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Evaluation of a dual-sorbent trap for monitoring organic compounds in air

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Abstract

The performance of a new kind of multi-sorbent trap for use in the simultaneous determination of compounds of different volatility and polarity was investigated. The adsorbents employed for this purpose were Carbograph 2 and Carbograph 5. The performance of this trap was evaluated in terms of thermal desorption and solvent extraction recoveries of substances belonging to the main classes of organic compounds, at different amounts and volumes of air sampled corresponding to concentrations ranging from 0.1 to 1000 mg/m³. The tubes examined allowed the trapping of the compounds used and their complete desorption with the procedure best suited to the analytical problem. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

The analysis of the volatile organic compounds (VOCs) present in the atmosphere and in the workplace is important to control human exposure to substances hazardous to health. Tubes containing solid sorbents, specifically designed for trapping of organic vapors from airborne samples without enriching water and carbon dioxide, are widely used for this purpose [1–18]. The choice of a suitable adsorbent is critical and requires a good knowledge of adsorbent properties. However, it is difficult for a single adsorbent to trap a wide range of organic compounds with different chemical structures and molecular masses. By combining more than one

adsorbent, a wider range of compounds can be explored. As a consequence, multi-sorbent traps have been receiving increasing attention [8,13–18].

In this study, the performance of a tube containing 150 mg of Carbograph 2 and 150 mg of Carbograph 5 was evaluated. Both adsorbents are graphitized carbons, a material with a graphite-like structure which interacts, mainly by dispersion forces, with organic compounds with a low affinity for water and which give low background on the chromatogram [19–21]. The main difference between the two adsorbents consists in their different surface area, 9 and 560 m²/g, respectively. In previous studies, Carbograph 5 was found to have a retention superior to that expected, given its surface area. This greater retention was probably due to the presence of geometrical active sites, in which a molecule interacts with more than one graphitic plane [7,19,20,22]. As a consequence, Carbograph 5 is able to retain

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light compounds and Carbograph 2 heavy compounds.

The evaluation consisted of placing different known amounts of a mixture of organic compounds in the tube and passing an air atmosphere through it (to simulate air sampling), followed by thermal desorption to determine the percent recoveries of the organic compounds from the tubes. The effect of varying sampling volumes and concentrations, as well as the effect of humidity and storage, was investigated.

With respect to solvent extraction, thermal desorption offers the advantages of greater sensitivity and the fact that it does not require the use of solvents hazardous to health and does not produce a solvent peak which could cover analyte peaks eluted too early. Therefore, it is the method of choice when evaluating light compounds or low concentrations. However, solvent extraction has the advantage that the analysis can be repeated [2,19,23]. Therefore, the tubes were also solvent-extracted and found to be suitable to trap mixtures of VOCs with different volatility and polarity.

2. Experimental

2.1. Adsorbents

Carbograph 2 (0.750–0.350 mm) was furnished by Supelco (Bellefonte, PA, USA); Carbograph 5 (0.750–0.350 mm) is a commercially available sample, supplied by LARA (Formello, Rome, Italy). The glass tubes, (11.8 cm×3 mm I.D.), were prepared in our laboratory from glass tubing. They were filled with 150 mg of Carbograph 2 (0.750–0.350 mm) and 150 mg of Carbograph 5 (0.750–0.350 mm) separated by a glass wool plug, and also plugged at the ends with the same material.

The tubes were preconditioned for 24 h at 300°C with nitrogen gas flowing through at 25 ml/min, and tested before use.

The blank chromatograms obtained by thermally desorbing the traps under the same conditions of analysis and at maximum sensitivity confirmed that no peaks of impurities were present which could disturb the gas chromatographic analysis.

2.2. Measurement of desorption recovery

The gas chromatograph employed for the analysis was a Carlo Erba GC 4300 equipped with a flame ionization detection (FID) system. The column used was a packed column (3 m×3 mm I.D.) filled with Carbograph 2+0.45% of Carbowax 20M, prepared in our laboratory.

The oven was kept for 2 min at 40°C, after which the temperature was increased by 25°C/min to 200°C.

A Model 890 thermal desorber manufactured by Dynatherm Analytical Instruments, Supelco was connected to the gas chromatography (GC) column by a transfer line maintained at 230°C.

