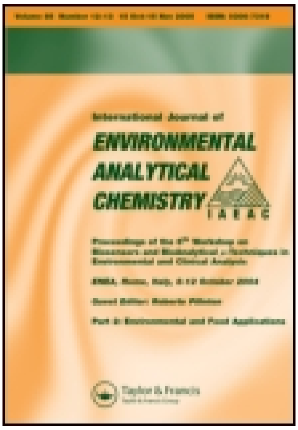

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Determination of volatile organic compounds in industrial wastewater plant air emissions by multi-sorbent adsorption and thermal desorption-gas chromatography-mass spectrometry

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Determination of volatile organic compounds in industrial wastewater plant air emissions by multi-sorbent adsorption and thermal desorption-gas chromatography-mass spectrometry

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This paper describes the process of determining the presence of volatile organic compounds in air emissions from industrial wastewater treatment plants (WWTP). The analytical method, based on thermal desorption-gas chromatography-mass spectrometry, was developed to simultaneously determine of 99 volatile organic compounds (VOCs) in air samples. This method is rapid, environmentally-friendly (since no organic solvents are used to extract the analytes) and compatible with a large range of thermally stable polar and apolar compounds. The target VOCs were selected on the basis of their occurrence in real samples and their adverse effects on the environment and human health. To cover the wide range of target compounds, multisorbent tubes filled with Tenax TA and Carbograph 1TD were used. Method validation showed good repeatabilities, low detection limits, a high linear range and good recoveries. At a fixed sample volume of 600 mL no significant losses for any of the target compounds were found in the samples. Stability during storage indicated that samples must be keep refrigerated at 4°C and analysed within three days of collection. Real samples were taken from air emissions of an industrial wastewater treatment plant located in the Southern Industrial Area of Tarragona (Spain) with the aim of studying its contribution as a source of atmospheric VOCs. This WWTP collects wastewater from several chemical factories which produce isocyanates, polyurethanes, chlorinated organics and functional chemicals among other products. Samples from the collecting tank after the primary sedimentation showed higher VOC concentrations than samples from the secondary treatment tank. The most abundant VOCs found in these emissions are included in the USEPA List of Hazardous Air Pollutants. The highest values correspond to acrylonitrile (up to 1843 $\mu g\,m^{-3}$) and styrene (up to 573.70 $\mu g\,m^{-3}$). The levels of chloroform, 1,4-dioxane, ethylbenzene, 1,2,3-trimethylbenzene and 1,4-diethylbenzene were also high.

Keywords: thermal desorption; industrial wastewater treatment plant emissions; quality air monitoring; volatile organic compounds

1. Introduction

The identification and measurement of volatile organic compounds (VOCs) in air is of considerable interest due to their direct or indirect impact on the global environment and human health. Several environmental effects of VOCs have been recognised, including

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their contribution to stratospheric ozone depletion; tropospheric photochemical ozone formation (which is the main cause of photochemical smog); enhancement of the global greenhouse effect; odour nuisance; and the accumulation and persistence in the environment of recalcitrant pollutants [1–3].

Furthermore, many VOCs have adverse effects on human health even at parts per billion (ppb) levels. These adverse effects include irritation of mucous membranes, neurotoxic effects (psychological stress and sensory irritation to behavioural function), epidemiology of respiratory disorders, negative impacts on reproductive systems and birth defects [4,5]. Ambient VOCs also have genotoxic effects. According to a study of the US Environmental Protection Agency (USEPA), ambient VOCs are responsible for between 35% and 55% of the outdoor air cancer risk in the US [6,7]. Hence, VOCs are considered an essential parameter for assessing the air quality in indoor and outdoor environments. It is, therefore, important to monitor these compounds in urban, industrial and rural ambient air and to determine their sources.

VOCs are released into the atmosphere as a result of natural and human activities. These activities include vehicle exhaust fumes, industrial activity, solvent usage, landfill waste and agriculture. Industrial applications of VOCs are very diverse, as they are used in the metal finishing industry, the synthetic organic chemical manufacturing industry, the petrochemical industry and the plastics industry. Industrial discharges are a source of VOCs in wastewater plants. It should be pointed out that whereas many VOCs are controlled by air quality legislation, only a few VOCs are listed in water quality legislation. For example, VOCs only account for a small number of the contaminants listed in the 'European Union list of priority pollutants for water policies' [8], whereas they account for most of the Hazardous Air Pollutants (HAPs) included in the US EPA Clean Air Act [9]. Therefore, a major concern regarding toxic VOCs in wastewater is the potential air emissions from wastewater treatment plants (WWTPs). Although several papers have focused on the monitoring of VOC emissions in industrial facilities [10–15], the emissions of VOCs from wastewaters in industrial-sewage treatment plants are often overlooked as sources of hazardous substances. Previous papers have shown the influence of urban WWTP emissions on air quality [16–21]. However, there are only a few studies on the composition of industrial WWTP emissions [22,23] and their relative importance as a potential source of specific hazardous air pollutants must be further investigated.

Due to the complexity of VOC composition and the low levels to be detected (from ppb down to ppt), several sampling and analytical strategies have been developed and applied to identifying and quantifying of VOC emissions [1,24–29]. Most of the methods that have been developed for determining VOC emissions from urban and industrial WWTPs are either canister-based [11,22] or sorbent-based [16,18,19,21,23]. New trends in VOC determination focus on the development of versatile, portable, low-cost and environmentally-friendly techniques without compromising the limit of detection. In this respect, preconcentration on solid sorbents followed by thermal desorption (TD) has been shown to be a highly advantageous technique [30–32]. Thermal desorption provides enhanced sensitivity, is compatible with thermally stable polar and apolar compounds, allows reuse of adsorbent tubes and minimises solvent usage with the consequent benefits for laboratory safety and waste disposal. In addition, the use of multiple-bed sorbent cartridges provides high breakthrough volumes and the quantitative retention and desorption of VOCs over a wide volatility range [14,28,33–35]. It should be noted, however, that if multisorbent adsorption tubes are used, the sample volume and the storage stability of each target compound must be evaluated [24].

This paper describes the development of a multisorbent adsorption and thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS) method for simultaneously monitoring 99 VOCs in air samples. This method was used to analyse the emissions of an industrial WWTP with the aim of studying its contribution as a source of atmospheric VOCs. The compounds studied include some hazardous VOCs like ozone precursors (alkanes, alkenes, aromatics and their halogenated derivatives) and some specifically industrial compounds such as acrylates, among others.

2. Experimental

2.1 *Chemical standards*

The list of the VOCs determined is shown in Table 1. A total of 99 target compounds were selected on the basis of their occurrence in industrial wastewater emissions and their adverse effects on the environment and human health. Thirty-four of the ninety-nine compounds determined are included in the list of Hazardous Air Pollutants (HAPs) of the US EPA Clean Air Act [9], eighteen of them are ozone precursors recommended for measurement by the Directive 2002/3/EC [36], eight of them are included in the European Union list of priority pollutants for water policies [8] and twelve of them are included as hazardous organic pollutants in the World Health Organization Air Quality Guidelines [4].

The standards of the 99 target compounds involve three mixtures of volatile organic compounds at 2000 $\mathrm{mg\,L^{-1}}$ in methanol (592/524 Volatile Organics Calibration Mix, EPA 524.2 Revision 4 Mix and 8270 Calibration Mix 5 from Supelco, Bellefonte, USA) and the individual standards of i-pentane, 1-pentene, n-pentane, 2-pentene (cis/trans mixture), isoprene, i-hexene, n-hexane, i-octane, n-heptane, n-octane, phenol, 1,2,3-trimethylbenzene (Aldrich, Steinheim, Germany), 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, 1,2-diethylbenzene, 1,3-diethylbenzene, 1,4-diethyilbenzene (Fluka, Buchs, Switzerland), and 2-methylnaphthalene (Riedel-deHaën, Seelze, Germany). The minimal purity of the standards was 98%. Toluene-d_8 from Aldrich was used as an internal standard, as recommended by the EPA [26].

