New approach to resolve the humidity problem in VOC determination in outdoor air samples using solid adsorbent tubes followed by TD-GC-MS.

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ABSTRACT

This study describes the humidity effect in the sampling process by adsorbent tubes followed by thermal desorption and gas chromatography-mass spectrometry (TD-GC-MS) for the determination of volatile organic compounds (VOCs) in air samples and evaluates possible solutions to this problem. Two multi-sorbent bed tubes, Tenax TA/Carbograph 1TD and Carbotrap B/Carbopack X/Carboxen 569, were tested in order to evaluate their behaviour in the presence of environmental humidity. Humidity problems were demonstrated with carbon-based tubes, while Tenax-based tubes did not display any influence. Silica gel, a molecular sieve and $CaCl_2$ were tried out as materials for drying tube to remove air humidity, placed prior to the sampling tube to prevent water from entering. The pre-tubes filled with 0.5 g of $CaCl_2$ showed the best results with respect to their blanks, the analytes recoveries and their ability to remove ambient humidity. To avoid the possible agglomeration of $CaCl_2$ during the sampling process in high relative humidity atmospheres, 0.1 g of diatomaceous earth were mixed with the desiccant agent. The applicability of the $CaCl_2$ pre-tube as drying agent prior to Carbotrap B/Carbopack X/Carboxen 569 tubes was tested in urban and industrial locations with samplings of air at high relative humidity. In addition, the results were compared with those obtained using Tenax TA/Carbograph 1TD tubes.

Keywords: thermal desorption; humidity; desiccant materials; gas chromatography; solid adsorbent tubes; volatile organic compounds

Abbreviations: Gas chromatography, GC; Volatile organic compounds, VOCs; Thermal desorption-gas chromatography-mass spectrometry; TD-GC-MS; Relative humidity, RH; Graphitized carbon black, GCB; Carbon molecular sieve, CMS; Tenax TA/Carbograph 1TD tubes, TC tubes; Carbotrap B/Carbopack X/Carboxen 569 tubes, CCC tubes

1. Introduction

Anthropogenic and biogenic volatile organic compounds (VOCs) are present as trace-levels gases in the atmosphere and they represent a potential threat to human health, animals and vegetation, even at low concentration levels (Cetin et al., 2003; Ras-Mallorquí et al., 2007). European Directive 2008/50/EC, recommends the measurement of some VOCs but only regulates the immission level of benzene to 5 μg m^{-3} as an annual average. Some of the effects originated from the photochemical reactivity of some of these compounds are well known, e.g. the formation of photochemical smog or the participation in the greenhouse effect, among others (Ras-Mallorquí et al., 2007).

The concentrations of these VOCs in the atmosphere, even near industries, are relatively low. Therefore, a preconcentration step is required prior the analysis by gas chromatography (GC). Reliable sampling methods based on bags and canisters are applied to collect samples in environmental analysis. However, numerous restrictions have been identified, such as handling difficulty, irreversibly adsorption of polar and heavy compounds in the walls and reaction of VOCs with other air components inside the canister or bag, and the need for an additional preconcentration step prior to GC analysis, among others, (Harper, 2000; Kumar and Víden, 2007). An alternative to sampling atmospheric VOCs is the retention into solid adsorbent technique, in passive or active sampling mode. These systems enable versatility due to the wide range of solid adsorbents commercially available, simple handling compared to canisters and selective trapping and the enrichment of the compounds during the sampling (Kumar and Víden, 2007). In active sampling mode, higher sampling volumes with less time and higher sensitivity are usually achieved compared to the passive solid adsorbent sampling technique. To extract the trapped compounds in the solid adsorbent, liquid desorption (LD) or thermal desorption (TD) can be used prior to GC analysis. Comparing both, TD offers the enrichment and subsequent desorption of the compounds in a single step without handling, thus avoiding analyte losses and possible contamination. In addition, the TD technique permits the compounds to enter fully into the chromatographic system and, thus, low limits of detection are achieved, whereas, in the LD technique only an aliquot of the extract is injected. However, when working with LD, adsorbents with a higher capacity are required to enable sampling of higher volumes and periods of time to counteract the dilution factor (Wong et al., 2013). Generally, for this technique, around 1,000 L of air is sampled with flow-rates about 700 mL min^{-1} during 24 h (Ramírez et al., 2012). In contrast, the TD technique is more suitable for lower sampling volumes and adsorbents with lower capacity are used, thus obtaining real-time concentrations. In this case, volumes of 1 to 20 L are usually sampled with flow-rates about 100 mL min^{-1} during short time periods, from minutes to a few hours (Ramírez et al., 2010; Ras et al., 2009a).

As mentioned above, there is a wide variety of commercial adsorbents that can be used with the TD technique. These adsorbents have different chemical structures, surfaces and porous structure in order to obtain specific intrinsic properties to retain different ranges of compounds. Some parameters, such as superficial area, thermal stability, hydrophobicity and the possible formation of artifacts, among others, play an important role in the adsorbent's capacity and in the breakthrough volumes of the analytes in the solid adsorbent. To be able to retain a wide range of VOCs, a suitable choice of the adsorbent or combination of different types of adsorbents is required. Nowadays, the TD technique and these multi-sorbent bed tubes have gained popularity and are used in various official methods to determine VOCs in outdoor and indoor airs (eg. EPA TO-17 USEPA, 1999, method 2549 NIOSH, 1996 and method D-6196-97 ASTM, 1997).

Apart from the complexity of air samples, some authors have reported that the main disadvantages of the enrichment onto solid adsorbents are related to the problems that may arise when atmospheres with high relative humidity are sampled (40-90%), making their analysis difficult (Idris et al., 2010; Ciccioli et al., 1992; Helmig and Vierling, 1995; Karbiwnyk et al., 2002; Kumar and Víden, 2007; Sampaolo et al., 1999; Woolfenden, 1997). Depending on the type of adsorbents used, environmental water vapour can modify and reduce the adsorption capacity of these adsorbents by competing for the active sites with the target compounds to be retained during sampling procedure. Therefore, breakthrough volumes of the target compounds can also be affected by the presence of humidity during the sampling (Helmig and Vierling, 1995). Moreover, water vapour may hydrolyse and chemically transform various analytes during the sampling or the analysis as well. Several authors have reported these problems in different types of adsorbents, with those based on porous polymers and graphitized carbons being less affected (Dutaur et al., 1998; Wong et al., 2013) than those based on carbon molecular sieves (Ciccioli et al., 1992; MDHS, 1992) due to their hydrophobicity. However, some studies do not mentioned any significant problems associated with the humidity in any kind of adsorbents used (Brown et al., 2014; Gallego et al., 2010; Idris et al., 2010; Sampaolo et al., 1999). Apart from the sampling problems mentioned, humidity can also cause several analytical problems. In TD, cryogenic methods are used and water may cause problems of ice accumulation in the cryogenic trap during the preconcentration step. A large amount of water can also cause changes in retention times and the detection of the organic compounds. In recent years, several authors have investigated possible approaches to resolve these problems. Specifically, some authors (Helmig, 1996, Dutaur et al., 1998;Ciccioli et al., 1992, Karbiwnyk et al., 2002 and Kumar and Víden, 2007) reported and summarised various strategies to achieve a reduction of water entering to the adsorbent TD tubes and to the chromatographic system. For example, using an in-home desorption unit for U-shaped traps, which led to the condensation of the water in the empty zone of the trap (Ciccioli et al., 1992), drying the flow through a trap containing a desiccant material prior to the chromatographic system (Helmig and Vierling, 1995; Kumar and Víden, 2007) or heating slightly the adsorbent TD tubes during the sampling (Karbiwnyk et al., 2002), among others.

