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Comparative study of the adsorption performance of a multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569) and a Tenax TA adsorbent tube for the analysis of volatile organic compounds (VOCs)

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ABSTRACT

A comparison between two types of adsorbent tubes, the commonly used Tenax TA and a multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569) tube developed in our laboratory, has been done to evaluate their usefulness in the analysis of VOCs in ambient air. Duplicate indoor and outdoor samples of Tenax TA and multi-sorbent tubes of 10, 20, 40, 60 and 90 l were taken in Barcelona city (Spain) on July and October of 2009. Breakthrough values (defined as %VOCs found in the back tube) were determined for all sampling volumes connecting two sampling tubes in series. The analysis was performed by automatic thermal desorption (ATD) coupled with capillary gas chromatography (GC)/mass spectrometry detector (MSD). Significant differences between the concentrations obtained-from multi-sorbent bed and Tenax TA tubes are observed for the very volatile compounds ($56\,^{\circ}\mathrm{C} <$ boiling point $< 100\,^{\circ}\mathrm{C}$ and $4\,\mathrm{kPa} <$ vapour pressure ($20\,^{\circ}\mathrm{C}$) $< 47\,\mathrm{kPa}$) (e.g. acetone, isopropanol, *n*-hexane) and for alcohols and chlorinated compounds (e.g. 1-butanol, carbon disulphide, dichloromethane, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene), being the concentrations found higher in multi-sorbent bed than in Tenax TA tubes. On the other hand, mainly all compounds with boiling points higher than 100 °C (except α-pinene, chlorinated and polar compounds) do not show significant differences between the obtained multi-sorbent bed and Tenax TA tube concentrations. For the concentrations obtained (5 ppt to 100 ppb), Tenax TA present high breakthrough values (from 0 to 77%) for mainly all compounds and sampling volumes studied. On the other hand, multi-sorbent bed tubes do not exhibit important breakthrough values for these compounds, except the VVOCs ethanol (for all sampled volumes), and acetone, dichloromethane and isopropanol (for sampling volumes over 40 l). The concentration differences observed between Tenax TA and multi-sorbent bed tubes are directly related to the high breakthrough values determined for Tenax TA adsorbent.

1. Introduction

Sorbent materials have a wide range of chemical forms and surface and porous structures, as it is observed in the variety of adsorbents that are commercially available both for industrial/occupational and environmental applications. For this reason, in air quality determination and pollution control it is necessary to establish the proper adsorbents to be used to determine the target compounds chosen. Ambient air is a very complex mixture of compounds, and has a very variable composition and concentration of pollutants. Hence, a good choice of sorbent or a good combination of different sorbents may allow the determination of a wide range of target compounds in air samples [1–8], as well as achieve high breakthrough volumes [9]. Nowadays, multi-sorbent beds are used in a high amount of validated methods for determining volatile toxic organic compounds in ambient air (e.g. NIOSH 2549 [10] and EPA TO-17 [11]).

Sampling through adsorbent materials serves to enrich the analytes in the sample, as they are generally found in trace and ultra-trace quantities in ambient air. The selective characteristics of the sorbent chosen would determine the removing of the target compounds from the air matrix [12]. On the other hand, a choice of a proper sorbent for the range of concentrations of the studied target compounds would eliminate problems derived from breakthrough [2]. Other factors different from the sorbent will influence in the choice of a proper sorbent, such as the type and

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concentration of target pollutants, the sampling equipment and the analytical technique (thermal desorption or solvent extraction), and the environmental conditions of sampling (mainly temperature and humidity) [13].

Tenax TA has been determined to be a not suitable adsorbent for very volatile organic compounds (VVOCs, 0 < boiling point < 50–100 °C [14]), mainly due to the displacement of the adsorbed volatile and polar compounds for non-polar high-molecular weight pollutants [15], as it has been described in previous studies [1,13,16–19]. However, Tenax TA continues being one of the most widely used adsorbents for the preconcentration of VOCs [19,20], in spite of its limited specific surface area (20–35 $m^2 g^{-1}$) and the possibility of suffering chemical decomposition and degradation of reactive analytes during sampling [1,18]. In addition to that, generally, a single adsorbent cannot be appropriate for the majority of compounds present in ambient air. Hence, a combination of several adsorbents, preferably carbon-based materials [17], may result in better performances. Consequently, if the analysis of the air sample would be done exhaustively, adsorbents that assure us a complete gathering without loss of sample would be needed.

In this paper, a comparison between two types of adsorbent tubes, one containing a mixture of three adsorbents (Carbotrap, Carbopack X, Carboxen 569) [7,21] and another containing Tenax TA was compared to evaluate their usefulness as active adsorbents of ambient air VOCs, including VVOCs.

2. Materials and methods

2.1. Chemicals and materials

Standards of VOCs, with purity not less than 98%, were obtained from Aldrich (Milwaukee, WI, USA), Merck (Darmstadt, Germany) and Fluka (Buchs, Switzerland). Perkin Elmer glass tubes (Pyrex, 6 mm external diameter, 90 mm long), unsilanised wool, Carbotrap (20/40 mesh), Carbopack X (40/60 mesh), Carboxen 569 (20/45 mesh) and Tenax TA (60/80 mesh) adsorbents were obtained from Supelco (Bellefonte, PA, USA).

2.2. Sampling

Duplicate samples of multi-sorbent bed and Tenax TA tubes of 10, 20, 40, 60 and 90 l of indoor and outdoor air were taken in Barcelona city (Spain) during the months of July and October 2009, respectively. The total number of tubes sampled was 40:20 multi-sorbent bed tubes and 20 Tenax TA tubes. Flow sampling rates were set at 70 ml min^{-1}. VOCs were dynamically sampled connecting custom packed glass multi-sorbent cartridge tubes (Carbotrap 20/40, 70 mg; Carbopack X 40/60, 100 mg and Carboxen 569 20/45, 90 mg) [7] and Tenax TA (60/80, 200 mg) tubes to air collector pump samplers specially designed in the LCMA-UPC laboratory [22]. To evaluate breakthrough values, two tubes were connected in series for each sample, letting us determine the amount of the studied compounds that were present in the back tube. On the other hand, the flow sampling rate was also evaluated. In October 2009, outdoor air samples of 90 l were taken at two different flow rates, 70 ml min^{-1} and 90 ml min^{-1}, for multi-sorbent bed and Tenax TA tubes. A total number of 16 samples were taken and analyzed: 8 multi-sorbent bed and 8 Tenax TA samples. The temperature and relative humidity during the sampling days were 29.8 °C (28–31 °C) and 43.3% (35–48%), and 22.6 °C (20–27 °C) and 56.5% (50–63%), for July and October 2009, respectively.

