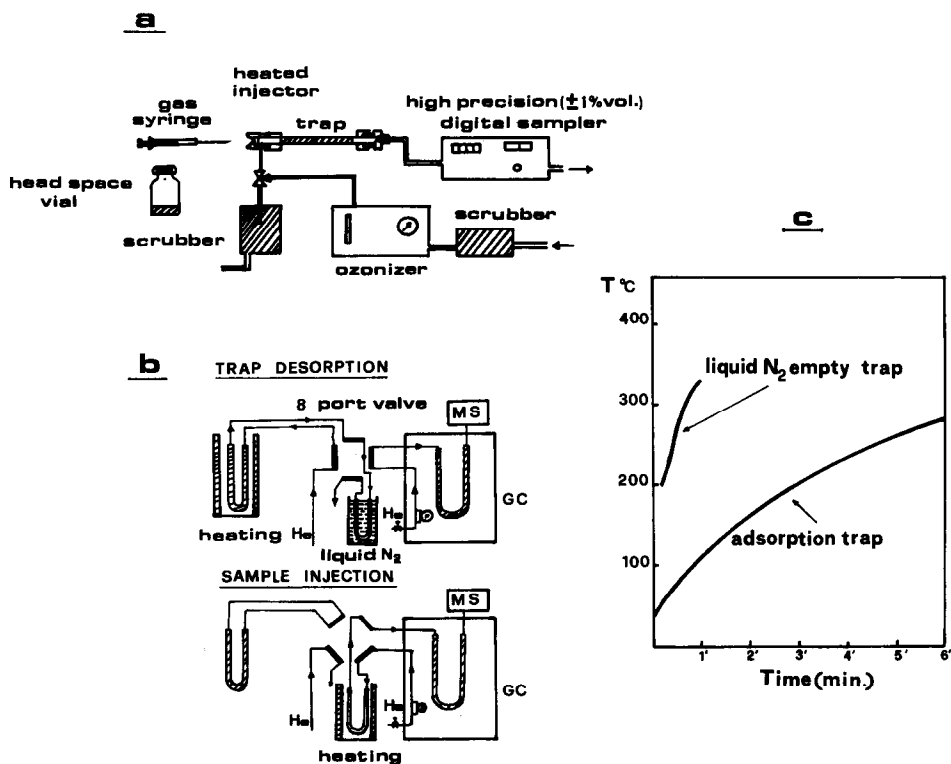


Fig. 1. (a) Experimental device for measuring the adsorption efficiency of the trapping materials. Part of this apparatus was also used for sampling volatiles in the atmosphere. (b) Schematic diagram of the thermal desorption system. (c) Temperature profiles of the gradients used during thermal desorption of volatile organics from adsorption traps.

the test compounds was injected into the traps, kept under a constant flow of air aspirated through the injector. The flow-rate (100 ml/min) was maintained constant by an electronically controlled device, which allowed measurement of the total volume sampled with an accuracy of  $\pm 1\%$ . The injector was kept at a temperature of 80°C in order to prevent condensation of the heaviest components. A trap was used to eliminate most of the reactive components in the atmosphere, but 1.9 ppm of methane, 0.05 ppb of C<sub>2</sub>–C<sub>4</sub> hydrocarbons and water were allowed to pass through it. The aspirating pump could be pre-set at any volume, ranging between 10 ml and 10 l. In the determination of the adsorption efficiency, carried out with test compounds, the volumes sampled were 2, 5 and 10 l. By switching a three-way valve, a known amount of ozone was generated in the air stream, and this allowed the evaluation of the effect of this pollutant on both the enriching material and the absorbed compounds. The ozone generator used was a part of a Monitor Lab 8500 Calibrator (San Diego, CA, U.S.A.), capable of generating known mixtures of ozone and air in the ppm–ppb range. By removing the heated injector and the ozone generator, the sampling device was assembled in a small, portable carriage, connected to a 12 V battery, and used for field measurements.

Fig. 1b is a schematic diagram of the thermal desorption apparatus, which was

connected to the gas chromatograph. To avoid thermal decomposition of the more reactive components, the traps were backflushed under temperature-programmed conditions, and the sample was transferred to an empty tube kept at the temperature of liquid nitrogen. After concentration, the organic compounds were injected into the GC column by removing liquid nitrogen, heating the tube and rapidly switching the four-way valve, connected to the GC inlet. The profiles of the temperature programmes used during the backflushing and injection steps are shown in Fig. 1c. It is worth noting that all the gas lines in contact with the sample were made of glass-coated metal tubes, as we have found that hot metal surfaces can decompose some natural components (e.g.,  $\alpha$ -terpinene).

The adsorption properties of Carbopack B and Tenax GC were measured by using small glass traps (150 × 4 mm), filled with the same volume of sorbent materials. To confirm the data obtained by thermal desorption, the amount of hydrocarbons recovered from Carbopack B was also checked by extracting the adsorbed compounds with 0.5 ml of carbon disulphide. The various components were recovered by forcing the extraction liquid through the trap with a syringe, inserted at the trap outlet.

Field measurements were carried out in a U-shaped 250 × 6 mm glass tube in order to ensure that none of the compounds of interest would be lost under the most critical sampling conditions (10 l sampling volume, 100% relative humidity and temperature 40°C). During field measurements, the traps were protected from dust by inserting a filter (0.25  $\mu$ m mean pore diameter) at the air inlet.

