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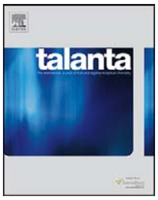

Comparative study of solvent extraction and thermal desorption methods for determining a wide range of volatile organic compounds in ambient air

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ABSTRACT

This paper compares two analytical methods for determining levels of 90 volatile organic compounds (VOCs) commonly found in industrial and urban atmospheres. Both methods are based on two official methods for determining benzene levels and involve collecting samples by active adsorptive enrichment on solid sorbents. The first method involves solvent extraction and uses activated charcoal as a sorbent. After sampling, the sorbent is extracted with 1 mL of carbon disulfide and then 1 μL of the extract is analysed in a GC–MS. The second method involves thermal desorption (TD) and uses Tenax TA and Carbograph 1TD as sorbents, which allows the whole sample to be analysed. In general, the thermal desorption method showed the best repetitivity and recovery and the lowest limit of detection and quantification for all target compounds. Because of its lower sensitivity, the solvent extraction method needs the preconcentration of large sample volumes of air (720 L vs. 2.64 L for the thermal desorption method) to yield similar limits of detection.

The performance of both methods in real samples was tested in a location near to a petrochemical complex. The results of the 24-h samples for the solvent extraction method were compared with the average of 12 2-h samples for the TD method. In some cases, both methods found differences in the VOC concentrations, especially in those compounds whose concentrations fluctuate significantly during the day.

1. Introduction

Volatile organic compounds (VOCs) have a significant impact on the environment and human health even at ppb levels. The environmental effects of VOCs include the accumulation and persistence of recalcitrant pollutants, the depletion of stratospheric ozone and the formation of tropospheric photochemical ozone [1–3]. Furthermore, VOCs have neurotoxic and genotoxic effects on human health and can cause respiratory and reproductive disorders [4–6].

Because of the complexity of the environmental air matrix and the usually low concentration of VOCs, from ppb down to ppt, reliably determining VOC levels in air requires the most efficient and sensitive sampling, preconcentration and analysis techniques. In this respect, adsorptive enrichment on solid sorbents is a well-established technique which allows sampling and preconcentration in one step. After the preconcentration step, analytes are removed from the sorbent and then determined by gas chromatography. Nowadays, most official agencies use two desorption methods for determining VOC levels: solvent extraction and thermal desorption.

Solvent extraction is the commonest method of VOC desorption. The main sorbent for this method is activated charcoal (usually coconut shell charcoal) [7–10]. Activated charcoal has a very complex surface structure containing a wide range of functional groups which allow the adsorption of a wide range of compounds [11,12]. The desorbing solvent most commonly used with activated charcoal is carbon disulfide due to its high volatility, its high adsorption heat on activated charcoal (which displaces other molecules), and its effectiveness at dissolving non-polar compounds. Moreover, it elutes rapidly at the front of the analysis on most common GC columns and has a very low response on FID [13].

The solvent extraction method is simple, compatible with high molecular mass and thermally unstable compounds and allows the preconcentration of high volumes of air. However, it has several drawbacks. The major disadvantage is that the sample is diluted with the desorbing solvent, which increases the method detection limit. As a consequence, this method requires long sampling periods and the preconcentration of large volumes of air. Moreover, polar and reactive compounds often have poor desorption efficiencies that can vary further with the presence of other polar species or water vapor [11,14–16]. These low recoveries can be associated

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Table 1

Target VOCs in chromatographic elution order showing retention times (t_R), repetitivity, recovery and method detection and quantification limit, expressed in $\mu g\,m^{-3}$, for the solvent desorption (method A) and the thermal desorption method (method B).