Collected ambient air samples were further analyzed by thermal desorption and gas chromatography–mass spectrometry (TD–GC/MSD) [7,21].

2.3. Analytical instrumentation

The analysis of VOCs was performed by automatic thermal desorption coupled with capillary gas chromatography/mass spectrometry detector, using a Perkin Elmer ATD 400 (PerkinElmer, Boston, MA, USA) and a Thermo Quest Trace 2000 GC (ThermoQuest, San Jose, CA, USA) fitted with a Thermo Quest Trace Finnigan MSD.

The methodology, validated for 57 compounds, is described elsewhere [7,21]. Mass spectral data are acquired over a mass range of 20–300 amu. Qualitative identification of target compounds is based on the match of the retention times and the ion ratios of the target quantification ions and the qualifier ions (Xcalibur 1.2 validated software package). Quantification of field samples is conducted by the external standard method [7]. Limits of detection (LOD), determined applying a signal-to-noise ratio of 3, range from 0.001 to 10 ng. The studied compounds show repeatabilities (% relative standard deviation values) ≤25% [7], accomplishing the EPA performance criteria [11]. Extreme precautions are established for quality assurance, injecting periodically blank samples and a known concentration of standards.

All concentration values were normalized by temperature (273 K) and pressure (760 mmHg).

The uncertainties shown in the text are one sigma.

3. Results and discussion

3.1. Multi-sorbent bed (Carbotrap, Carbopack X, Carboxen 569)–Tenax TA concentrations comparative

Differences between multi-sorbent bed and Tenax TA tube concentrations are shown in Tables 1 and 2 for indoor and outdoor air, respectively. Average ± standard deviation and median values for all sampled volumes are shown ($n = 10$). In addition to that, boiling point (°C) and vapour pressure at 20 °C (kPa) are also presented for each evaluated compound. Significant differences between the concentrations obtained from multi-sorbent bed and Tenax TA tubes (t-test, $p < 0.05$ (normal data) and U of Mann–Whitney, $p < 0.05$ (not normal data)) are observed for the very volatile compounds (56 °C < boiling point < 100 °C and 4 kPa < vapour pressure (20 °C) < 47 kPa) (e.g. acetone, isopropanol, carbon disulphide, *n*-hexane) and for alcohols and chlorinated compounds (e.g. 1-butanol, phenol, dichloromethane, chloroform, carbon tetrachloride, trichloroethylene, tetrachloroethylene); being higher the concentrations found in multi-sorbent bed than in Tenax TA tubes. On the other hand, mainly all compounds with boiling points higher than 100 °C (except α-pinene, chlorinated and polar compounds) do not show significant differences between the concentrations obtained through multi-sorbent bed and Tenax TA tubes, both for indoor and outdoor air concentrations. The boiling point of 100 °C is often advised as a guidance value below which the adsorption of the compounds is not satisfying for Tenax TA [19]. In addition to that, a displacement of the adsorbed volatile and polar compounds for non-polar high-molecular weight pollutants in Tenax TA adsorbent has been observed in previous studies [15]. Hence, the behaviour observed for alcohols and chlorinated compounds may be determined by their polarity, being these polar pollutants displaced by high-molecular weight compounds.

In Fig. 1, multi-sorbent bed and Tenax TA concentrations are plotted for some of the studied compounds both for indoor and outdoor air. For the very volatile and polar compounds (e.g. acetone and isopropanol) differences are observed between the regression line obtained from multi-sorbent bed and Tenax TA correlation and the 1:1 line; however, compounds with boiling points over 100 °C, such as ethylbenzene and $m + p$-xylenes, show good correlations

Table 1

Average ± standard deviation for all samples and median indoor air concentrations ($\mu g\, m^{-3}$) for multi-sorbent bed and Tenax TA tubes ($n = 10$). Compounds are listed by elution order.

Compounds	Average ± SD		Median		Boiling point (°C)	Vapour pressure (20 °C, kPa)
	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA		
Ethanol[a]	30 ± 24	27 ± 19	21	21	79	5.8
Acetone[a,†]	205 ± 213	14 ± 15	73	6	56	24
Isopropanol[a,‡]	23 ± 17	1.0 ± 0.8	15	0.8	82	4.4
Carbon disulphide[a,‡]	0.9 ± 0.4	0.2 ± 0.1	1	0.1	46	41.1
Dichloromethane[a,†]	14 ± 15	0.5 ± 0.5	6	0.4	69	47.4
n-Hexane[a,‡]	4.7 ± 0.9	0.4 ± 0.2	5	0.4	61	17
Chloroform[a,‡]	34 ± 15	1 ± 1	27	0.7	61	21.1
Carbon tetrachloride[b,‡]	6 ± 3	0.7 ± 0.4	7	0.7	118	1.5
Acetic acid[a]	98 ± 22	107 ± 77	96	75	77	12.2
Benzene[a,‡]	7 ± 3	0.9 ± 0.4	7	0.9	80	10
n-Heptane[a,†]	15 ± 10	5 ± 1	13	5	98	4.6
1-Butanol[b,‡]	11 ± 4	3 ± 2	11	2	118	0.6
Trichloroethylene[a,†]	1.2 ± 0.5	0.2 ± 0.2	1	0.2	87	7.8
Methylisobuthylketone[b]	1.1 ± 0.2	0.7 ± 0.4	1	0.7	117	2.1
Toluene[b,‡]	83 ± 23	52 ± 13	78	49	111	2.9
Tetrachloroethylene[b,‡]	1.2 ± 0.4	0.6 ± 0.3	1	0.6	121	1.9
Butyl acetate[b]	4 ± 1	5 ± 1	4	5	126	1.2
NN-dimethylformamide[b]	7 ± 4	5 ± 3	5	5	153	0.4
Ethylbenzene[b]	31 ± 17	27 ± 13	33	27	137	1.2
m + *p*-Xylene[b]	74 ± 29	68 ± 25	71	63	139/138	0.8/0.9
o-Xylene[b]	34 ± 16	28 ± 11	33	26	145	0.7
2-Buthoxyethanol[b]	9 ± 5	8 ± 2	8	7	171	0.1
α-Pinene[b,‡]	4.8 ± 0.9	0.8 ± 0.5	5	0.6	157	0.4
Benzaldehyde[b]	5 ± 1	6 ± 2	5	5	178	0.1
Limonene[b]	17 ± 10	13 ± 7	13	12	177	0.2
p-Dichlorobenzene[b]	0.09 ± 0.02	0.09 ± 0.01	0.09	0.09	174	0.2
Phenol[b,‡]	1.7 ± 0.4	2.7 ± 0.3	2	3	182	0.1

[a] The compound has a boiling point <100 °C.