Usually, 10 l of air were more than sufficient for detecting the compounds of interest. Rainwater was sampled with a laboratory-made, dry/wet deposimeter, driven by an electronic circuit that opens the PTFE cap of the glass container when a droplet sensor is activated. When the rainfall stops and the sensor becomes dry, the electronic circuit moves the cap back over the bottle and protects the sample from dust. Prior to the enriching process, the water was passed first through a pre-cleaned glass column, filled with glass-wool to remove small insects, pollen and large particles, and then filtered through a PTFE filter having a mean pore size of 0.25  $\mu$ m. The organic compounds were removed by pumping water through a 10 cm × 4 mm glass trap, packed with Carbopack B (20–40 mesh). Both ends of the trap were filled with glass-wool. After the pre-concentration step, the trap was dried with helium and the carbon extracted in a 40 ml Soxhlet extractor with benzene–methanol (4:1) for 6 h at 80°C. The extract, dried under a flow of nitrogen, was dissolved in 10  $\mu$ l of dichloromethane, and small aliquots (2  $\mu$ l) were analysed by gas chromatography–mass spectrometry (GC–MS).

Fig. 2 shows the apparatus developed to retain the polyaromatic compounds desorbed from the filter during sampling of particulate matter. In this instance, Carbopack B was inserted into a small chamber between the filter and the aspirating device. The chamber had a diameter of 47 mm and was 10 mm deep. An exploded diagram of the chamber, containing the adsorbent, is shown in Fig. 2b.

Particles were collected on a pre-cleaned Spectrograde quartz filter (Gelman, Instruments, Milan, Italy). The particulate matter collected from the stack of an industrial plant was sampled isokinetically using a Gelaire 4000 (Gelman), capable of maintaining a constant flow-rate throughout the entire system. Diesel particulates, emitted from a commercial vehicle, were sampled by inserting the exhaust pipe into

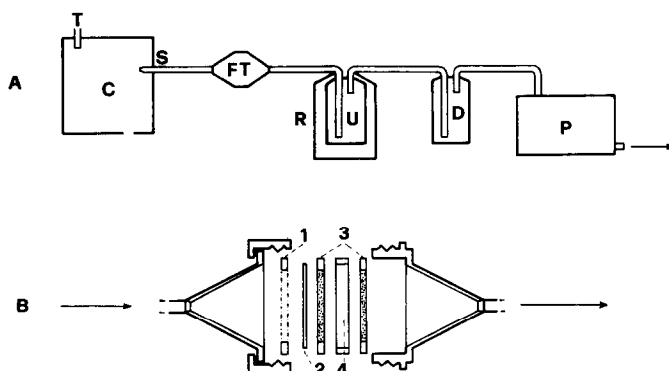


Fig. 2. (a) Schematic diagram of the sampling device used for collecting particulate matter and vapours emitted from industrial emissions and diesel exhausts. T = pipe; C = expansion chamber; S = nozzle; F = filter; T = trap; R,U = water trap; D = drier; P = pump. During sampling of industrial emissions, T and C were removed. (b) Exploded diagram of the filter holder and the chamber containing the adsorbing material. 1 = O-ring; 2 = filter; 3 = metal fritted filters; 4 = adsorbent.

a 10-l expansion chamber. This laboratory-made device was used to obtain more accurate sampling by preventing turbulent motion of the particles. The aspirating device was the same as that used for sampling the industrial emission and was operated at a flow-rate of 15 l/min. After sampling, the adsorbent was removed from the chamber and extracted in a Soxhlet apparatus. The same procedure was applied to the particles collected on the filter.

#### *Chromatographic separation and detection methods*

The separation of the light components recovered from the absorption traps was carried out on a 3 m × 2 mm I.D. packed column, filled with Carbo-pack B (80–100 mesh) coated with 0.5% SP-1000 (Supelco). After 1 min at 70°C, the temperature of the column was increased linearly to 235°C at 3°C/min. The column was installed in a Dani 3900 (Dani, Monza, Italy) gas chromatograph, equipped with a flame ionization detector and connected to a VG 70-70 F double-focusing mass spectrometer (VG Analytical, Altrincham, U.K.) through a jet separator.

Specific detection of natural and anthropogenic hydrocarbons in air samples was accomplished by operating the MS apparatus in the selected-ion-detection (SID) mode. The separation of rainwater extracts was carried out on a 25-m × 0.32 mm I.D. fused-silica capillary column (J. & W. Scientific, Rancho Cordova, CA, U.S.A.). The liquid coating was DB 5 and the film thickness was 0.17 μm. The column was installed in the Dani 3900 gas chromatograph, equipped with a temperature-programmed vaporizer (TPV) injector. The column outlet was connected directly to the mass spectrometer. Reconstructed chromatograms and normalized mass spectra were stored and generated by a VG 2350 data system, interfaced with the mass spectrometer.

The soluble organic fraction, extracted from the samples collected from the industrial plant emission, was pre-fractionated on an HPLC column (250 × 4 mm I.D.), filled with 10-μm Erbasil silica particles (Carlo Erba), prior to the GC determination. PAHs were separated from their polar derivatives by gradient elution, using

*n*-hexane and dichloromethane as mobile phases. The column was eluted with *n*-hexane for 8 min, then dichloromethane was added at a rate of 2%/min. When the eluent was 100% dichloromethane, the isocratic conditions were maintained for at least 10 min. HPLC separations were carried out on a Varian 3000 liquid chromatograph (Varian Instruments, Palo Alto, CA, U.S.A.), equipped with a Rheodyne 7125 injection valve (Rheodyne, Berkeley, CA, U.S.A.) with a 20- $\mu$ l loop and a variable-wavelength UV detector. The HPLC fractions containing PAHs were collected, dried and dissolved in dichloromethane. Aliquots were subjected to GC and GC-MS analysis on the same capillary column as that used for separating the rainwater concentrate. Diesel exhaust was pre-fractionated on a semi-preparative LC column (180  $\times$  8 mm I.D.) filled with basic alumina (70–150 mesh) (Woelm) (Carlo Erba), activated at 250°C for 12 h in order to separate the PAHs and nitro-PAHs from alkanes and other polar components. The separation was carried out by sequential elution with *n*-hexane, dichloromethane, and methanol. The dichloromethane fraction, containing PAHs and nitro-PAHs, was further separated on the Erbasil HPLC column by gradient elution with *n*-hexane and dichloromethane. The nitro-PAHs recovered from the eluate were analysed by capillary GC and detected with a nitrogen-phosphorus detector supplied by Carlo Erba. The instrument was equipped with a TPV injector. Positive identification of the various components was carried out by the same GC-MS combination as described above. More details of the fractionation scheme and the identification procedure are reported in ref. 12.