No.	Target VOCs	t_R (min)	Repetitivity[a] (%RSD, $n = 5$)		% recoveries[b] ($n = 3$)		MDL[c] ($\mu g\,m^{-3}$)		MQL[d] ($\mu g\,m^{-3}$)	
			Met. A	Met. B	Met. A	Met. B	Met. A	Met. B	Met. A	Met. B
1	i-Pentane[e]	3.87	0.66	2.49	99.2	85.0	0.69	0.04	1.39	0.19
2	1-Pentene[e]	4.08	3.87	2.45	96.3	99.8	0.69	0.19	1.39	0.38
3	n-Pentane[e]	4.20	2.11	2.42	99.5	99.7	0.28	0.02	0.69	0.04
4	Diethyl ether	4.30	8.79	2.67	99.0	99.8	0.69	0.04	1.39	0.19
5	2-Trans-pentene[e]	4.35	0.99	1.75	98.7	99.6	0.28	0.04	0.69	0.19
6	Isoprene[e]	4.38	1.68	3.38	97.4	94.9	0.69	0.28	1.39	0.38
7	2-Cis-pentene[e]	4.49	4.03	2.87	97.3	96.1	0.69	0.04	1.39	0.19
8	1,1-Dichloroethylene	4.59	3.77	1.14	96.1	95.7	0.28	0.03	0.69	0.04
9	Acrylonitrile[f,g]	4.63	7.06	0.99	100.1	100.0	0.14	0.002	0.69	0.02
10	1-Hexene	5.37	12.39	2.13	88.0	95.2	0.69	0.04	1.39	0.19
11	Trans-1,2-dichloroethene	5.63	4.52	3.27	95.4	97.9	0.69	0.02	1.39	0.04
12	Methyl-tercbutylether[f]	5.69	5.01	0.86	96.5	85.9	0.07	0.04	0.14	0.19
13	Propionitrile	5.88	8.30	1.21	97.4	100.1	0.07	0.04	0.14	0.19
14	1,1-Dichloroethane	6.00	7.13	2.38	96.3	100.2	1.39	0.02	2.78	0.04
15	n-Hexane[e,f]	6.54	2.67	2.10	96.7	96.6	0.28	0.03	0.69	0.04
16	Methacrylonitrile	6.55	4.45	1.45	96.8	99.8	0.01	0.004	0.07	0.04
17	Cis-1,2-dichloroethylene	6.92	5.58	2.32	100.2	99.9	0.69	0.02	1.39	0.04
18	Methylacrilate	7.10	3.95	0.98	95.9	99.8	0.69	0.004	1.39	0.04
19	2,2-Dichloropropane	7.14	4.40	3.48	97.7	84.1	0.28	0.02	0.69	0.04
20	Bromochloromethane	7.26	6.08	1.46	95.4	99.6	0.07	0.03	0.14	0.04
21	Chloroform[f]	7.33	7.15	1.85	100.8	99.8	0.01	0.02	0.07	0.04
22	Tetrahydrofuran	7.60	4.92	0.67	98.8	99.9	0.14	0.11	0.69	0.19
23	1,1,1-Trichloroethane[f]	8.29	6.86	2.75	101.3	97.5	0.07	0.02	0.14	0.19
24	1-Chlorobutane	8.40	9.02	2.24	65.1	99.5	0.07	0.01	0.14	0.19
25	1,2-Dichloroethane[g]	8.42	2.29	2.36	101.6	99.4	0.69	0.004	1.39	0.04
26	1,1-Dichloropropene	8.66	7.60	2.67	97.8	99.5	0.28	0.02	0.69	0.04
27	Benzene[e,f,g]	8.92	0.96	1.47	98.3	100.0	0.28	0.16	0.69	0.38
28	Carbon tetrachloride[f]	8.97	5.66	3.75	101.4	95	0.69	0.02	0.69	0.19
29	Chloroacetonitrile	9.41	10.29	3.68	87.6	99.7	0.07	0.04	0.14	0.19
30	i-Octane[e]	9.83	4.03	3.01	100.5	97.7	0.28	0.02	0.69	0.04
31	n-Heptane[e]	10.28	2.38	2.96	98.3	100.0	0.28	0.03	0.69	0.19
32	2-Nitropropane[f]	10.29	5.35	1.15	99.0	99.5	0.07	0.004	0.14	0.02
33	1,2-Dichloropropane[f]	10.38	4.94	0.41	99.5	99.6	0.07	0.01	0.14	0.02
34	Trichloroethene[f,g]	10.41	8.26	2.01	100.9	99.5	0.28	0.004	0.69	0.02
35	Dibromomethane	10.51	5.96	0.83	100.3	99.8	0.14	0.02	0.69	0.04
36	1,4-Dioxane[f]	10.68	5.96	6.34	100.2	99.4	0.07	0.30	0.14	0.38
37	Methylmethacrylate[f]	10.78	5.64	2.68	91.2	99	0.07	0.004	0.14	0.38
38	Bromodichloromethane	10.77	4.90	1.56	101.4	99.3	0.07	0.004	0.14	0.04
39	Cis-1,3-dichloropropene	12.02	5.90	1.46	102.0	99.5	0.14	0.02	0.69	0.04
40	Trans-1,3-dichloropropene	13.05	5.25	2.89	101.9	99.7	0.14	0.02	0.69	0.04
41	Toluene[e,f,g]	13.23	5.95	1.05	99.9	99.6	0.07	0.23	0.14	0.38
42	1,1,2-Trichloroethane[f]	13.41	7.88	3.55	102.6	100.0	0.14	0.004	0.69	0.04
43	Ethylmethacrylate	13.77	3.86	3.40	102.8	99.8	0.07	0.004	0.14	0.04
44	1,3-Dichloropropane	13.87	12.92	2.21	104.7	99.3	0.14	0.004	0.69	0.04
45	n-Octane[e]	14.36	6.45	1.94	99.5	96.9	0.07	0.01	0.14	0.19
46	Dibromochloromethane	14.49	8.54	2.62	101.5	99.4	0.07	0.004	0.14	0.02
47	1,2-Dibromoethane	14.89	6.86	2.95	99.4	99.7	0.07	0.01	0.14	0.02
48	Tetrachloroethene[f,g]	14.95	16.93	0.43	102.3	98.7	0.07	0.002	0.14	0.02
49	Chlorobenzene[f]	16.48	5.01	3.07	100.5	99.3	0.07	0.002	0.14	0.02
50	1,1,1,2-Tetrachloroethane	16.60	4.26	2.82	99.6	99.1	0.28	0.004	0.69	0.02
51	Ethylbenzene[e,f]	16.99	4.66	2.59	101.7	99.2	0.07	0.04	0.14	0.08
52,53	m,p-Xylene[e,f]	17.31	4.55	2.51	99.8	98.9	0.01	0.02	0.07	0.04
54	Bromoform[f]	18.10	11.94	4.08	101.7	99.5	0.07	0.01	0.14	0.02
55	Styrene[f,g]	18.13	3.45	3.63	91.1	99.6	0.01	0.15	0.07	0.19
56	o-Xylene[e,f]	18.22	4.17	3.84	97.5	100.3	0.07	0.0004	0.14	0.04
57	1,1,2,2-Tetrachloroethane[f]	18.91	3.93	4.67	100.4	99.6	0.07	0.01	0.14	0.02
58	1,2,3-Trichloropropane	19.17	4.10	1.76	101.4	99.8	0.28	0.02	0.69	0.04
59	1,4-Dichloro-2-butene	19.24	1.40	3.95	103.7	99.7	0.07	0.03	0.14	0.04
60	Isopropylbenzene[f]	19.32	4.15	3.18	100.2	99.8	0.01	0.003	0.07	0.02
61	Bromobenzene	19.75	0.82	3.72	99.2	99.4	0.07	0.004	0.14	0.02
62	n-Propylbenzene	20.38	2.55	3.34	93.0	100.1	0.07	0.004	0.14	0.02
63	2-Chlorotoluene	20.42	4.47	3.61	96.5	99.9	0.01	0.01	0.07	0.02
64	4-Chlorotoluene	20.60	4.76	3.61	95.8	99.5	0.01	0.004	0.07	0.02
65	3-Ethyltoluene	20.62	5.02	3.58	93.2	99.5	0.01	0.002	0.07	0.004
66	4-Ethyltoluene	20.71	2.99	3.89	90.7	99.9	0.01	0.40	0.07	0.45
67	1,3,5-Trimethylbenzene[e]	20.87	4.51	3.80	95.5	99.9	0.01	0.002	0.07	0.004
68	2-Ethyltoluene	21.30	4.44	3.25	95.9	99.3	0.01	0.004	0.07	0.04
69	Pentachloroethane	21.35	10.85	4.03	82.4	99.7	0.07	0.02	0.14	0.04
70	tert-Butylbenzene	21.72	4.59	3.19	99.5	99.4	0.01	0.004	0.07	0.02
71	1,2,4-Trimethylbenzene[e]	21.78	1.90	3.52	95.9	98.2	0.01	0.01	0.07	0.02
72	1,3-Dichlorobenzene	22.30	2.46	4.56	90.4	98.3	0.07	0.004	0.14	0.02
73	sec-Butylbenzene	22.31	4.61	3.85	99.4	99.4	0.07	0.002	0.14	0.004

Table 1 (*Continued*).

No.	Target VOCs	t_R (min)	Repetitivity[a] (%RSD, $n = 5$)		% recoveries[b] ($n = 3$)		MDL[c] ($\mu g\,m^{-3}$)		MQL[d] ($\mu g\,m^{-3}$)	
			Met. A	Met. B	Met. A	Met. B	Met. A	Met. B	Met. A	Met. B
74	1,4-Dichlorobenzene[f]	22.52	0.71	4.04	90.3	99.6	0.01	0.004	0.07	0.02
75	p-Isopropyltoluene	22.69	4.00	3.65	100.3	99.6	0.01	0.01	0.07	0.02
76	1,2,3-Trimetylbenzene[e]	22.73	2.67	3.63	88.8	98.3	0.01	0.004	0.07	0.01
77	Benzyl alcohol	22.93	5.35	1.57	82.6	95.0	0.01	0.0004	0.07	0.002
78	1,2-Dichlorobenzene	23.20	2.77	2.96	97.7	99.2	0.01	0.004	0.07	0.02
79	1,3-Diethylbenzene	23.34	2.51	4.23	85.3	99.5	0.01	0.004	0.07	0.02
80	1,4-Diethylbenzene	23.56	2.44	4.09	93.4	99.5	0.01	0.004	0.07	0.02
81	n-Butylbenzene	23.58	5.35	2.14	88.1	98.3	0.01	0.002	0.07	0.004
82	1,2-Diethylbenzene	23.72	3.81	4.02	91.1	97.2	0.01	0.004	0.07	0.02
83	Hexachloroethane[f]	24.37	4.83	3.80	97.6	95.1	0.07	0.02	0.14	0.04
84	1,2-Dibromo-3-chloropropane	24.45	6.28	4.09	97.0	98.6	0.28	0.02	0.69	0.04
85	1,2,4-Trichlorobenzene	26.53	1.44	4.09	82.2	99.6	0.01	0.004	0.07	0.04
86	Naphthalene[f,g]	26.79	8.28	1.33	78.3	92.0	0.07	0.04	0.14	0.10
87	Hexachlorobutadiene	27.17	3.45	4.16	100.6	99.5	0.07	0.004	0.14	0.02
88	1,2,3-Trichlorobenzene	27.24	7.98	3.60	87.8	99.3	0.01	0.004	0.07	0.02
89	2-Methylnaphtalene[f,g]	28.77	8.47	1.70	47.4	91.5	0.07	0.02	0.14	0.04
90	1-Methylnaphtalene[f,g]	29.11	8.01	1.50	47.0	91.2	0.04	0.002	0.07	0.004

