Novel family of multi-layer cartridges filled with a new carbon adsorbent for the quantitative determination of volatile organic compounds in the atmosphere

Enzo Brancaleoni[a],*, Mirco Scovaventi[b], Massimiliano Frattoni[a], Rosanna Mabilia[a], Paolo Ciccioli[a]

[a]*Istituto sull'Inquinamento Atmosferico del CNR, Area della Ricerca di Roma, Via Salaria km 29.300, C.P. 10-00016 Monterotondo Scalo, Italy*
[b]*Centro Tecnico Chimico Fisico e Biologico dell'Esercito Italiano, S.S. Braccianese Claudia km 67,300, 00053 Civitavecchia, Italy*

Abstract

The ability of a new graphitized carbon black adsorbent (Carbograph 5) to retain volatile organic compounds (VOCs) in air has been investigated through laboratory experiments performed by frontal chromatography. An artificial mixture containing 19 different compounds from C_1 to C_7 at levels of 50 ppb (v/v) each was used as eluent. The amounts of VOCs retained by Carbograph 5 were determined by high-resolution GC–flame ionization detection after thermal desorption at 250°C. The retention features of this adsorbent were compared with those provided by Carbograph 1 and Carbograph 2, two graphitic carbons equivalent in specific surface area and adsorption properties to Carbopack B and Carbopack C, respectively. It was found that Carbograph 5 exhibits safe sampling volumes of VOCs much higher than those of Carbograph 1 and is the only hydrophobic material providing performances comparable to those of some molecular sieve adsorbents. Results obtained indicate that Carbograph 5 can be used alone or in combination with other materials. When combined with lighter adsorbents, it allows the quantitative collection of polar and non-polar VOCs with carbon number higher than 3 in air volumes larger than 5 l at any relative humidity. In combination with stronger carbon molecular sieve adsorbents, it makes possible the quantitative collection of components with volatilities ranging from C_2 to C_7 in small samples. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The content of volatile organic compounds (VOCs) in air is considered a fundamental parameter for assessing the quality of the atmosphere because some compounds are acting as precursors of photochemical smog formation [1,2] whereas others represent a potential threat to human health. In addition to

this, some specific components can contribute to global change, by depleting the stratospheric ozone (such as chlorofluorocarbons) [1,3], and/or to the radiative forcing of the earth (such as methane, chlorofluorocarbons and dimethylsulfide) [1,4].

Due to the complexity of VOC composition in the atmosphere [5], the low levels to be detected [from ppb (v/v) (ppbv) down to ppt (v/v) (pptv)] [6] and the specific task for which monitoring of VOCs is required [1], different sampling and analytical strate-

*Corresponding author.

gies have been developed and applied for the identification and quantification of VOCs in air [7]. With few exceptions, sample enrichment is needed in order to meet the sensitivity of the detection systems presently available. However, different sampling and analytical methods are necessary to cover the full range of VOCs released or formed in air [1,7].

If very volatile VOCs (i.e. compounds with vapor pressure higher than ca. 15 kPa) need to determined, sampling is usually performed on passivated canisters [8,9]. Since this system does not provide sample preconcentration, VOCs must be concentrated prior to being analyzed by capillary GC. Usually, this step is performed by refocusing the sample on micro-traps filled with light adsorbents kept at ca. $-180°C$ [10–13]. Cryogenic cooling is also needed if sampling of very volatile VOCs is performed with traps filled with solid sorbents. Good recoveries of components from C_2 to C_7 were indeed reported when cartridges were maintained at temperatures ranging from $+5$ to $-15°C$ [13–15]. Whichever the sampling approach is, water condensation limits the collected volume to 0.2–0.5 l when the relative humidity of the atmosphere exceeds 70%. Although dehydrating agents have been used to make possible the collection of large volumes of air any relative humidity, these devices are not free from artifacts. Selective losses of VOCs have been reported with magnesium perchlorate [16] and potassium carbonate [17] whereas sample contamination [17,18] and selective removal of VOCs [19,20] have been observed with Nafion tubes.

Water condensation problems can be prevented by sampling VOCs on traps filled with hydrophobic materials kept at room temperature [7,13,20–23]. Since a single adsorbent is unable to efficiently collect a wide volatility range of VOCs [24], multi-layer traps filled with different combinations of hydrophobic materials have been proposed for collecting VOCs at any relative humidity. Among them, those based on graphitic carbons and poly-2,6-diphenyleneoxide porous polymers (Tenax polymers) are the most widely used [7,22]. Since both adsorbents are thermally stable and essentially non-specific, a quantitative release of polar and non-polar components up to 20 carbon atoms is obtained by heating the trap at 250°C. These features, combined with the low mass of artifacts provided by these

adsorbents [7], explain why multi-layer tubes filled with graphitized Tenax (Tenax-GR) and Carbopack B set in series are recommended by the US Environmental Protection Agency (EPA) (Method TO-17) for the sampling of VOCs at any relative humidity [25]. Similar performances are provided by traps filled with combinations of Carbopack C and Carbopack B [20,26–27]. In combination with mass spectrometry [26], this last method has made possible the identification of more than 350 different components in tropospheric samples collected worldwide [5,26]. Since in both cases the strongest trapping material used is, however, Carbopack B, the range of VOCs that can be determined in 2 l samples is restricted to components with carbon number higher than ca. 5 [25]. Quantification of some important compounds potentially toxic to man (such as 1,3-butadiene) or relevant to tropospheric ozone formation (such as isoprene, methacrolein and methylvinyl ketone) is possible with these methods only when their aerometric concentrations are sufficiently high that volumes equal or smaller than 0.5 l are sufficient for the analysis [5,15]. According to the EPA [25], it is also possible to determine VOCs ranging in volatility from C_3 to C_{12} in 2 l samples. Since these methods involve the use of hydrophilic materials, their application is limited to samples with relative humidity lower than 65%.