## RESULTS AND DISCUSSION

### *Volatile organic compounds in air*

Fig. 3a and b show the recovery of olefinic and alkylbenzenic compounds, respectively, measured when 2, 5 and 10 l of air were passed through traps containing equal volumes of adsorbent. This laboratory experiment was carried out by injecting

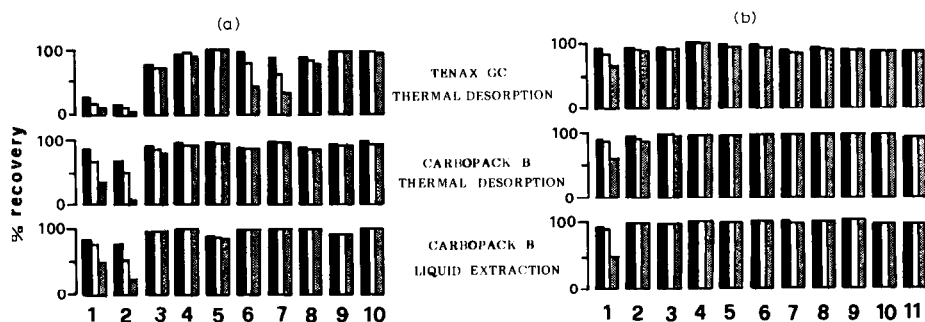


Fig. 3. Percentage of test compounds recovered from Carbopack B and Tenax GC when 2 (closed bars), 5 (open bars) and 10 l (shaded bars) of air were passed through the adsorption traps. (a) Olefins and monoterpenes: 1 = 1-hexene; 2 = bicycloheptadiene; 3 = 1-heptene; 4 = vinylcyclohexene; 5 = 1-octene; 6 = *cis,cis*-octadiene; 7 =  $\alpha$ -pinene; 8 = carene; 9 =  $\alpha$ -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.

a known volume of standard mixture into the traps and measuring the amount of each component recovered when the air, sampled with the apparatus shown in Fig. 1b, was allowed to flow through the adsorbent. The trapping efficiency of Carboxpack B was also measured by extracting the sample with 0.5 ml of CS<sub>2</sub> in order to ensure that no artifacts, arising from thermal decomposition of the adsorbed organics or the carbonaceous material, were formed during the desorption step. The precision of the measurements, based on at least three injections, was *ca.* 2%. Although some differences do exist between the two sets of histograms obtained with Carboxpack B, they are very small and can be attributed mainly to the low trapping efficiency of the liquid nitrogen tube. In spite of these small uncertainties, Fig. 3 allows a fair comparison between the adsorption efficiencies of Tenax GC and Carboxpack B and clearly shows that the latter is a better material for the enrichment of low-boiling compounds and particularly those natural hydrocarbons (*e.g.*,  $\alpha$ -pinene and carene) which are known to be emitted in large amounts from pine forests. Although important, this comparison cannot be taken by itself as a good reason for the choice of one of the two adsorbents, as it is always possible to increase the volume of the solid material in order to obtain a comparable recovery. More important is the observation we made when 500 ppb of ozone was added to the air flowing through the traps. While the recovery measured with olefins and arenes was, within experimental error, the same as that shown in Fig. 3a and b, serious decomposition of the polymeric matrix of Tenax GC was observed and substantial amounts of interfering compounds were detected by chromatographic analysis. As the same components were produced when no test compounds were injected into the Tenax GC trap, it was evident that they were formed by interaction between the oxidant, added to the eluting air, and the surface of the adsorbent.

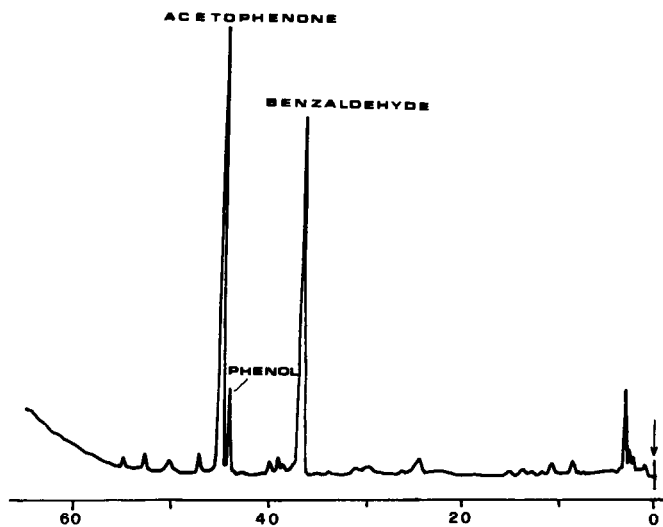


Fig. 4. GC-MS profile of the decomposition products released by the Tenax GC trap when 5 l of air, containing 500 ppb of ozone, were passed through the adsorbent. To detect the products better, the starting temperature of the column was 40°C in this instance, whereas the temperature gradient was the same as that reported under Experimental.