[a] Repetitivity expressed as relative standard deviation (%RSD) for the analysis of 1 ng VOCs standard ($n = 5$).

[b] Recoveries calculated as the percentage recovery of the response obtained by the triplicate analysis of a 1 ng standard using method A or method B, compared with the response obtained by direct injection of the same amount of standard under the same split conditions.

[c] Method detection limit (MDL), expressed in $\mu g\,m^{-3}$, calculated for a sampling volume of air of 720 L (method A) and 2.64 L (method B).

[d] Method quantification limit (MQL), expressed in $\mu g\,m^{-3}$, calculated for a sampling volume of air of 720 L (method A) and 2.64 L (method B).

[e] Ozone precursors recommended for measurement by the Directive 2002/3/EC [26].

[f] Compounds included in the USEPA List of Hazardous Air Pollutants [25].

[g] Compounds included as hazardous organic pollutants in the WHO Air Quality Guidelines [4].

with the strength of multiple binding interactions and even irreversible adsorptions and catalytic transformations of the analytes into different products. Regarding the solvent, CS_2 can react with certain compounds such as amines, which can interfere with the analysis of volatile chlorinated carbons and may vaporise some very volatile molecules during the procedure because of the heat of the desorption [13]. Furthermore, CS_2 has highly toxic health effects [4], causes serious environmental damage and has a high response on MS.

Thermal desorption is a good alternative to solvent desorption and is also used in several official methods like the UNE-EN 14662-1 for benzene and the EPA TO-17 for VOCs [17,18]. This method provides enhanced sensitivity (since the whole sample is analysed), is compatible with thermally stable polar and apolar compounds, enables the reuse of the adsorbent tubes, avoids the use of toxic solvents in the extraction step and, in consequence, prevents the solvent's signal from masking the analyte peaks in the sample chromatograms. There is a wide variety of commercial sorbents that can be used with the thermal desorption technique. The main types of sorbents used in air monitoring are porous organic polymers, graphitised carbon blacks and carbon molecular sieves [1,11,19]. The selection of a suitable sorbent depends not only on the physical and chemical characteristics of the VOC studied, but also on sampling conditions such as the meteorological conditions, time of sampling and sample volume. Consequently, recent studies tend to use multiple-bed sorbent cartridges which provide high breakthrough volumes and the quantitative retention and desorption of VOCs over a wide volatility range [20–24]. The main drawbacks of thermal desorption are: the initial cost of the equipment; the possible degradation of those sorbents that generate artefacts and blanks of some analytes, which can interfere in the analysis; and the consumption of the sample in a single analysis (although modern equipment allows the recollection of split samples in a fresh tube). Moreover, thermal desorption is not recommended for thermally unstable compounds and for compounds with high boiling points (above 300 °C) because the desorption efficiencies decrease.

Since the solvent and thermal desorption methods are based on quite different physical and chemical processes, it is important to study how this affects the accuracy and precision of the overall emission estimates. Hence, the aim of this paper is to compare two methods used for monitoring VOCs: one based on solvent extraction (method A) and one based on thermal desorption (method B). Both methods were used to determine the levels of 90 VOCs that are commonly found in industrial and urban atmospheres and that have a wide range of different physical and chemical characteristics. Both methods were tested using real atmospheric samples taken from a location situated next to a petrochemical complex. As far as we know, this is the first study to compare the performance in real samples of both methods and the results when used to determine 90 compounds. Hence, this study should help in defining the most appropriate method for monitoring these compounds.

2. Experimental

2.1. Chemical standards

The list of the 90 target VOCs is shown in Table 1. The VOCs were selected on the basis of their occurrence in industrial and urban air and their adverse effects on the environment and human health. Twenty-seven of the ninety compounds are included in the list of Hazardous Air Pollutants (HAPs) of the US EPA Clean Air Act [25], eighteen of them are ozone precursors recommended for measurement by the Directive 2002/3/EC [26] and ten of them are included as hazardous organic pollutants in the World Health Organization Air Quality Guidelines [4].

The standards of the 90 target compounds involve two mixtures of volatile organic compounds at 2000 mg L^{-1} (592/524 Volatile Organics Calibration Mix and EPA 524.2 Revision 4 Mix in methanol, from Supelco, Bellefonte, USA) and the individual standards of i-pentane, 1-pentene, n-pentane, 2-pentene (cis/trans mixture), isoprene, 1-hexene, n-hexane, i-octane, n-heptane, 1,4-dioxane, n-octane, 1,2,3-trimethylbenzene, benzyl alcohol (Sigma–Aldrich, Steinheim, Germany), 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, 1,2-diethylbenzene, 1,3-diethylbenzene, 1,4-diethylbenzene (Fluka, Buchs, Switzerland), 1-methylnaphthalene and 2-methylnaphthalene (Riedel-deHaën, Seelze, Germany). The minimal purity of the standards was 97%.

Toluene-d_8 from Aldrich was used as an internal standard for method A as recommended by the UNE-EN 14662-2 [10].

The standards were diluted in methanol for gas chromatography with purity >99.9% (SDS, Peypin, France) and with a toluene-d_8 constant concentration of 5 mg L^{-1} for method A. All the standards were prepared on the day of use, and stored at 4 °C in 10 mL Certan® capillary vials provided by Supelco. Nitrogen gas of 99.999% purity was used to activate the thermal desorption sorbent tubes and 99.999% pure helium gas was used for the chromatographic analysis (Carburos Metálicos, Barcelona, Spain). Carbon disulfide from Sigma–Aldrich (purity 99.9% with lees than 0.001% of benzene) was used for the solvent extraction method.

2.2. Analytical methods

2.2.1. Method A

Standard charcoal tubes Orbo™-32 (provided by Supelco) were used for the solvent extraction method. These cartridges are glass tubes with both ends flame sealed (7 cm long × 6 mm o.d.) and contain two sections of 20/40 mesh coconut activated charcoal separated by a 2-mm portion of urethane foam. The adsorbing section, which is the longest, contained 100 mg of charcoal and the back-up section 50 mg.