To widen the range of VOCs that can be determined at any relative humidity and simplify the sampling of very volatile VOCs at ambient temperature, the adsorption features of a new graphitized carbon black material characterized by a surface area 5 times higher than Carbopack B were investigated for the first time. Based on the results obtained, it has been possible to design multi-layer traps suitable the determination of polar and non-polar VOCs with carbon number higher than 3 in 5 l samples at any relative humidity. Traps containing Carbograph 5 are also proposed for the collection of very volatile VOCs at ambient temperature.

2. Experimental

2.1. Trapping materials and trap geometry

The materials used in our investigation were

Carbograph 1, Carbograph 2, Carbograph 5 and Carbosieve S III. The former three adsorbents were all supplied by Lara (Rome, Italy) in particles having a size ranging between 20 and 40 mesh and they were characterized by a specific surface area of 90, 12 and 560 m^2 g^{-1}, respectively. The corresponding bulk densities were 0.422, 0.840 and 0.407 g ml^{-1}. They can be all classified as non-porous, non-specific, graphitized carbon blacks belonging to Class I of the scheme proposed by Matisova and Skrabakova [22]. Comparative studies [28] have shown that Carbograph 1 and Carbograph 2 exhibit retention properties quite similar to materials produced by Supelco (Bellefonte, PA, USA). In particular, Carbograph 1 can be considered equivalent to Carbopack B whereas Carbograph 2 can be considered equivalent to Carbopack C. Carbosieve S III, a carbon molecular sieve adsorbent characterized by a surface area of 800 m^2 g^{-1}, was instead supplied by Supelco in particles ranging between 40 and 60 mesh.

Adsorbents used were placed in glass tubes 16 cm long characterized by an external diameter of 6 mm and an internal diameter of 3 mm. This geometry was selected to enable the release of VOCs with the thermal-desorption cold trap (TCT) injector system available from Chrompack (Middleburg, Netherlands). It was also compatible, however, with the desorption unit built in our laboratory. Quartz wool was used to keep in place the adsorbents inside the tube. Before the use, traps were all cleaned at 300°C under a flow rate of helium (100 ml min^{-1}). They were purged for 10 min at least. After cleaning, they were closed with tight connectors and stored in large (10 l) sealed glass containers according to the procedure described in Ref. [19].

2.2. Analytical procedure for the determination of the safe sampling volume (SSV) of hydrocarbons from C_2 to C_7 and for the quantification of very volatile VOCs in air samples

A cylinder of artificial air containing 19 components from C_1 to C_7 at levels of 50 ppbv each was used as eluant in the frontal chromatography experiments aimed at determining the SSVs on different graphitized carbon black adsorbents. The pressurized standard mixture (100 kg cm^{-2}) was supplied by Siad (Bergamo, Italy). The content and purity of the mixture were controlled with the methodology described in Ref. [12].

The standard mixture was passed through the cartridges at a flow rate of 200 ml min^{-1}. Amounts retained were determined by thermal desorption using a laboratory-made unit [12]. It was coupled to a Fractovap 4160 gas chromatograph (Carlo Erba, Milan, Italy) through a four-way valve. The inlet of the chromatographic apparatus was equipped with a cryofocusing injection system consisting of a microtrap filled with 0.005 g of Carbotrap from Supelco to allow the analysis of VOCs by capillary GC [12]. By switching the four-way valve, traps were connected to the cryofocusing system kept at −150°C. VOCs, released by heating the traps at a rate of 30°C min^{-1}, were transferred into the cryofocusing unit by using a flow rate of He of 15 ml min^{-1}. Complete desorption of VOCs from graphitic carbons was achieved by setting the final temperature of the furnace at 250°C. With traps containing Carbosieve S III, a final temperature of 280°C was, instead, necessary. Injection of VOCs into the GC column was accomplished by rising the temperature of the microtrap from −150°C to 200°C in 3 min.

Desorbed compounds were analyzed on a 50 m× 0.53 mm I.D. capillary column internally coated with Al_2O_3 and Na_2SO_4 supplied by Chrompack. The flow rate of the carrier gas (helium) was 0.3 ml min^{-1}. After sample injection, the column temperature was kept at 60°C for 3 min and then increased at a rate of 3°C min^{-1} until a final temperature of 200°C was reached. The final temperature was maintained for 30 min. Detection was accomplished by flame ionization detection (FID). Since the column used separates all alkanes, alkenes, alkynes and arenes from C_2 to C_9 but completely retains all polar components [12], the analytical procedure described above was also used for the determination of very volatile VOCs sampled on traps filled with Carbotrap 5 and Carbosieve S III.

2.3. Analytical procedure for the analysis of polar and non-polar VOCs on multi-layer traps filled with hydrophobic adsorbents

For the analysis of VOCs sampled on traps filled

with hydrophobic adsorbents a different analytical procedure was adopted. To allow the identification and quantification of polar and non-polar components, the sample was injected into a 50 m×0.32 mm I.D. capillary column coated with a thin film (0.40 μm) of CP-Sil-5 CB-MS supplied by Chrompack. The column was connected to a Hewlett-Packard (Palo Alto, CA, USA) gas chromatograph (model 5890) coupled to a 5970B mass selective detector provided by the same company. Thermal desorption was carried out with the TCT unit supplied by Chrompack. With this system, VOCs released by heating the traps at 250°C were cryofocused in an empty liner kept at −180°C. They were injected into the analytical column by rising the temperature of the liner from −180 to 200°C at a rate of 15°C s^{-1}. To optimize the separation of VOCs, the column was maintained at 0°C for 3 min after the injection and then the temperature raised to 50°C at a rate of 3°C min^{-1}. From 50 to 220°C the temperature was increased at a rate of 5°C min^{-1}. The final temperature was maintained for 30 min.