A GC analysis of the major decomposition products arising from the oxidation of the polymeric material is shown in Fig. 4. The products concerned were subjected to GC-MS analysis and the major compounds were identified as benzaldehyde, acetophenone and phenol. The amount of decomposition products (several micrograms) was produced by passing 5 l of air containing 500 ppb of ozone through the adsorbent. The presence of these compounds is in complete agreement with the observations of Krost *et al.*<sup>11</sup>, but some details seem to contradict their suggestion that water is equally important in producing the decomposition of the polymer. In our experiment, water was always present during sample collection at 50% relative humidity, but the production of benzaldehyde, phenol and benzophenone was observed only

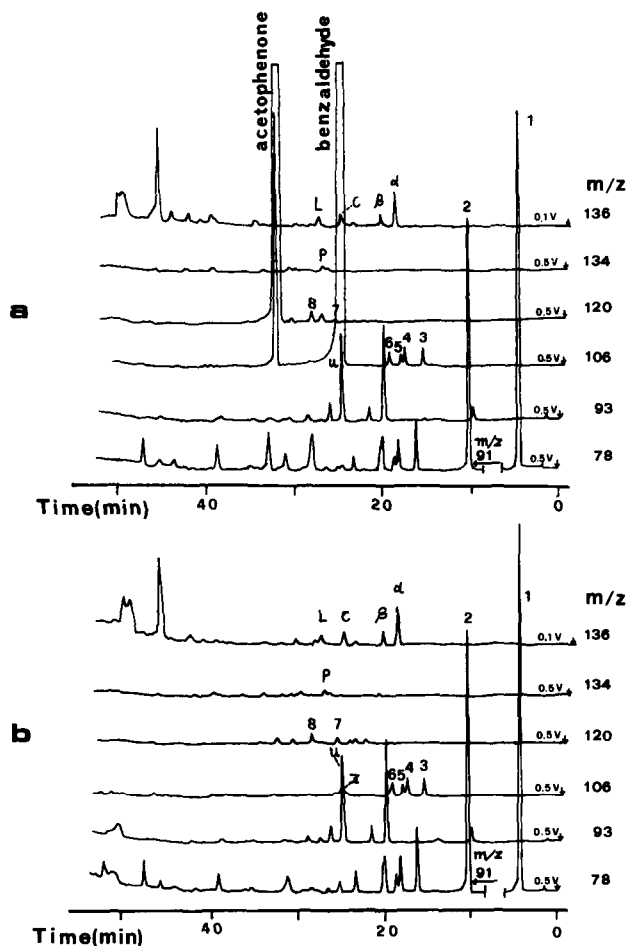


Fig. 5. Selected-ion detection chromatographic profiles obtained by analysing 10 l of an air sample collected at noon in a pine forest. (a) Tenax GC; (b) Carboxpack B. 1 = Benzene (0.016 ppb); 2 = toluene (0.086 ppb); 3 = ethylbenzene (0.015 ppb); 4 = *m*-xylene (0.009 ppb); 5 = *p*-xylene (0.004 ppb); 6 = *o*-xylene (0.006 ppb); 7 = 2-ethyltoluene (0.0005 ppb); 8 = 1,2,4-trimethylbenzene (0.005 ppb);  $\alpha$  =  $\alpha$ -pinene (0.08 ppb);  $\beta$  =  $\beta$ -pinene (0.01 ppb); c = carene (0.007 ppb); L = limonene (0.01 ppb); p = *p*-cymene (0.004 ppb); u = unknown; z = benzaldehyde.

when ozone was added to the mixture. It is likely that water becomes effective when other pollutants (such as  $\text{NO}_2$  and  $\text{SO}_2$ ), which were not present in our mixture, are added to the air stream.

Although important, the experiment we performed in the laboratory could be questioned as, in the real world, ozone concentrations seldom exceed 100–200 ppb, and one could argue that, in fact, such concentrations may not be as critical as we believe. In order to forestall this criticism, we performed the sampling of hydrocarbons in a suburban atmosphere when certain photochemical smog conditions, commonly observed in the spring and summer season throughout Italy, were established at the sampling site. Concurrent with the determination of hydrocarbons, other parameters that were suspected to influence the decomposition of Tenax GC were monitored. In order to check whether benzaldehyde, phenol and benzophenone, released from the Tenax GC trap were produced by chemical decomposition of the polymeric matrix, the air was collected in a small forest not directly exposed to anthropogenic sources and a trap of Carbopack B was sampled in parallel. The measurements were carried out at noon, when the concentration of ozone was 120 ppb and the relative humidity was 50%. The concentrations of  $\text{NO}_2$  and  $\text{SO}_2$ , measured at the same site, were 10 and 8  $\mu\text{g}/\text{m}^3$ , respectively. In order to allow a fair comparison between the two adsorbents, the volume of solid material contained in the traps was increased to a point where no losses of  $\text{C}_6$ – $\text{C}_{10}$  hydrocarbons took place when 10 l of air were enriched. Such a volume was considered to be necessary for the accurate detection of the various components that were present in the atmosphere at ppb–ppt levels, because of the lack of anthropogenic sources in our site and the high photochemical reactivity of hydrocarbons occurring at noon.

Fig. 5a and b show the SID tracings recorded when the traps containing Tenax GC and Carbopack B, respectively, were analysed. Although the contents of natural and anthropogenic hydrocarbons measured with the two traps are almost the same, a very significant interference from decomposition products is seen in the chromatogram of the compounds recovered from Tenax GC. Considering that the amount of organic material released in the form of benzophenone and benzaldehyde was at least two orders of magnitude higher than the most abundant components detected in the chromatogram, whereas the concentrations of water,  $\text{SO}_2$  and  $\text{NO}_2$  in our sample were relatively low, it is reasonable to conclude that, in agreement with laboratory experiments, ozone is likely to be the main cause of the decomposition of the Tenax GC adsorbent. As the concentration of ozone, commonly found in urban atmospheres, can be much higher than that measured during our experiment, and daily variations can be large during photochemical smog events, it appears that the use of traps packed with Tenax GC can lead to erroneous results in the evaluation of organics in air. The possibility of sampling artifacts is also increased by the fact that a higher free acidity in the atmosphere (*e.g.*,  $\text{HNO}_2$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) can be observed concurrently with high levels of ozone. For a full understanding of the limitations connected with the presence of these decomposition products, it must also be recalled 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.