In the present study, two different types of multi-sorbent bed tubes (Tenax TA/Carbograph 1TD and Carbotrap B/Carbopack X/Carboxen 569) were evaluated for their behaviour when several polar and non-polar VOCs with a wide range of carbon number are determined in air matrices with different relative humidity content. Tenax TA/Carbograph 1TD adsorbent tubes (TC tubes) are one of the most commonly used type of multi-sorbent beds for the determination of a wide range of VOCs, up to more than 90 compounds (Ramírez et al., 2011; Woolfenden, 1997). This material combination is suitable for sampling medium to high boiling compounds ($C_{5/6}$ to C_{30}) (Markes International Ltd, 2014). Meanwhile, Carbotrap B/Carbopack X/Carboxen 569 tubes (CCC tubes) have a higher surface area than TC tubes, thus their adsorption capacity is greater and low boiling compounds can be retained onto them (Kim and Kim, 2015). Comparing both types of tubes, CCC tubes present better blanks because these materials exhibit minimal inherent artifact levels (Kumar and Víden, 2007) and the intrinsic amount of some target compounds is lower than 0.1 ng, as indicated by the manufacturer (Markes International Ltd, 2014). Therefore, this kind of tubes allows lower instrumental limits of detection and lower method limits of detection to be achieved, due to their capacity, as the air volume sampled can be higher. Meanwhile, TC tubes present some artifact levels and an inherent amount of various analyzed compounds below 1 ng (e.g. benzene and toluene) (Harper, 1994; Helmig, 1996; Wong et al., 2013). However, as indicated by the manufacturer, these type of tubes are more hydrophobic than CCC tubes and prevent water from entering them, thereby preventing potential humidity problems (Markes International Ltd, 2014).

2. Experimental part

2.1. Reagents and standards

The standards of the 90 VOCs studied (Table 1) include two different standard commercial mixtures at a concentration of 2,000 µg mL^{-1} in methanol (SS 502/524 Volatile Organics Calibration Mix and EPA 524.2 Revision 4 Mix both supplied by Supelco, Bellefonte, USA) and individual solutions of i-pentane, 1-pentene, 2-pentene (50% cis/trans mixture), isoprene, i-hexene, n-hexane, i-octane, n-heptane, n-octane, 1,4-dioxane (Sigma-Aldrich, Steinheim, Germany), 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, 1,2-diethyltoluene, 1,3-diethyltoluene, 1,4-diethyltoluene (Fluka, Buchs, Switzerland), 1-methylnaphtalene and 2-methylnaphtalene (Riedel-deHaën, Seelze, Germany) were prepared in methanol at concentrations of 2,000 µg mL^{-1} and stored at 4ºC. A working mixture solution of all the target compounds at 100 µg mL^{-1} was prepared in methanol and stored at 4ºC. More diluted standard level solutions were prepared in methanol on the day of use. Methanol was GC grade with purity >99.9% from J.T. Baker (Teugseweg, Deventer, Netherlands).

Nitrogen gas used for conditioning the adsorbent tubes and helium gas utilized for the calibration and chromatographic analysis, both with a purity of 99.999% were supplied by Carburos Metálicos (El Morell, Tarragona, Spain).

The desiccant materials evaluated in in-house drying pre-tubes were as follows: silica gel, anhydrous calcium chloride and a molecular sieve, all purchased from Sigma-Aldrich (Steinheim, Germany). Diatomaceous earth (Thermo Scientific, Barcelona, Spain) was also used as dispersing agent in the drying pre-tubes.

Table 1. Target compounds, their retention times (t_R) and quantifier and qualifier ions. Reproducibility, expressed as relative standard deviation (%RSD) for the analysis of 2.5 ng of VOCs standard (n=5), method's detection limits (MDL) and method's quantification limits (MQL) for both methods.

No.	Compound	t_R (min.)	Quant. ion	Qualifier ions	TC tubes method[a]			CCC tubes method[b]		
					MDL ($ng\ m^{-3}$)	MQL ($ng\ m^{-3}$)	Reproducibility (%RSD)	MDL ($ng\ m^{-3}$)	MQL ($ng\ m^{-3}$)	Reproducibility (%RSD)
1	i-Pentane	5.50	41	43(105%) 42(89%) 57(89%)	42	167	6	42	167	11
2	1-Pentene	5.75	55	70(75%) 41(55%)	83	333	7	42	167	8
3	n-Pentane	5.89	43	42(59%) 41(51%) 57(20%)	83	333	6	42	167	9
4	Ethyl ether	5.98	59	74(80%) 45(57%)	42	167	19	17	42	9
5	2-trans-Pentene	6.05	55	70(50%) 42(27%) 39(27%)	42	83	20	4	17	8
6	Isoprene	6.10	67	68(68%) 53(55%) 40(20%)	17	83	21	2	8	6
7	2-cis-Pentene	6.20	55	70(53%) 42(29%) 39(26%)	83	333	22	17	83	10
8	1,1-Dichloroethylene	6.31	61	96(89%) 40(67%) 98(66%)	42	83	15	42	167	14
9	Acrylonitrile	6.35	53	52(84%) 51(37%)	8	42	10	2	8	22
10	Allyl Chloride	6.60	41	39(77%) 76(58%) 78(16%)	42	167	15	17	42	12
11	Carbon disulfide	6.83	76	44(11%) 78(11%)	42	83	18	17	42	23
12	trans-1,2-Dichloroethylene	7.32	61	96(96%) 98(70%) 60(50%)	42	83	13	4	17	14
13	tert-Butyl methyl ether	7.39	73	43(27%) 57(18%) 41(16%)	42	167	17	4	17	13
14	Propionitrile	7.60	54	52(21%) 51(15%) 55(15%)	8	42	7	17	83	20
15	1,1-Dichloroethane	7.69	63	65(36%) 83(20%) 85(10%)	42	83	11	17	83	12
16	1-Hexene	8.00	56	41(91%) 55(67%)	83	333	18	17	42	13
17	n-Hexane	8.24	57	43(55%) 56(51%) 42(29%)	167	417	18	17	42	20
18	Methacrylonitrile	8.26	67	52(51%) 40(42%) 66(37%)	42	83	8	17	42	9

19	cis-1,2-Dichloroethylene	8.56	96	61(96%) 98(64%) 63(34%)	42	83	9	4	17	11
20	Methyl acrylate	8.70	55	85(26%) 58(10%) 42(10%)	42	83	7	2	8	10
21	2,2-Dichloropropane	8.80	77	79(35%) 97(23%)	83	167	11	17	42	16
22	Chloroform	8.85	83	85(65%) 87(10%)	8	42	8	4	17	10
23	Bromochloromethane	8.86	130	128(76%) 93(29%)	42	83	10	42	167	17
24	Tetrahydrofurane	9.22	42	71(60%) 72(60%) 41(56%)	42	83	7	17	42	7
25	1,1,1-Trichloroethane	9.87	97	99(66%) 61(31%) 119(17%)	42	83	11	17	42	9
26	1,2-Dichloroethane	9.94	62	64(35%) 49(23%) 63(18%)	42	83	21	17	42	7
27	1-Chlorobutane	9.94	56	41(47%) 43(19%) 39(12%)	17	83	15	17	42	10
28	1,1-Dichloropropene	10.21	75	110(46%) 39(36%) 112(31%)	42	83	9	17	42	9
29	Benzene	10.47	78	77(22%) 51(13%) 52(12%)	83	333	16	17	42	6
30	Carbon tetrachloride	10.47	117	119(95%) 121(30%) 82(18%)	42	83	10	17	42	16
31	Chloroacetonitrile	10.68	75	48(48%) 77(44%) 40(25%)	42	83	10	17	83	9
32	i-Octane	11.26	57	56(32%) 41(22%) 99(8%)	42	83	14	4	17	8
33	n-Heptane	11.63	71	57(117%) 56(32%)	167	333	15	2	8	13
34	1,2-Dichloropropane	11.71	63	62(73%) 65(32%)	8	42	8	4	17	8
35	Trichloroethene	11.75	130	132(95%) 95(77%) 97(51%)	42	83	10	2	8	8
36	Dibromomethane	11.84	174	93(57%) 172(55%) 176(53%)	42	83	10	2	8	9
37	1,4-Dioxane	11.95	88	58(70%) 43(25%)	167	417	23	17	42	10
38	Bromodichloromethane	11.99	83	85(65%) 129(14%) 47(13%)	42	83	8	17	42	10
39	Methyl methacrylate	12.04	69	41(97%) 100(52%) 39(49%)	17	83	10	17	42	10
40	cis-1,3-Dichloropropene	13.21	75	77(32%) 39(39%) 110(29%)	42	83	9	4	17	12
41	trans-1.,3-Dichloropropene	14.09	75	110(32%) 77(32%) 39(31%)	83	167	9	4	17	4
42	Toluene	14.34	91	92(60%) 65(9%) 63(6%)	83	333	8	17	42	10