The MSD unit was operated in the scan mode by collecting all ions ranging from m/z 20 to 200. When possible, the identification of components was performed by analyzing the entire spectrum. For co-eluted components or species present at trace levels, positive identification was achieved by combining retention index and reconstructed mass chromatogram information. Selective ions and time sequences used for positive identification of VOCs can be found in Ref. [26].

Quantification of individual components by mass-spectrometry was achieved with different methods. Isoprene was exactly quantified by using a standard gaseous mixture containing 2.98 ppbv of this component. Eleven independent laboratories using different sampling and analytical techniques certified the pressured mixture, supplied by the National Physical Laboratory (Teddington, Middlesex, UK) within the frame of a European Intercalibration Project on VOCs called AMOHA. Monoterpenes and the most abundant semi-volatile carbonyls were quantified by using diffusion tubes and liquid standard solutions according to the procedure described by Larsen et al. [27]. Traps containing liquid standards were analyzed after removing the solvent with 2 l of clean air.

3. Results and discussion

3.1. SSVs of VOCs on Carbograph 5

As a first approach, the ability of Carbograph 5 to retain VOCs more strongly than the other two graphitized carbon black adsorbents tested was investigated. Preliminary experiments were conducted by passing equal volumes (1 l) of the standard solution of VOCs from C_1 to C_7 through traps completely filled with Carbograph 1, Carbograph 2 and Carbograph 5. The amounts of VOCs retained by each adsorbent were determined by high-resolution (HR) GC–FID after thermal desorption at 250°C. While the comparison with Carbograph 1 was useful to evaluate the retention features of Carbograph 5, the comparative study with the lighter adsorbent (Carbograph 2) served to test the ability of Carbograph 5 to completely release adsorbed compounds at 250°C and to verify the consistency of data obtained with previous studies [20,28].

The largest volume of adsorbent that was compatible with the heating zone of the TCT unit was used for these experiments. By considering that this zone was 10 cm long and 2 cm of the trap were occupied by quartz wool, the portion of the tube containing the adsorbent was 8 cm. This length corresponded to a volume of 0.56 ml, a value quite close to that typically used in tubes supplied by commercial companies. Due to the constraints posed by the desorption system, results obtained on a volume basis were considered more useful than those obtained on a weight basis for comparing the maximum performances provided by materials characterized by different bulk densities and specific surface areas.

Experiments were performed in frontal chromatography as this approach provides more realistic indications than pulsed injection on the trapping capabilities of the various materials under atmospheric condition [29]. Although the concentrations present in the mixture (50 ppbv for each component) were suitable for simulating very polluted situations, data obtained could also be applied to remote and rural areas as it has been shown that retention of VOCs slightly increases by decreasing their concentration in air [29–31].

The results of repeated experiments carried out on

three independent traps for each adsorbent tested are summarized in Fig. 1. Data reported clearly indicate that Carbograph 5 is much more efficient than other graphitized adsorbents in the collection of VOCs. It is able to completely retain 14 of the 19 components present in the standard mixture. The list includes quite volatile components (such as butanes, butenes, pentanes and pentenes) that are completely or partly lost on traps filled with the Carbograph 1 or Carbograph 2. The percent retention of propane and propene (31 and 40%, respectively) is also very interesting as it suggests that quantitative collection of these components can be achieved with air volumes smaller than ca. 0.3 l.

To more precisely assess the adsorption features of Carbograph 5, SSVs of VOCs present in the standard mixtures were determined. The percent of each component retained by the trap was measured by passing increasing volumes of the mixture though the adsorbent. The maximum volume for which the percent retention was higher, within the experimental errors ($\pm$ 4%), than 99% was taken as the SSV. Data were collected for volumes of Carbograph 5 ranging from 0.14 to 0.56 ml. Similar experiments were carried with Carbograph 1 in order to evaluate what fraction of Carbograph 5 was able to provide a retention equivalent to that of cartridges completely filled with Carbograph 1. As an example of the procedure used, we have reported in Fig. 2(a and b) the percent retention of propane that was measured when increasing volumes of the hydrocarbon mixture where passed through traps filled with different amounts of Carbograph 5 and Carbograph 1, respectively. The SSVs of 18 hydrocarbons for different amounts of Carbograph 5 and Carbograph 1 are shown, instead, in Tables 1 and 2, respectively. Data reported in these Tables suggest that traps containing 230 mg of Carbograph 5 were able to retain all VOCs above C_3 on 5 l samples and their collection efficiency was better to that provided by a 65 cm column filled with 1887 mg of Carbograph 1. By considering that traps filled with 0.56 ml of Carbograph 1 and Carbograph 5 were characterized by total carbon surfaces available for the adsorption of 21 and 129 m^2, respectively, the actual retention of Carbograph 5 measured by frontal chromatography was much higher ($>$30%) than that derived from

theoretical considerations based on the specific surface areas of the adsorbents investigated. This large deviation from theoretical expectations suggested that deactivation of the carbon surface caused by adsorbed molecules played an important role in determining the SSVs of Carbograph 1. Since in frontal chromatography the degree of coverage of the carbon surface is strictly related to the concentration of the material present in the eluent, additional experiments were performed to check how a substantial dilution of the hydrocarbon mixture would have affected the retention properties of Carbograph 5. The results obtained by passing hydrocarbon mixtures at different concentrations through cartridges containing 115 mg of Carbograph 5 are shown in Fig. 3. Data reported refer to total volumes of 10 l. They show that substantial increases in retention where observed for those VOCs whose break though volume was close to 10 l and complete recovery of these components could be achieved for volumes comprised between 5 and 10 l when diluted samples were collected. However, increments observed were not large enough to substantially widen the range of VOCs retained by Carbograph 5.