Samples were collected by active sampling at the large section end of the tube. A volatile organic compounds sampler CPV-COV-S (MCV, Collbató, Spain) with a module that allows the sequential sampling of up to nine samples was used to pump air samples at a flow rate of 500 mL min^{-1}, for 24 h, thus collecting 720 L of air. After sampling, the charcoal tubes were removed from the sampler and the two open sides were tightly closed with special PTFE caps to avoid undesirable desorption. Then samples were stored in hermetic glass jars at −20 °C until the analysis, in order to prevent the risk of contamination and deterioration. Samples were analysed no later than 1 week after collection. To detect possible contamination, weekly field blanks were tested by putting a charcoal tube with broken ends in a channel of the sampler but without passing any air sample though it. The blank tube was then collected and analysed.

In preparation for the analysis, each charcoal tube was scored with a quartz blade (Orbo™ tube cutter, Supelco) in the front of the first section (i.e. the adsorbing section) of charcoal and broken open. The glass wool was removed and discarded. The charcoal in the adsorbing section was transferred to a 2-mL capped vial. The separating foam was removed and discarded; the second section (back-up section) was transferred to another capped vial. These two sections were analysed separately.

To desorb the samples, 1 mL of desorbing solution was pipetted into each sample vial. The desorption solution consisted of 5 ppm of internal standard solution in carbon disulfide. The sample vials were capped with PTFE as soon as the solution was added. Desorption was done for 30 min with occasional shaking.

Immediately after the solvent process, 1 μL of sample extract was injected into a split/splitless inlet port. Chromatographic conditions are detailed in Section 2.3.

2.2.2. Method B

The cartridges used for the thermal desorption method were stainless-steel tubes (89 mm long × 6.4 mm o.d.) filled with a multisorbent bed of approximately 350 mg of Tenax/Carbograph 1TD (Markes International Limited, Llantrisant, UK). The selection of the two sorbent materials was based on previous studies [13,20,27].

Before each use, tubes were conditioned by thermal cleaning (100 °C for 15 min, 200 °C for 15 min and 325 °C for 30 min) under a nitrogen flow rate of 100 mL min^{-1} (purity 99.999%, Carburos Metálicos, Tarragona, Spain). After conditioning, the tubes were sealed with Swagelok end caps fitted with PTFE ferrules and stored in hermetically sealable glass jars with desiccant material in order to prevent any ambient contamination of the sorbents.

An MTS-32™ sequential tube sampler coupled with a constant flow sampling pump (FLEC Air Pump 1001, from Markes) was used to pump air samples. This equipment allows the sequential sampling of 32 tubes. The sampling volume was fixed at 22 mL min^{-1}, for 2 h and 2.64 L of air were collected. Samples were collected at the Tenax TA end of the tube in order to collect the heaviest hydrocarbons first. The Tenax TA end of the tubes were capped with DiffLok™ caps which allow air to pass when sampling while also protecting the sample tubes for up to 8 days. Blanks of the total process were checked by putting two blank tubes into the sequential tube sampler every sampling day without passing any air sample through it.

Desorption of the analytes retained on the Tenax TA–Carbograph 1TD sorbent tubes was carried out in a Unity Thermal Desorption system connected to an Ultra A automatic sampler (both from Markes International Limited, Llantrisant, UK). In the primary desorption the sorbent tubes were heated to 275 °C with a helium flow rate of 30 mL min^{-1} for 10 min and no split. The desorbed VOCs were refocused into a cold trap, filled with Tenax TA and Carbograph 1TD and cooled at −5 °C. In the secondary desorption the cold trap was flash-heated at 300 °C for 3 min, with a split flow of 5 mL min^{-1}, and analytes were injected into the chromatographic column. Additional details about the thermal desorption system were given in previous studies [20,27].

2.3. Chromatographic conditions

In both methods, separation and detection were performed in a 6890N gas chromatograph and 5973 inert mass spectrometer (Agilent Technologies. Palo Alto, USA), using a TRACSIL Meta.X5 capillary column (60 m, 0.32 mm, 1.0 μm, provided by TEKNOKROMA, Barcelona, Spain). Analyses with method A were performed by injecting 1 μL of extract in a split/splitless port at 180 °C with a split of 5 mL/min and a helium flow rate of 1.2 mL min^{-1}. The oven temperature of the GC was initially held at 40 °C for 5 min, then raised to 140 °C at a rate of 6 °C min^{-1} and then raised again to 220 °C at a rate of 15 °C min^{-1} and held at that temperature for 8 min.

For method B, the interface between the thermal desorption system and the GC was set at 200 °C. The analyses were performed with a helium flow rate of 1.5 mL min^{-1} and the same GC oven program of temperatures as method A. The flow rate for method B was higher than for method A because higher flow rates were needed for the completely trap desorption.

In both methods, the GC–MS interface was set at 280 °C. The mass spectrometer acquired data in scan mode with an m/z interval from 35 to 280 and an electron impact energy of 70 eV. Qualitative identification of target VOCs was based on the match between the retention times and the ion ratios of the target quantifier and qualifier ions. The retention times are shown in Table 1. The quantifier and qualifier ions for each target compound have been published elsewhere [27]. The internal standard calibration method was used for the GC–MS quantification in method A and the external standard calibration was used in method B.

2.4. Calibration

Calibration in both methods was done by enriching the sorbent tubes with the liquid standards using a Calibration Solution Loading Rig (Markes International Limited, Llantrisant, UK). Volumes of between 1 and 5 μL were injected into the sorbent tubes while a flow of 100 mL min^{-1} of helium passed through the tube to carry the analytes into the sorbent. To ensure the full retention of the analytes and the repeatability of the injection, the syringe was placed in the sorbent for 20 s and in the helium stream for 5 min before the tubes were sealed and immediately desorbed and analysed as described above.

2.5. Sampling sites

Field samples were taken at Perafort (Tarragona, Spain). This location is sited less than 1 km from the North Industrial Complex and about 15 km from the main city, Tarragona. Some of the products manufactured at this complex are vinyl acetate, benzene, chloroform, methylene chloride, acrylonitrile, methylmethacrylate, ethylbenzene, styrene, fuels, propane and kerosene [28]. Samples were collected in October and November 2008.

3. Results and discussion

3.1. Comparison of the analytical methods

Although both analytical methods have been proposed by several official organisations for monitoring benzene and other VOCs in air, they differ regarding the sorbent used for the preconcentration step in the analyte extraction method. These differences were tested for the 90 target VOCs because they affect the analytical parameters.