[b] The compound has a boiling point >100 °C.

[†] Significant differences observed between the concentrations obtained from multi-sorbent bed and Tenax TA tubes (*U* of Mann–Whitney, $p < 0.05$). Not normal data.

[‡] Significant differences observed between the concentrations obtained from multi-sorbent bed and Tenax TA tubes (*t*-test, $p < 0.05$). Normal data.

Table 2

Average ± standard deviation for all samples and median outdoor air concentrations ($\mu g\, m^{-3}$) for multi-sorbent bed and Tenax TA tubes ($n = 10$). Compounds are listed by elution order.

Compounds	Average ± SD		Median		Boiling point (°C)	Vapour pressure (20 °C, kPa)
	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA		
Ethanol[a]	7 ± 3	6 ± 3	6	5	79	5.8
Acetone[a,‡]	23 ± 9	1.5 ± 0.8	21	1	56	24
Isopropanol[a,‡]	21 ± 22	0.5 ± 0.4	13	0.4	82	4.4
Carbon disulphide[a,‡]	0.4 ± 0.2	0.05 ± 0.04	0.4	0.03	46	41.1
Dichloromethane[a,‡]	7 ± 3	0.2 ± 0.1	7	0.1	69	47.4
n-Hexane[a,‡]	2.6 ± 0.7	0.3 ± 0.2	3	0.2	61	17
Chloroform[a,†]	41 ± 57	3 ± 3	10	1	61	21.1
Carbon tetrachloride[b,‡]	1.2 ± 0.2	0.1 ± 0.1	1	0.1	118	1.5
Acetic acid[a]	20 ± 6	16 ± 8	21	16	77	12.2
Benzene[a,‡]	3 ± 1	0.4 ± 0.3	3	0.3	80	10
n-Heptane[a,‡]	3 ± 1	1.0 ± 0.4	3	1	98	4.6
1-Butanol[b,‡]	5 ± 4	0.4 ± 0.3	4	0.4	118	0.6
Trichloroethylene[a,‡]	0.6 ± 0.4	0.07 ± 0.04	0.5	0.1	87	7.8
Methylisobuthylketone[b]	0.2 ± 0.1	0.15 ± 0.04	0.2	0.2	117	2.1
Toluene[b,‡]	32 ± 9	19 ± 6	34	18	111	2.9
Tetrachloroethylene[b,‡]	5 ± 2	3 ± 2	5	3	121	1.9
Butyl acetate[b]	2 ± 1	1.3 ± 0.7	1	1	126	1.2
NN-dimethylformamide[b]	6 ± 4	4 ± 4	5	2	153	0.4
Ethylbenzene[b]	4 ± 2	4 ± 1	5	4	137	1.2
m + *p*-Xylene[b]	14 ± 5	14 ± 4	16	15	139/138	0.8/0.9
o-Xylene[b]	4 ± 2	4 ± 1	5	4	145	0.7
2-Buthoxyethanol[b]	1.0 ± 0.6	1.2 ± 0.4	0.9	1	171	0.1
α-Pinene[b,‡]	0.9 ± 0.7	0.1 ± 0.1	0.8	0.1	157	0.4
Benzaldehyde[b,‡]	1.4 ± 0.6	2.8 ± 0.8	1	3	178	0.1
Limonene[b,‡]	0.4 ± 0.4	0.1 ± 0.1	0.4	0.1	177	0.2
p-Dichlorobenzene[b]	0.06 ± 0.03	0.06 ± 0.03	0.06	0.07	174	0.2
Phenol[b,‡]	0.3 ± 0.1	1.4 ± 0.5	0.3	1	182	0.1

[a] The compound has a boiling point <100 °C.

[b] The compound has a boiling point >100 °C.

[†] Significant differences observed between the concentrations obtained from multi-sorbent bed and Tenax TA tubes (*U* of Mann–Whitney, $p < 0.05$). Not normal data.

[‡] Significant differences observed between the concentrations obtained from multi-sorbent bed and Tenax TA tubes (*t*-test, $p < 0.05$). Normal data.

