DEVELOPMENT OF A METHOD FOR THE MONITORING OF ODOUR-CAUSING COMPOUNDS IN ATMOSPHERES SURROUNDING WASTEWATER TREATMENT PLANTS

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ABSTRACT

This study describes the development of an analytical method based on active collection in a multisorbent Tenax TA/Carbograph 1TD tube, followed by thermal desorption and gas chromatography-mass spectrometry for the determination of 16 volatile organic compounds in air samples. The analysed compounds include ozone precursors and odour-causing compounds belonging to different chemical families (sulphur- and nitrogen-containing compounds, aldehydes and terpenes). Two types of sorbents were tested and desorption conditions (temperature, time, and sampling and desorption flow) were evaluated. External calibration was carried out using the multisorbent bed . Method detection limits in the range 0.2-2.0 $\mu g \cdot m^{-3}$ for 1 L samples were obtained. The method was applied for determining the target compounds in air samples from two different wastewater treatment plants. Most of the compounds were detected and toluene, limonene and nonanal were found in particularly high concentrations with maximum values of 438 $\mu g \cdot m^{-3}$, 233 $\mu g \cdot m^{-3}$ and 382 $\mu g \cdot m^{-3}$, respectively.

Key words: air analysis; gas chromatography-mass spectrometry; malodours; thermal desorption; volatile organic compounds.

1 Introduction

Interest in the characterization of individual volatile organic compounds (VOCs) in air has increased over the last decades as their emissions have been associated with environmental effects [1,2] and several adverse effects on human health [3,4]. Malodour pollution associated to industrial or animal activities has become an important issue because human tolerance to offensive smells is gradually decreasing [5]. Some VOCs have been related to the perception of odours in environments such as the vicinity of wastewater treatment plants (WWTPs) [6-8] or animal facilities [9].

Gaseous emissions from WWTPs are complex mixtures which include many different volatile compounds , particularly hydrogen sulphide, ammonia, carbon dioxide, and

methane. Other odorous compounds such as mercaptans, organic sulphides, nitrogen-containing compounds (e.g. amines, indole, and skatole) and oxygenated compounds (e.g. aldehydes, alcohols, organic acids, and ketones) can also be found in these emissions at lower concentrations [6,10]. The complexity of these emissions and the low odour threshold limits of many odorous compounds points to the need for highly sensitive analytical techniques for the determination of target VOCs. Sampling and preconcentration have been performed in different ways: active or passive sampling using adsorption tubes followed by thermal desorption-gas chromatography (TD-GC) [6-8,11-18], grab sampling followed by solid-phase microextraction (SPME) as the preconcentration technique [10,19,20], and other recently developed methodologies such as micro sorbent-traps [21].

Solid sorbent capture has become a reference methodology for the sampling of VOCs in air samples [14]. There is a wide variety of commercially available sorbents and the selection of the most appropriate one depends on the physical and chemical characteristics of the target analytes, the time of sampling, the sampling volume, and the presence of other interfering compounds (matrix effect). Dincer et al. [6] collected air samples from WWTPs and sludge management areas using a Tenax TA/Carboxen 1000 trap and identified 29 compounds belonging to different chemical families. A group of seven volatile organic sulphur compounds was determined in air samples from two WWTPs using a dual-bed of Tenax TA/Unicarb [7]. Ambient air samples from different locations of Delhi were analysed for the determination of toxic organic compounds using an activated charcoal sorbent tube and a total of 77 VOCs were identified [16], many of them appearing in the US-EPA list of hazardous air pollutants. Another method was developed for the determination of VOCs in an urban airborne environment close to a municipal incinerator, a waste collection centre and a wastewater treatment plant [8]. Tubes containing Chromosorb-106 were used and a total of 148 VOCs were identified. Air-quality and malodorous episodes in urban, rural and industrial environments were evaluated with a method using multisorbent tubes containing Carbotrap, Carbopack X and Carboxen 569 [12]. 48 VOCs were analysed in air

samples collected near to an industrial complex and a petroleum refinery in Singapore using Tenax/Carbopack X sorbent tubes [22]. High concentrations of toluene, ethylbenzene, xylene isomers, 2-butanone, and hexane were constantly detected. Three types of sorbent tubes were evaluated for the analysis of 12 VOCs considered as representative of emissions from sewer networks [18]. The compounds that showed the largest levels were trichloromethane, toluene, xylene isomers, and limonene. Active sampling on solid sorbents presents good stability of the target analytes during transport and storage (several months [23]) and allows on-site concentration of the compounds.