Due to the dilution of the sample with the extraction solvent, method A needs a high volume of air to be preconcentrated in order to achieve acceptable limits of detection, whereas a low volume is enough for method B. Prior to determining the sample volume for each method, blank signals of the sorbents were checked because they affect the method detection limits and overall performance. To quantify these blanks, the responses of the blank tubes were compared with the responses obtained by directly injecting the standards under the same split conditions. Blanks of the activated charcoal tubes (method A) were determined by extracting and analysing the sorbent, from the adsorbing section of eight new tubes under the same conditions as the samples (see Section 2.2.1). These blanks showed the presence of only two of the target compounds: n-hexane (0.09 ± 0.05 ng per tube) and benzene (0.07 ± 0.04 ng per tube). Blanks of the thermal desorption tubes (method B) were checked by analysing eight freshly cleaned sorbent tubes also under the same conditions as the samples (see Section 2.2.2). A total of 21 target VOCs were found in the method B tubes in amounts ranging from 0.0012 ± 0.0003 ng for the o-xylene, to 0.30 ± 0.25 ng for 4-ethyltoluene. The method B blanks for n-hexane and benzene were 0.03 ± 0.01 ng and 0.23 ± 0.07 ng, respectively. The values of the average blank concentrations for the remaining compounds in method B were similar to those reported in a previous paper [27]. The subsequent analysis of real samples showed that amounts of VOCs in the blank tubes were less than 5% of the average amounts found in samples, as recommended by EPA [18].

To fix the sample volume, breakthrough tests were performed for both methods. For method A, the back-up section of the charcoal tubes was analysed under the same conditions as the adsorptive section. In the eight samples analysed with method A the concentration of the target VOCs in the back-up section was under the method quantification limit at the fixed rate of 500 mL min^{-1} for 24 h (720 L of air collected). To set the sampling volume of method B, two fresh cleaned sorbent tubes were connected in series so that the back tube would retain the analytes eluted from the front tube. Although the recommended sampling volume for method A for benzene is 10 L [17], the presence of more volatile target analytes caused the rate to be set at 22 mL min^{-1} for 2 h, which meant that 2.64 L of air was collected. At this volume, 10 target compounds were present in the second tube at concentrations ranging from 2.4% for chloroform to 4.8% for n-pentane, compared with their respective concentrations in the first tube. This does not exceed the 5% recommended by the EPA [18].

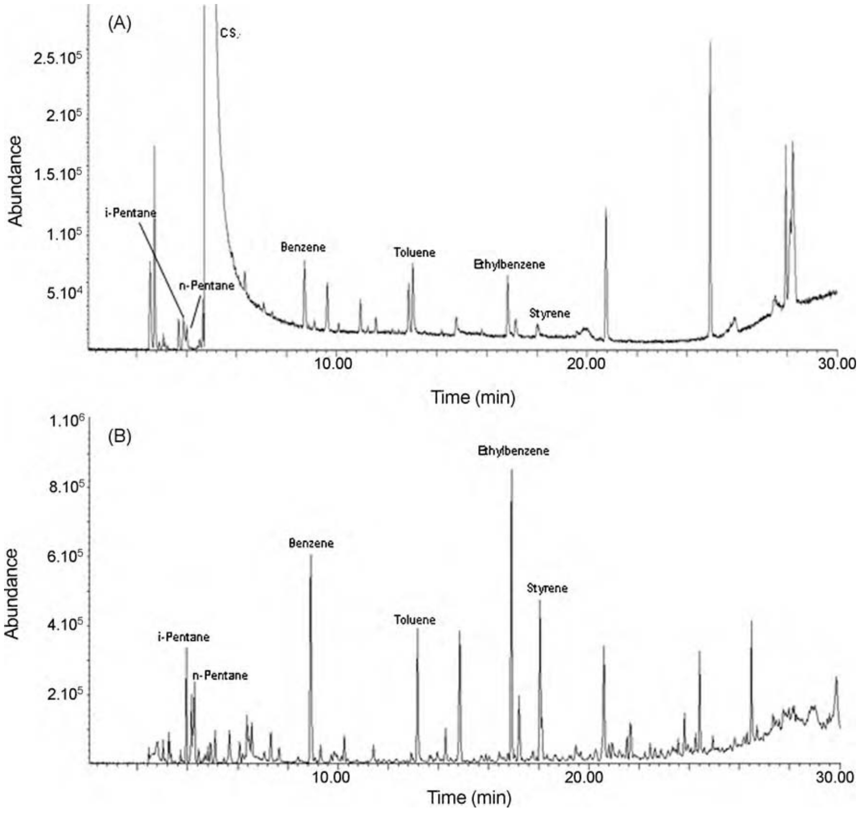

Fig. 1. Total ion chromatograms of an air sample by method A (A) and by method B (B). Some of the most representative compounds are marked.

Table 2
Average concentration, expressed in $\mu g\, m^{-3}$, of target compounds found in real samples by the solvent extraction method (A) and the thermal desorption method (B).