The advantages of using Carbopack B traps for detecting small variations in the organic components involved in photochemical reactions and their products can

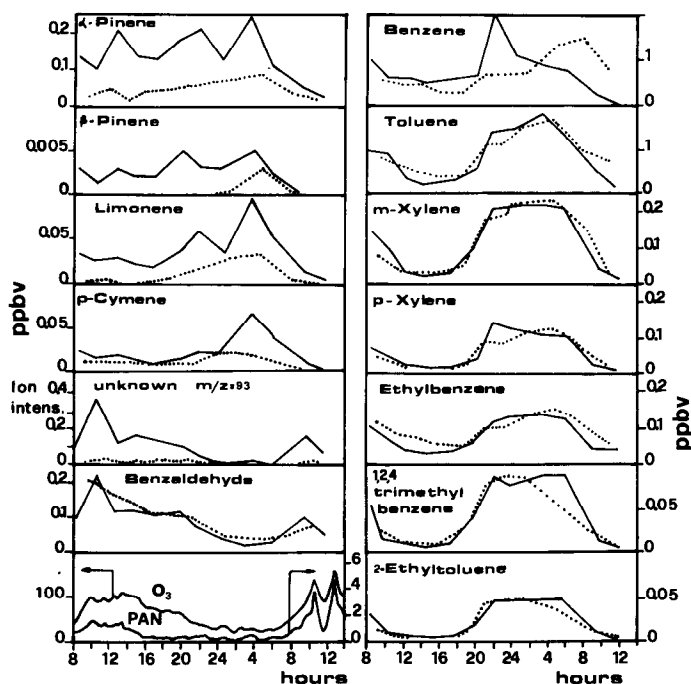


Fig. 6. Diurnal variations of natural and anthropogenic hydrocarbons, benzaldehyde, ozone and PAN, measured in a suburban forest (30 km from Rome) during a photochemical smog episode in July. . . . ., Concentrations measured above the canopy (12 m); —, concentrations measured below the canopy. All samples were enriched on Carboxpack B traps.

be better understood by examining the results shown in Fig. 6, where hourly concentrations of the most significant gaseous components measured in a forested area located downwind of Rome during a photochemical smog event are shown. The solid lines refer to the measurements carried out 1 m above the ground, whereas the dotted lines indicate the concentrations measured above the canopy (12 m above the ground). The trends of ozone and peroxyacetyl nitrate (PAN) have been added in order to give an idea of the degree of photochemical pollution, measured at the sampling site. The results reported illustrate well the high accuracy ( $\pm 2\%$ ) and sensitivity (ppt levels) that can be achieved through the use of traps packed with Carboxpack B. The possibility of detecting the small differences between the concentrations measured below and above the canopy in fact permits a differentiation between hydrocarbons emitted within the forest (terpenes, unknown product) and those diffusing into it (alkylbenzenes, benzaldehyde). The fact that the decrease in the concentrations of all alkylbenzene hydrocarbons observed at noon is concurrent with the increase in the concentration of benzaldehyde fits well the hypothesis that this compound is generated by the reaction of alkylbenzenes with OH radicals. The similarity observed in the diurnal trends of benzaldehyde and the unknown component recorded at  $m/z = 93$  suggests that the latter is likely to be produced by photochemical conversion of hydrocarbons. The difference in its concentrations measured above

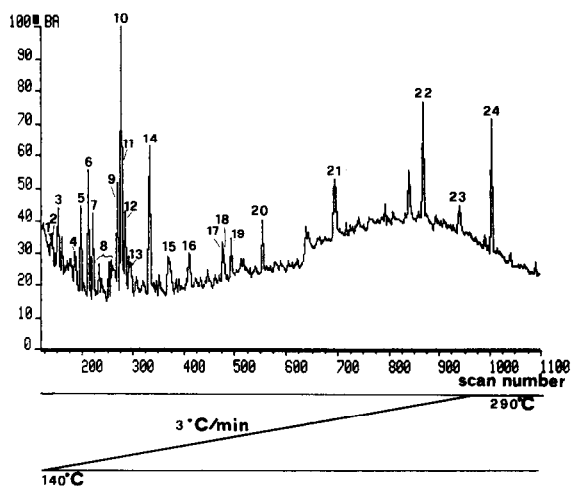


Fig. 7. GC-MS profile obtained from the analysis of a 100-ml rainwater sample, collected at the same site as that in Fig. 6. The sample was enriched on a Carbo-pack B trap. For peak numbers, see Table I.

and below the canopy can be taken as a diagnostic symptom, if this unknown product is formed by photochemical conversion of naturally emitted compounds.

The consistency of these observations with the trends of ozone and PAN can be taken as further confirmation that no artifacts arising from the use of this absorbent were occurring during the monitoring of volatile compounds in air.