The standards were diluted in methanol for gas chromatography with purity >99.9% (SDS, Peypin, France) and ranged between 0.01 and 500 $\mathrm{mg\,L^{-1}}$ with a toluene-d_8 constant concentration of 5 $\mathrm{mg\,L^{-1}}$. All the standards were prepared on the day of use, and stored at 4°C in 10 mL Certan® capillary vials provided by Supelco.

2.2 *Two-bed sorbent tubes*

A two-bed sorbent cartridge was chosen to cover the wide range of target compounds in this study. The cartridges were stainless-steel tubes (length: 3 in. × 0.5 in.; o.d.: 0.25 in.) filled with a multisorbent bed of approximately 350 mg of Tenax/Carbograph 1TD (Markes International Limited, Llantrisant, UK). The two sorbent materials were selected on the basis of previous studies [14,24].

Before each use, tubes were conditioned by thermal cleaning (100°C for 15 minutes, 200°C for 15 minutes and 325°C for 30 minutes) under a nitrogen flow rate of 100 $\mathrm{mL\,min^{-1}}$ (purity 99.999%, Carburos Metálicos, Tarragona, Spain). After conditioning, the tubes were sealed with Swagelok end caps fitted with PTFE ferrules and stored in

Table 1. Target compounds, in chromatographic elution order, their retention times (t_R), quantifier and qualifier ions, repetitivity (expressed as relative standard deviation (%RSD) for the analysis of 100 ng of VOCs standard ($n = 5$) and calculated without and with an internal standard), method detection (MDL) and quantification limit (MQL) (expressed in µg m^{-3} and calculated for a sampling volume of 600 mL) and the instrumental recoveries (%Rec.).

No.	Target VOCs	t_R (min)	Quantifier ion	Qualifier ions[1]			Repetitivity (%RSD, $n = 5$)		MDL (µg m^{-3})	MQL (µg m^{-3})	%Rec. ($n = 3$)
							No I.S.	I.S.			
1	i-Pentane[b]	3.87	43	57 (71)	72 (7)		2.49	1.48	0.17	0.83	85.0
2	1-Pentene[b]	4.08	42	55 (78)	70 (49)	39 (46)	2.45	1.26	0.83	1.67	100.0
3	n-Pentane[b]	4.20	43	57 (16)	72 (10)		2.42	1.06	0.08	0.17	100.0
4	Diethyl ether	4.30	59	74 (84)	45 (62)	41 (12)	2.67	0.55	0.17	0.83	100.0
5	2-Trans-pentene[b]	4.35	55	70 (43)	42 (40)	41 (30)	1.75	0.55	0.17	0.83	100.0
6	Isoprene[b]	4.38	67	68 (66)	53 (72)	40 (26)	3.38	0.35	1.23	1.67	94.9
7	2-Cis-pentene[b]	4.49	55	70 (44)	42 (33)	41 (24)	2.87	1.57	0.17	0.83	96.1
8	1,1-Dichloroethylene	4.59	61	96 (63)	98 (41)		1.14	0.69	0.13	0.17	95.7
9	Acrylonitrile[a,d]	4.63	53	52 (82)	50 (81)	38 (7)	0.99	0.99	0.01	0.08	100.0
10	3-Chloropropene[a]	4.89	39	76 (50)	78 (19)		2.24	2.24	0.17	0.83	97.0
11	Dichloromethane[a,c,d]	4.88	49	84 (83)	86 (53)	51 (31)	4.9	1.87	1.00	1.67	100.0
12	Carbon disulphide[a,d]	5.05	76	44 (12)	78 (9)		3.2	4.75	0.07	0.83	86.7
13	1-Hexene	5.37	43	56 (65)	69 (23)	84 (16)	2.13	0.08	0.17	0.83	95.2
14	Trans-1,2-dichloroethene	5.63	61	96 (71)	98 (46)		3.27	0.29	0.08	0.17	97.9
15	Methyl-tercbutylether[a]	5.69	73	57 (21)	43 (21)	41 (20)	0.86	0.12	0.17	0.83	85.9
16	Propionitrile	5.88	54	55 (15)	38 (4)		1.21	0.80	0.17	0.83	100.0
17	1,1-Dichloroethane	6.00	63	65 (32)	83 (13)		2.38	0.19	0.08	0.17	100.0
18	n-Hexane[a,b]	6.54	57	86 (16)	71 (6)	43 (70)	2.10	0.02	0.12	0.17	96.6
19	Methacrylonitrile	6.55	41	67 (70)	52 (26)	66 (24)	1.45	0.80	0.02	0.17	100.0
20	Cis-1,2-dichloroethylene	6.92	61	96 (80)	63 (31)		2.32	1.46	0.08	0.17	99.9
21	Methylacrilate	7.10	55	85 (19)	42 (10)		0.98	0.17	0.02	0.17	99.8
22	2,2-Dichloropropane	7.14	77	79 (31)	97 (20)		3.48	2.22	0.08	0.17	84.1
23	Bromochloromethane	7.26	130	128 (76)	93 (32)		1.46	0.89	0.13	0.17	99.6
24	Chloroform[a,c]	7.33	83	85 (64)			1.85	1.06	0.08	0.17	99.8
25	Tetrahydrofuran	7.60	42	71 (46)	72 (47)	41 (58)	0.67	0.07	0.50	0.83	99.9
26	1,1,1-Trichloroethane[a]	8.29	97	99 (62)	61 (40)	119 (13)	2.75	1.37	0.08	0.83	97.5
27	1-Chlorobutane	8.40	56	41 (59)	63 (5)	49 (4)	2.24	0.96	0.05	0.83	99.5
28	1,2-Dichloroethane[c,d]	8.42	62	64 (31)	49 (21)	63 (14)	2.36	1.54	0.02	0.17	99.4