No.	Target VOCs	Day 1		Day 2		Day 3		Day 4		Day 5		Day 6		Day 7		Day 8	
		A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
1	i-Pentane	3.90	33.04	6.90	32.25	3.70	17.94	5.90	54.90	10.60	49.49	9.90	76.85	5.10	52.09	5.40	61.44
3	n-Pentane	2.80	10.55	3.50	12.53	2.80	9.57	3.50	19.82	5.20	20.55	4.00	17.51	2.70	11.74	2.80	15.92
4	Diethyl ether	n.d.	0.09	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
5	2-Trans-pentene	n.d.	1.15	n.d.	2.86	n.d.	1.23	n.d.	1.79	n.d.	2.57	n.d.	1.16	n.d.	1.17	n.d.	1.61
6	Isoprene	n.d.	4.21	n.d.	4.87	n.d.	2.05	n.d.	3.84	n.d.	3.97	n.d.	1.31	n.d.	0.87	n.d.	1.88
7	2-Cis-pentene	n.d.	1.43	n.d.	4.50	n.d.	1.41	n.d.	2.09	n.d.	2.32	n.d.	1.18	n.d.	1.46	n.d.	1.74
9	Acrylonitrile	n.d.	0.95	n.d.	2.45	n.d.	2.82	n.d.	26.59	n.d.	6.64	n.d.	42.01	n.d.	47.77	n.d.	6.05
11	Trans-1,2-dichloroethene	n.d.	0.88	n.d.	0.39	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
13	Propionitrile	n.d.	0.54	n.d.	0.13	n.d.	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15	n-Hexane	1.40	2.38	1.70	5.84	2.30	2.47	2.30	4.17	3.70	6.69	2.20	4.74	2.00	2.58	1.90	4.20
20	Bromochloromethane	n.d.	1.08	n.d.	0.38	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
21	Chloroform	0.80	0.69	0.80	1.20	0.80	0.36	0.80	0.52	0.90	0.64	0.80	0.32	0.80	0.38	0.80	0.71
22	Tetrahydrofuran	n.d.	0.98	n.d.	0.33	n.d.	0.15	n.d.	0.38	n.d.	0.27	n.d.	0.11	n.d.	0.53	n.d.	0.55
25	1,2-Dichloroethane	n.q.	1.68	n.d.	3.25	n.d.	0.22	n.d.	0.82	1.50	2.96	n.d.	0.13	n.d.	0.31	n.q.	3.81
27	Benzene	1.40	2.53	1.60	7.77	2.90	8.52	3.60	17.15	6.40	14.46	4.00	14.10	1.70	10.50	1.30	9.18
28	Carbon tetrachloride	1.30	1.04	1.40	1.00	1.50	1.06	1.60	1.08	2.20	1.16	1.30	0.84	1.20	0.96	1.20	1.29
31	n-Heptane	1.30	0.77	1.60	2.62	1.50	0.86	1.50	1.47	2.10	2.35	1.60	1.65	n.d.	1.03	n.d.	1.58
32	2-Nitropropane	0.80	0.66	1.00	2.34	0.90	0.67	0.90	1.04	1.40	1.53	1.10	1.17	1.30	0.79	1.40	1.15
34	Trichloroethene	2.10	0.69	2.10	0.54	2.00	0.08	2.00	0.15	2.00	0.25	2.00	0.10	0.70	0.10	0.80	0.28
36	1,4-Dioxane	n.d.	0.86	n.d.	0.02	n.d.	n.d.	n.d.	0.02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.10
37	Methylmethacrylate	n.d.	0.67	0.70	4.05	n.d.	0.25	n.d.	1.42	n.d.	0.24	0.80	1.11	0.50	0.63	n.d.	0.18
41	Toluene	3.90	8.60	5.20	12.08	3.60	5.05	4.10	8.18	3.90	8.96	3.90	6.64	2.20	3.93	2.50	6.17
45	n-Octane	n.d.	0.44	1.20	1.59	1.10	0.40	1.20	0.87	1.10	1.32	1.30	0.71	1.10	0.72	1.20	0.98
48	Tetrachloroethene	0.20	0.87	0.20	0.81	n.q.	0.31	0.10	0.48	n.q.	0.62	n.q.	0.28	n.q.	0.25	n.q.	0.58
51	Ethylbenzene	1.40	1.68	1.90	3.50	1.50	1.57	4.60	13.60	5.70	7.06	5.60	13.76	2.20	5.13	1.80	3.88
52, 53	m,p-Xylene	1.50	2.23	1.90	3.29	1.20	0.94	1.30	1.55	2.00	1.87	1.40	1.28	1.10	0.82	1.20	1.42
55	Styrene	1.30	0.54	1.60	2.67	1.70	1.82	2.80	4.45	3.50	4.09	4.30	5.74	3.20	7.52	1.70	1.59
56	o-Xylene	1.10	1.00	1.68	1.53	1.00	0.46	1.00	0.79	1.50	0.88	1.10	0.61	0.70	0.44	0.90	0.65
60	Isopropylbenzene	n.d.	0.08	n.d.	0.12	n.d.	0.05	n.d.	0.05	n.d.	0.04	n.d.	0.05	n.d.	0.02	0.80	0.04
62	n-Propylbenzene	n.d.	0.26	n.d.	0.61	n.d.	0.20	n.d.	0.35	n.d.	0.28	n.d.	0.26	n.d.	0.18	n.d.	0.24
65	3-Ethyltoluene	n.d.	0.34	n.d.	0.56	n.d.	0.22	n.d.	0.34	n.d.	0.37	n.d.	0.28	n.d.	0.21	n.d.	0.29
66	4-Ethyltoluene	n.d.	0.84	n.d.	2.43	n.d.	0.82	n.d.	1.56	n.d.	0.76	n.d.	0.61	n.d.	0.29	n.d.	0.65
67	1,3,5-Trimethylbenzene	n.d.	0.29	n.d.	0.45	n.d.	0.18	n.d.	0.22	n.d.	0.24	n.d.	0.18	n.d.	0.13	n.d.	0.19
68	2-Ethyltoluene	n.d.	0.10	n.d.	0.22	n.d.	0.03	n.d.	0.09	n.d.	0.10	n.d.	0.07	n.d.	0.03	n.d.	0.06
70	tert-Butylbenzene	n.d.	0.09	n.d.	0.09	n.d.	0.06	n.d.	0.06	n.d.	0.05	n.d.	0.02	0.70	0.04	0.70	0.02
71	1,2,4-Trimethylbenzene	n.d.	0.36	n.d.	1.13	n.d.	0.22	0.90	0.49	n.d.	0.56	0.90	0.34	n.d.	0.21	n.d.	0.35
73	sec-Butylbenzene	n.d.	0.10	n.d.	0.13	n.d.	0.05	n.d.	0.07	n.d.	0.06	n.d.	0.05	0.90	0.03	0.90	0.05
74	1,4-Dichlorobenzene	n.d.	0.15	n.d.	0.13	n.d.	0.07	n.d.	0.06	n.d.	0.02	n.d.	0.01	n.d.	n.d.	n.d.	0.01
75	p-Isopropyltoluene	0.80	0.24	n.d.	1.44	n.d.	0.01	n.d.	0.06	n.d.	0.07	n.d.	0.03	n.d.	0.01	0.80	0.02
76	1,2,3-Trimetylbenzene	n.d.	0.07	n.d.	0.42	n.d.	0.04	n.d.	0.07	n.d.	0.08	n.d.	0.04	n.d.	0.02	0.80	0.04
77	Benzyl alcohol	n.d.	2.01	n.d.	4.33	n.d.	0.04	n.d.	0.80	n.d.	0.64	n.d.	0.00	n.d.	1.17	n.d.	0.07
79	1,3-Diethylbenzene	n.d.	0.04	n.d.	0.08	n.d.	0.11	n.d.	0.15	n.d.	0.12	n.d.	0.14	n.d.	0.08	n.d.	0.08
80	1,4-Diethylbenzene	n.d.	0.25	n.d.	0.29	n.d.	0.19	n.d.	0.26	n.d.	0.28	n.d.	0.20	n.d.	0.15	n.d.	0.19
81	n-Butylbenzene	n.d.	0.03	n.d.	0.35	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
85	1,2,4-Trichlorobenzene	n.d.	0.18	n.d.	0.13	n.d.	0.17	n.d.	0.12	n.d.	0.02	n.d.	0.04	n.d.	0.01	n.d.	n.d.
86	Naphthalene	n.d.	n.d.	n.d.	2.98	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
88	1,2,3-Trichlorobenzene	n.d.	0.19	n.d.	0.13	n.d.	0.17	n.d.	0.12	n.d.	0.01	n.d.	0.05	n.d.	0.02	n.d.	0.01
89	2-Methylnaphtalene	n.d.	0.02	n.d.	1.45	n.d.	0.02	n.d.	n.d.	n.d.	0.06	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
90	1-Methylnaphtalene	n.d.	n.d.	n.d.	2.36	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Total VOCs	25.70	88.12	34.60	134.7	28.50	63.22	38.10	172.1	63.90	145	46.20	195.7	28.30	154.4	28.90	134.1

n.d.: compound not detected (value < MDL) and n.q.: compound not quantified (value < MQL).

Table 1 shows the repetitivity and recovery as well as the method detection and quantification limit for the 90 target VOCs determined by both methods.

The repetitivity of both methods was calculated as the relative standard deviation (%RSD) of the analyses of five replicates of 1 ng from VOC standard mixture. The method A tubes were filled with 1000 ng of each VOC, extracted with 1 mL of solvent (see Section 2.2.1) and then 1 μL of the extract was analysed. The method B tubes were directly filled with 1 ng of standard mixture and then analysed (see Section 2.2.2). Repetitivities of method A (ranging from 0.66% RSD for i-pentane to 12.9% RSD for 1,3-dichloropropene) were generally higher than those of method B (ranging from 0.41% RSD for 1,2-dichloropropane to 6.34% RSD for 1,4,-dioxane). None of them exceeded the 25% recommended by EPA [29].