#### *Organics dissolved in rainwater*

The need to know the extent to which organic compounds dispersed in air are removed by wet deposition has necessitated their determination in rainwater samples. As the pH of water ranges between 5 and 3, the enrichment must be carried out on absorbents that do not undergo chemical decomposition in the presence of acidic compounds. Moreover, the surface of the sorbent material should be non-selective and possibly hydrophobic so that adsorption can be competitive with solution. In other words, the ideal sorbent should behave like an active reversed-phase column packing material. Our previous investigations on the use of Carbo-pack B in HPLC<sup>13,14</sup> have shown that this material exhibits such features to some extent. It behaves like a reversed-phase packing for LC, but the interaction with this organic material is much stronger than with chemically bonded phases, so that even with pure methanol, it is difficult to elute compounds with more than two benzene rings in a reasonable time. This capability to retain organic materials dissolved in polar solvents and the chemical stability down to pH 1 or 2 has been exploited for the enrichment of organics in rainwater.

Fig. 7 shows the GC-MS analysis of a rainwater sample enriched on Carbo-pack B. The rainwater was collected during a storm in springtime. The sampling site was located in a suburban area, where emissions from anthropogenic activities were contributing to a minor extent to the total content of particulate matter. The choice of sample was purposely made so as to show possible sampling artifacts arising from PAHs, which are always present in carbonaceous materials.

TABLE I

ORGANIC COMPOUNDS FOUND IN A RAINWATER SAMPLE COLLECTED IN A SUBURBAN AREA AND ENRICHED ON CARBOPACK B

No.	Species	Molecular weight	Most abundant fragments ( <i>m/z</i> )
1	Phenol	94	94, 66, 65
2	Decane	142	43, 57, 41, 92, ..., 142
3	2-Methyl-5-isopropylfuran	124	109, 124, 43, 53
4	Naphthalene	128	128
5	Unknown	—	43, 84, 135
6	1-Indanone	132	132, 104, 10, 131, 78, 77
7	Unknown	—	341, 73, 147, 325
8a	Tentatively identified as ketofurans	166	43, 84, 105, 151, 166, 139
8b		166	43, 96, 124, 166
8c		166	123, 43, 66, 55, 81
9	Suspected to be oxygen- ated cyclic compounds	210	109, 43, 82, 55, 71, ..., 210
10		210	43, 82, ..., 210
11		148	148, 43, 105, 130, 102, 77, 76, 119
12	Unknown	—	73, 147, 281, 327
13	4-Methyl-2,6-di- <i>tert.</i> - butylphenol	220	205, 220, 206, 55, 57, 145,
14	Unknown	—	43, 71, 41, 56, 55, 111, 159
15	Suspected to be an oxygen- ated cyclic compound	210	43, 109, 82, 55, 97, 71, 127
16	Unknown	—	43, 71, 55, 57, 85, 152
17	Unknown	—	43, 58, 71, 85, 109
18	Trimethylidihydropurinedione	194	194, 109, 55, 67
19	Phthalate ester	—	149, 57, 43, 223, 167
20	Phthalate ester	—	149, 43, 57, 223, 205
21	Bromourate compound	234	236, 234, 155, 235, 233, 208
22	Phthalate ester	—	149, 167, 279
23	Unknown	—	43, 55, 57, 69, 71, 83
24	Unsaturated primary alcohol	—	69, 81, 41, 42, 95, 40, 137, 55, 121

The analysis of the mass spectra recorded during GC-MS analysis did not show any PAHs (except naphthalene), and this was consistent with the fact that the adsorbent was clean, the suspended particulate matter contained compounds of natural origin and the air masses were not travelling over industrial areas. However, an unambiguous identification of many of the compounds shown in the chromatogram of Fig. 7 has not been possible, and only a few of them have provided information about the origin of the sample. A list of the compounds subjected to the GC-MS analysis is given in Table I. For the unidentified compounds the most intense peaks are reported. Although it was impossible to attribute an exact molecular formula to the peaks on the basis of the mass spectra alone, an analysis of the various fragments indicated that many of the chromatographic peaks were oxygenated compounds and some of them certainly contained a furan ring. As these last components closely resemble the organic compounds found in essential oils extracted from plants, it is likely that they were present in the sample.

Extraction with solvents of the water sample after passage through the Carpack B trap did not show any organic components with more than five or six

carbon atoms, and this confirmed that no artifacts were formed during the sample enrichment. It is worth noting that only 100 ml of water were sampled for this determination, and that this was more than sufficient for obtaining intense mass spectra of the major components. Considering that the concentrations of the major components present in our sample ranged between 10 to 20 ng/l and several liters of clean water are needed for the elution of compounds with more than two benzene rings, the use of Carboxack B traps should be suitable for the determination of pollutants present in the sample at ppb–ppt levels.

*Polyaromatic compounds volatilized during sampling of particulate matter*

Another important field of application for trapping materials is the collection of high-molecular-weight compounds that are not retained on filter media or volatilized during sampling of particulate matter. In this instance, chemical and thermal stability are required of the adsorbent. Both are important, as large amounts of free acids ( $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and  $\text{HCl}$ ), water and polar organic compounds may be present in industrial and vehicular emissions, and high temperatures are often reached in the stacks during combustion processes. Graphitic carbons fit these requirements well, as they can be heated to  $2000^\circ\text{C}$  without changing their chemical and structural features and they do not react with strong acids. Using graphitic carbons with a surface area greater than  $50\text{ m}^2/\text{g}$ , it is also possible to retain relatively heavy compounds, even in the presence of large amounts of organic materials. Carboxack B, which has a surface area of  $90\text{ m}^2/\text{g}$ , is a sufficiently strong adsorbent for the enrich-