43	1,1,2-Trichloroethane	14.38	97	83(73%) 99(63%) 85(48%)	42	83	8	17	42	8
44	Ethyl methacrylate	14.72	69	41(55%) 39(27%) 99(25%)	42	83	6	17	42	12
45	1,3-Dichloropropane	14.87	76	41(43%) 78(33%) 39(15%)	42	83	8	17	42	8
46	n-Octane	15.30	85	57(67%) 71(60%)	83	333	13	4	17	11
47	Dibromochloromethane	15.39	129	127(77%) 131(25%) 79(9%)	42	83	9	4	17	10
48	1,2-Dibromomethane	15.84	107	109(95%) 188(6%) 93(5%)	42	83	9	4	17	13
49	Tetrachloroethene	15.97	166	164(77%) 131(55%) 129(54%)	42	83	10	2	4	14
50	Chlorobenzene	17.31	112	77(42%) 114(33%)	42	83	9	2	4	10
51	1,1,1,2-Tetrachloroethane	17.35	131	133(94%) 117(63%) 119(61%)	42	83	8	2	8	9
52	Ethylbenzene	17.78	91	106(35%)	17	83	10	2	4	9
53, 54	m,p-Xylene	18.06	91	106(56%) 105(24%) 77(11%)	42	167	14	2	4	9
55	Bromoform	18.75	173	171(50%) 175(48%) 93(14%)	42	83	8	4	17	11
56	Styrene	18.84	104	103(46%) 78(35%)	42	83	10	2	8	11
57	o-Xylene	18.93	91	106(53%) 105(20%) 77(11%)	42	83	8	2	4	9
58	1,1,2,2-Tetrachloroethane	19.42	83	85(65%) 95(16%) 131(14%)	42	83	7	4	17	9
59	1,2,3-Trichloropropane	19.69	75	110(45%) 77(32%) 112(28%)	42	83	7	4	17	8
60	trans-1,4-Dichloro-2-butene	19.82	75	89(57%) 53(55%) 88(42%)	83	167	10	41	167	21
61	Isopropylbenzene	19.90	105	120(29%) 77(12%) 79(10%)	4	17	8	1	2	9
62	Bromobenzene	20.33	156	158(98%) 77(89%) 51(20%)	42	83	9	4	17	10
63	n-Propylbenzene	20.84	91	120(28%)	42	83	8	1	2	7
64	2-Chlorotoluene	20.91	126	89(34%) 128(31%)	42	83	8	2	8	9
65	4-Chlorotoluene	21.04	91	126(36%) 125(13%)	8	42	9	2	8	8
66	3-Ethyltoluene	21.05	120	79(25%) 103(19%) 65(16%)	42	83	14	2	8	10
67	4-Ethyltoluene	21.10	120	79(21%) 103(17%) 65(14%)	42	83	23	2	8	8

68	1,3,5-Trimethylbenzene	21.24	105	120(55%) 119(14%) 77(10%)	8	42	7	2	8	9
69	Pentachloroethane	21.60	167	165(77%) 117(72%) 119(67%)	42	83	7	4	17	11
70	2-Ethyltoluene	21.61	105	120(38%) 91(11%) 77(8%)	42	83	15	2	4	9
71	tert-Butylbenzene	21.92	119	91(56%) 134(56%)	4	17	8	2	8	9
72	1,2,4-Trimethylbenzene	21.97	105	120(57%)	42	83	8	2	4	9
73	1,3-Dichlorobenzene	22.38	146	148(62%) 111(30%)	4	17	9	2	8	10
74	sec-Butylbenzene	22.39	105	134(20%)	4	17	9	1	2	8
75	1,4-Dichlorobenzene	22.52	146	148(64%) 111(29%) 117(17%)	4	17	8	2	4	10
76	p-Isopropyltoluene	22.65	119	134(30%) 91(20%)	8	42	9	1	2	10
77	1,2,3-Trimethylbenzene	22.74	105	120(50%) 77(10%) 91(8%)	42	83	15	2	4	8
78	1,2-Dichlorobenzene	23.11	146	148(64%) 111(32%) 75(17%)	4	17	8	2	4	9
79	1,3-Diethylbenzene	23.19	119	105(95%) 134(53%) 91(20%)	42	83	17	2	4	10
80	1,4-Diethylbenzene	23.35	119	120(10%) 117(8%)	8	42	16	4	8	10
81	n-Butylbenzene	23.36	92	65(20%) 39(12%)	4	17	8	4	8	10
82	1,2-Diethylbenzene	23.52	105	119(98%) 134(62%) 91(25%)	42	83	16	4	8	8
83	Hexachloroethane	24.00	201	117(74%) 119(72%) 203(68%)	42	83	7	8	42	14
84	1,2-Dibromo-3-chloropropane	24.08	157	155(73%) 75(48%) 159(24%)	42	83	11	4	17	16
85	Nitrobenzene	24.17	77	123(69%) 51(38%) 93(15%)	42	83	16	4	83	4
86	Naphthalene	26.03	128	127(13%) 129(11%) 126(7%)	42	83	10	2	8	11
87	Hexachlorobutadiene	26.37	225	223(64%) 227(64%) 190(38%)	8	42	9	2	4	10
88	1,2,3-Trichlorobenzene	26.47	180	182(95%) 184(32%) 145(25%)	4	17	10	2	4	11
89	2-Methylnaphthalene	27.85	142	141(85%) 115(25%) 63(8%)	8	42	20	2	8	11
90	1-Methylnaphthalene	28.19	142	141(85%) 115(30%) 63(8%)	8	17	18	2	8	9

[a] MDLs and MQLs calculated for 2.64 L of sample.

[b] MDLs and MQLs calculated for 6 L of sample.

2.2. Adsorbent TD tubes

The stainless-steel adsorbent tubes for TD (Markes International Limited, Llantrisant, UK , length 89 mm x 6.4 mm o.d. x 5 mm i.d.) tested in this study were as follows: (i) a multi-sorbent bed of about 350 mg of a porous polymer, Tenax TA 35/60 mesh, and graphitized carbon black (GCB), Carbograph 1TD 40/60 mesh (TC tubes); (ii) a multi-sorbent bed of about 260 mg of two GCB, Carbotrap B 20/40 mesh and Carbopack X 40/60 mesh and carbon molecular sieve (CMS) Carboxen 569 20/45 mesh (CCC tubes), both purchased from Markes International Limited, Llantrisant, UK.

TC and CCC tubes were activated before their first use according to the supplier's recommendations and then, previously to each use, were conditioned using a pure nitrogen gas flow of 100 mL min^{-1} at 335ºC for 30 min in the case of TC tubes, while the CCC tubes were conditioned at 100ºC, 200ºC, 300ºC and 380ºC, maintaining each temperature for 15 min. All of the clean tubes were capped with ¼ in. brass long-term storage caps with ¼ in. combined PTFE ferrules, stored in hermetically sealable glass jars containing a desiccant material in order to prevent any ambient contamination of the adsorbents, and used for new analyses within 1 week.