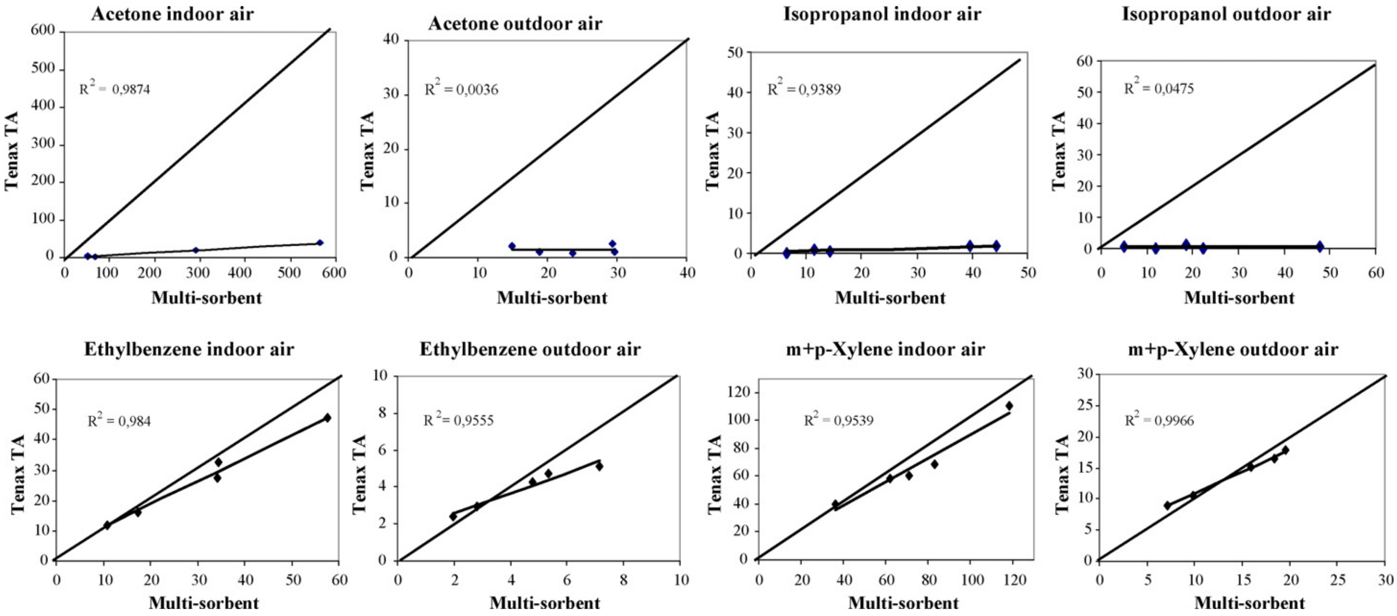

Fig. 1. Comparison of different compound concentrations (μg m^{-3}) using multi-sorbent bed tubes (Carbotrap, Carbopack X and Carboxen 569) and Tenax TA tubes.

between multi-sorbent bed and Tenax TA obtained concentrations. In Table 3, correlation coefficients between multi-sorbent bed and Tenax TA tube concentrations, slope and intercept values for all the studied compounds are shown. Mainly all compounds that present boiling points above 100 °C and vapour pressures (20 °C) lower than 2–3 kPa, exhibit significant correlations and do not show significant differences in concentrations between multi-sorbent bed and Tenax TA tubes (Tables 1 and 2). The correlation coefficients between the compounds that do not present significant differences between the two types of adsorbents and show good correlations range between 0.773–0.954 and 0.950–0.997 for indoor and outdoor air, respectively (Table 3). On the other hand, these compounds present slope values near to 1 both for indoor and outdoor concentrations.

Ethanol, acetone, isopropanol and dichloromethane present significant correlations between multi-sorbent bed and Tenax TA tube

Table 3

Correlation coefficients (r^2 values), slope and intercept for linear regressions between multi-sorbent bed (x axis) and Tenax TA (y axis) tubes for indoor and outdoor VOCs concentrations.

Compounds	Correlation coefficient (r^2)		Slope		Intercept	
	Indoor	Outdoor	Indoor	Outdoor	Indoor	Outdoor
Ethanol[a]	0.777*	0.002	0.69	0.04	6.95	5.59
Acetone[a]	0.987*	0.004	0.07	0.01	−3.23	1.36
Isopropanol[a]	0.939*	0.048	0.04	−0.01	0.01	0.61
Carbon disulphide[a]	0.123	0.552	0.10	0.14	0.05	−0.01
Dichloromethane[a]	0.945*	0.027	0.03	−0.01	0.10	0.21
n-Hexane[a]	0.055	0.602	0.05	−0.27	0.61	0.98
Chloroform[a]	0.020	0.398	−0.01	0.14	1.52	−0.48
Carbon tetrachloride[b]	0.347	0.002	1.50	−0.03	−40.02	0.17
Acetic acid[a]	0.144	0.104	0.10	0.59	0.11	3.67
Benzene[a]	0.022	0.556	−0.02	−0.23	1.01	0.98
n-Heptane[a]	0.252	0.167	0.05	−0.13	3.94	1.33
1-Butanol[b]	0.669	0.353	0.38	0.15	−1.49	−0.36
Trichloroethylene[a]	0.546	0.258	0.24	−0.05	−0.06	0.10
Methylisobuthylketone[b]	0.727	0.499	1.37	0.24	−0.75	0.09
Toluene[b]	0.381	0.134	0.35	−0.20	22.43	25.33
Tetrachloroethylene[b]	0.773*	0.443*	0.75	0.53	−0.29	0.04
Butyl acetate[b]	0.894*	0.954*	0.93	0.74	0.55	0.25
NN-dimethylformamide[b]	0.042	0.019	0.19	0.07	4.01	3.36
Ethylbenzene[b]	0.984*	0.956*	0.76	0.55	3.38	1.48
m + *p*-Xylene[b]	0.954*	0.997*	0.85	0.70	4.52	3.92
o-Xylene[b]	0.937*	0.981*	0.68	0.84	5.27	0.61
2-Buthoxyethanol[b]	0.827*	0.951*	0.34	0.62	4.53	0.59
α-Pinene[b]	0.002	0.026	−0.03	0.01	0.87	0.08
Benzaldehyde[b]	0.901*	0.084	1.27	−0.38	−0.28	3.30
Limonene[b]	0.927*	0.950*	0.62	0.29	3.04	0.01
p-Dichlorobenzene[b]	0.271	0.649	1.28	0.82	−0.03	0.01
Phenol[b]	0.847*	0.038	0.71	−0.81	1.54	1.63

[a] The compound has a boiling point <100 °C.

[b] The compound has a boiling point >100 °C.

* Significant correlations obtained from multi-sorbent bed and Tenax TA tubes (F-Snedecor, $p < 0.05$).

Table 4

Average ± standard deviation for each volume breakthrough values (%VOC found in the back tube) for multi-sorbent bed and Tenax TA tubes ($n = 2$). Indoor air sampling. Compounds are listed by elution order.