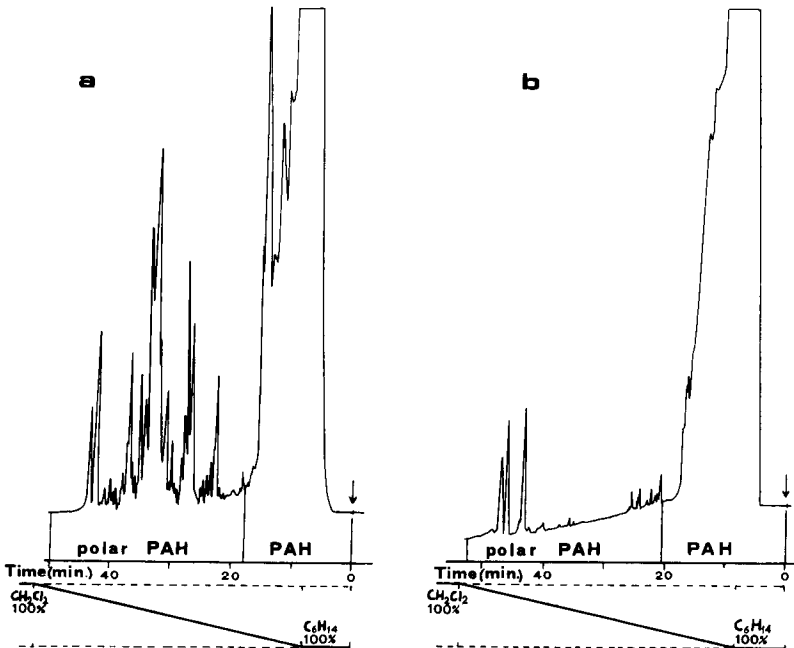


Fig. 8. HPLC fractionation of PAHs emitted from an industrial plant. (a) PAHs extracted from the filter; (b) PAHs extracted from the Carboxack B trap, placed after the filter.

ment of this type of sample, and it has been applied to the determination of the PAHs that are at the focus of public concern because of their high carcinogenic and mutagenic activity.

The first example of the application of this adsorbent was the determination of PAHs emitted from the stack of a chemical plant where coke residue was used during the industrial process. As the particulate matter was found to contain mainly PAHs with 3–4 benzene rings and the temperature within the stack was sufficiently high to cause conversion of the particles into vapour, the use of an adsorbing trap

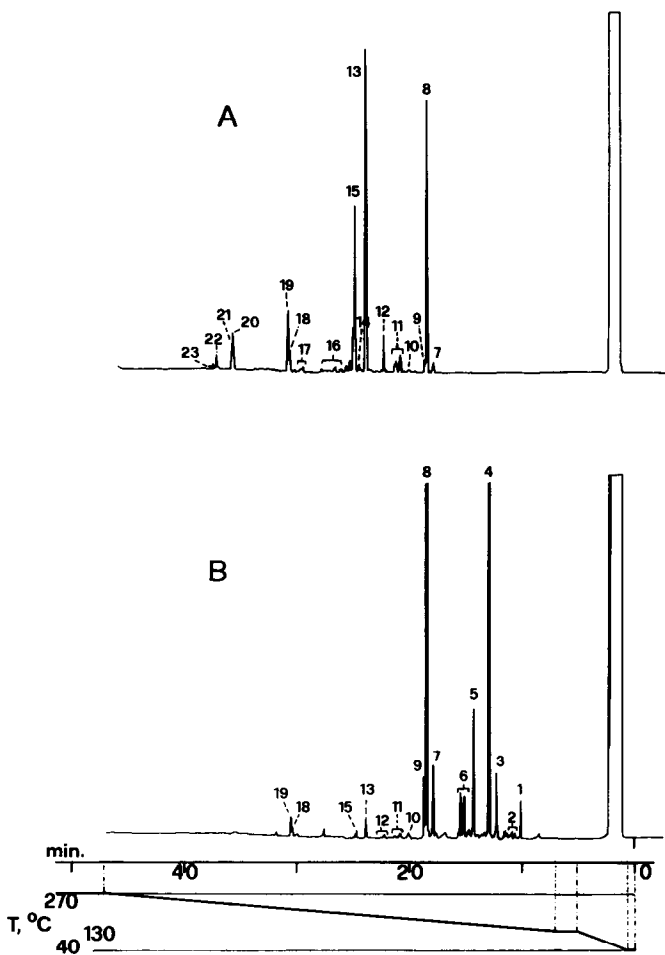


Fig. 9. GC separations of PAHs emitted from the same industrial plant as that in Fig. 8. (a) PAHs extracted from the filter; (b) PAHs extracted from the Carboxpack B trap, placed after the filter. 1 = 1,1'-Biphenyl; 2 = dimethylnaphthalenes; 3 = acenaphthene; 4 = dibenzofuran; 5 = 9H-fluorene; 6 = methyl dibenzofurans; 7 = dibenzothiophene; 8 = phenanthrene; 9 = anthracene; 10 = phenylnaphthalene; 11 = methylphenanthrenes/anthracenes; 12 = phenylnaphthalene; 13 = fluoranthene; 14 = benzo[def]dibenzothiophene; 15 = pyrene; 16 = methylfluoranthenes/pyrenes; 17 = benzonaphthothiophenes; 18 = benz[a]anthracene; 19 = chrysene; 20 = benzo[k]fluoranthene; 21 = benzo[b]fluoranthene; 22 = benzo[e]pyrene; 23 = benzo[a]pyrene.

concurrently with the sampling of particulate matter was believed to be necessary for an accurate evaluation of the total amount of PAHs released into the environment.

Fig. 8a and b show the HPLC profiles obtained by analysis of the soluble organic fraction extracted from the particulate matter and Carbopack B trap, respectively. The chromatogram in Fig. 8b has been scaled down by injecting a smaller aliquot of the extract, because the amount of PAHs in the adsorbent was five times greater than that found in the filter. A comparison between these two chromatograms reveals that, when the trapping material was not placed in series with the filter, neither the total amount nor the actual composition of the emission could be measured. The advantage of using Carbopack B instead of impingers filled with organic solvents was shown by sampling the same emission in parallel. Only a minor portion of these compounds was found in the solvent used for collecting PAHs, so that the total emission measured with this method was between three and four times smaller than that determined by using the solid adsorbent.