29	1,1-Dichloropropene	8.66	75	110 (37)	39 (53)	77 (30)	2.67	0.77	0.08	0.17	99.5
30	Benzene[a,b,c,d]	8.92	78	77 (23)	51 (15)	52 (15)	1.47	0.03	0.72	1.67	100.0
31	Carbon tetrachloride[a]	8.97	117	119 (93)	121 (31)	82 (21)	3.75	2.89	0.08	0.83	95.0
32	Chloroacetonitrile	9.41	75	40 (23)	48 (47)	77 (32)	3.68	2.47	0.17	0.83	99.7
33	i-Octane[b]	9.83	57	56 (34)	41 (26)	99 (5)	3.01	2.57	0.08	0.17	97.7
34	n-Heptane[b]	10.28	71	57 (54)	100 (18)		2.96	2.10	0.15	0.83	100.0
35	2-Nitropropane[a]	10.29	43	41 (87)	39 (31)		1.15	0.74	0.02	0.08	100.0
36	1,2-Dichloropropane[a]	10.38	63	76 (38)			0.41	0.28	0.05	0.08	99.6
37	Trichloroethene[a,d]	10.41	130	132 (86)	95 (92)		2.01	1.43	0.02	0.08	99.5
38	Dibromomethane	10.51	174	93 (80)	95 (73)	172 (53)	0.83	0.26	0.08	0.17	99.8
39	1,4-Dioxane[a]	10.68	88	58 (49)	43 (16)	57 (15)	6.34	3.35	1.33	1.67	99.4
40	Methylmethacrylate[a]	10.78	41	100 (35)	69 (80)	39 (55)	2.68	2.40	0.02	1.67	100.0
41	Bromodichloromethane	10.77	83	85 (52)	129 (12)		1.56	1.26	0.02	0.17	99.3
42	Cis-1,3-dichloropropene	12.02	75	39 (45)	77 (31)	110 (23)	1.46	0.73	0.08	0.17	99.5
43	Pyridine trifluoroacetate	12.17	79	52 (48)	51 (22)	39 (4)	5.65	3.21	0.02	0.17	97.4
44	Trans-1,3-dichloropropene	13.05	75	110 (24)	39 (43)	77 (30)	2.89	2.41	0.08	0.17	99.7
45	Toluene[a,b,d]	13.23	91	92 (59)			1.05	0.34	1.00	1.67	99.6
46	1,1,2-Trichloroethane[a]	13.41	97	83 (81)	99 (60)	85 (52)	3.55	0.81	0.02	0.17	100.0
47	Ethylmethacrylate	13.77	69	41 (68)	99 (22)	86 (17)	3.40	0.52	0.02	0.17	100.0
48	1,3-Dichloropropane	13.87	76	41 (62)	78 (31)	39 (21)	2.21	1.37	0.02	0.17	99.3
49	n-Octane[b]	14.36	85	71 (60)	57 (86)	114 (14)	1.94	1.58	0.03	0.83	96.9
50	Dibromochloromethane	14.49	129	127 (77)	131 (24)		2.62	1.63	0.02	0.08	99.4
51	1,2-Dibromoethane	14.89	107	109 (93)			2.95	0.52	0.05	0.08	99.7
52	Tetrachloroethene[a,d]	14.95	166	164 (79)	129 (67)	131 (65)	0.43	0.04	0.01	0.08	98.7
53	Chlorobenzene[a]	16.48	112	77 (55)	114 (31)	51 (17)	3.07	0.3	0.01	0.08	99.3
54	1,1,1,2-Tetrachloroethane	16.60	131	133 (95)	117 (65)	119 (63)	2.82	1.2	0.02	0.08	99.1
55	Ethylbenzene[a,b]	16.99	91	106 (31)			2.59	2.20	0.17	0.33	99.2
56, 57	m,p-Xylene[a,b]	17.31	91	106 (56)	105 (25)	77 (14)	2.51	2.13	0.16	0.34	98.9
58	Bromoform[a]	18.10	173	171 (51)	93 (16)	81 (13)	4.08	2.81	0.05	0.08	99.5
59	Styrene[a,d]	18.13	104	103 (46)	78 (40)		3.63	3.24	0.67	0.83	99.6
60	o-Xylene[a,b]	18.22	91	106 (47)	105 (22)	77 (17)	3.84	1.47	0.003	0.17	100.3
61	1,1,2,2-Tetrachloroethane[a]	18.91	83	85 (64)	95 (15)	131 (11)	4.67	2.93	0.05	0.08	99.6
62	1,2,3-Trichloropropane	19.17	75	110 (34)	77 (31)	97 (18)	1.76	1.37	0.08	0.17	99.8
63	1,4-Dichloro-2-butene	19.24	75	53 (69)	89 (52)	124 (20)	3.95	2.7	0.12	0.17	99.7
64	Isopropylbenzene[a]	19.32	105	120 (28)	77 (15)	79 (13)	3.18	2.79	0.01	0.08	99.8
65	Bromobenzene	19.75	77	156 (71)	158 (69)	51 (28)	3.72	1.17	0.02	0.08	99.4

(*continued*)

Table 1. Continued.

No.	Target VOCs	t_R (min)	Quantifier ion	Qualifier ions[1]			Repetitivity (%RSD, $n=5$)		MDL (μg m^{-3})	MQL (μg m^{-3})	%Rec. ($n=3$)
							No I.S.	I.S.			
66	n-Propylbenzene	20.38	120	105 (16)			3.34	2.95	0.02	0.08	100.1
67	2-Chlorotoluene	20.42	126	125 (25)	128 (30)		3.61	3.22	0.05	0.08	99.9
68	4-Chlorotoluene	20.60	91	126 (33)	125 (13)	128 (10)	3.61	3.22	0.02	0.08	99.5
69	3-Ethyltoluene	20.62	105	120 (31)	77 (11)		3.58	3.19	0.01	0.02	99.5
70	4-Ethyltoluene	20.71	105	120 (29)	77 (11)	91 (10)	3.89	3.50	1.77	2.00	99.9
71	1,3,5-Trimethylbenzene[b]	20.87	105	120 (49)	119 (12)	77 (11)	3.80	3.41	0.01	0.02	99.9
72	Phenol[a]	20.99	94	66 (30)	55 (7)	50 (5)	4.48	4.10	2.33	2.50	102.3
73	Aniline[a]	21.21	93	66 (30)	65 (14)	52 (3)	6.91	0.18	0.002	0.02	96.8
74	2-Ethyltoluene	21.30	105	120 (31)	91 (11)	77 (11)	3.25	2.87	0.02	0.17	99.3
75	Pentachloroethane	21.35	167	117 (96)	165 (77)	130 (31)	4.03	3.64	0.08	0.17	99.7
76	tert-Butylbenzene	21.72	119	91 (63)	134 (21)		3.19	2.80	0.02	0.08	99.4
77	1,2,4-Trimethylbenzene[b]	21.78	105	120 (58)			3.52	3.13	0.03	0.08	98.2
78	1,3-Dichlorobenzene	22.30	146	148 (63)	111 (36)	75 (26)	4.56	4.17	0.02	0.08	98.3
79	sec-Butylbenzene	22.31	105	134 (24)			3.85	3.46	0.01	0.02	99.4
80	1,4-Dichlorobenzene[a]	22.52	146	148 (62)	111 (35)	75 (25)	4.04	3.65	0.02	0.08	99.6
81	p-Isopropyltoluene	22.69	119	134 (31)	91 (25)	117 (15)	3.65	3.27	0.03	0.05	99.6
82	1,2,3-Trimetylbenzene[b]	22.73	105	120 (44)	77 (12)	91 (9)	3.63	3.24	0.02	0.05	98.3
83	Benzyl alcohol	22.93	79	108 (60)	107 (43)	51 (16)	1.57	1.48	0.005	0.01	95.0

84	1,2-Dichlorobenzene	23.20	146	148 (63)	111 (38)	75 (25)	2.96	2.57	0.02	0.08	99.2
85	1,3-Diethylbenzene	23.34	105	119 (98)	134 (48)	91 (24)	4.23	3.84	0.02	0.08	99.5
86	1,4-Diethylbenzene	23.56	119	105 (82)	77 (23)		4.09	3.71	0.02	0.08	99.5
87	n-Butylbenzene	23.58	91	92 (61)	134 (32)	65 (12)	2.14	1.75	0.01	0.02	98.3
88	1,2-Diethylbenzene	23.72	105	119 (87)	134 (50)	77 (17)	4.02	3.63	0.02	0.08	97.2
89	Hexachloroethane[a]	24.37	201	117 (95)	199 (62)	166 (48)	3.80	3.41	0.08	0.17	95.1
90	1,2-Dibromo-3-chloropropane	24.45	157	155 (78)	75 (74)		4.09	3.71	0.08	0.17	98.6
91	Nitrobenzene[a]	24.52	77	123 (51)	51 (46)	93 (13)	4.25	3.86	0.08	0.17	95.2
92	1,2,4-Trichlorobenzene[c]	26.53	180	182 (96)	184 (30)	145 (27)	4.09	3.71	0.02	0.17	99.6
93	Naphthalene[a,c,d]	26.79	128	127 (18)	129 (15)		1.33	0.94	0.17	0.83	92.0
94	Hexachlorobutadiene[c]	27.17	225	227 (64)	223 (62)	190 (39)	4.16	3.77	0.02	0.08	99.5
95	1,2,3-Trichlorobenzene[c]	27.24	180	182 (90)	184 (28)	145 (25)	3.60	3.22	0.02	0.08	99.3
96	2-Methylnaphtalene[a,d]	28.77	142	141 (85)	115 (28)		1.70	3.41	0.08	0.17	91.5
97	1-Methylnaphtalene[a,d]	29.11	142	141 (95)	115 (38)		1.50	3.59	0.01	0.02	91.2
98, 99	2,3,4,5-Tetrachlorophenol/ 2,3,4,6	34.40	232	131 (29)	166 (19)		6.12	0.96	0.0003	0.003	92.3

Notes: [1] The value in brackets next to qualifier ions represents per cent abundances of each ion for that compound.