3.2. Practical applications of traps containing Carbograph 5 for the enrichment of VOCs in air

Data reported in Table 1 and Fig. 3 clearly indicate that Carbograph 5 is suitable for collecting VOCs in urban, suburban and remote areas. The range of volatility that can be covered is, however, quite limited as traps filled with 230 mg of adsorbents make it possible to quantify all components ranging in volatility from C_4 to C_7 in 5 l air samples. It is only possible to extend the range of VOCs to components with 3 carbon atoms by drastically decreasing the sampled volume to 0.2 l. Basically, the retention provided by Carbograph 5 is comparable to that of carbon molecular sieve adsorbents (e.g. Carboxen 563, Carboxen 564 and Carboxen 569) characterized by similar values of the specific surface area [22]. It is definitely lower, however, than that afforded by Carbosieve S III or Spherocarb. With respect to hydrophilic adsorbents with comparable specific surface areas, Carbograph 5 offers the advantage, however, that water condensation is
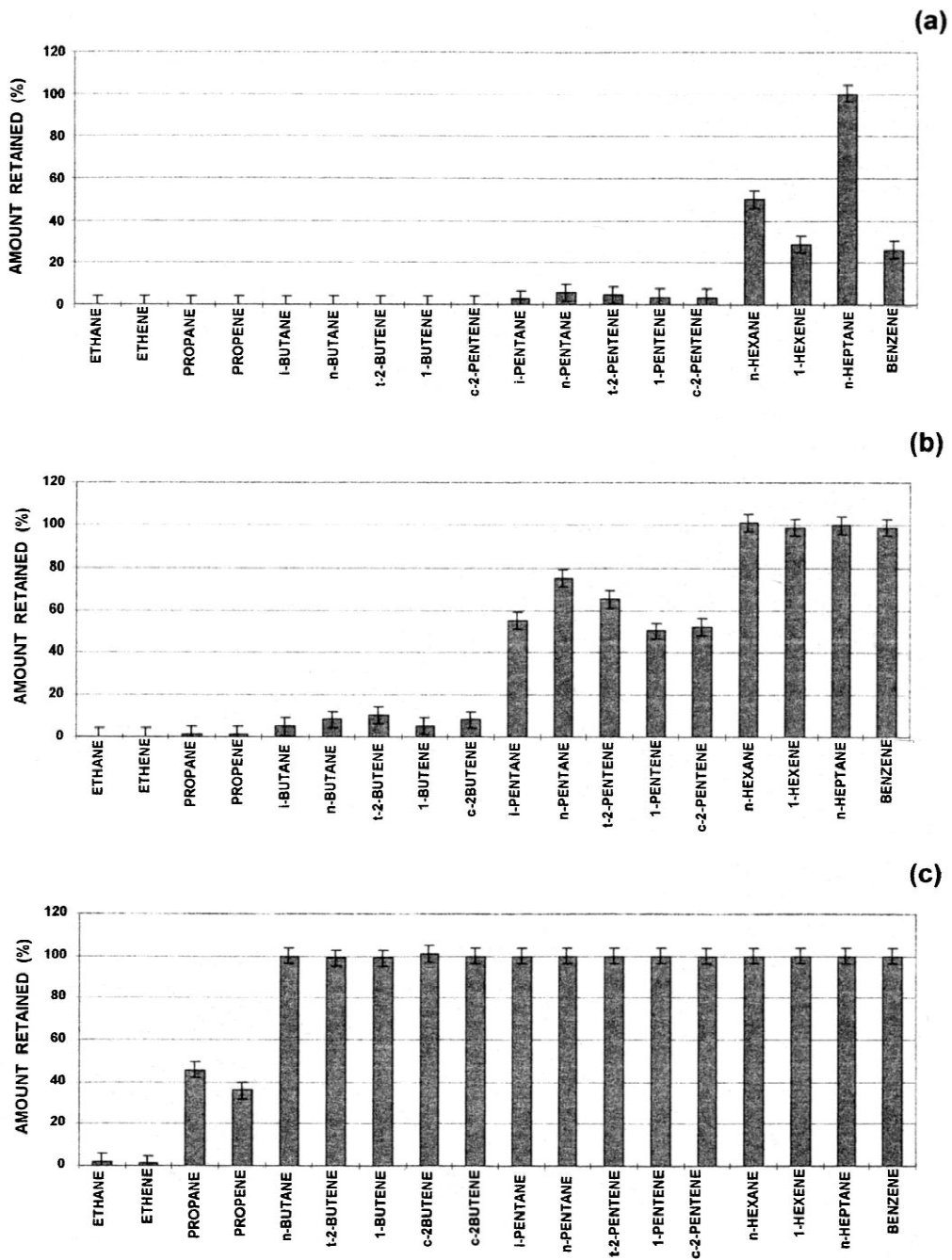
Fig. 1. Percent amount of individual VOCs from C_2 to C_7 that were retained on 8 cm traps filled with 0.56 ml of (a) Carbograph 2, (b) Carbograph 1 and (c) Carbograph 5 when 1 l of the hydrocarbon mixture was passed through the them.
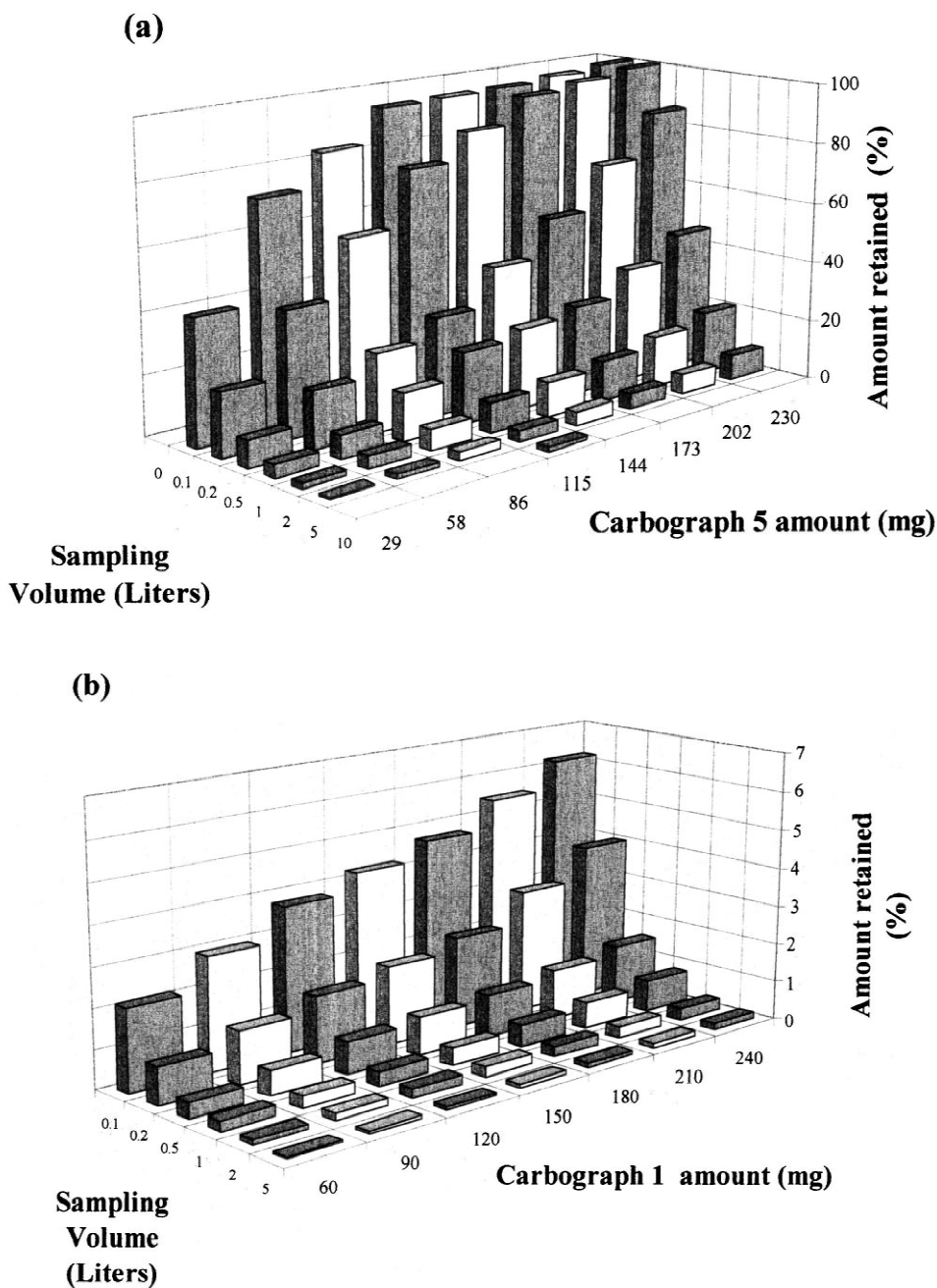
(a)