Compounds	10 l		20 l		40 l		60 l		90 l	
	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA
Ethanol[a]	34 ± 2	54 ± 1	19 ± 1	54 ± 4	27 ± 9	55 ± 2	53 ± 2	51 ± 2	56 ± 1	46 ± 1
Acetone[a]	0.6 ± 0.3	54 ± 2	1 ± 1	55 ± 4	6 ± 3	54 ± 3	16 ± 9	42 ± 3	26 ± 3	42 ± 2
Isopropanol[a]	2 ± 1	54 ± 3	4 ± 2	56 ± 3	10 ± 1	56 ± 4	31 ± 2	49 ± 1	63 ± 17	56 ± 2
Carbon disulphide[a]	3.7 ± 0.2	44 ± 4	4 ± 1	40 ± 15	6 ± 4	41.8 ± 0.3	4 ± 3	51 ± 16	10 ± 8	56 ± 23
Dichloromethane[a]	6 ± 2	53 ± 2	7 ± 3	54 ± 3	22 ± 15	51 ± 1	31 ± 3	50 ± 7	61 ± 1	58 ± 3
n-Hexane[a]	0.4 ± 0.2	56 ± 3	0.46 ± 0.01	59 ± 2	0.8 ± 0.2	59 ± 5	0.2 ± 0.1	56 ± 10	0.055 ± 0.004	60 ± 3
Chloroform[a]	0.3 ± 0.1	56 ± 2	0.3 ± 0.1	57 ± 5	1 ± 1	53 ± 2	0.29 ± 0.01	51 ± 1	13 ± 11	58 ± 4
Carbon tetrachloride[b]	0	51 ± 3	0	55 ± 5	0.1 ± 0.1	62 ± 3	0	52 ± 10	0.1 ± 0.2	57 ± 3
Acetic acid[a]	0.8 ± 0.7	22 ± 4	1.0 ± 0.7	30 ± 16	0.7 ± 0.3	44 ± 2	0.5 ± 0.3	42 ± 6	1.6 ± 0.1	47 ± 14
Benzene[a]	0.6 ± 0.9	49 ± 4	0.9 ± 0.1	60 ± 2	0.8 ± 0.1	56 ± 5	1 ± 2	57 ± 1	0.1 ± 0.1	63 ± 3
n-Heptane[a]	0.3 ± 0.4	26 ± 4	0.1 ± 0.1	45 ± 8	0.1 ± 0.1	52 ± 2	0.04 ± 0.05	47 ± 2	0.051 ± 0.003	77 ± 6
1-Butanol[b]	0.7 ± 0.9	46 ± 15	0.8 ± 0.1	52 ± 14	0.6 ± 0.3	44 ± 30	0.214 ± 0.003	42 ± 22	0.5 ± 0.2	44 ± 24
Trichloroethylene[a]	0	55 ± 4	0	58 ± 5	0	57 ± 3	0	42 ± 1	0	58 ± 3
Methylisobuthylketone[b]	0	15 ± 4	0	22 ± 4	0.4 ± 0.2	35 ± 1	0	46 ± 3	0	64 ± 1
Toluene[b]	0.5 ± 0.3	19 ± 2	0.2 ± 0.2	42 ± 11	0.2 ± 0.1	50.1 ± 0.3	0.1 ± 0.1	42 ± 5	0.1 ± 0.1	61 ± 5
Tetrachloroethylene[b]	0	16 ± 2	0	34 ± 12	0.3 ± 0.1	44 ± 1	0	53 ± 1	0	62 ± 4
Butyl acetate[b]	0.3 ± 0.4	2.1 ± 0.3	0.39 ± 0.04	4 ± 2	0	6 ± 1	0	19 ± 1	0.1 ± 0.03	40 ± 2
NN-dimethylformamide[b]	0	8 ± 1	0	22 ± 5	0	31 ± 4	0	49 ± 3	0.6 ± 0.8	64 ± 2
Ethylbenzene[b]	0.1 ± 0.2	1.9 ± 0.1	0.2 ± 0.2	5 ± 2	0.07 ± 0.01	9 ± 4	0.02 ± 0.01	17 ± 1	0.04 ± 0.03	37 ± 2
m + *p*-Xylene[b]	0.2 ± 0.2	1.7 ± 0.2	0.2 ± 0.1	5 ± 3	0.06 ± 0.01	7 ± 3	0.03 ± 0.02	22 ± 3	0.1 ± 0.1	42 ± 2
o-Xylene[b]	0.1 ± 0.2	2.1 ± 0.1	0.1 ± 0.1	4 ± 2	0.07 ± 0.03	7 ± 2	0.02 ± 0.01	14.6 ± 0.2	0.1 ± 0.1	38 ± 2
2-Buthoxyethanol[b]	0	1.7 ± 0.3	0	3.5 ± 0.2	0.5 ± 0.1	8.6 ± 0.2	0.2 ± 0.1	31 ± 1	0.2 ± 0.1	24 ± 2
α-Pinene[b]	0	48 ± 4	0	57 ± 5	0.1 ± 0.1	55 ± 2	0	48 ± 4	0.01 ± 0.02	60 ± 2
Benzaldehyde[b]	0.6 ± 0.8	3.0 ± 0.4	0.6 ± 0.2	3.4 ± 0.1	1.1 ± 0.3	3.5 ± 0.3	0.9 ± 0.3	7 ± 1	0.8 ± 0.1	9 ± 3
Limonene[b]	0	0.6 ± 0.1	0.1 ± 0.1	1 ± 1	0.1 ± 0.1	2 ± 1	0	6.2 ± 0.2	0.02 ± 0.01	12 ± 4
p-Dichlorobenzene[b]	0	0	0	0	0	1 ± 1	0	1 ± 1	0.9 ± 0.1	2 ± 2
Phenol[b]	0.6 ± 0.8	8.8 ± 0.3	2 ± 1	5 ± 1	1.4 ± 0.2	5 ± 1	2.6 ± 0.4	8 ± 2	2 ± 1	14 ± 5

[a] The compound has a boiling point <100 °C.

[b] The compound has a boiling point >100 °C.

Table 5

Average ± standard deviation for each volume breakthrough values (%VOC found in the back tube) for multi-sorbent bed and Tenax TA tubes ($n = 2$). Outdoor air sampling. Compounds are listed by elution order.