Recoveries were measured as the percentage recovery of the response obtained by the triplicate analysis of 1 ng of VOCs using method A or method B and compared with the response obtained by direct injection of the same amount of VOCs under the same split conditions. Recoveries for most of the target compounds were higher than 95% for both methods. However, polar compounds tended to show lowest recoveries with method A. For instance, 1-chlorobutane had a recovery of 65.1% with method A and 99.5% with method B and benzyl alcohol had a recovery of 82.6% for method A and 95% for method B. The same trend was seen with voluminous compounds like naphthalene (78.3% with method A vs. 92% with method B), 2-methylnaphthalene (47.4% with method A, 91.5% with method B) and 1-methylnaphthalene (47% method A, 91.2% method B). These results agree with similar trends that have previously been reported [11,13,30].

The method detection limits (MDLs) of both methods were evaluated in two ways. For target compounds without blank signal, MDLs were determined as the concentrations corresponding to three times the noise signal of the quantifier ion. For target compounds which present a signal in the blank, the MDLs were established as the sum of the average concentrations of the blank responses plus three times the standard deviation of this signal ($n = 8$). For all target VOCs the method quantification limits (MQLs) were fixed as the lowest calibration level. The MDLs of method A for 720 L of sample (ranging from 0.01 $\mu g\,m^{-3}$ for several compounds such as methacrylonitrile or m,p-xylene, to 1.39 $\mu g\,m^{-3}$ for 1,1-dichloroethane) were generally higher than those of method B for 2.64 L of sample (ranging from 4×10^{-4} $\mu g\,m^{-3}$ for o-xylene and benzyl alcohol, to 0.4 $\mu g\,m^{-3}$ for 4-ethyltoluene). Exceptions were 1,4-dioxane (0.07 $\mu g\,m^{-3}$ by method A and 0.3 $\mu g\,m^{-3}$ by method B), toluene (0.07 $\mu g\,m^{-3}$ by method A, 0.23 $\mu g\,m^{-3}$ by method B), styrene (0.01 $\mu g\,m^{-3}$ by method A and 0.15 $\mu g\,m^{-3}$ by method B) and 4-ethyltoluene (0.01 $\mu g\,m^{-3}$ by method A and 0.40 $\mu g\,m^{-3}$ by method B) because of the presence of a signal of both compounds in the blanks of method B sorbent tubes.

Similarly, MQLs for method A were generally higher than those for method B. For method A MQLs ranged from 0.07 $\mu g\,m^{-3}$ for some compounds such as m, p-xylene and n-propylbenzene, to 2.78 $\mu g\,m^{-3}$ for 1,1-dichloroethane. For method B MQLs ranged from 0.002 $\mu g\,m^{-3}$ for benzyl alcohol to 0.45 for 4-ethyltoluene. Exceptions were also 1,4-dioxane (0.14 $\mu g\,m^{-3}$ by method A and 0.38 $\mu g\,m^{-3}$ by method B), toluene (0.14 $\mu g\,m^{-3}$ by method A, 0.38 $\mu g\,m^{-3}$ by method B), styrene (0.07 $\mu g\,m^{-3}$ by method A and 0.19 $\mu g\,m^{-3}$ by method B) and 4-ethyltoluene (0.07 $\mu g\,m^{-3}$ by method A and 0.45 $\mu g\,m^{-3}$ by method B). These results agree with those reported in a previous study, which compared the solvent extraction and the thermal desorption method for eight VOCs (benzene, toluene, ethylbenzene, m,p,o-xylene and 1,2,4 and 1,3,5-trimetylbenzene), and also showed lower detection limits and better instrumental repetitivities for the thermal desorption method [31].

3.2. Comparison of the performance in real samples

Results of both methods in real samples were compared by sampling atmospheric air over 8 days in a location situated next to a petrochemical complex. Eight samples collected for 24 h and analysed by method A were compared with the mean daily values of 96 samples (12 per day) collected for 2 h and analysed by method B in the same period of time. Fig. 1 shows the typical chromatograms of the samples with method A (Fig. 1A) and with method B (Fig. 1B). Some of the most representative compounds of each sample are marked. Of particular note in Fig. 1A is the high and wide signal of carbon disulfide, the extraction solvent.

Table 2 shows the average concentrations of the compounds found in the samples by both methods. Signals of the target compounds in field blanks were taken into account when calculating sample concentrations. It is worth mentioning that in the period sampled only 18 of the 90 VOCs were detected and quantified by method A, while method B quantified 50 of them. In general concentrations from method A were lower than the daily average concentrations obtained from method B. However, some compounds showed occasionally higher concentrations with method A, for instance, chloroform, carbon tetrachloride, n-heptane, trichloroethene, n-octane, m,p-xylene, styrene, o-xylene and p-isopropyltoluene. The analytes which had the highest differences in the values obtained by both methods were i-pentane, n-pentane, benzene, toluene and ethylbenzene. These compounds also showed the highest concentrations and the highest dispersion of the values in the 12 2-h samples collected per day by method B. For example, Fig. 2A and B shows, for benzene and o-xylene, respectively, the correlation between the values for method A and the average values of the 12 method B samples for each sampled day. These figures show some correlation between the results obtained by both methods for both compounds. However, the slope of benzene, which showed high concentration values for both methods and high dispersion for method B (method A 2.9 ± 1.8 $\mu g\,m^{-3}$, method B 10.5 ± 12.4 $\mu g\,m^{-3}$), is further from the ideal slope 1 than that of o-xylene, which had low concentration values for both methods and less dispersion for method B (method A 1.1 ± 0.2 $\mu g\,m^{-3}$, method B 0.8 ± 0.7 $\mu g\,m^{-3}$).

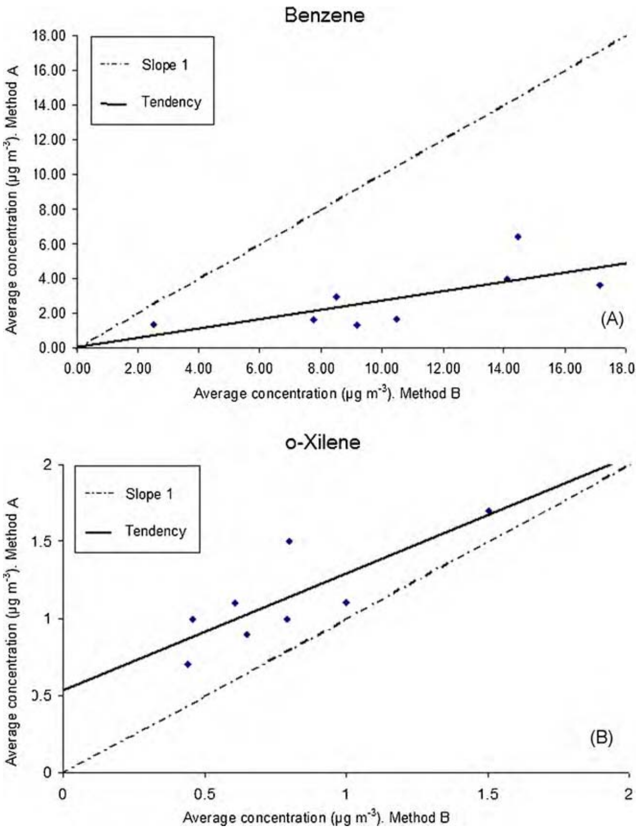

Fig. 2. Correlations of the average concentrations, in $\mu g\,m^{-3}$, obtained by both methods for benzene (A) and o-xylene (B).