(b)

Fig. 2. Percent retention of propane measured when increasing volumes of the air mixture were passed through traps filled with different amounts Carbograph 5 (a) and Carbograph 1 (b).

prevented and sampling can be performed at any relative humidity.

Based on these considerations, the features of Carbograph 5 can be better exploited by combining this adsorbent with other hydrophobic materials, such as Carbopack B and Carbopack C (or materials

Table 1
Safe Sampling Volume (SSV) values (liters) of different hydro-carbons measured on increasing volumes of Carbograph 5 in the traps. The average error in the SSVs was ±0.5% of the sampled volume

Amount (mg)	29	58	115	173	230
Volume (ml)	0.07	0.14	0.28	0.42	0.56
Length of the trap (cm)	1	2	4	6	8
Compound					
Ethane	<0.1	<0.1	<0.1	<0.1	<0.1
Ethene	<0.1	<0.1	<0.1	<0.1	<0.1
Propane	<0.1	<0.1	<0.1	<0.1	0.2
Propene	<0.1	<0.1	0.1	0.1	0.2
Isobutane	0.5	1	2	>5	>5
n-Butane	1	1	5	>5	>5
trans-2-Butene	1	2	5	>5	>5
1-Butene	1	1	2	>5	>5
cis-2-Butene	1	1	5	>5	>5
iso-Pentane	>5	>5	>10	>10	>10
n-Pentane	>5	>5	>10	>10	>10
trans-2-Pentene	>5	>5	>10	>10	>10
1-Pentene	>5	>5	>10	>10	>10
cis-2-Pentene	>5	>5	>10	>10	>10
n-Hexane	>5	>5	>10	>10	>10
1-Hexane	>5	>5	>10	>10	>10
n-Heptane	>5	>5	>10	>10	>10
Benzene	>5	>5	>10	>10	>10

Table 2
Safe Sampling Volume (SSV) values (liters) of different hydro-carbons measured on increasing volumes of Carbograph 1 in the traps. The average error in the SSVs was ±0.5% of the sampled volume