2.2. Sampling process

The pre-tubes were filled with the different desiccant materials to evaluate and were placed before the TD tubes as can be seen in Figure 1. These materials were tested for their suitability for preventing humidity from entering the TD tubes during the sampling process without affecting the representativeness of the sample. Pre-tubes were prepared in-house with an empty stainless-steel tube (length 89 mm x 6.4 mm o.d. x 5 mm i.d.), a gauze retaining spring, two sorbent-retaining springs (Markes International Limited) and filled with the desiccant material to be tested, as shown in Figure 1.

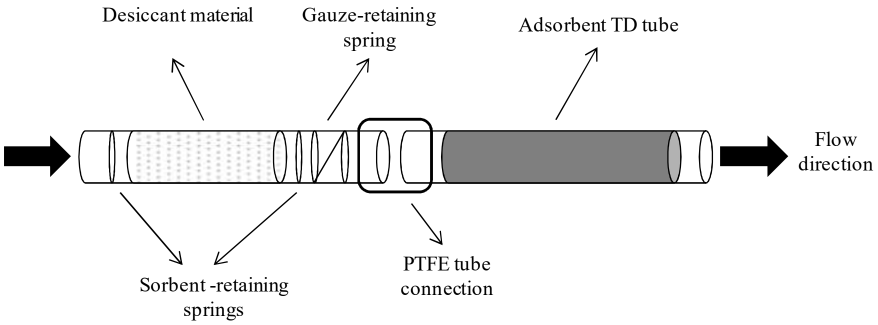

Figure 1. Sampling setup with drying pre-tubes and an in-house drying pre-tubes preparation scheme.

Drying pre-tubes used in series with CCC tubes were filled with a homogeneous mixture of 0.5 g $CaCl_2$ and 0.1 g diatomaceous earth as a dispersant and antiblocking agent, following the protocol described above, to prevent the packaging of $CaCl_2$ when high humidity air is sampled. These in-house drying pre-tubes were prepared and were activated by heating at 200ºC under a nitrogen gas flow of 100 mL min^{-1} for 1 h.

The samples were collected by using air-sampling pumps (ACTI-VOC low-flow sampling pump) from Markes International Limited. For the tests with TC tubes, the sampling flow-rate was set at 22 mL min^{-1} for 2 h, with a total volume of pumped air of 2.64 L (Ramírez et al., 2010; Ras et al., 2009b). For CCC tubes, the flow-rate was set at 50 mL min^{-1} for 2 h, collecting a final volume of 6 L. The pumps were calibrated using an ADM3000 universal gas flow meter (Agilent Technologies, Palo Alto, USA) before and after each sampling. Once sampled, the tubes were capped and analysed the same day, or kept in the refrigerator (4ºC) during storage and analysed the day after the sampling.

2.3. *Desorption and chromatographic analysis*

Desorption of the VOCs retained on the adsorbent 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 case of TC tubes, the adsorbent tube was pre-purged for 1 min at room temperature at a flow-rate of 30 mL min^{-1} of pure helium gas, trapping the compounds in line. In this step, a split of 5 mL min^{-1} was applied. Then, the tube was heated to 275ºC for 10 min, while the same flow-rate of pre-purge was passed through the tube to desorb the analytes and focus them into a hydrophobic and general purpose cold trap, packed with a graphitized carbon black and Tenax, which was kept at -10ºC. A split flow was not applied in this step. Afterwards, the trap was heated to 300ºC with the most energetic temperature ramp possible for 5 min. The VOCs were quickly desorbed from the trap in a narrow band and injected into the chromatographic column through the flow path heated at 190ºC. A split flow of 5 mL min^{-1} was applied in this step.

For CCC tubes, the pre-purge step was the same as described above with a flow-rate of 50 mL min^{-1}. Tube desorption was performed at the same flow-rate for 10 min and heating the tube at 350ºC. Compounds desorbed from the tube were focused in a general-purpose GCB cold trap kept at -10ºC in splitless mode. Trap desorption took place at 330ºC for 10 min with a split flow of 5 mL min^{-1} and the analytes were transferred to the GC system via flow path heated at 190ºC. Table 2 summarises the experimental conditions for both types of tubes.

Separation and detection were performed in a 6890N gas chromatograph and a 5973 inert mass spectrometer simple quadrupole from Agilent Technologies, using a Zebron ZB-5 (5% phenyl-95% dimethylpolysiloxane) capillary column (60 m × 0.32 mm, 1.0 µm) (Micron Phenomenex, Torrance, California, USA). Pure helium gas (99.999% purity) was used as the carrier at a flow-rate of 1.2 mL min^{-1}. The oven temperature of GC was initially held at 50ºC for 5 min, increased to 140ºC at a rate of 6ºC min^{-1}, and then to 220ºC at a rate of 15ºC min^{-1} and kept at that temperature for 8 min, with the total analysis time being 33.33 min. The mass spectrometer detection was in scan mode with an m/z interval from 35 to 280 at electron impact energy of 70 eV. Transfer line, MS source and quadrupole temperatures were 280ºC, 230ºC and 150ºC, respectively. Table 2 summarises the experimental conditions for the chromatographic analysis. Qualitative identification of the target VOCs was based on the coincidence of the retention times and the ratio of quantifier and qualifier ions. Quantification was performed by integrating the peak area of the quantifier specific ion for each compound. Table 1 summarises the retention times and quantifier and qualifier ions for each compound.

Table 2. Experimental conditions for sampling, thermal desorption and GC-MS analysis for VOCs determination using TC and CCC tubes.

			TC tubes	CCC tubes
Sampling		**Adsorbent**	350 mg of Tenax TA (35/60 mesh)/Carbograph 1TD (40/60 mesh)	260 mg of Carbotrap B (20/40 mesh)/Carbopack X (40/60 mesh)/Carboxen 569 (20/45 mesh)
		Flow-rate	22 mL min^{-1}	50 mL min^{-1}
		Time	120 min	120 min
		Volume	2,640 mL	6,000 mL
Thermal Desorption	**Pre-purge**	**Flow, time and temperature**	30 mL min^{-1}, 1 min, Room temp.	50 mL min^{-1}, 1 min, Room temp.
		Split	5 mL min^{-1}, trap in line	5 mL min^{-1}, trap in line
	Tube (1st desorption)	**Tube desorption**	10 min, 275°C, split off	10 min, 350°C, split off
		Desorption flow	30 mL min^{-1}	50 mL min^{-1}
		Trap temperature	- 10°C	- 10°C
	Trap (2nd desorption)	**Adsorbent**	General purpose hydrophobic cold trap	General purpose GCB cold trap
		Trap desorption	5 min, 300 °C, split on	10 min, 330 °C, split on
		Desorption flow	6.2 mL min^{-1}	6.2 mL min^{-1}
		Split flow	5 mL min^{-1}	5 mL min^{-1}
		Flow path temperature	190°C	190°C
Analysis GC-MS	**GC**	**Column**	ZB-5 capillary column (60m × 0.32mm, 1μm thickness)	
		Column flow	1.2 mL min^{-1}	
		Oven program	50°C for 5 min 6°C min^{-1} to 140°C 15°C min^{-1} to 220°C, for 8 min	
	MS	**Ionization source**	EI, 70eV, 230°C	
		Analyzer	Quadrupole, 150°C	
		Transfer line temperature	280°C	
		Mode	Full-scan	
		m/z range	35 to 280	
		Quantification	By quantifier ion	

Injection of the standards was performed by preparing the diluted standard levels from the working mix solution (see the Section 'Reagents and standards'). The diluted standards levels were loaded into both adsorbent tubes by using Calibration Solution Loading Ring purchased from Agilent Technologies as described in a previous studies

(Ras-Mallorquí et al., 2007; Ras et al., 2010). This procedure is also specified in Section 4.2.9 of the regulation UNE-EN 14662-1, 2006. The spiked tube was then immediately desorbed and analysed under the same conditions as the samples, depending on the type of adsorbent tube.