[a] Compounds included in the USEPA List of Hazardous Air Pollutants [9].

[b] Ozone precursors recommended for measurement by the Directive 2002/3/EC [36].

[c] Compounds included in the European Union list of priority pollutants for water policies [8].

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

hermetically sealable glass jars with desiccant material in order to prevent any ambient contamination of the sorbents.

2.3 *Calibration*

The external liquid standards and the internal standard were loaded into the two-bed sorbent tubes using a Calibration Solution Loading Rig (Markes International Limited, Llantrisant, UK) which allows a 99.999% pure Helium flow (Carburos Metálicos, Tarragona, Spain) to pass through the tube at a fixed flow rate of 100 mL min^{-1}. The cartridges were attached to the end of the weak sorbent (Tenax TA) in the same position as in the sample collection. A conventional GC syringe was used to inject 1 μL of each dilution of the standard solution into the sorbent cartridges. After the injection, a short time (approximately 20 s) was allowed to elapse before removing the needle from the sorbent to enable the target compounds to be fully evaporated and retained on the sorbent bed. To ensure the repeatability of the injection and the total evaporation of the solvent, the helium stream was maintained for 5 minutes before the tubes were sealed with Difflok caps and then immediately analysed. If this procedure was followed, there was no sign of methanol in the standard solution chromatograms.

2.4 *Thermal desorption GC-MS analysis*

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 first step, primary desorption, tubes were heated to 275°C with a helium flow rate of 30 mL min^{-1} for 10 min. This was done to desorb the analytes which were refocused on a hydrophobic general purpose cold trap, filled with Tenax TA and a graphitised carbon, cooled at −10°C. A split flow was not applied in this step, so all the mass desorbed from the tubes went into the cold trap. After flash-heating of the cold trap at 300°C during 3 min, analytes were injected into the chromatographic column. A split flow of 5 mL min^{-1} was applied in this step. The parameters of this method were based on a previous work [14] and optimised for the 99 target VOCs.

Separation and detection were performed in a 6890N gas chromatograph and 5973 *inert* mass spectrometer (Agilent Technologies. Palo Alto, USA), using a TRACSIL MetaX5 capillary column (60 m, 0.32 mm, 1.0 μm, provided by TEKNOKROMA, Barcelona, Spain) and helium gas as the carrier at a flow rate of 1.5 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 3 min.

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, operating at an electron impact energy of 70 eV. Qualitative identification of the target VOCs was based on the match of the retention times and the ion ratios of the target quantifier and qualifier ions. The retention times and the quantifier and qualifier ions for each target compound are shown in Table 1. The internal standard calibration method was used for the GC-MS quantification.

2.5 *Sample collection*

The Tarragona area is an important industrial centre mainly based on the chemical industry. Most of the chemical industries are located in two areas: the North Industrial Complex, which has a surface area of 470 ha and an oil refinery, and the South Industrial Complex, which occupies an area of 717 ha with several chemical and petrochemical plants. In this study, field samples were taken from an industrial WWTP located in the South Industrial Complex, near some tourist locations (see Figure 1). This WWTP collects wastewater from four chemical factories which produce a wide variety of products such as isocyanates, polyurethanes, chlorinated organics, polymerisates, functional chemicals, surfactants and adhesives. The samples were collected in November 2008 in two locations: the collecting tank after the primary sedimentation and the secondary treatment tank.

Samples were collected at the Tenax TA end of the tube in order to collect the heaviest hydrocarbons first. The tubes were placed in the headspace of the tanks at approximately 1 m from the wastewater. An air sampling pump (SKC, Eighty Four, USA) was used to pump air samples at a flow rate of 50 mL min^{-1}, for 12 min. The pump was calibrated with a flowmeter before and after sampling (Altech, Deerfield, UK) and the flow average was used to determine the volume of air sampled.

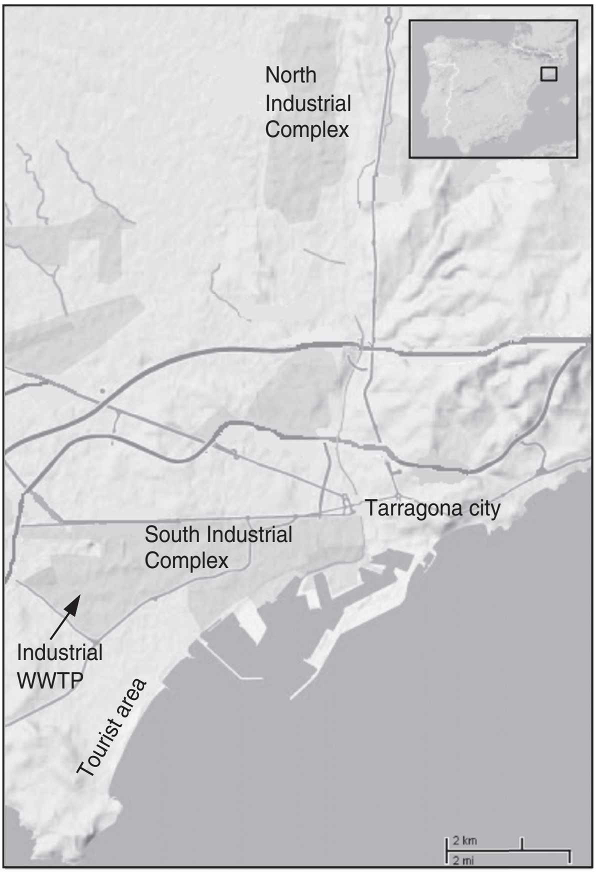

Figure 1. Map of the Tarragona area showing the location of the North and the South Industrial complexes, the sampled industrial WWTP, the main location (Tarragona city) and the tourist area.

3. Results and discussion

3.1 *Analytical method*

3.1.1 *Method optimisation*

All the parameters of the instrumental method were optimised using liquid standards of the 99 target VOCs and the internal standard. Although the matrix in which the standards are dissolved can affect the calibration, accurate gas external standards for a wide range of target compounds are not easy to generate. For this reason, recent studies have shown that liquid standards loaded in the sorbents in the appropriate conditions are a reliable alternative [30,37].

For the thermal desorption system, previous studies showed that while low desorption temperature, time and flow result in poor recovery of the target compounds, high values of these variables increase the number of artefacts and shorten the life of the sorbents [14,34]. For the 99 target VOCs, the tube and trap desorption temperature, the time and the flow, explained in section 2.4 above, were optimised to ensure the highest recoveries and the lowest artefacts [14].

Chromatographic separation was satisfactory for most of analytes (see retention times in Table 1) and the co-eluted analytes were quantified using characteristic ions. Only *m*-xylene and *p*-xylene and 2,3,4,5-tetrachlorophenol and 2,3,4,6-tetrachlorophenol were quantified together as they exhibited identical mass spectra.

Sample volume for real samples was fixed to ensure that no analytes had broken through the sorbent bed during sampling. Two identical sorbent tubes were connected in series, so that the back tube would retain the analytes eluted from the front tube, and air emitted by the collecting tank after the primary treatment (the most contaminated area) was pumped though them at different sampling rates (from $100\,\mathrm{mL\,min^{-1}}$ to $20\,\mathrm{mL\,min^{-1}}$) and periods of time (from 30 to 10 minutes). After each sampling both tubes were analysed. This test was conducted on different dates and under different atmospheric conditions (temperatures ranging from 5°C to 25°C, humidity between 60% to 90% and wind speeds up to $60\,\mathrm{km\,h^{-1}}$). The flow rate of the sampling was fixed at $50\,\mathrm{mL\,min^{-1}}$ for 12 minutes collecting 600 mL of air. Under these conditions, only eleven target VOCs were present in the second tube, with concentrations between 0.45 and 4.47% of their respective concentrations in the first tube, as is shown in Table 2. The highest value was 4.47% for the 1,4-dioxane but this does not exceed the 5% recommended by the EPA [38].