Amount (mg)	60	119	179	238
Volume (ml)	0.14	0.28	0.42	0.56
Length of the trap (cm)	2	4	6	8
Compound				
Ethane	<0.1	<0.1	<0.1	<0.1
Ethene	<0.1	<0.1	<0.1	<0.1
Propane	<0.1	<0.1	<0.1	<0.1
Propene	<0.1	<0.1	<0.1	<0.1
Isobutane	<0.1	<0.1	<0.1	<0.1
n-Butane	<0.1	<0.1	<0.1	<0.1
trans-2-Butene	<0.1	<0.1	<0.1	<0.1
1-Butene	<0.1	<0.1	<0.1	<0.1
cis-2-Butene	<0.1	<0.1	<0.1	<0.1
iso-Pentane	<0.1	0.1	0.1	0.2
n-Pentane	0.1	0.2	0.2	0.5
trans-2-Pentene	<0.1	<0.1	0.2	0.2
1-Pentene	<0.1	<0.1	0.2	0.2
cis-2-Pentene	<0.1	<0.1	0.1	0.2
n-Hexane	2	>5	>5	>5
1-Hexane	2	>5	>5	>5
n-Heptane	>5	>5	>5	>5
Benzene	1	2	2	>5

equivalent to them). With respect to existing methods, traps containing suitable amounts of Carbograph 5 make it possible, indeed, to widen the range of components that can be determined at any relative humidity and to achieve higher sensitivities. To optimize the distribution of VOCs with different volatilities among the various adsorbents used, traps containing 118 mg of Carbograph 2, 60 mg of Carbograph 1 and 115 mg of Carbograph 5 were tested. This arrangement was selected to ensure that compounds with volatities ranging from C_7 to C_{10} were retained by Carbograph 1 whereas those with volatilities ranging from C_4 to C_7 were adsorbed on Carbograph 5 when samples of 5 l were collected. The role of Carbograph 2 was to prevent that semi-volatile VOCs reached Carbograph 1. This distribution of VOCs among the various graphitic adsorbents used ensured also the complete recovery of compounds from C_4 to C_{20} at 250°C. Laboratory experiments performed with gaseous and liquid standard mixtures showed that the only effect produced by

sampling 10 l of air through multi-layer traps filled with Carbograph 2, Carbograph 1 and Carbograph 5 was the partial loss of C_4 components.

This type of traps were tested in the field for one month to check if their performances were definitely superior to those provided by cartridges filled with combinations of Carbopack B and Carbopack C. Sampling was carried out in a holm oak (*Quercus ilex* L.) forest located inside the presidential estate of Castelporziano near Rome. The site, not far from the seashore, was particularly suitable for testing the ability of multi-layer traps to collect both polar and non-polar VOCs of different origin in humid samples. Data collected in previous investigations have definitely established that levels of VOCs in this site were one order of magnitude lower than those occurring the suburban area of Rome [5,32] and the composition was dominated by aldehydes from C_2 to C_{10}, 6-methyl-5-heptene-2-one, arenes and mono-terpene compounds [32]. They also suggested that emission from local pines (*Pinus pinea* L.) and oaks (*Quercus ilex* L.) was the main source of mono-
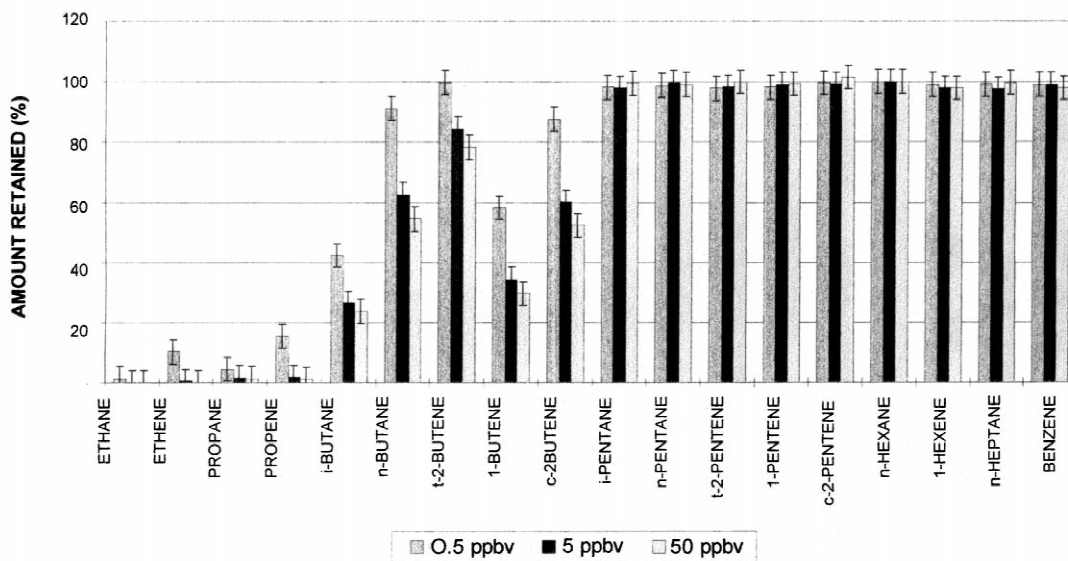
Fig. 3. Effect on the percent amount of VOCs retained on Carbograph 5 as a function of the concentration of the air mixture used as eluant. The volume passed through the cartridge was 10 l. The amount of carbon was in the trap was 115 mg.