2.5. Sampling sites

Tarragona is a city in Catalonia (Spain) located on the Mediterranean coast and is characterised by high industrial activity. It is surrounded by two large industrial parks, called North and South. This industrial activity is mainly based on the chemical industry and processing oil derivates. Tarragona also has one of the biggest industrial sea harbours in the country.

The method was applied at two different locations. The first one is the village of Constantí (Tarragona, Spain), which is located at 2 km of the Industrial North Park and is influenced by it. The second is inside the Tarragona sea harbour within its sphere of industrial activity.

3. Results and discussion

3.1. Desiccant agents tested

The ideal desiccant material should remove water from the sample, be environmental friendly, not interfere with the sampling process and not contaminate the sample, as well as being simple and easy to handle. Due to their ability to remove humidity from the environment, the following drying materials were tested: silica gel, a molecular sieve and calcium chloride. These materials were examined in series prior to CCC tubes because a number of authors have reported that relative humidity affects the retention of compounds onto this kind of adsorbent TD tubes (Helmig and Vierling, 1995; Woolfenden, 1997).

Prior to checking the desiccant agents' ability to remove water from air samples, blanks of the different drying materials were performed. These blanks were carried out using the Calibration Solution Ring. A pre-tube filled with the corresponding previously conditioned drying material was connected in series before a CCC tube and they were placed in the tube insert of the Calibration Solution Ring. This device allowed a flow of pure helium stream to be passed through both tubes at room temperature. In all the tests for the drying materials, the helium flow-rate was 50 mL min^{-1} for 2 h to recreate the sampling conditions. Subsequently, the CCC tube used was analysed by TD-GC-MS as described in Section 2.3. These tests evaluate whether the desiccant material lets some interfering or target compounds enter the CCC tubes, hindering the real sampling process. Similar blank results were obtained when working with 1 g of silica gel or 1 g of molecular sieve. Their blanks showed a few target compounds such as ethyl ether, chloroform, carbon tetrachloride, styrene and p-isopropyltoluene, all of them with concentration below LOQ, and only isoprene, chloroform and p-isopropyltoleuene were found in 1 g of $CaCl_2$ blanks at concentrations below the LOQ. The rest of peaks that appear in the chromatogram did not interfere with the determination of the target compounds.

In the same way, to observe whether the analytes would be retained in the drying pre-tube during the sampling process, a pre-tube was connected in series with a CCC tube and they were spiked at 2.5 ng under a constant flow-rate of pure helium of 50 mL min^{-1} for 2 h. The results were compared to those obtained with a single CCC tube spiked at the same concentration level under the same spiking conditions. The pre-tube tests performed with 1 g of silica gel or 1 g of molecular sieve showed similar recoveries, in both cases lower than 10% (n=5) for the heaviest compounds,as can be seen in Figure 2, showing the retention of these compounds in both desiccant materials (Figures 2A and 2B compared to 2D). Otherwise, the lightest compounds showed recoveries between 68 and 108%, except for a few compounds that exhibit lower recovery values. Meanwhile, recoveries higher than 80% (2.5 ng, n=5) were obtained for all the target compounds with 1 g of $CaCl_2$ used in the pre-tube. The similarity between both chromatograms (Figures 2C and 2D) can be observed in Figure 2. Therefore, $CaCl_2$ material was selected for further studies.

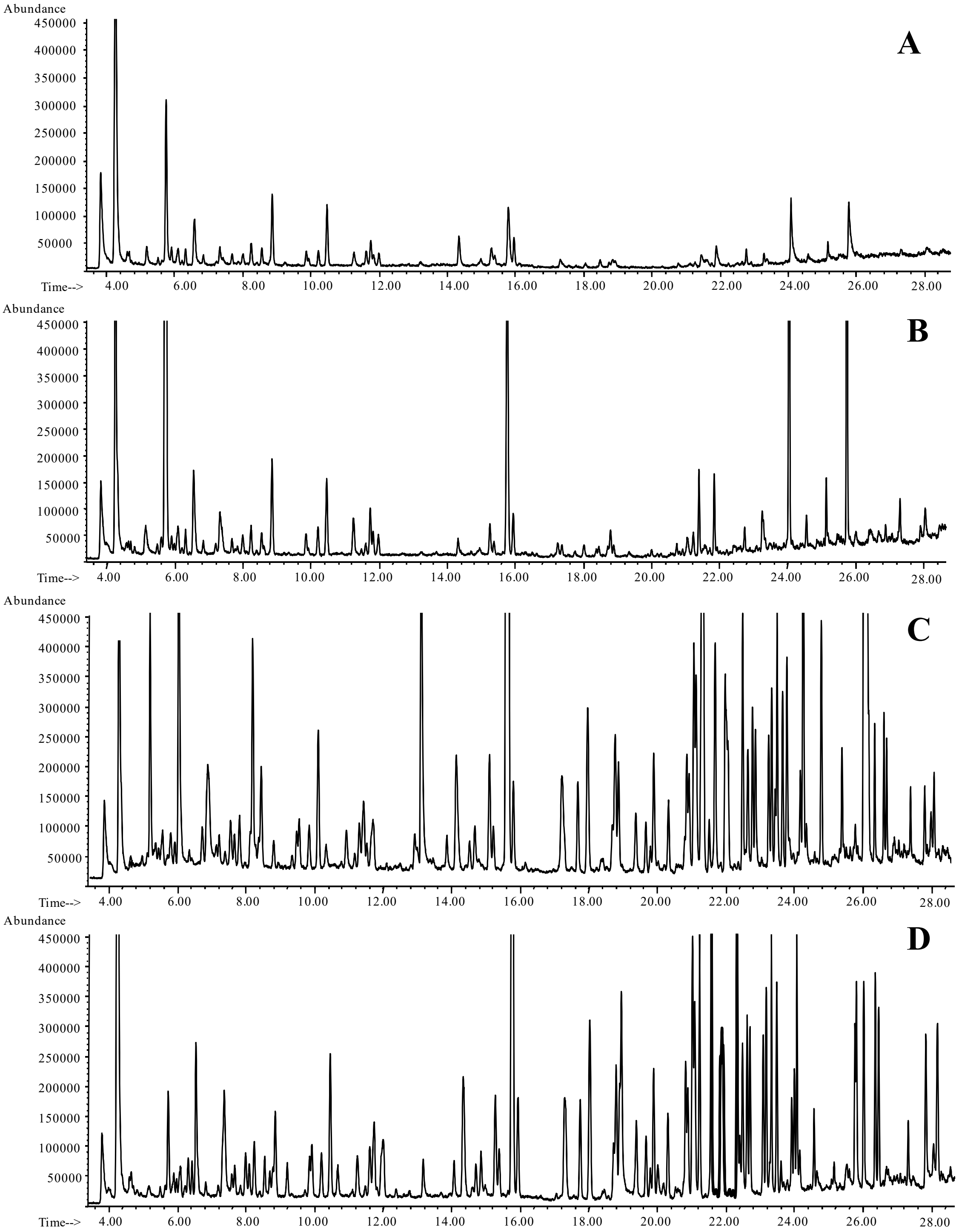

Figure 2. Chromatograms corresponding to the enrichment of 2.5 ng using: 1 g of silica gel (A), 1 g of molecular sieve (B) and 1 g of $CaCl_2$ (C) as drying pre-tubes prior to the CCC tube. Chromatogram (D) corresponds to the enrichment of 2.5 ng in to a CCC tube without any drying pre-tube.