Compounds	10 l		20 l		40 l		60 l		90 l	
	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA	Multi-sorbent	Tenax TA
Ethanol[a]	36 ± 1	47 ± 2	45 ± 6	39 ± 5	25 ± 1	53 ± 10	48 ± 25	37 ± 7	53 ± 21	36 ± 1
Acetone[a]	1.3 ± 0.4	48 ± 1	3 ± 1	38 ± 7	3 ± 1	48 ± 12	7 ± 3	41 ± 9	12 ± 5	27 ± 1
Isopropanol[a]	1 ± 1	57.7 ± 0.2	5 ± 2	50 ± 3	3 ± 1	69 ± 4	8 ± 7	46 ± 8	14 ± 11	43 ± 6
Carbon disulphide[a]	3.3 ± 0.4	50 ± 3	5 ± 7	43 ± 4	8.8 ± 0.2	51 ± 1	12 ± 1	48 ± 8	14 ± 16	43 ± 2
Dichloromethane[a]	10 ± 1	57 ± 4	8 ± 2	58 ± 4	9 ± 1	62 ± 7	28 ± 10	53 ± 9	32 ± 18	44 ± 8
n-Hexane[a]	0.3 ± 0.5	51 ± 6	1 ± 1	49 ± 1	1.4 ± 0.2	58 ± 2	0.4 ± 0.3	67 ± 9	0.4 ± 0.1	60 ± 1
Chloroform[a]	1 ± 1	59 ± 1	0.5 ± 0.4	42 ± 4	0.8 ± 0.7	81 ± 8	6 ± 5	47 ± 12	1.4 ± 0.3	50 ± 3
Carbon tetrachloride[b]	0	46 ± 5	0	53 ± 1	0	60 ± 4	0	56 ± 2	0	57 ± 3
Acetic acid[a]	0	22 ± 4	1.1 ± 0.3	30 ± 16	0.3 ± 0.4	44 ± 2	0	42 ± 6	0.4 ± 0.6	47 ± 14
Benzene[a]	0	47 ± 7	0	45 ± 5	0	52 ± 9	0	63 ± 2	0	48 ± 1
n-Heptane[a]	0	26 ± 4	0	31 ± 2	0	53 ± 3	0	51.1 ± 0.2	0	69 ± 2
1-Butanol[b]	2 ± 2	45 ± 2	3 ± 4	34 ± 5	1 ± 1	57.6 ± 0.3	0.8 ± 0.6	62 ± 2	0.5 ± 0.4	62 ± 2
Trichloroethylene[a]	0	51 ± 7	0	50 ± 3	0	68 ± 7	0	70 ± 4	0	71 ± 5
Methylisobuthylketone[b]	0	9 ± 3	0	16 ± 3	0	33 ± 4	0.5 ± 0.2	29 ± 3	0.2 ± 0.2	45 ± 5
Toluene[b]	0.6 ± 0.3	15 ± 7	0.7 ± 0.6	25 ± 6	0.3 ± 0.1	50 ± 6	0.3 ± 0.3	50 ± 5	0.20 ± 0.04	59 ± 2
Tetrachloroethylene[b]	0	7 ± 6	0.18 ± 0.02	47 ± 6	0.11 ± 0.03	23 ± 2	1 ± 1	37 ± 2	0.1 ± 0.1	60 ± 5
Butyl acetate[b]	0	0	0	1 ± 2	0	8 ± 2	0.2 ± 0.3	7.0 ± 0.1	0	21 ± 5
NN-dimethylformamide[b]	0	4 ± 5	0	10 ± 14	0	34 ± 9	0	33 ± 21	0	35 ± 19
Ethylbenzene[b]	0.9 ± 0.2	2 ± 2	0.8 ± 0.8	3 ± 2	0.10 ± 0.03	13 ± 2	0.14 ± 0.01	11 ± 2	0.1 ± 0.1	24 ± 6
m + *p*-Xylene[b]	0.5 ± 0.1	2 ± 1	0.5 ± 0.4	3 ± 2	0.11 ± 0.01	13 ± 3	0.1 ± 0.1	11 ± 2	0.08 ± 0.03	26 ± 6
o-Xylene[b]	0.6 ± 0.1	2 ± 2	0.7 ± 0.3	3 ± 2	0.12 ± 0.01	11 ± 1	0.1 ± 0.1	10 ± 1	0.07 ± 0.03	19 ± 4
2-Buthoxyethanol[b]	0	0	0	3.7 ± 0.4	0	13 ± 2	0	8 ± 1	0	16 ± 1
α-Pinene[b]	0	48 ± 9	0	58 ± 5	0	71.7 ± 0.1	0.1 ± 0.1	70 ± 3	0.2 ± 0.1	64 ± 1
Benzaldehyde[b]	0.7 ± 0.3	8 ± 1	0.5 ± 0.3	5 ± 1	0.19 ± 0.01	6 ± 1	0.3 ± 0.2	10 ± 1	0.05 ± 0.02	11 ± 3
Limonene[b]	0	0	0	0	0	8 ± 2	1.9 ± 0.3	5 ± 1	0.1 ± 0.1	12 ± 2
p-Dichlorobenzene[b]	0	0	0	0	1 ± 1	0	0	0	0	1 ± 2
Phenol[b]	0	11 ± 4	0.59 ± 0.01	10 ± 1	0.2 ± 0.3	10.8 ± 0.01	0	10 ± 1	2 ± 1	13 ± 4

[a] The compound has a boiling point <100 °C.

[b] The compound has a boiling point >100 °C.

concentrations in indoor air. However, slope values are really different from 1. These correlations cannot be taken into account due to the fact that the high breakthrough values obtained for these compounds both in multi-sorbent bed (for some of the sampling volumes) and Tenax TA tubes (for all sampling volumes) vary the real concentrations that would be obtained if breakthrough values were within acceptable ranges.

On the other hand, benzaldehyde and phenol do not present significant correlations in outdoor air since their concentrations both for multi-sorbent bed and Tenax TA tubes at the different sampled volumes are very similar, being all points of the correlation curve near to each other.

3.2. *Breakthrough comparative*

Breakthrough values can be influenced by weather variables such as temperature and relative humidity [11,18]. In the present study, average values of temperature and relative humidity were of 29.8 °C and 43.3%, and 22.6 °C and 56.5% for the samplings of July and October of 2009, respectively, as it has been said before. In general, important increases in temperature could lead to a reduction in breakthrough values [11]. However, it is unlikely that the 7 °C difference observed between temperature average values would account for an important degree of discrepancy between the obtained breakthrough values, as it has been observed in previous studies [23]. On the other hand, concerning relative humidity, a competition for the adsorbent active surface area would occur between water and the target compounds [24], reducing the adsorption capacity of the sorbent [25]; leading to different breakthrough values depending on the humidity of the environments. In this case, the hydrophobic properties of the sorbent would be crucial for the obtention of reliable results [11,26]. All sorbents used in the present study present high hydrophobicity, therefore, no differences in breakthrough values due to the differences observed in relative humidity among the sampling days would be expected.