terpenes in air [33] whereas transport from the city of Rome under land-breeze conditions accounted for the presence of anthropogenic VOCs [34]. These investigations were unable to assess, however, if and to what extent soil vegetation releasing isoprene was contributing to the whole biogenic emission from forested areas. Since the lack of detection of isoprene in air was mainly due to the low sensitivity afforded by existing methods, 10 l samples were collected on multi-layer filled with Carbograph 5. Sampling was performed 2 m above the canopy of the holm oak forest. Traps were collected 5 times a week for one month. More than 20 cartridges were analyzed and parallel sampling with traps containing Carbopack B and Carbopack C was performed in many instances. Fig. 4a reports an example of the total ion current profile obtained by submitting to GC–MS determination a sample collected on multi-layer traps containing Carbograph 2, Carbograph 1 and Carbograph 5. Results of parallel sampling showed that GC–MS profiles and aerometric concentrations obtained with combinations of Carbopack B and Carbopack C were, within an experimental error of ±5%, the same as those obtained with traps containing Carbograph 5 for compounds with volatilities larger than C_5 (for comparison see the caption of Fig. 4a). These field experiments confirmed that traps containing Carbograph 5 were able to release polar components present in forest and remote areas with the same efficiency as recommended methods. They offered the unique advantage, however, to quantitatively retain isoprene in large air volumes thus allowing its quantification at pptv levels. The presence of this biogenic component in our samples was unambiguously assessed by the presence in the chromatogram of a peak characterized by the same retention index (503.6) and fragmentation pattern of isoprene [26]. In particular, it was checked that the areas of mass-chromatographic peaks generated by plotting the fragments with m/z 68, 53 and 39 provided, within an experimental error of ±3%, the correct ratio relatively to the area of the mass chromatographic peak generated by the ion with m/z 67 (64, 78 and 92%, respectively). The exact position of isoprene in the chromatogram and the intensity of the peak produced by the concentration present in the sample (50 pptv) is shown in Fig. 4b where the selected ion profile obtained with the fragment m/z 67 is shown. By using multi-layer traps containing Carbograph 5 it was possible to definitely assess that emission from soil vegetation did not substantially contribute to the whole biogenic emission of the holm oak forest. This
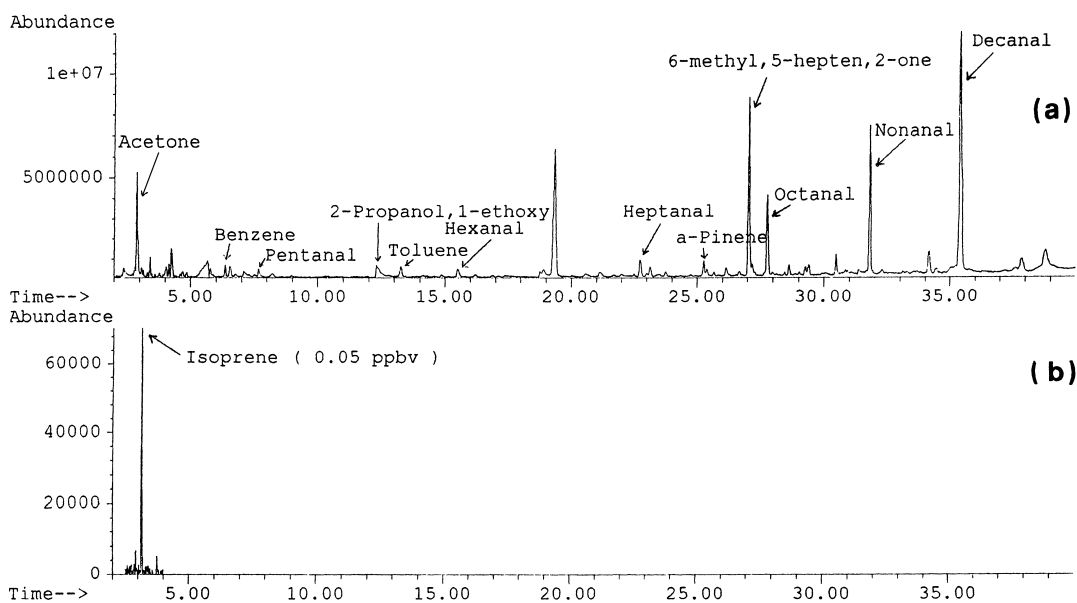
Fig. 4. (a) Total ion current GC–MS profile of a 10 l air sample collected over the canopy of the holm oak forest of Castelporziano (Rome, Italy). The trap used was filled with 118 mg of Carbograph 2, 60 mg of Carbograph 1 and 115 mg of Carbograph 5 set in series. The main components are indicated in the mass-chromatogram. The levels measured were: benzene (0.11 ppbv, +1%), toluene (0.17 ppbv, +1%), nonanal (0.52 ppbv, −2%), decanal (0.93 ppbv, +3%), 6-methyl-5-heptene-2-one (0.73 ppbv, +4%), α-pinene (0.06 ppbv, +2%). The number following the value of the mixing ratio represented the deviation from the concentrations determined with parallel sampling performed on multi-layer traps filled with 76 mg Carbopack C and 180 mg Carbopack B. (b) Selected ion profile recorded at 67 m/z showing the presence of 50 pptv of isoprene.

was probably due to the limited penetration of sunlight through the canopy and the lower temperatures experienced by the leaves.