The pre-tube filled with 1 g of $CaCl_2$ was tested in a real atmosphere (from a suburban area subject to man-made emissions: traffic and industries) in order to ascertain whether it has the capacity to remove humidity before it enters the adsorbent TD tube. Several samplings of two samples in parallel with CCC tubes were performed in the same place but on different days and time slots with different relative humidity. One of the samples in parallel was sampled with the $CaCl_2$ pre-tube prior to the adsorbent TD tube, and the other one without it. Some problems were found when air with medium-high relative humidity content (40-90% RH) was sampled for 2 h at a flow-rate of 50 mL min^{-1} using 1 g of $CaCl_2$ for the pre-tube. These problems were related to the compacting of the desiccant material in the pre-tube caused by the humidity, thus the sampling pump was not able to suck out and it stopped. In order to resolve it, the same tests described above were performed filling the pre-tube with a smaller quantity (0.5 g of $CaCl_2$), trying to avoid the compacting while obtaining the same performance. The results obtained were similar to the previous ones, with no significant differences being observed between the two amounts tested, and diatomaceous earth (DE) was tested as dispersive agent to be mixed with the 0.5 g of $CaCl_2$, in an attempt to prevent the agglomeration of $CaCl_2$ during the sampling. Various blanks (n=5) of a pre-tube filled with 0.1 g of DE were performed as described above and no target compound was present in the chromatograms. Spiked tests (2.5 ng, n=3) with these DE pre-tubes were also performed to ensure that the analytes were not retained in this material. The recoveries of this step were higher than 90% for all of the compounds. Accordingly, 0.1 g of DE were mixed with 0.5 g of $CaCl_2$ to fill the pre-tube to achieve the optimal conditions.

Figure 3A shows three overlaid chromatograms of three samples collected using CCC tubes at the same site but with different relative humidity, without using the desiccant pre-tube. As can be seen in Figure 3A, at RH higher than 30-40%, the baseline distortion and the retention times of some compounds slightly increased. Therefore, RH significantly affects the determination of VOCs when CCC tubes are used in the sampling. However, as shown in Figure 3B, a significant difference was observed between the chromatograms obtained with the sampling at about 60% RH. The chromatogram obtained using a drying pre-tube of $CaCl_2$ (Figure 3B, orange line) showed a better baseline, avoiding the distortions due to water entering the chromatographic system, more target compounds present in chromatogram and higher peak areas compared to the chromatogram obtained working with a single CCC tube. Overall, the results obtained using 0.5 g of $CaCl_2$ plus 0.1 g of DE pre-tube prior to CCC tubes showed an improvement of the chromatogram baseline when atmospheric air with medium-high %RH (40-90%) was sampled. The signals of most analytes also increased in comparison to the results of the same tests performed without the drying pre-tube and the agglomeration problem was avoided. Therefore, the efficacy of the $CaCl_2$ pre-tube for preventing water from entering the adsorbent tube was demonstrated.

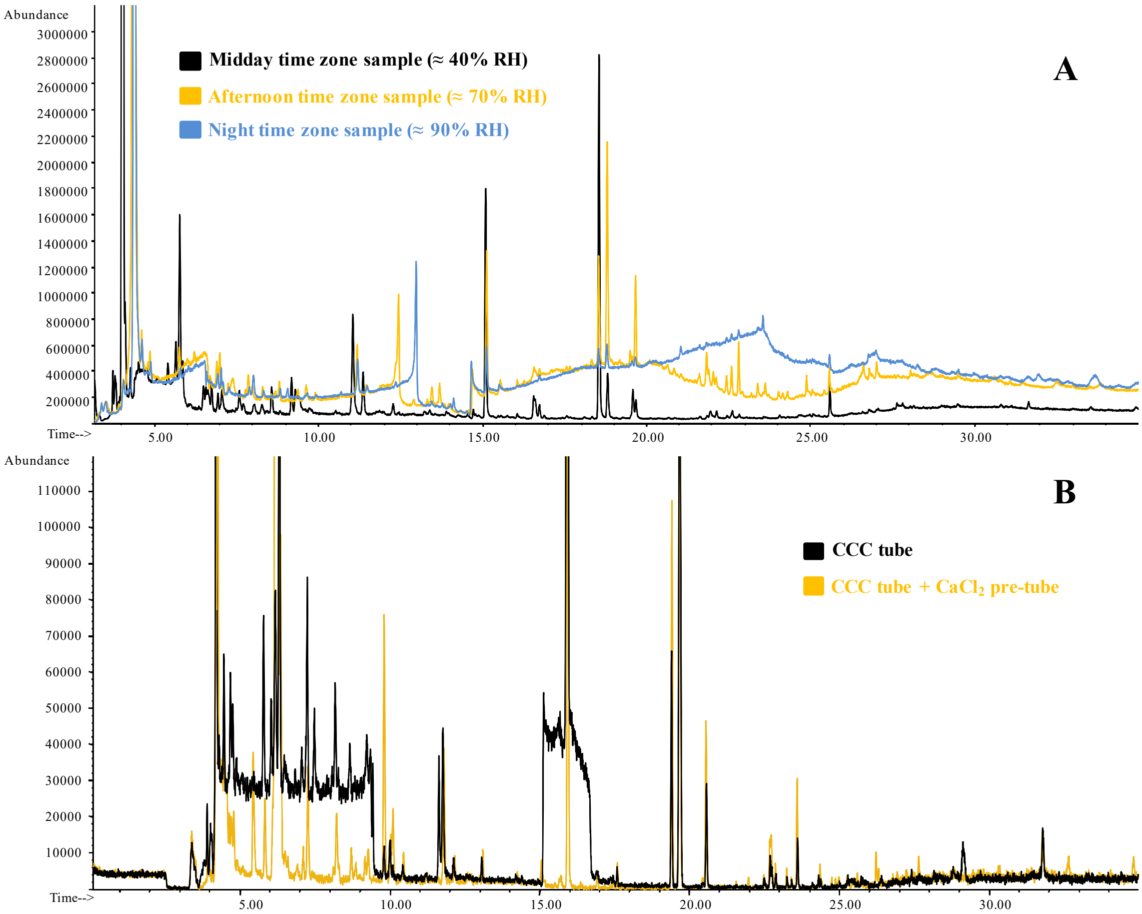

Figure 3. (A) three overlaid chromatograms corresponding to three samples taken with the CCC tubes at the same site during different time zones of a day without be used the drying pre-tube. (B) two chromatograms corresponding to a CCC tubes parallel sampling using $CaCl_2$ + DE pre-tube (orange line) and without be used it (black line).

In the suburban samples collected using 0.5 g of $CaCl_2$ plus 0.1 g of DE as the drying pre-tube in series with CCC tubes, only a few target compounds were found in almost all samples: benzene, toluene, ethylbenzene, m,p-xylene, o-xylene, ethyl ether, tetrachloroethylene, 1,2-dichloroethane, carbon tetrachloride, n-heptane, styrene, n-propylbenzene, i-propylbenzene, 1,3,5-trimethylbenzene, 2-ethyltoluene, 1,2,4-trimethylbenzene, p-isopropyltoluene and 1,2,3-trimethylbenzene. The influence of humidity on these compounds was evaluated based on the correlation between the relative humidity at the time of the samplings and the quotient of the ratio between the results obtained from the samplings in parallel (without and with the $CaCl_2$ pre-tube). Generally, when the RH was higher than 40%, a humidity effect was observed for all the sampling tests. Some compounds, such as benzene, ethyl ether, 1,2-dichloroethane and carbon tetrachloride, showed a clear linear trend decreasing while the RH was rising, probably due to the competition between the water molecules and the compounds of interest for the active sites of the adsorbent. Therefore, a decrease in their concentrations was observed when the pre-tube was not used. Figure 4A (black markers) shows a graph as an example of the linear trend decreasing for benzene's ratios versus the average of the RH in each sampling. Meanwhile, the rest of the compounds found were affected differently by the presence of humidity and they did not display a clearly decrease. For example, similar behaviour was observed for toluene, ethylbenzene, m,p-xylene, o-xylene and n-heptane, which presented low dispersion in their results of around 40% RH but, when the RH was increased, the dispersion rose with a non-excessive decline at high humidity (more than 70%). Figure 4B (black markers) shows an example for ethylbenzene in CCC tubes, which presents a clear dispersion on the sampling results and a decrease when air with more than 40% RH is sampled. The rest of the compounds did not show dispersion in the results obtained when atmospheric air with about 40% RH was sampled while the results of the samples taken at higher relative humidity exhibited a clear dispersion without any trend. To illustrate, Figure 4C (black markers) shows the graph for n-propylbenzene and the random dispersion in the results can be seen at RH higher than 40%.