3.1.2 *Artefact evaluation*

Blank signals of the tubes and the formation of artefacts affect the method detection limit and the overall method performance. Although blank levels can be made extremely low by meticulous conditioning of the solid adsorbents and by properly storage [39], artefact formation may be unavoidable and needs to be taken into account [40]. Furthermore, the degradation products of Tenax TA are well known and have been widely studied [41,42]. Blanks of the tubes were checked by analysing the 20 freshly cleaned sorbent tubes involved in this study. Their responses were compared with the responses obtained by direct injection of the standards under the same split conditions. A total of 24 target VOCs were found in these tubes in amounts ranging from 0.0012 ng, for the o-xylene, to 1.2 ng for the phenol. Table 3 shows the average concentrations and the standard deviation of the blanks of the target compounds found. The average blank concentrations were included in the calibration curves of these 24 target VOCs.

Table 2. VOCs detected in the second tube in breakthrough tests and their % concentrations compared with their respective concentrations in the first tube.

No.	Target VOCs	%
9	Acrylonitrile	0.62
24	Chloroform	0.94
39	1,4-Dioxane	4.47
55	Ethylbenzene	2.57
56, 57	m,p-Xylene	1.62
59	Styrene	1.63
69	3-Ethyltoluene	0.65
71	1,3,5-Trimethylbenzene	0.52
77	1,2,4-Trimethylbenzene	0.73
82	1,2,3-Trimetylbenzene	0.45
86	1,4-Diethylbenzene	0.60

3.1.3 *Method validation*

To determine the instrumental repeatability, five cartridges filled with 100 ng of VOC standard were analysed on the same day. Although the EPA recommends the use of internal standards in the determination of VOCs by thermal desorption [26], internal standards are not always used in these kind of studies [33,34]. To evaluate the need for an internal standard, the relative standard deviation of the results was calculated with and without the internal standard (see Table 1). Although the repeatabilities without using the internal standard are quite good (ranging from 0.41 to 6.91% RSD), in most of the cases the use of the internal standard gave better values (ranging from 0.02 to 4.1% RSD). Thus, toluene-d_8 was used as an internal standard in this study.

The instrumental limit of detection (LOD) and the instrumental limit of quantification (LOQ) were evaluated in two ways. For target compounds without blank signal, LODs were determined as the concentrations corresponding to three times the noise signal of the quantifier ion and LOQs as the lowest calibration level. For target compounds which present a signal in the blank, the LODs and LOQs were established as the sum of the average concentrations of the blank responses plus three times the standard deviation of this signal, for the LOD, and plus ten times the standard deviation of the signal for the LOQ ($n = 20$). The lowest values of LOD and LOQ correspond to the sum of 2,3,4,5 and 2,3,4,6-tetrachlorophenol (0.0001 ng and 0.001 ng, respectively) and the highest values were for phenol (1.4 ng and 1.5 ng, respectively), which has a high blank signal.

The linear range was evaluated within a VOC amount ranging from LOQ of each compound to 1500 ng. All calibration curves showed a good linearity in that range with determination coefficients (r^2) higher than 0.990 for all compounds. Once the linear range had been tested, calibration curves at amounts ranging from LOQ of each compound and 100 ng were used to quantify the samples. Due to the high concentrations of acrylonitrile and styrene found in the samples, the ranges of their calibration curves were wider (0.05–1200 ng and 0.5–500 ng, respectively).

Instrumental recoveries were measured as the percentage recovery of the response obtained by the triplicate analysis of a 100 ng standard using the TD-GC-MS method and were compared with the response obtained by direct injection of the same amount of standard under the same split conditions. As Table 1 shows, most of the target compounds

Table 3. Blank concentrations of target VOCs in the freshly cleaned tubes and their standard deviation in ng.

No.	Target VOCs	Average concentration (ng)	s.d. (ng, $n=20$)
6	Isoprene	0.25	0.16
11	Dichloromethane	0.29	0.10
12	Carbon disulphide	0.012	0.009
18	n-Hexane	0.03	0.01
24	Chloroform	0.14	0.01
25	Tetrahydrofuran	0.09	0.07
30	Benzene	0.23	0.07
34	n-Heptane	0.05	0.01
39	1,4-Dioxane	0.18	0.18
45	Toluene	0.22	0.13
49	n-Octane	0.010	0.003
55	Ethylbenzene	0.05	0.02
56, 57	m,p-Xylene	0.02	0.01
59	Styrene	0.08	0.11
60	o-Xylene	0.0012	0.0003
64	Isopropylbenzene	0.020	0.001
70	4-Ethyltoluene	0.30	0.25
72	Phenol	1.2	0.5
77	1,2,4-Trimethylbenzene,	0.010	0.004
81	p-Isopropyltoluene	0.010	0.003
82	1,2,3-Trimetylbenzene	0.010	0.001
93	Naphthalene	0.04	0.02
96	2-Methylnaphtalene	0.02	0.01
97	1-Methylnaphtalene	0.002	0.001

have recoveries higher than 95% ($n=3$, %RSD between 0.02 and 4.06). The lowest recoveries correspond to i-pentane, methyl-tercbutylether and carbon disulphide (85, 86 and 87%, respectively).

The method detection limit (MDL) and the method quantification limit (MQL) ranged from 0.0003 to 2.3 $\mu g\,m^{-3}$ and from 0.003 to 2.5 $\mu g\,m^{-3}$, respectively (see Table 1).The precision in real samples was determined by sampling two sorbent tubes connected in parallel at the same time and under the same conditions. The analysis of these tubes showed similar results.

3.1.4 *Stability during storage*

The stability during storage was investigated by analysing twelve replicates of freshly cleaned cartridges filled with 100 ng of standard solution. Three of these were immediately analysed and the others were sealed with Swagelok end caps fitted with PTFE ferrules and stored at 4°C in hermetically sealable glass jars with desiccant material. Three of these cartridges were analysed after being stored for one day, three of them after three days and the last three after one week. Toluene-d_8 was used as the internal standard in the analysis of all samples. Figure 2 shows the fresh sample relative responses against the corresponding results for 3 days and 7 days of storage. Good correlations ($r^2 > 0.990$) and slopes close to the ideal 1 were observed after up to three days of storage (Figure 2a). After one week of storage (Figure 2b), however, the amount of carbon disulphide and n-hexane increased in the stored tubes, possibly due to the degradation of some analytes.