Fig. 9a and b show the GC profiles of the PAH fraction present in the dust sample and in the Carbopack B trap, respectively. A comparison between the distribution of the PAHs in the solid and in the vapour phase gives a good clue to the volatilization process and confirms the usefulness of the technique described. As only very small amounts of PAHs were found in the water condensed past the trap, it was concluded that the carbon trap was able to retain up to 2 mg of PAHs, which was present in 1 m<sup>3</sup> sample. It must be stressed that the surface features of Carbopack B were completely restored after the extraction, in spite of the fact that substantial amounts of water, NO<sub>2</sub> and SO<sub>2</sub> had passed through the adsorbent and that the material could be used for further sampling.

The last application of Carbopack B traps relates to the determination of volatile nitro-PAHs emitted from a diesel exhaust. The importance of this determination is related to the fact that these compounds are known to act as direct mutagens in

TABLE II  
NITRO-PAH CONTENT IN A DIESEL EXHAUST EMISSION

No.	Compound	Particulate matter ( $\mu\text{g/g}$ )	Volatiles* ( $\mu\text{g/N m}^3$ )
1	1-Nitronaphthalene	2	0.2
2	<i>x</i> -Methyl-1-nitronaphthalene	5	0.4
3	2-Nitronaphthalene	3	0.8
4	<i>x</i> -Nitrofluorene	1	2
5	2-Nitrofluorene	1	1.5
6	9-Nitroanthracene	4	0.7
7	<i>x</i> -Nitroanthracene	2	0.4
8	Dinitronaphthalenes	1	0.4
9	Dimethylnitronaphthalenes	0.5	—
10	1-Nitropyrene	20	—
11	2,7-Dinitrofluorene	0.3	—
12	Methylnitropyrenes	1	—
13	<i>x</i> -Nitrobenzo[ <i>a</i> ]pyrene	0.2	—
14	<i>x,y</i> -Dinitropyrene	0.3	—

\* These compounds were sampled on the Carbopack B trap.



the Ames assay. Here also it is important to provide evidence that such emissions contain large amounts of NO<sub>2</sub>, water and CO, and that detectable amounts of HNO<sub>3</sub> are also present.

In order to establish the extent to which nitro-PAHs can be volatilized from the filter, we sampled the particulate matter by the same procedure as that followed for determining industrial emissions. The concentrates of the two extracts were fractionated according to the procedure described previously<sup>1,2</sup>, and the eluates containing nitro-PAHs were subjected to GC analysis using a nitrogen-phosphorus specific detector. The results of this investigation are reported in Table II. Considering that *ca.* 50 mg of particulate matter are present in 1 m<sup>3</sup> of exhaust, the amount of nitro-PAHs found in the trap cannot be neglected if the total content of nitrated organics is to be determined accurately. Although the components found in the adsorbent are not likely to act as strong direct mutagens, this portion of nitro-PAHs should be added to that extracted from the particulate matter when samples are submitted for microbiological tests. We would like to reiterate here that the analysis of diesel emissions represents a severe test for the adsorbent and the fact that no high-molecular-weight components were found in the trap can be taken as measure of the chemical stability of Carbopack B and its suitability for this type of determination.

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#### REFERENCES

- 1 W. Bertsch, T. C. Chang and A. Zlatkis, *J. Chromatogr. Sci.*, 12 (1974) 175.
- 2 B. Versino, M. de Groot and F. Geiss, *Chromatographia*, 7 (1974) 302.
- 3 E. D. Pellizzari, J. E. Bunch, R. E. Berkley and J. McRae, *Anal. Chem.*, 48 (1976) 83.
- 4 R. Perry and J. D. Twibell, *Atmos. Environ.*, 7 (1973) 929.
- 5 S. Van Tassel, N. Amalfitano and R. Singh Narang, *Anal. Chem.*, 53 (1981) 2130.
- 6 A. Raymond and G. Guiochon, *Environ. Sci. Technol.*, 8 (1974) 143.
- 7 P. Ciccioi, G. Berton, E. Brancaleoni, R. Fratarcangeli and F. Bruner, *J. Chromatogr.*, 126 (1976) 757.
- 8 H. Knoepfel, B. Versino, H. Schlitt, A. Peil, H. Schauenburg and H. Vissers, in B. Versino and H. Ott (Editors), *Proceedings of the First European Symposium on the Physico-Chemical Behaviour of the Atmospheric Pollutants, Ispra, 16-18 October, 1979*, CEC, Brussels, 1980, p. 25.
- 9 P. Ciccioi, E. Brancaleoni, M. Possanzini, A. Brachetti and C. Di Palo, in B. Versino and G. Angeletti (Editors), *Proceedings of the Third European Symposium on the Physico-chemical Behaviour of Atmospheric Pollutants, Varese, 10-12 April, 1984*, Reidel, Dordrecht, 1984, p. 62.
- 10 E. D. Pellizzari and K. J. Krost, *Anal. Chem.*, 56 (1984) 1813.
- 11 K. J. Krost, E. D. Pellizzari, S. G. Walburn and S. A. Hubbard, *Anal. Chem.*, 54 (1982) 810.
- 12 A. Liberti, P. Ciccioi, A. Cecinato, E. Brancaleoni and C. Di Palo, *J. High Resolut. Chromatogr. Chromatogr. Commun.*, 7 (1984) 389.
- 13 P. Ciccioi, R. Tappa, A. Di Corcia and A. Liberti, *J. Chromatogr.*, 206 (1981) 35.
- 14 P. Ciccioi and R. Tappa, *J. Chromatogr.*, 269 (1983) 47.