Data reported in Table 1 and Fig. 3 indicate also that Carbograph 5 could have also been used for the collection of very volatile components at ambient temperature if combined with stronger adsorbents able to retain compounds with volatility ranging from C_2 to C_3. To explore this possibility, multi-layer traps containing 57 mg of Carbograph 5 and 285 mg of Carbosieve S III were tested. Although, in principle, such a combination was suitable for sampling quite large volumes of air, water condensation problems and poor recovery of VOCs from Carbosieve S III drastically limited the size of the sample available to the analysis. Tests carried out by passing increasing volumes of the hydrocarbon mixture from C_1 to C_7 through traps filled with Carbosieve S III showed that recoveries lower than 80% were obtained for unsaturated components with carbon number equal or higher than 4 when the

sampling volume exceeded 0.2 l. Since this volume was not much different, however, from that necessary (0.25 l) for quantifying VOCs from C_2 to C_7 with passivated canisters, traps containing Carbograph 5 and Carbosieve S III were considered a possible alternative for sampling very volatile VOCs in air. With respect to canisters, traps are, indeed, easier to handle and less prone to contamination. In addition to this, they do not require expensive apparatuses for sample collection and cleaning. Due to limited volume required, sampling can be simply performed by using glass syringes of 250 ml.

Tests carried out on samples circulated during the intercalibration exercise carried out within the frame of the AMOHA project showed that results obtained with traps containing Carbograph 5 and Carbosieve S III provided results quite consistent with direct analysis. For most of the components present in the mixture deviations from canister values never exceeded ±5%. Based on these results, additional tests were performed by collecting samples in the urban
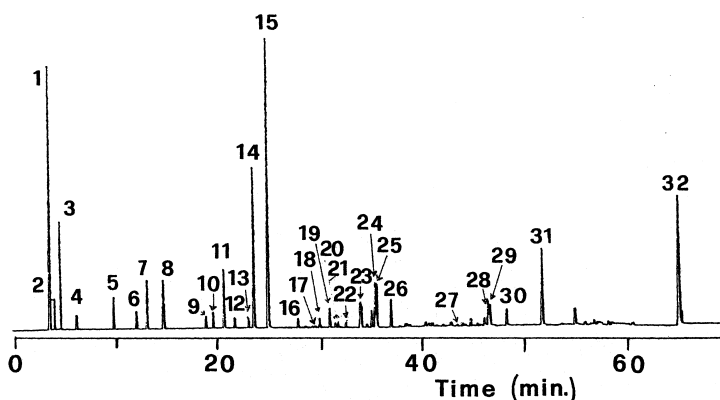
Fig. 5. GC–FID profile obtained by sampling on a multi-layer trap filled with Carbograph 5 and Carbosieve S III set in series. The amount of each material is reported in Table 2. The volume sampled was 200 ml. The sample was collected in downtown Rome in wintertime. The number following the value of the mixing ratio represents the percent deviation from canister determinations carried out on the same sample. (1) Methane, (2) ethane (14.6 ppbv, +4%), (3) ethene (54.2 ppbv, +3%), (4) propane (3.8 ppbv, −1%), (5) propene (10.0 ppbv, +2%), (6) isobutane (5.0 ppbv, +1%), (7) *n*-butane (15.8 ppbv, −2%), (8) acetylene (16.7 ppbv, −3%), (9) *trans*-2-butene (3.8 ppbv, −5%), (10) 1-butene (5.0 ppbv, −2%), (11) isobutene (18.8 ppbv, −2%), (12) *cis*-2-butene (2.9 ppbv, −2%), (13) cyclopentane (2.8 ppbv, +5%), (14) isopentane (39.6 ppbv, −4%), (15) *n*-pentane (56.3 ppbv, −4%), (16) 1,3-butadiene (2.9 ppbv, −4%), (17) cyclopentene (1.3 ppbv, −3%), (18) *trans*-2-butene (4.3 ppbv, −2%), (19) 2-methyl-2-butene (6.3 ppbv, −3%), (20) 1-pentene (2.1 ppbv, −2%), (21) 2-methyl-1-butene (1.2 ppbv, −1%), (22) *cis*-2-pentene (2.3 ppbv, +3%), (23) 2,2-dimethylbutane (7.2 ppbv, +1%), (24) 3-methylpentane (24.4 ppbv, +1%), (25) 2-methylpentane (15.6 ppbv, −5%), (26) *n*-hexane (10.5 ppbv, +4%), (27) 1-hexene (1.8 ppbv, −2%), (28) 3-methylhexane (10.1 ppbv, −3%), (29) 2-methylhexane (7.8 ppbv, −2%), (30) *n*-heptane (5.6 ppbv, +8%), (31) benzene (36.5 ppbv, +20%), (32) toluene (83.3 ppbv, +8%).

air of Rome. An example of the GC–FID profile obtained during these experiments is reported in Fig. 5. With the only exception of benzene, the composition reported in Fig. 5 was perfectly consistent with that provided by samples collected on passivated canisters. Since results obtained with multi-layer traps better matched the profile of car emissions, the lower levels of benzene (20%) systematically measured with canisters could be attributed to partial adsorption of this component on the walls or in the pump. This conclusion was supported by the fact that concentrations measured with multi-layer traps (see the caption of Fig. 5) were in better agreement with the data published by Brocco et al. [35] who monitored VOCs with an automatic analyzer for more than 3 years.

4. Conclusions

The availability of a graphitic carbon with adsorption features comparable to those of some carbon molecular sieve adsorbents has made it possible to widen the range of polar and non-polar VOCs that can be collected at any relative humidity. Multi-layer traps containing combinations of Carbograph 5 and other hydrophobic sorbents provide better sensitivity than existing methods as they allow the complete retention of VOCs with volatility higher than C_3 up to 5 l samples. In combination with stronger adsorbent, traps filled with Carbograph 5 provide performances equivalent to those obtained by canister sampling for compounds ranging in volatility from C_2 to C_7. Although more detailed investigations are needed for validating this method, preliminary results are quite promising. If they will be confirmed, the sampling of very volatile VOCs can be greatly simplified.

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