The injector and detector temperatures were 230°C and 200°C, respectively. The nitrogen carrier gas flow was 30 ml/min.

The traps were loaded with four different amounts of each mixture and for the same amount four different air volumes were tested.

The two mixtures examined were: (a) methyl ethyl ketone, methyl isobutyl ketone, hexane, styrene, ethoxyethyl acetate, 2-butoxyethanol and (b) ethyl acetate, 2-methoxyethanol, 1,1,2,2-tetrachloroethane, *o*-xylene, 1,2,4-trimethylbenzene.

The lowest amounts were obtained by a gaseous standard mixture and the highest by a liquid standard mixture.

The gaseous standard mixture was prepared by injection with a standard liquid syringe of 2.5 µl of each pure compound into a 1-l glass flask previously evacuated with a rotary pump. Before use, the glass flask was brought to atmospheric pressure with nitrogen. The traps were loaded by injecting 100 µl or 500 µl (about 200 ng or 1 µg) of each gaseous standard mixture with a gas-tight syringe.

The highest amounts were obtained loading the traps with 0.35 µl or 1.5 µl (about 50 µg or 200 µg) of a liquid mixture containing the same weighed amount of each pure compound.

The loading procedure was carried out using the desorber apparatus switched to the sample preparation mode and kept at 200°C. For each amount, four different volumes (2 l, 1 l, 500 ml, 200 ml) were allowed to pass through the trap at 25°C and at a flow-rate of 50 ml/min.

The desorption procedure was carried out switch-

ing the desorber apparatus into the desorption mode. The analysis was performed immediately; the traps were backflushed and desorbed at 300°C for 6 min under a 30 ml/min stream of nitrogen. Recoveries were calculated by comparison with the same standard sample amount injected into an empty glass tube in the thermal desorber connected to the GC system.

In all cases, a back-up trap was connected with a PTFE tube to the first trap and analyzed in order to verify the loss of more volatile compounds, attributable to the insufficient trapping capacity of the first trap at the sampling temperature employed (25°C in all the breakthrough experiments).

Five traps were tested for each amount and air volume sampled.

The desorption recoveries were also evaluated after different storage periods (one week and one month). The dual-sorbent traps were spiked at a concentration of 200 ng with an air volume flowing through of 200 ml. Then, they were sealed with metal connectors equipped with PTFE ferrules, wrapped in aluminium foil and stored in a tightly closed glass container (1 l) in the presence of active charcoal to prevent contamination of the trapping materials at 25°C. One sealed trap was used as a blank to check whether accidental exposure of the container to contaminants would cause passive collection of the pollutants in the sampled traps [21]. The traps were stored in the glass container for one week or for one month and then analyzed.

The same volumes, but of moist air, with relative humidity adjusted to 50% via a water-sparging vessel, passed through the tubes spiked with analytes as described above. Before analysis 30 ml of pure dry nitrogen were passed through in order to remove any traces of water.

2.3. Measurement of solvent extraction recovery

The performance of this dual-sorbent trap with solvent extraction was also evaluated. The tubes to be solvent extracted were cleaned before use with 10 ml of carbon disulfide or with 5 ml of a methylene dichloride–methanol (1:1) mixture, followed by 5 ml of methylene dichloride to eliminate possible impurities present on the graphitized carbon surface. After drying with dry pure nitrogen gas flowing

through at 20 ml/min and heating at 300°C temperature for 1 h before spiking, the tubes were loaded with 1.5 μ l of one of the liquid mixtures. The compounds were eluted with 1 ml of carbon disulfide or with 1 ml of methylene dichloride. The traps were spiked with the highest concentration (200 μ g) to obtain a concentration compatible with the detection limit (ng) of the FID system. Three measurements were made for the eluate of each trap and three traps were examined for each solvent used. The eluate was analyzed in the gas chromatographic system and the quantitative recoveries are shown in Section 3 (Table 3).

Blank experiments performed by extracting the tubes with 1 ml of solvent without spiking did not show any peaks at the time of elution of the analytes.

The quantitative recoveries were calculated by comparison with a standard solution at the same concentration injected into the gas chromatograph under the conditions described above.