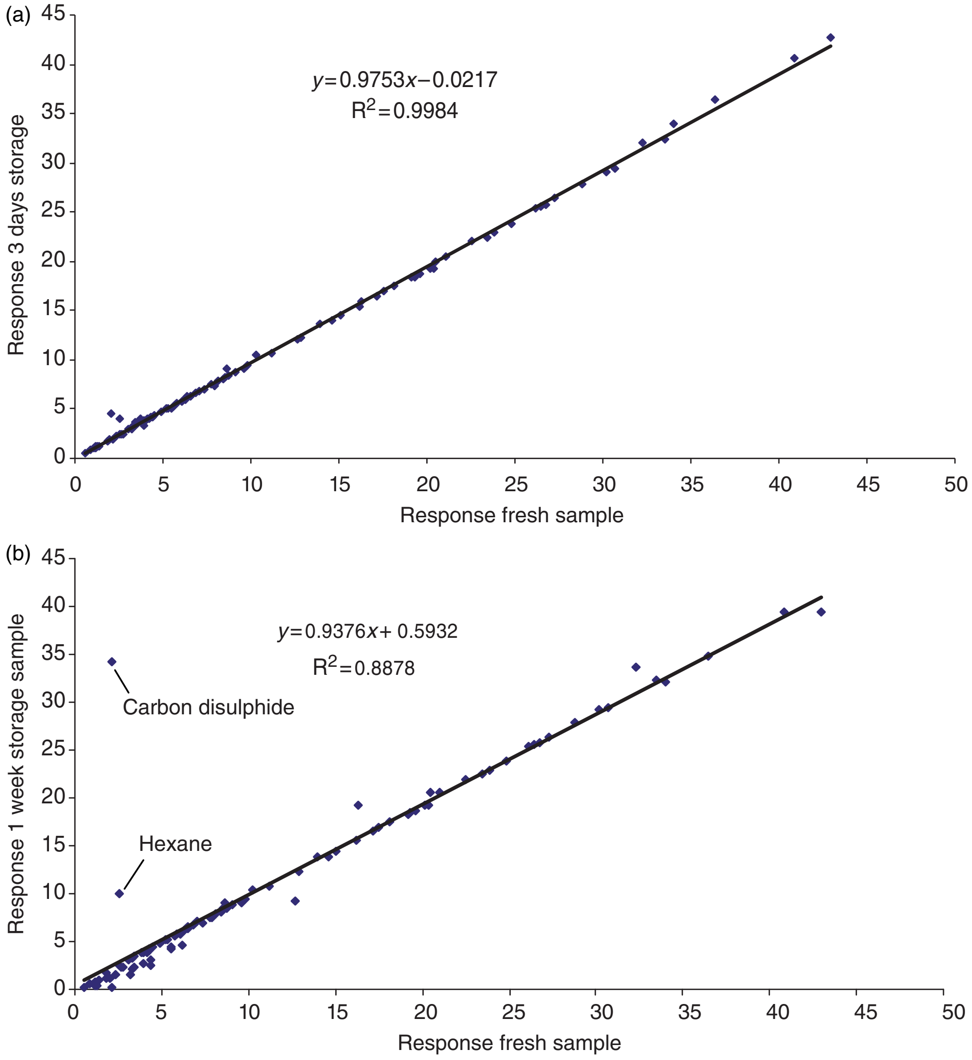

Figure 2. Correlations of the 99 target compounds after three days (a) and after one week of storage (b).

Furthermore, the losses of the most volatile target VOCs after one week storage, ranging between the 20% and the 50%, indicate that the samples should be analysed within three days of collection.

3.2 *Analysis of real samples*

Sixteen samples were taken in the industrial WWTP in November 2008. A total of 65 of the 99 VOCs were detected in these samples and 55 of these 65 were quantifiable by the proposed method. Table 4 shows the average, maximum and minimum concentrations found in the collecting tank after the primary sedimentation (site 1) and in the secondary treatment tank (site 2). Figure 3 shows the typical chromatogram for site 1 (Figure 3a) and for site 2 (Figure 3b). The most characteristic VOCs of each site are indicated. The highest concentration in site 1 was for acrylonitrile, with a maximum concentration of 1843 $\mu g\,m^{-3}$ and an average concentration of 843 $\mu g\,m^{-3}$. In this site, high concentrations of styrene were also found, between 408 and 574 $\mu g\,m^{-3}$. Also worthy of note were the high concentrations of chloroform (2.22–155 $\mu g\,m^{-3}$), 1,4-dioxane (14.2–104 $\mu g\,m^{-3}$), ethylbenzene (20.5–96.9 $\mu g\,m^{-3}$), m,p-xylene (35.3–136 $\mu g\,m^{-3}$), 1,2,3-trimethylbenzene (56.9–104 $\mu g\,m^{-3}$) and 1,4-diethylbenzene (<0.08–120 $\mu g\,m^{-3}$).

In contrast, levels of most compounds were lower in site 2 than in site 1. This is to be expected because in the secondary treatment tank is where the organic matter is biologically degraded and evaporation processes take place [43]. The exceptions were: i-Pentane, with concentrations between 6.13 and 20.08 $\mu g\,m^{-3}$ in site 1 and between 7.08 and 33.35 $\mu g\,m^{-3}$ in site 2; n-pentane (site 1: 1.27–9.08 $\mu g\,m^{-3}$, site 2: 6.13–15.8 $\mu g\,m^{-3}$), 2-cis-pentene (site 1: <0.17–1.50 $\mu g\,m^{-3}$, site 2: 1.27–2.27 $\mu g\,m^{-3}$) and n-heptane (site 1: <0.83–1.15 $\mu g\,m^{-3}$, site 2: <0.83–2.47 $\mu g\,m^{-3}$). A plausible explanation is that these VOCs may be degradation products of some other organic water pollutants. Finally, it is important to note that the levels of 1,4-dioxane were similar in both sampling sites which may indicate that the biological degradation of this compound did not occur.

To the best of our knowledge, this is the first study of the emissions of these 99 VOCs in this kind of industrial WWTP. Therefore, the results found could only be compared to those reported for petrochemical and urban WWTPs. For example, studies of air emissions from two petrochemical WWTPs in Taiwan reported concentrations of up to 620 $mg\,m^{-3}$ of benzene, 370 $mg\,m^{-3}$ of styrene and 53 $mg\,m^{-3}$ of acrylonitrile [11,22,23] which are much higher than the levels found in this study. In addition, the concentrations of VOCs reported for studies in urban WWTPs were generally higher than those reported in this paper except for acrylonitrile, chloroform and styrene [18,44]. Also worthy of note are the higher levels of chlorinated VOCs in urban WWTPs such as 1,1,1-trichloroethane (up to 82 $\mu g\,m^{-3}$) and tetrachloroethane (up to 40 $\mu g\,m^{-3}$).

It is significant that the most abundant VOCs found in the samples are all included in the USEPA List of Hazardous Air Pollutants [9]. Of these, acrylonitrile and styrene, which have the highest concentration levels, are also considered hazardous organic pollutants in the WHO Air Quality Guidelines [4]. Acrylonitrile is an anthropogenic product with carcinogenic effects in animals and humans. Although no safe level for acrylonitrile in air is established by the WHO, this organisation estimates a lifetime risk of $2 \cdot 10^5$ at an air concentration of 1 $\mu g\,m^{-3}$. As indicated in this section, the levels of acrylonitrile in this study were up to 1843 $\mu g\,m^{-3}$. As for styrene, it is one of the most important monomers worldwide and also occurs naturally as a degradation product of some organisms. A weekly average of 260 $\mu g\,m^{-3}$ is established as a guideline value for this compound. In the collected samples, styrene concentrations were higher than this guideline value (up to 574 $\mu g\,m^{-3}$). The high concentrations of these two compounds together with the remaining 63 VOCs found in the samples show the importance of industrial WWTPs as a source of hazardous air pollutants and the need for adequate analytical methods to monitor these compounds.

4. Conclusions

An analytical method for simultaneously determining 99 volatile organic compounds in air samples by TD-GC-MS was successfully optimised and evaluated. This method involves

Table 4. Target compounds found in real samples and their average, maximum and minimum concentrations in site 1 and 2.