Multi-sorbent bed and Tenax TA breakthrough values for the different volumes sampled are shown in Tables 4 and 5 for indoor and outdoor air, respectively. Typical VOCs recommended breakthrough value is <5% [11]. For the concentrations obtained, Tenax TA present high breakthrough values for mainly all compounds and sampling volumes studied. However, butyl acetate, ethylbenzene, *m* + *p*-xylene, *o*-xylene, and 2-buthoxyethanol present acceptable Tenax TA breakthrough values for sampling volumes up to 20 l. In addition to that, limonene and *p*-dichlorobenzene present breakthrough acceptable values up to 40 and 90 l, respectively. For compounds with boiling points below 100 °C and vapour pressures (20 °C) higher than 2 kPa, breakthrough values for Tenax TA tubes are very similar for each sample volume. However, breakthrough concentrations increase when increasing the sample volume for compounds that present boiling points above 100 °C and vapour pressures (20 °C) lower than 2–3 kPa (Tables 4 and 5).

On the other hand, multi-sorbent bed tubes do not exhibit important breakthrough values for these compounds, except the VVOCs ethanol (for all sampled volumes), and acetone, dichloromethane and isopropanol (for sampling volumes over 40 l).

The significant differences observed between multi-sorbent bed and Tenax TA concentrations, being the concentrations higher in multi-sorbent bed tubes, are directly related to the high breakthrough values determined for Tenax TA adsorbent. High breakthrough values represent a transfer of the target compounds from the front tube to the back tube; hence, lower concentrations are expected in the front tube. Tenax TA has a surface area of 20–35 $m^2\,g^{-1}$, whereas Carbotrap, Carbopack X and Carboxen 569 have surface areas of 95–100 $m^2\,g^{-1}$, 240–250 $m^2\,g^{-1}$ and

Table 6
Average ± standard deviation outdoor air concentrations ($\mu g\,m^{-3}$) and average ± standard deviation breakthrough values (%) for 70 $ml\,min^{-1}$ and 90 $ml\,min^{-1}$ sampling rates using multi-sorbent bed tubes ($n = 2$). Sample volume: 90 l. Compounds are listed by elution order.

Compounds	Multi-sorbent bed			
	Concentration ($\mu g\,m^{-3}$)		Breakthrough (%)	
	70 $ml\,min^{-1}$	90 $ml\,min^{-1}$	70 $ml\,min^{-1}$	90 $ml\,min^{-1}$
Ethanol[a]	2 ± 1	3 ± 1	64 ± 12	43 ± 8
Acetone[a]	27 ± 2	12.4 ± 0.7	8 ± 4	11 ± 4
Isopropanol[a]	3.9 ± 0.5	2.1 ± 0.1	19 ± 8	23 ± 7
Carbon disulphide[a,‡]	0.5 ± 0.1	0.05 ± 0.01	3 ± 2	8 ± 2
Dichloromethane[a]	3.2 ± 0.8	2.1 ± 0.4	33 ± 18	26 ± 1
n-Hexane[a]	5.9 ± 0.5	5.0 ± 0.6	0.022 ± 0.003	0.029 ± 0.004
Chloroform[a]	3.4 ± 0.1	2.7 ± 0.6	1.3 ± 0.6	2.2 ± 0.1
Carbon tetrachloride[b]	1.04 ± 0.02	0.8 ± 0.2	0	0
Acetic acid[a]	15 ± 7	16 ± 4	0.5 ± 0.1	0.4 ± 0.4
Benzene[a]	4.1 ± 0.4	3.6 ± 0.7	0.15 ± 0.04	0.15 ± 0.04
n-Heptane[a]	3.7 ± 0.7	3.6 ± 0.2	0	0
1-Butanol[b]	0.955 ± 0.002	1.3 ± 0.8	2 ± 1	1 ± 1
Trichloroethylene[a]	0.45 ± 0.01	0.3 ± 0.1	0	0
Methylisobuthylketone[b]	0.26 ± 0.02	0.15 ± 0.03	0.3 ± 0.2	0
Toluene[b]	37 ± 3	34 ± 2	0.054 ± 0.001	0.041 ± 0.004
Tetrachloroethylene[b]	2.5 ± 0.3	2.3 ± 0.3	0.4 ± 0.1	0.25 ± 0.02
Butyl acetate[b,‡]	2.4 ± 0.2	1.2 ± 0.2	0	0
NN-dimethylformamide[b,‡]	10 ± 2	1 ± 1	0	0
Ethylbenzene[b]	7 ± 1	6 ± 1	0.025 ± 0.004	0.0166 ± 0.0001
m + *p*-Xylene[b]	21 ± 2	20 ± 1	0.05 ± 0.01	0.024 ± 0.001
o-Xylene[b]	7 ± 1	6.7 ± 0.4	0.04 ± 0.01	0.022 ± 0.004
2-Buthoxyethanol[b]	0.9 ± 0.2	0.77 ± 0.02	0	0
α-Pinene[b]	1.3 ± 0.2	1.2 ± 0.2	0.07 ± 0.04	0
Benzaldehyde[b]	1.0 ± 0.3	0.9 ± 0.1	1.0 ± 0.3	0.86 ± 0.04
Limonene[b]	0.4 ± 0.1	0.5 ± 0.1	0	0
p-Dichlorobenzene[b]	0.10 ± 0.03	0.07 ± 0.02	0	0
Phenol[b]	0.18 ± 0.02	0.12 ± 0.01	0	0

[a] The compound has a boiling point <100 °C.

[b] The compound has a boiling point >100 °C.

[‡] Significant differences observed between the concentrations obtained from 70 $ml\,min^{-1}$ and 90 $ml\,min^{-1}$ (*t*-test, $p < 0.05$).

Table 7
Average ± standard deviation outdoor air concentrations (μg m^{-3}) and average ± standard deviation breakthrough values (%) for 70 ml min^{-1} and 90 ml min^{-1} sampling rates using Tenax TA tubes ($n = 2$). Sample volume: 90 l. Compounds are listed by elution order.