3. Results and discussion

The trap was tested using 11 compounds belonging to the main classes of organic compounds in order to evaluate trapping efficiency, desorption recovery and stability after storage.

The amounts spiked ranged from 200 ng to 200 μ g (that is, considering the air volume, the corresponding concentrations ranged from 0.1 to 1000 mg/m^3). The threshold limit values are in the order of hundreds of mg/m^3 in the workplace, and in the order of $\mu\text{g}/\text{m}^3$ in the atmosphere [24].

It should be outlined that the tests were performed in a situation far from real sampling conditions. In fact, all the analytes of the examined mixture were spiked on the top of the tube at the beginning of the experiments, then pure air was passed through. These conditions were harsher than real sampling conditions.

The sorbent packings, being graphitized carbons, are not polar; therefore, non-polar compounds would be expected to be best retained. The behavior of the tube with polar compounds was less predictable. In fact, it is known to depend not only on the surface area of the graphitized carbon but above all on the “active sites”, (chemical or mostly surface ir-

regularities), present on it, which vary among graphitized carbons according to their origin and manufacture [7]. These active sites may be supposed to have some catalytic activity. Therefore, the tube behavior needed to be tested in order to verify if organic compounds of different volatility and chemical structure were efficiently adsorbed (breakthrough experiments) and desorbed (desorption recovery measurements).

A back-up tube was connected in series to the traps in all the experiments to check that breakthrough had not occurred during sampling. The tested compounds were found to be efficiently trapped by the main trap and the back-up trap contained less than 1% of the tested compounds in all the experiments. Light polar compounds such as ethyl acetate, methoxyethanol and methyl ethyl ketone were well retained at all the spiked amounts and air volumes tested. It should be underlined that these compounds were poorly retained by traditional graphitized carbons [7].

The desorption recoveries were also satisfactory for all the compounds tested, including the polar ones. In fact, thermal decomposition or irreversible adsorption did not occur at the desorption temperature of 300°C used in all the experiments. These data are reported in Table 1 and the corresponding chromatograms are shown in Figs. 1 and 2.

Therefore, the dual-sorbent tube is suitable to trap

and desorb mixtures of compounds of different volatility and polarity. It is of note that the tube was packed with only graphitized carbons which have two positive characteristics: they are hydrophobic and do not undergo decomposition, as, for example, does Tenax, which in highly oxidizing atmospheres generate oxygenated compounds [6,8]. Most of the multi-sorbent traps discussed in the literature contain activated charcoals or molecular sieves (see, for example, Refs. [6,8,14,18]). Tubes packed with graphitized carbons (such as Carboxpack C and/or B) and molecular sieves (for example Carboxieve S-III) are the best choice for trapping and thermally desorbing very volatile hydrocarbons C_2 – C_3 . In fact, ethane exhibits a breakthrough volume of 2.95 l/g on Carboxieve S-III [18] vs. the 0.1 l/g value on Carboxigraph 5 [20]. However, molecular sieves cause enriching water, especially when the relative humidity is higher 50%, leading to problems in performing the analysis [6,8]. A drastic reduction in adsorption properties was also observed at this percentage of relative humidity [6,14]. Ciccioli et al. used a trap packed with graphitized carbons (Carboxigraph B and C) in the case of humidity higher than 50% to perform quantitative analysis of C_6 – C_{14} compounds. The use of the dual-trap containing Carboxigraph 5 should also consent the analysis of lighter (C_3 – C_4) compounds. In fact, propane has a breakthrough volume of 2.4 l/g on Carboxigraph 5 and unsaturated

Table 1
Percent recoveries at several sampling volume and concentration levels obtained by thermal desorption (300°C for 6 min)^a