		Site 1 (μg m^{-3})			Site 2 (μg m^{-3})		
No.	Target VOCs	Average	Maximum	Minimum	Average	Maximum	Minimum
1	i-Pentane	10.1	20.1	6.1	15.6	33.3	7.08
3	n-Pentane	3.64	9.08	1.27	6.52	15.8	6.13
5	2-Trans-pentene	0.004	0.03	n.q.	0.12	0.65	0.05
6	Isoprene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
7	2-Cis-pentene	0.19	1.50	n.d.	1.44	2.27	1.27
8	1,1-Dichloroethylene	0.2	1.60	n.d.	0.62	1.68	1.62
9	Acrylonitrile	843	1843	260	7.63	15.3	3.00
11	Dichloromethane	4.16	9.62	1.67	2.71	4.22	2.17
12	Carbon disulphide	1.01	6.07	n.q.	1.94	7.28	1.72
14	Trans-1,2-dichloroethene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
16	Propionitrile	0.40	3.22	n.d.	0.31	2.50	n.d.
18	n-Hexane	0.81	4.43	n.q.	1.04	4.20	n.q.
24	Chloroform	56.9	155	2.22	4.80	9.52	1.27
25	Tetrahydrofuran	0.57	2.38	n.q.	0.60	1.40	n.q.
26	1,1,1-Trichloroethane	0.51	1.42	1.35	1.03	1.42	1.33
27	1-Chlorobutane	n.d.	n.d.	n.d.	0.61	4.85	n.d.
28	1,2-Dichloroethane	0.68	2.10	0.63	1.37	3.72	0.53
30	Benzene	1.31	5.03	n.q.	1.46	2.98	n.q.
31	Carbon tetrachloride	1.31	1.48	1.13	1.34	1.45	1.15
33	i-Octane	0.61	1.35	0.95	0.47	1.28	1.22
34	n-Heptane	0.14	1.15	n.q.	0.56	2.47	n.q.
35	2-Nitropropane	0.14	0.60	n.q.	0.31	1.30	n.q.
37	Tricloroethene	0.28	2.22	n.q.	0.12	0.75	n.q.
39	1,4-Dioxane	42.0	105	14.2	43.8	63.1	21.6
40	Methylmethacrylate	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
41	Bromodichloromethane	0.06	0.48	n.d.	0.17	0.58	0.38
43	Pyridine trifluoroacetate	n.d.	n.d.	n.d.	1.01	8.12	n.d.
45	Toluene	5.71	19.1	n.q.	3.05	5.55	n.q.
49	n-Octane	0.23	1.82	n.q.	0.24	1.03	n.q.
50	Dibromochloromethane	0.16	0.38	0.15	0.17	0.47	0.10
52	Tetrachloroethene	0.88	1.63	0.38	0.91	3.00	0.17
53	Chlorobenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
55	Ethylbenzene	55.6	96.9	20.5	5.7	19.7	1.02
56, 57	m,p-Xylene	76.9	137	35.3	2.54	8.13	0.52
58	Bromoform	0.04	0.23	n.q.	0.06	0.25	n.q.
59	Styrene	574	775	409	4.23	6.12	3.02
60	o-Xylene	8.73	25.9	n.q.	0.77	3.02	n.q.
64	Isopropylbenzene	0.04	0.28	n.q.	0.13	1.02	n.q.
65	Bromobenzene	n.d.	n.d.	n.d.	0.08	0.67	n.d.
66	n-Propylbenzene	0.81	5.55	n.q.	0.61	3.95	n.q.
69	3-Ethyltoluene	25.7	59.1	n.q.	2.18	7.95	n.q.
70	4-Ethyltoluene	14.7	56.5	23.5	3.04	15.5	2.93
71	1,3,5-Trimethylbenzene	7.83	21.2	n.q.	0.85	4.10	n.q.
72	Phenol	n.d.	n.d.	n.d.	1.22	9.78	n.d.
74	2-Ethyltoluene	8.29	27.0	n.q.	0.80	2.85	n.q.
76	Tert-Butylbenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
77	1,2,4-Trimethylbenzene	28.9	70.8	n.q.	1.85	7.92	n.q.
78	1,3-Dichlorobenzene	n.q.	n.q.	n.q.	n.d.	n.d.	n.d.
79	sec-Butylbenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
80	1,4-dichlorobenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
81	p-Isopropyltoluene	1.22	4.25	n.q.	0.21	0.93	n.q.
82	1,2,3-Trimetylbenzene	81.7	104	56.9	2.65	10.6	0.05
83	Benzyl alcohol	n.q.	n.q.	n.q.	0.1	0.78	n.q.
84	1,2-Dichlorobenzene	n.q.	n.q.	n.q.	n.d.	n.d.	n.d.
85	1,3-Diethylbenzene	4.59	16.8	n.q.	0.44	1.95	n.q.

(*continued*)

Table 4. Continued.

No.	Target VOCs	Site 1 ($\mu g\ m^{-3}$) Average	Site 1 Maximum	Site 1 Minimum	Site 2 ($\mu g\ m^{-3}$) Average	Site 2 Maximum	Site 2 Minimum
86	1,4-Diethylbenzene	57.5	120	n.q.	3.84	15.7	n.q.
87	n-Butylbenzene	2.03	10.6	n.q.	0.13	0.68	n.q.
88	1,2-Diethylbenzene	0.49	2.40	n.q.	0.05	0.27	n.q.
91	Nitrobenzene	n.d.	n.d.	n.d.	0.31	1.37	n.q.
92	1,2,4-Trichlorobenzene	n.q.	n.q.	n.q.	n.q.	n.q.	n.q.
93	Naphthalene	0.60	4.82	n.q.	0.14	1.15	n.q.
94	Hexachlorobutadiene	0.23	0.5	0.42	0.19	0.40	n.d.
95	2-Methylnaphthalene	7.80	34.9	n.q.	0.19	0.97	n.q.
97	1-Methylnaphtalene	11.3	32.9	9.32	0.14	3.13	1.52

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

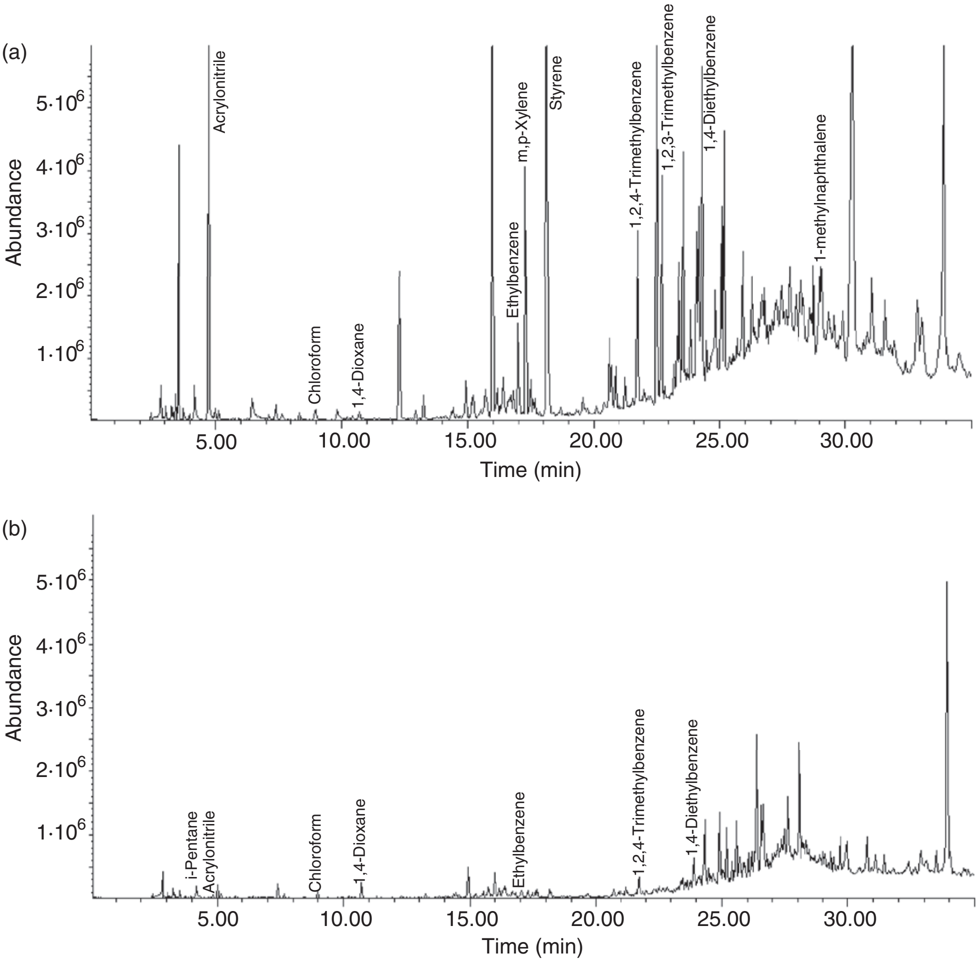

Figure 3. Chromatograms from site 1 (a) and from site 2 (b).

only 12 minutes of sampling and a low preconcentration volume of air (600 mL). The analysis of blanks showed the presence of some compounds of interest, mainly phenol, isoprene, dichloromethane, benzene and toluene, which affect the detection limits of these compounds. However, the high levels of the compounds in real samples indicate that the method can be useful in determining these. Although most of the compounds were stable during one week of storage at 4°C, the losses of the most volatile compounds and the increases in the concentration of carbon disulphide and n-hexane indicate that samples should be analysed within three days of collection.