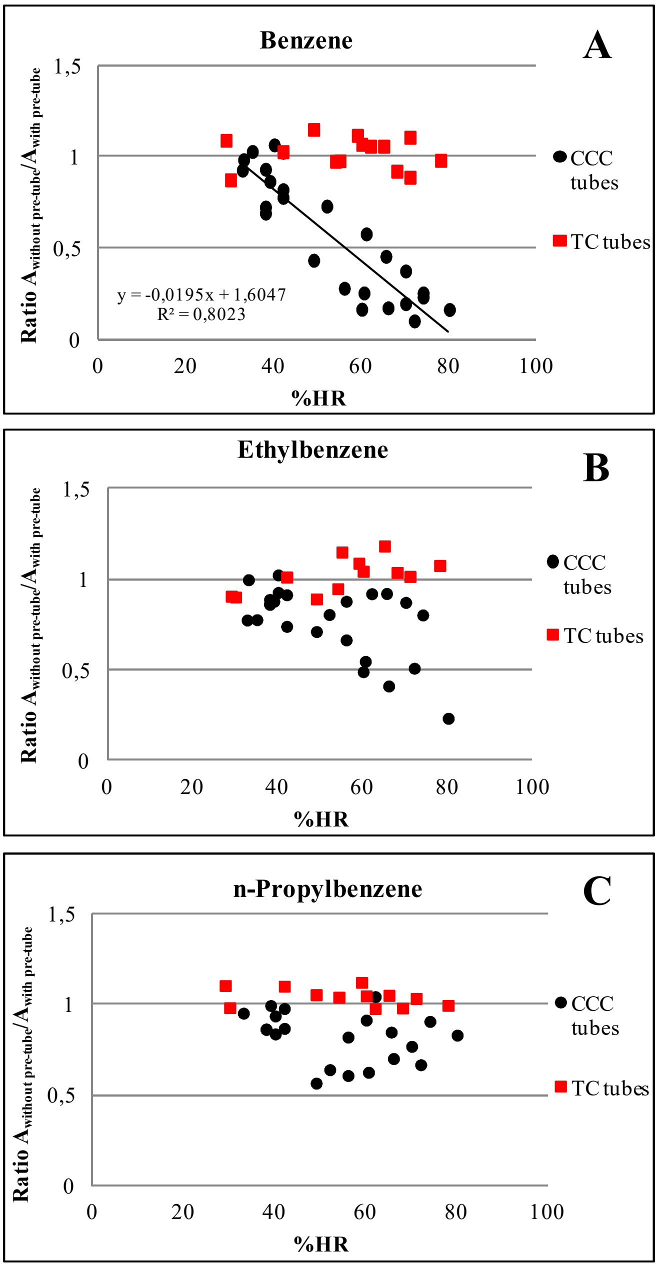

Figure 4. Graphs corresponding to the quotient between the results of a CCC tubes parallel real sampling without using the $CaCl_2$ pre-tube and with it vs. the relative humidity (%) at the sampling moment. (A) is for the case of benzene, (B) for ethylbenzene and (C) for n-propylbenzene.

For comparison purposes, some suburban real atmospheric samples were taken in parallel with and without the drying pre-tube, using TC tubes in order to check the humidity effect on them. None of the compounds found were affected by the presence of RH at the time of the sampling. This fact is demonstrated in Figure 4 (red markers) which shows no significant differences between the ratios throughout all the relative humidity values tested for the three examples. Hence, it is not necessary to use a drying pre-tube when TC tubes are used, which is in line with the results found in literature (Gallego et al., 2010; Idris et al., 2010).

3.2. TD-GC-MS validation

The CCC tubes method were evaluated and compared with the TC tubes method, for these reason both methods were validated under the optimised thermal desorption conditions described in Section 2.3. Several blanks (*n*=5) of the two types of multi-bed adsorbent tubes evaluated in this study were carried out. In the case of TC tubes, the target compounds that appeared in their blanks were as follows: benzene, toluene, ethylbenzene, m,p-xylene, styrene and naphthalene, which agree with these described in previous studies (Ras-Mallorquí et al., 2007). Meanwhile, for CCC tubes only benzene, toluene and naphthalene were found in the blanks. It is important to point out that, for both types of adsorbent TD tube analysed, all of the compounds found were present in their blanks at concentrations below the limit of quantification (LOQ). However, higher levels of these compounds were observed in TC tubes blanks than in CCC tubes (Woolfenden, 1997).

In order to validate the methods, repeatability and reproducibility (expressed as relative standard deviation, %RSD), linear range and method detection (MDLs) and quantification (MQLs) limits were determined for the studied compounds in both types of tubes.

Repeatability and reproducibility of the TD-GC-MS method were evaluated for both kinds of adsorbent TD tubes spiked at 2.5 ng (n=5). The results were expressed as relative standard deviations (%RSD). Both methods showed good intra-day and inter-day precision for all compounds, with most of the %RSD values below 14%, except for a few compounds, with %RSD values below 23%. Table 1 shows the reproducibility values for both methods. These results comply the performance guidelines set by USEPA, 1999, which require %RSD values below 25% in the case of VOCs.

An external calibration method was used for the quantification of target analytes in which 1 µL of the corresponding standard solutions was loaded into each kind of adsorbent TD tube, as mentioned in Section 2.3. and the tube was then immediately desorbed. Seven calibration levels were used by loading for each kind of adsorbent TD tubes (TC and CCC tubes) at amounts between 0.005 and 100 ng, except for pentanes and benzene which were validated up to 300 ng due to the high concentrations found in some samples. Calibration curves showed good linearity, with determination coefficients (r^2) higher than 0.990 for all of the compounds in both adsorbent TD tubes. Instrumental detection limits (LODs) were taken as three times the ratio signal/noise of the quantifier ion, taking into account the tube blanks of each type of adsorbent TD tube. Instrumental quantification limits (LOQs) were the lowest point in the calibration curves.

The final sample volume for each type of adsorbent TD tube has to be determined in order to ensure that there are no analytes losses during the sampling process by leaking through the adsorbent bed (USEPA, 1999). The breakthrough volume for target compounds in TC tubes was evaluated in previous studies (Ramírez et al., 2010; Ras et al., 2009b) and the sampling conditions were set at flow-rate of 22 mL min^{-1} for 2 hours, collecting 2.64 L of air. In this study, the breakthrough volumes for the target analytes on CCC tubes were determined by placing two identical freshly cleaned CCC tubes in a highly contaminated atmosphere. They were connected in series, so that the back tube would retain the analytes eluted from the front tube and air was pumped through them using a sampling pump (USEPA, 1999). Several samplings were performed at a fixed flow-rate of 50 mL min^{-1} for different times (2, 4, 8, 15, 24 h) resulting in sampling volumes between 6 L to 72 L. Analytes were present in second tube with 24 L of sampled air, with losses about 20-30 % for most compounds. Lower losses were observed when 12 L of air was sampled; some compounds showed losses ranging from 2-5%, except in the case of hexane, benzene, toluene, styrene and xylenes, which present losses more than 5%. Therefore, the sample volume was set at 6 L (50 mL min^{-1} during 2 h), which involves losses of about 1-2% for only few compounds, according to the EPA's recommendations, suggesting losses lower than 5%.