Compound	Recovery (%): $\bar{x} \pm RSD$ (%)															
	200 ng				1 μ g				50 μ g				200 μ g			
	200 ml	500 ml	1 l	2 l	200 ml	500 ml	1 l	2 l	200 ml	500 ml	1 l	2 l	200 ml	500 ml	1 l	2 l
Methyl ethyl ketone	92±4	93±5	95±5	91±6	100±4	100±4	100±5	101±5	103±6	102±5	100±5	100±4	92±5	105±4	99±5	100±5
Methyl isobutyl ketone	101±5	99±5	103±5	102±5	99±4	100±5	102±4	102±4	97±3	104±5	102±5	103±5	91±4	93±5	95±4	90±4
Ethyl acetate	99±6	103±4	91±5	98±5	95±6	98±5	97±5	96±5	98±4	96±5	95±6	91±6	100±5	96±5	98±4	100±4
2-Methoxyethanol	90±4	95±5	89±6	96±4	89±6	90±6	92±5	92±5	93±5	96±5	95±4	94±5	93±5	91±6	95±5	92±6
n-Hexane	99±4	97±4	100±3	99±3	98±4	99±3	102±5	101±4	100±4	102±3	93±4	99±4	101±4	99±3	96±5	102±5
Styrene	100±3	98±4	99±3	97±5	102±4	100±3	101±4	98±3	96±4	100±4	98±5	103±5	103±4	98±4	99±4	100±4
o-Xylene	97±4	98±3	99±4	101±4	94±5	97±4	95±4	94±5	92±4	98±5	100±4	96±4	100±3	97±4	99±3	100±3
Ethoxyethyl acetate	100±4	97±5	98±5	96±5	92±6	97±5	100±4	100±6	93±5	95±6	94±5	103±5	92±6	97±4	97±5	103±6
1,1,2,2-Tetrachloroethane	95±4	96±5	98±3	95±4	96±4	95±5	96±4	97±4	95±4	94±4	96±3	96±3	99±4	95±4	94±5	97±4
1,2,4-Trimethylbenzene	95±5	100±4	97±4	101±4	102±5	97±4	95±5	99±5	98±4	92±4	92±5	92±5	100±4	91±6	103±4	96±4
2-Butoxyethanol	90±6	87±7	88±5	89±7	103±5	90±6	95±6	85±6	92±4	102±5	104±6	105±6	91±6	100±5	97±5	95±6

^a The RSD was calculated on five repeats.

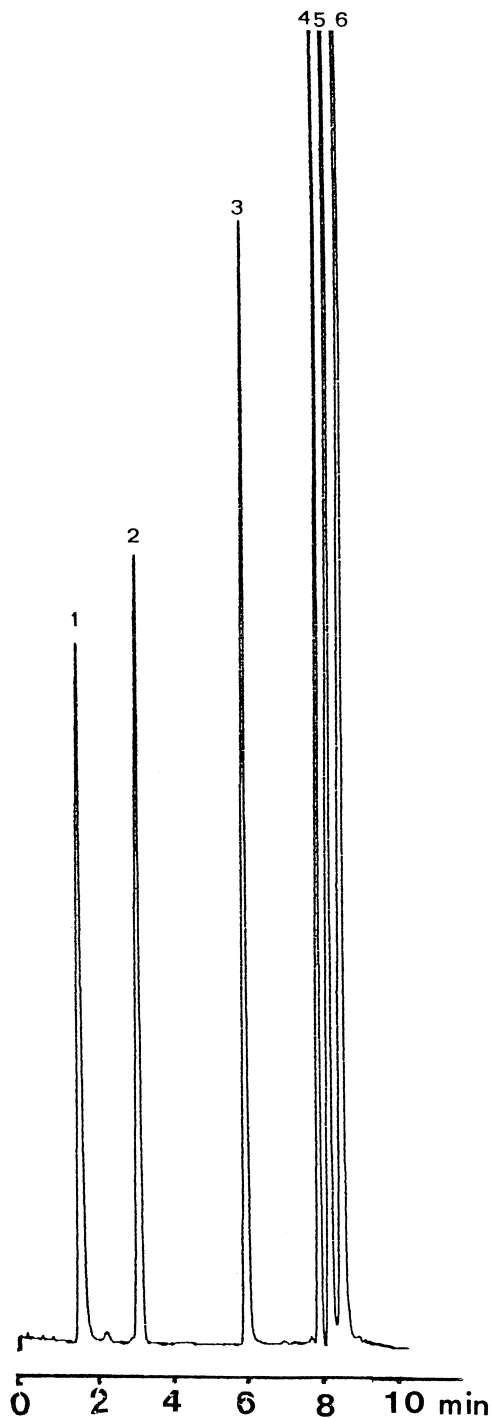


Fig. 1. Chromatographic separation obtained by thermal desorption of a trap loaded with 200 ng of each compound followed by 2 l of pure air flowing through the trap: (1) methyl ethyl ketone, (2) methyl isobutyl ketone, (3) hexane, (4) styrene, (5) ethoxyethyl acetate, (6) 2-butoxyethanol.