When the method was applied to air emissions from an industrial WWTP, the concentrations of target compounds were found to be higher in the collecting tank after the primary sedimentation than in the secondary treatment tank. Acrylonitrile and styrene were the most abundant and the levels of chloroform, 1,4-dioxane, ethylbenzene, 1,2,3-trimethylbenzene and 1,4-diethylbenzene were also high.

The wide variety of hazardous VOCs found in the industrial WWTP emissions and the high concentrations of acrylonitrile and styrene indicate the importance of industrial WWTPs as a source of hazardous air pollutants and the need for fast and environmentally-friendly analytical methods that should be able to monitor a large number of these compounds. The TD-GC-MS method proposed has these characteristics and has been demonstrated to perform well in real samples.

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References

[1] J. Dewulf and H. Van Langenhove, J. Chromatogr. A **843**, 163 (1999).
[2] R.G. Derwent, M.E. Jenkin, and S.M. Saunders, Atmos. Environ. **30**, 181 (1996).
[3] R. Atkinson, Atmos. Environ. **34**, 2063 (2000).
[4] WHO – World Health Organisation, *Air Quality Guidelines for Europe*, 2nd ed. WHO Regional Publications, European Series, No. 29 (Copenhagen, 2000).
[5] A.P. Jones, Atmos. Environ. **33**, 4535 (1999).
[6] USEPA – US Environmental Protection Agency, Office of Air Quality Planning, *Cancer Risk from Outdoor Exposure to Air Toxics*. EPA-450/1-90-004a (Washington, 1990).
[7] P.W.G. Liu, Y.C. Yao, J.H. Tsai, Y.C. Hsu, L.P. Chang, and K.H. Chang, Sci. Total Environ. **398**, 154 (2008).
[8] Decision No. 2455/2001/EC of the European Parliament and of the Council of 20 November 2001 establishing the list of priority substances in the field of water policy and amending Directive 2000/60/EC. Official Journal of the European Communities L331/4, 15/12/2001: 1–5.
[9] USEPA – US Environmental Protection Agency, Office of Air Quality Planning, Amendments to 1990 Clean Air Act-List of 189 Hazardous Air Pollutants (Washington, 1994).
[10] E. Cetin, M. Odabasi, and R. Seyfioglu, Sci. Total Environ. **312**, 103 (2003).
[11] T.Y. Lin, U. Sree, S.H. Tseng, K.H. Chiu, C.H. Wu, and J.G. Lo, Atmos. Environ. **38**, 4111 (2004).
[12] Y.C. Hsu, S.K. Chen, J.H. Tsai, and L. Chiang, J. Air Waste Manag. Asso. **57**, 698 (2007).
[13] C.L. Chen, C.M. Shu, and H.Y. Fang, Environ. Monit. Asses. **120**, 487 (2006).
[14] M.R. Ras-Mallorqui, R.M. Marce-Recasens, and F. Borrull-Ballarin, Talanta **72**, 941 (2007).

[15] F. Dincer and A. Muezzinoglu, Atmos. Environ. **40**, 4210 (2006).

[16] A.P. Bianchi and M.S. Varney, Ann. Occ. Hyg. **41**, 437 (1997).

[17] A.K. Oskouie, D.T. Lordi, T.C. Granato, and L. Kollias, Atmos. Environ. **42**, 4530 (2008).

[18] J. Leach, A. Blanch, and A.C. Bianchi, Atmos. Environ. **33**, 4309 (1999).

[19] E. Atasoy, T. Dogeroglu, and S. Kara, Water Res. **38**, 3265 (2004).

[20] A. Escalas, J.M. Guadayol, M. Cortina, J. Rivera, and J. Caixach, Water Res. **37**, 3913 (2003).

[21] M.R. Ras, F. Borrull, and R.M. Marce, Talanta **74**, 562 (2008).

[22] B.Z. Wu, T.Z. Feng, U. Sree, K.H. Chiu, and H.G. Lo, Anal. Chim. Acta **576**, 100 (2006).

[23] W.H. Cheng and M.S. Chou, J. Environ. Sci. Health Part A-Toxic/Hazard. Subst. Environ. Eng. **38**, 2521 (2003).

[24] M. Harper, J. Chromatogr. A **885**, 129 (2000).

[25] J. Dewulf and H. Van Langenhove, Trac-Trends Anal. Chem. **21**, 637 (2002).

[26] USEPA – US Environmental Protection Agency. Compendium Method TO-17: Determination of Volatile Organic Compounds in Ambient Air Using Active Sampling Onto Sorbent Tubes, EPA/625/R-96/010b (Washington, 1999).

[27] D.K.W. Wang and C.C. Austin, Anal. Bioanal. Chem. **386**, 1099 (2006).

[28] K. Demeestere, J. Dewulf, B. De Witte, and H. Van Langenhove, J. Chromatogr. A **1153**, 130 (2007).

[29] M.R. Ras, F. Borrull, and R.M. Marcé, TrAC Trends Anal. Chem. **28**, 347 (2009).

[30] K. Demeestere, J. Dewulf, K. De Roo, P. De Wispelaere, and H. Van Langenhove, J. Chromatogr. A **1186**, 348 (2008).

[31] E. Baltussen, C.A. Cramers, and P.J.F. Sandra, Anal. Bioanal. Chem. **373**, 3 (2002).

[32] M. Czaplicka and K. Klejnowski, J. Chromatogr. A **976**, 369 (2002).

[33] A. Ribes, G. Carrera, E. Gallego, X. Roca, M.J. Berenguer, and X. Guardino, J. Chromatogr. A **1140**, 44 (2007).

[34] O.O. Kuntasal, D. Karman, D. Wang, S.G. Tuncel, and G. Tuncel, J. Chromatogr. A **1099**, 43 (2005).

[35] J.D. Donaldson, S.M. Grimes, L. Mehta, and A.J. Jafari, J. AOAC Int. **86**, 39 (2003).

[36] Decision No. 2455/2001/EC of the European Parliament and of the Council of 12 February 2002 relative to ozone in air. Official Journal of the European Communities L67/14, 09/03/2002: 1–17.

[37] N.A. Martin, N. Barber, J.K. Black, R.P. Lipscombe, and C.A. Taig, Atmos. Environ. **41**, 7666 (2007).

[38] USEPA – US Environmental Protection Agency, Compendium Method TO-15: Determination Of Volatile Organic Compounds (VOCs) In Air Collected In Specially-Prepared Canisters And Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), EPA/625/R-96/010b (Washington, 1999).

[39] D. Helmig, J. Chromatogr. A **732**, 414 (1996).

[40] C.H. Wu, M.N. Lin, C.T. Feng, K.L. Yang, Y.S. Lo, and J.G. Lo, J. Chromatogr. A **996**, 225 (2003).

[41] J.F. Walling, J.E. Bumgarner, D.J. Driscoll, C.M. Morris, A.E. Riley, and L.H. Wright, Atmos. Environ. **20**, 51 (1986).

[42] P.A. Clausen and P. Wolkoff, Atmos. Environ. **31**, 715 (1997).

[43] WEF-ASCE – Water Environment Federation-American Society of Civil Engineers, *Toxic Air Emissions from Wastewater Treatment Facilities* (Alexandria, VA, USA, 1995).

[44] F. Dincer and A. Muezzinoglu, J. Environ. Sci. Health Part A – Toxic/Hazard. Subst. Environ. Eng. **43**, 1569 (2008).