Furthermore, Fig. 3 compares the results obtained in the real samples by both methods for four compounds: benzene, m,p-xylene, styrene and o-xylene (Fig. 3A–D, respectively). In these figures it can be observed that the variability in the concentrations of the investigated compounds that can be detected by method B is not detected by method A. Specifically, the high increases in the concentrations detected by method B do not correspond to a proportional increase in the average concentration detected by method A. For instance, the maximal concentration of benzene that was detected on the 4th day of sampling between 12 and 14 h (70.4 $\mu g\,m^{-3}$, Fig. 3A) and which considerably increases the average concentration of this compound for method B does not correspond to a proportional increase in the average concentration detected by method A. However, in the case of styrene (Fig. 3C), method A and method B seemed to correlate on most of the days sampled except for the 7th day. Hence, in most cases method A does not detect the dynamics of changes in ambient air quality over small periods of time.

Moreover, method B identifies which compounds could have the same origin. For instance, the similar profile of concentrations in method B for m,p-xylene and o-xylene (Fig. 3B and D) can indicate the same focus of emission and similar behaviour in atmospheric samples. Other analytes showed similar profiles in method B, such as i-pentane, n-pentane (figures not shown).

As far as we know, this is the first study to compare the performance of both methods in real samples. Nevertheless, some

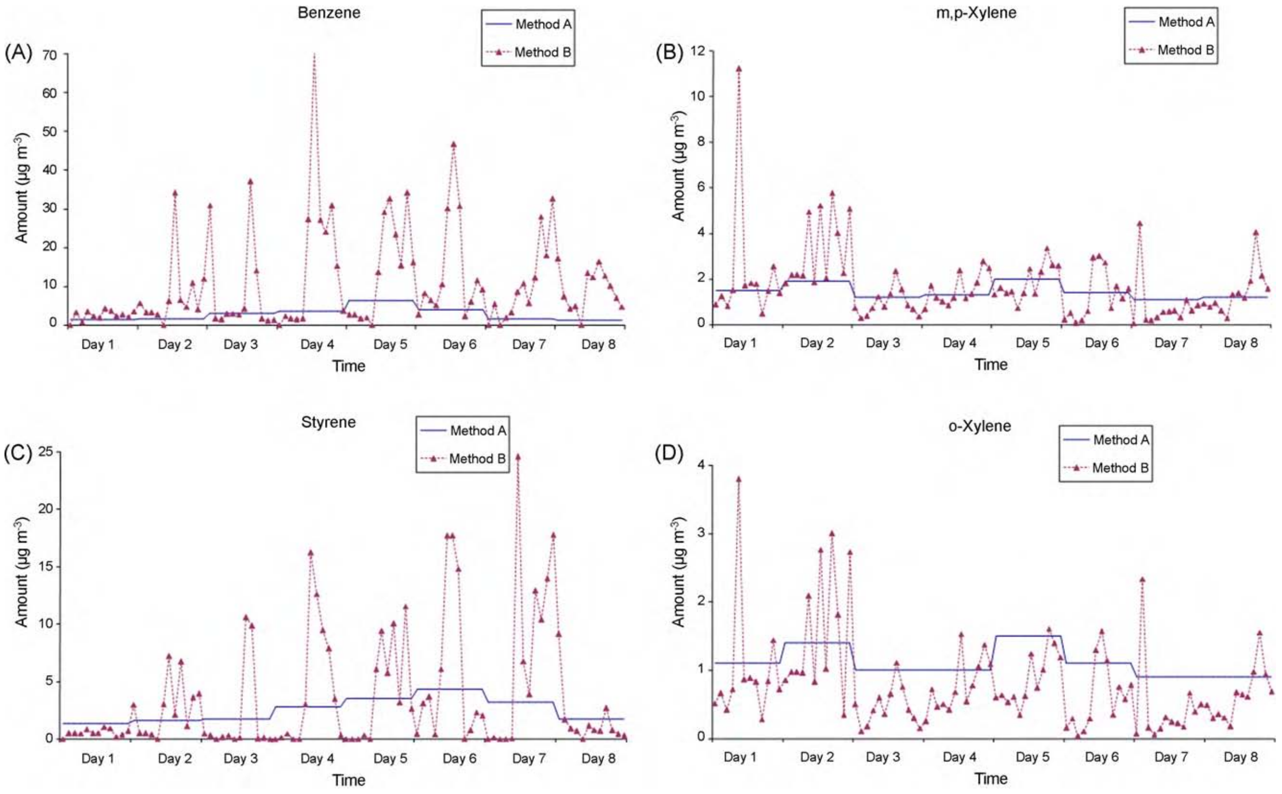

Fig. 3. Concentrations, in µg m^{-3}, obtained by both methods for some of the main compounds: benzene (A), m,p-xylene (B), styrene (C) and o-xylene (D).

authors have studied the factors which can affect the performance of both methods. For example, it is known that meteorological conditions, particularly humidity, can considerably influence the methods [11,13]. The sorbents used in method B (Texax TA and Carbograph 1TD) are relatively hydrophobic and are poorly affected by ambience humidity [13]. However, when relative humidity is greater than 50%, water can be adsorbed in the active sorbent centres of the activated charcoal surface, which becomes hydrophilic. The water adsorbed can displace organic molecules, react with them or form an immiscible phase on desorption into which polar molecules can partition and essentially be lost to analysis [13]. It should be noted that the relative humidity of the sampled days was higher than 50% (from 62% to 95%). Nevertheless, in this study there was no correlation between the different values of method A and method B and the increased humidity. Moreover, the activated charcoal can have chemical reactions with other inorganic compounds present in industrial air such as NO_2, Cl_2, H_2S, SO_2 and ozone, which can also decrease the active sorbents centres [12]. Furthermore, it is also known that the precision and the accuracy of the solvent extraction method can be affected by the presence of other polar compounds in the air samples which do not affect the thermal extraction method [11,13].

4. Conclusions

This study compared the performance of two analytical methods for determining 90 VOCs in air. The repetitivity, recovery and detection and quantification limit of the thermal desorption method were generally better than those of the solvent extraction method for the target compounds. However, blanks of the thermal desorption sorbent tubes showed the signal of 21 target VOCs whereas blanks of the solvent extraction tubes showed only signals of low concentrations of hexane and benzene.

Performance in real samples showed in some cases differences in the VOC concentrations, with those determined by thermal desorption generally being higher. Furthermore, the thermal desorption method allows short periods of sampling and can give more precise information about the daily variability of the VOC concentration whereas the solvent extraction method, which gives daily average values, cannot reflect punctual emissions of the pollutants.

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