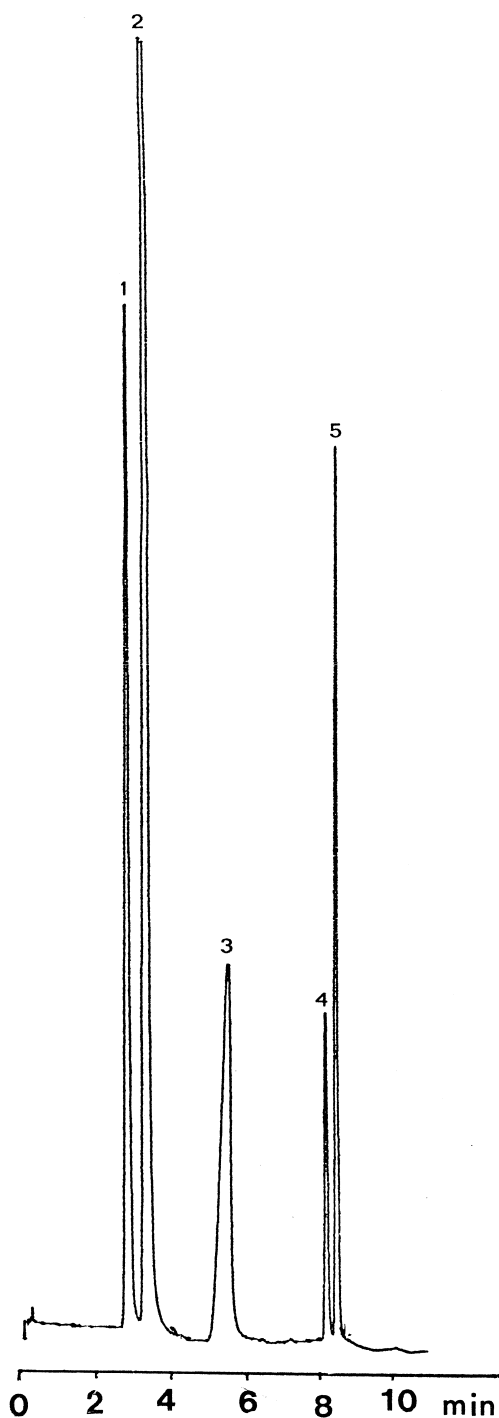


Fig. 2. Chromatographic separation obtained by thermal desorption of a trap loaded with 200 ng of each compound followed by 2 l of pure air through the trap: (1) ethyl acetate, (2) 2-methoxyethanol, (3) 1,1,2,2-tetrachloroethane, (4) *o*-xylene, (5) 1,2,4-trimethylbenzene.

hydrocarbons (propene and propine) have greater breakthrough volumes because they interact more strongly with the graphitic planes [20].

The dual-sorbent tube is not suitable for trapping at ambient temperature of mixtures containing very volatile polar compounds such as methanol, which has a breakthrough volume of 0.6 l/g on Carbograph 5 [20].

The effect of humidity was also tested. The presence of 50% humidity did not alter the recoveries obtained. However, after the moist air was passed through the trap and before desorption, the tubes were rinsed with 30 ml of dry nitrogen in order to eliminate water, which could disturb the analysis. This dry purge seemed to work satisfactorily [14,25]. The volume of dry nitrogen necessary was very low. In fact, the breakthrough volume of water on Carbograph 5 was 0.003 l/g [20]. Furthermore, the adsorption capacity of Carbograph 5 is 10 mg of water/g [20] and that of Carbograph 2 was about 1 mg/g, in contrast with the water trapping capacity of 400 mg/g of carbon molecular sieves [26].