Compounds	Tenax TA			
	Concentration (μg m^{-3})		Breakthrough (%)	
	70 ml min^{-1}	90 ml min^{-1}	70 ml min^{-1}	90 ml min^{-1}
Ethanol[a]	2.2 ± 0.3	1.8 ± 0.4	45 ± 2	44 ± 6
Acetone[a]	0.5 ± 0.1	0.49 ± 0.04	29 ± 4	34 ± 2
Isopropanol[a]	0.10 ± 0.01	0.094 ± 0.001	46 ± 4	53.52 ± 0.02
Carbon disulphide[a]	0.011 ± 0.001	0.013 ± 0.002	47 ± 4	46 ± 1
Dichloromethane[a]	0.04 ± 0.01	0.026 ± 0.002	46 ± 6	58 ± 5
n-Hexane[a]	0.2 ± 0.1	0.16 ± 0.03	56 ± 7	54 ± 1
Chloroform[a]	0.10 ± 0.02	0.025 ± 0.001	54 ± 7	57 ± 1
Carbon tetrachloride[b]	0.062 ± 0.003	0.045 ± 0.001	47 ± 3	58 ± 2
Acetic acid[a]	4.7 ± 0.3	4.3 ± 0.8	45 ± 8	54 ± 11
Benzene[a,‡]	0.28 ± 0.01	0.14 ± 0.02	47 ± 2	49.6 ± 0.3
n-Heptane[a]	0.9 ± 0.2	0.5 ± 0.2	29 ± 3	42 ± 6
1-Butanol[b]	0.07 ± 0.01	0.07 ± 0.01	61 ± 22	55 ± 1
Trichloroethylene[a,‡]	0.048 ± 0.002	0.12 ± 0.01	55 ± 2	47 ± 4
Methylisobuthylketone[b,*]	0.093 ± 0.002	0.12 ± 0.02	31 ± 1	36.6 ± 0.3
Toluene[b,‡,*]	9.6 ± 0.3	7.2 ± 0.3	43 ± 3	56.2 ± 0.2
Tetrachloroethylene[b,*]	0.552 ± 0.003	0.7 ± 0.1	47 ± 2	54 ± 1
Butyl acetate[b,*]	2 ± 1	1.2 ± 0.3	8 ± 3	22 ± 4
NN-dimethylformamide[b,‡]	1 ± 1	3.5 ± 0.1	30 ± 6	48 ± 6
Ethylbenzene[b,*]	3.26 ± 0.03	2.7 ± 0.5	13 ± 2	27 ± 3
m + *p*-Xylene[b,*]	11.0 ± 0.1	9 ± 1	11 ± 2	27 ± 3
o-Xylene[b,*]	2.68 ± 0.04	2.0 ± 0.4	9 ± 2	23 ± 4
2-Buthoxyethanol[b,*]	0.67 ± 0.02	0.6 ± 0.1	3.3 ± 0.1	7 ± 1
α-Pinene[b,*]	0.10 ± 0.01	0.043 ± 0.004	48 ± 5	66 ± 4
Benzaldehyde	1.8 ± 0.4	2 ± 1	3.59 ± 0.04	7 ± 3
Limonene[b,*]	0.05 ± 0.01	0.03 ± 0.01	3 ± 1	12 ± 2
p-Dichlorobenzene[b]	0.0440 ± 0.0002	0.06 ± 0.03	0	0.5 ± 0.3
Phenol[b,*]	0.78 ± 0.02	0.8 ± 0.3	5.1 ± 0.2	10 ± 2

[a] The compound has a boiling point <100 °C.
[b] The compound has a boiling point >100 °C.
[*] Significant differences observed between breakthrough values obtained from 70 ml min^{-1} and 90 ml min^{-1} (*t*-test, $p < 0.05$).
[‡] Significant differences observed between the concentrations obtained from 70 ml min^{-1} and 90 ml min^{-1} (*t*-test, $p < 0.05$).

387–485 $m^2 g^{-1}$, respectively. Total surface areas of the tubes are approximately of 6 and 70 m^2 for Tenax TA and multi-sorbent bed, respectively. Therefore, multi-sorbent bed tubes have approximately 12 times more surface area to retain compounds than Tenax TA tubes. Due to its low specific surface area, Tenax TA has low adsorption capacity, and it is only suitable for the sampling of medium to high boiling compounds (50–100 °C < boiling point < 240–260 °C and 0.1 kPa < vapour pressure (20 °C) < 3–4 kPa [14]), e.g. C_6–C_{26} hydrocarbons, as it has been observed in several previous studies [1,4,27].

3.3. *Sampling flow rates comparative*

Two sampling rates, of 70 ml min^{-1} and 90 ml min^{-1}, were evaluated to determine if differences in breakthrough values were observed for the same volumes sampled using different sampling rates. The sample volume was established at 90 l, being the worst case. In Tables 6 and 7, average ± standard deviation of concentrations and breakthrough values at the two different sampling rates are shown for multi-sorbent bed and Tenax TA tubes, respectively. Significant differences are observed between Tenax TA breakthrough values for compounds with boiling points above 100 °C and vapour pressures (20 °C) lower than 2–3 kPa, being higher the ones corresponding to 90 ml min^{-1} (Table 7). On the other hand, no differences are observed between breakthrough values of 70 ml min^{-1} and 90 ml min^{-1} sampling rates for multi-sorbent bed tubes (Table 6). Hence, even at 90 l of sample volume and at a sampling rate of 90 ml min^{-1}, multi-sorbent bed tubes present acceptable breakthrough values for the majority of studied compounds (except ethanol, acetone, isopropanol and dichloromethane) as it has been said previously. However, Tenax TA tubes present unacceptable breakthrough values for mainly all studied compounds, and worse values are obtained when increasing the sampling rate.

4. Conclusions

Multi-sorbent bed tubes show better performance than Tenax TA tubes for very volatile organic compounds, being the first type of sorbent tube more appropriate for the adsorption of this kind of compounds, especially for those presenting boiling points lower than 100 °C and vapour pressures (20 °C) above 3 kPa. On the other hand, compounds with boiling points higher than 100 °C and vapour pressures lower than 2–3 kPa, show similar achievements in multi-sorbent bed and Tenax TA tubes. Tenax TA present unacceptable breakthrough values for mainly all compounds and sampling volumes studied. However, multi-sorbent bed tubes do not exhibit important breakthrough values for these compounds. Hence, if an exhaustive analysis of ambient air would be done, sorbent tubes that assure us a complete gathering of very volatile organic compounds without loss of sample would be more appropriate, such as a multi-sorbent bed of carbonaceous adsorbents.

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