Method detection limits (MDLs) and method quantification limits (MQLs) were calculated taking into account the final sampling volume for each type of adsorbent TD tube: 2.64 L for TC tubes and 6 L for CCC tubes. MDLs for TC tubes ranged from 4 ng m^{-3} to 167 ng m^{-3} and decreased to values between 1 ng m^{-3} to 42 ng m^{-3} with CCC tubes. In the same way, the MQLs obtained for TC tubes ranged from 17 ng m^{-3} to 417 ng m^{-3} and from 4 ng m^{-3} to 167 ng m^{-3}for CCC tubes. MDLs and MQLs values for both adsorbent TD tubes are summarised in Table 1. As can be seen, lower values were achieved for CCC tubes, enabling the compounds to be determined at lower concentrations.

4. Applications

The efficacy of $CaCl_2$ pre-tube to prevent water from entering was confirmed by analysing more complex samples taken in urban and industrial locations with high relative humidity content.

In the case of urban samples in Constantí, three samples in parallel were taken: one with a single CCC tube, another one with a $CaCl_2$ drying pre-tube prior to a CCC tube and the last one with a TC tube. Several compounds were found in those samplings in parallel due to the proximity to an industrial park. Table 3 shows the concentrations values for all the analytes quantified in those samples. Comparing the concentrations found in the samples with CCC tubes, it can be seen that the highest values were obtained using the drying pre-tube, as is shown by the concentration ratios between them. This fact confirms the effect of humidity on this kind of adsorbent tube, changing its capacity when it is used. With respect to the results of the more volatile compounds, it can be seen that they are more influenced by humidity than the others. This fact could be explained by their retention onto the CMS of the CCC tubes. It is the strongest adsorbent and the most hydrophilic, so also therefore the most influenced by humidity. Regarding the chromatograms acquired for both CCC samples, the result was an improvement of the baseline and higher peaks using the desiccant, as expected. Comparing the samples using the TC tube and the CCC tube with the $CaCl_2$ pre-tube, the concentration ratios between them showed values close to 1, which means that there were no significant differences between them. These results were expected because it had previously demonstrated that TC tubes are not affected by the relative humidity and that the drying pre-tube removes the environmental humidity. Therefore, using the desiccant agent, CCC tubes were not affected by relative humidity, and they enable sampling higher volumes than with TC tubes, due to its capacity.

Table 3. VOCs concentrations found in Constantí sampling point (75% RH), as well as concentration ratios between the CCC tubes using the $CaCl_2$ pre-tube and without be used it and between the CCC with the $CaCl_2$ pre-tube and the TC tube.

No.	Compound	CCC tube (μg m^{-3})	$CaCl_2$ pre-tube + CCC tube (μg m^{-3})	TC tube (μg m^{-3})	Concentration ratio CCC tube/CCC tube + $CaCl_2$ pre-tube	Concentration ratio $CaCl_2$ pre-tube + CCC tube/TC tube
1	i-Pentane	16.5	46.9	36.9	0.35	1.27
3	n-Pentane	12.6	42.8	45.9	0.30	0.93
17	n-Hexane	7.6	10.9	14.7	0.70	0.74
29	Benzene	0.8	3.0	3.2	0.26	0.93
30	Carbon tetrachloride	0.3	1.7	1.4	0.20	1.17
33	n-Heptane	3.0	3.6	3.9	0.83	0.91
42	Toluene	3.7	5.0	4.7	0.75	1.06
46	n-Octane	6.5	3.5	3.9	1.84	0.91
52	Ethylbenzene	2.4	3.8	3.7	0.63	1.03
53, 54	m,p-Xylene	2.1	2.9	3.1	0.73	0.93
56	Styrene	1.1	1.8	2.1	0.61	0.89
57	o-Xylene	1.6	2.1	2.1	0.75	1.00
61	Isopropylbenzene	0.2	0.3	0.3	0.80	0.89
63	n-Propylbenzene	0.4	0.4	0.4	0.85	0.93
66	3-Ethyltoluene	1.2	1.4	1.1	0.83	1.22
67	4-Ethyltoluene	0.5	0.6	0.5	0.83	1.14
68	1,3,5-Trimethylbenzene	0.5	0.7	0.6	0.74	1.23
70	2-Ethyltoluene	0.4	0.5	0.4	0.87	1.07
72	1,2,4-Trimethylbenzene	1.4	1.8	1.5	0.75	1.21
76	p-Isopropyltoluene	0.2	0.3	0.3	0.64	1.03
77	1,2,3-Trimethylbenzene	0.4	0.6	0.7	0.68	0.88
80	1,4-Diethylbenzene	0.2	0.3	0.4	0.80	0.81
86	Naphthalene	0.1	0.2	0.2	0.58	0.86

For industrial environment, samples were taken in a location inside the Tarragona harbour. High levels of benzene are present due to its storage and transportation in this place. These high values enabled the linear trend previously obtained to be confirmed. Therefore, only the results of benzene are shown. Table 4 shows the results for the samples: the %RH during in each sampling, the concentrations (μg m^{-3}) with and without the $CaCl_2$ drying pre-tube, the experimental ratio between the peak areas obtained with and without the use of pre-tube and the theoretical ratio calculated by the linear regression curve done for benzene (Figure 5A). As expected, with high %RH, the concentrations found in both samples using the drying pre-tube were higher (41.4 and 26.6 μg m^{-3}) than those obtained working without it (8.3 and 4.1 μg m^{-3}, respectively). In the same way, in these results, no significant differences were observed in both samplings between the experimental and theoretical ratios. This fact demonstrates the losses of benzene at high %RH and the applicability of the drying pre-tube method even in samplings at different sites and under different conditions.

Table 4. Benzene results for the real samplings in Tarragona harbor.

Sampling	%RH	CCC tube ($\mu g\ m^{-3}$)	$CaCl_2$ pre-tube + CCC tube ($\mu g\ m^{-3}$)	Experimental ratio	Theoretical ratio
1	75	8.3	41.4	0.21	0.22
2	81	4.1	26.6	0.16	0.11

5. Conclusions

The effect of ambient humidity on the capacity of adsorbent TD tubes has been demonstrated when carbon-based solid adsorbents were used in the sampling process. It can be concluded that Carbotrap B/Carbopack X/Carboxen 569 adsorbent TD tubes were affected by the presence of humidity at values higher than 40% of RH. It confirms that the capacity of these adsorbent tubes is reduced. Placing a pre-tube filled with a desiccant material, $CaCl_2$ with diatomaceous earth, prior to the CCC tubes in the sampling process prevents the water from entering the adsorbent tube. Not all the compounds exhibited the same behaviour in the presence of RH; with some showing a high dispersion in their results at RH higher than 40%, while others presented a slight reduction with a notably dispersion in their response when the RH was increased and, lastly, some compounds showed a clearly linear decreasing trend in their concentrations as the RH increased. Moreover, it was also confirmed that Tenax TA/Carbograph 1TD adsorbent TD tubes, which are fairly hydrophobic, were not affected by the presence of relative humidity even at high values. The applicability of both methods had been demonstrated on industrial and urban samples, making it clear that the drying pre-tube must be used when CCC tubes are utilised, while, in the samplings with TC tubes, it is not necessary. However, it has also been demonstrated that, with CCC tubes, higher sample volumes can be sampled and, therefore, lower limits of detection can be achieved.

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