The desorption storage recoveries given in Table 2 demonstrate that the stored traps did not show any losses if examined after one week. However, a longer period of storage (one month) led to a severe loss of alcohols and ketones. This loss was probably due to a series of factors which are difficult to control and to identify [14]. Accordingly, the sampled tubes should preferably be analyzed within one week.

Table 2
Percent recoveries obtained by thermal desorption after one month's storage^a

Compound	200 ng (200 ml) $\bar{x} \pm \text{RSD} (\%)$
Methyl ethyl ketone	60 ± 9
Methyl isobutyl ketone	31 ± 15
Ethyl acetate	107 ± 13
2-Methoxyethanol	52 ± 10
<i>n</i> -Hexane	103 ± 8
Styrene	103 ± 6
<i>o</i> -Xylene	93 ± 7
Ethoxyethyl acetate	98 ± 6
1,1,2,2-Tetrachloroethane	111 ± 18
1,2,4-Trimethylbenzene	83 ± 5
2-Butoxyethanol	20 ± 19

^a The RSD was calculated on five repeats.

Many studies have shown that storage on adsorbents can be improved by keeping the spiked tubes at sub-ambient temperature [27–32]. This is particularly useful when very volatile compounds, for which the trap exhibits low breakthrough volumes, have been sampled. However, it must also be kept in mind that uptake of ambient contaminants can be greater at lower temperatures. In our experiments, the losses were more meaningful for polar compounds such as alcohols or ketones, and they were greater for the heavier compounds. Thus, it can be supposed that losses are mainly attributable to decomposition phenomena rather than to losses. However, the effect of temperature on the rate of decomposition phenomena deserves further investigation.

The traps were also solvent extracted. Solvent extraction can be an alternative to thermal desorption when the concentration is high enough to allow a final concentration of the solution compatible with the detector limit of the instrument, and also allows injection to be repeated. However, the chromatographic column must be chosen with care. In fact, lighter compounds must be retained well enough to be separated from the solvent peak. Furthermore, solvent extraction implies the use of solvents which, posing risks to health, need to be eliminated from analytical procedures.

The solvent extraction procedure gave, as expected, the good recoveries shown in Table 3. The use of 1 ml of solvent gave complete recoveries with both carbon disulfide and methylene dichloride. However, when using FID carbon disulfide, which has a less intense response, may be preferable.

When investigating the workplace environment, where the concentrations of volatile organic pollutants are in the parts per million range, there are generally no problems in terms of concentration of the pollutants, while in the atmosphere they are present in concentrations at least three-orders of magnitude lower. As a consequence, the possibility of using solvent desorption is linked to the volume which can be sampled before the lighter components in the mixture start to be eluted: that is, to their breakthrough volumes [24,33,34].

Thus, the choice of the desorption method is a function of the breakthrough volumes of the pollutants to be monitored, of their concentration and of

Table 3
Percent recoveries obtained by solvent extraction^a

Compound	$\bar{x} \pm \text{RSD} (\%)$	
	200 μg Carbon disulfide	200 μg Methylene dichloride
Methyl ethyl ketone	100 \pm 4	–
Methyl isobutyl ketone	100 \pm 3	92 \pm 3
Ethyl acetate	85 \pm 5	–
2-Methoxyethanol	99 \pm 4	–
<i>n</i> -Hexane	101 \pm 3	–
Styrene	101 \pm 3	97 \pm 3
<i>o</i> -Xylene	101 \pm 3	97 \pm 2
Ethoxyethyl acetate	101 \pm 4	90 \pm 4
1,1,2,2-Tetrachloroethane	97 \pm 3	99 \pm 3
1,2,4-Trimethylbenzene	98 \pm 3	93 \pm 3
2-Butoxyethanol	103 \pm 4	95 \pm 4

^a The RSD was calculated on five repeats.

the kind of measurements which need to be performed.

4. Conclusion

Complete trapping and desorption of a mixture of hazardous organic substances was obtained using a dual-sorbent trap containing 150 mg of Carbograph 5 and 150 mg of Carbograph 2. This procedure was successful when the traps were desorbed within one week after sampling. Either thermal desorption or solvent extraction can be used. The same results were obtained in the presence of 50% humidity. Therefore, this dual-sorbent trap can be a useful instrument with which to address different analytical problems.

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