In an attempt to go one step further, a new study has been undertaken to evaluate solid sorbent capture as a preconcentration technique for odorous VOCs in the air of WWTPs. We have evaluated a method based on active adsorption in multi-bed sorbent tubes, thermal desorption with cryofocusing in a cold trap, and GC-MS analysis for the determination of a group of 16 VOCs including odour-causing compounds belonging to different chemical families and ozone precursors, whose determination is recommended by European legislation regarding ozone in ambient air (EU Directive 2002/3/CE). The thermal desorption conditions have been evaluated and the developed method has been validated. The proposed method has then been applied to the analysis of air samples from two wastewater treatment plants.

2 Experimental

2.1 Chemicals

The standards contained a mixture of BTEX compounds at 2000 $mg \cdot L^{-1}$ (BTEX Mix in Methanol, Supelco, Bellefonte, PA, USA) and the individual standards of 1,4-dioxane (99.8%), dimethyl disulphide (DMDS, 99%), 1,2,3-trimethylbenzene (90%), (R)-(+)-limonene (99%), 1,4-diethylbenzene (96%), *m*-cresol (99.7%), nonanal (95%), benzothiazole (90%), (-)-carvone (99%), indole (99%), and skatole (98%). All of these compounds were obtained from Sigma-Aldrich (Steinheim, Germany). Phenol (99.5%) was obtained from Dr. Ehrenstorfer (Augsburg, Germany).

Stock solutions in methanol for gas chromatography with purity >99.9% (SDS, Peypin, France) were prepared and stored at 4°C for up to a week. Working solutions were prepared at the moment of calibration.

2.2 Sorbent tubes

Commercially available stainless-steel tubes from Markes International Limited (Llantrisant, UK) (89 mm length × 6.4 mm o.d. × 5 mm i.d.) were used. Two sorbent configurations were evaluated: firstly, a single sorbent trap with 150 mg of Tenax TA; and, secondly, a two-sorbent bed containing 350 mg of Tenax TA/Carbograph 1TD. Before use, tubes were activated and conditioned by passing 99.999% pure nitrogen gas (Carburos Metálicos, Barcelona, Spain) at a flow of 100 mL·min^{-1}. The two-sorbent bed cartridges were conditioned at 100, 200, 300 and 335°C for 1h each, while Tenax TA cartridges were activated at 320°C for 2h followed by 30 min at 335°C, in accordance with the supplier's recommendations.

2.3 Sampling

Air samples were obtained from two WWTPs located in Reus (Tarragona, Spain) and Castell d'Aro (Girona, Spain). A Sidekick air sampling pump (SKC Ltd., Dorset, UK) was used, which was calibrated using an ADM 3000 digital flow-meter (Agilent Technologies, Palo Alto, CA, USA). Air samples were pumped through preconditioned tubes at a flow rate of 35 mL·min^{-1} to collect 1 L air volume. After sampling, tubes were immediately sealed with end caps fitted with PTFE ferrules and stored at 4°C in glass jars. They were then transported to the laboratory, stored in a refrigerator at 4°C, and analysed before 24h.

2.4. TD-GC-MS equipment and conditions

Desorption was carried out in a UNITY thermal desorber (Markes). The sorbent tube was loaded from an ULTRA automatic sampler (Markes). For tube desorption, the sorbent tube was heated to 275°C for 10 min with a helium flow rate of 30 mL·min^{-1}. The

desorbed compounds were refocused into a general purpose hydrophobic cold trap filled with Tenax TA/Carbograph 1TD (Markes) at –10°C using splitless mode. The next step consisted on the cold trap desorption, which was carried out at 300°C for 10 min using a split flow of 10 mL·min^{-1} (split ratio 1:10).

Analytes were separated and detected in a 6890N gas chromatograph and a 5973 inert mass spectrometer (Agilent Technologies). A ZB-5 capillary column (60 m × 0.32 mm i.d., 1 µm film thickness) from Micron Phenomenex (Torrance, CA, USA) was used with 99.999% pure helium (Carburos Metalicos) as the carrier gas at a constant inlet flow rate of 1 mL·min^{-1}. The oven temperature was initially held at 40°C for 5 min; ramped at 5°C/min to 150°C and then ramped at 15°C/min to 250°C, and held for 5 min: the whole run lasted 38 min.

The GC-MS interface was set at 280°C. The mass spectrometer acquired data in scan mode with an *m/z* interval from 40 to 300 amu and an electron impact energy of 70eV. Chromatographic data was acquired by means of MSD ChemStation software (Agilent Technologies). Compounds were quantified by a target ion and identified by qualifier ions and retention times. The target compounds are shown in Table 1 with their respective odour threshold concentrations (OTCs) and details of the GC-MS analysis.

For calibration purposes, liquid standards were loaded into sorbent tubes using a Calibration Solution Loading Ring (Agilent Technologies). A conventional GC syringe was used to inject volumes of between 1 and 5 µL of each standard while a flow of 100 mL·min^{-1} of 99.999% pure helium passed through the tube flowing in the direction of the injection. After the injection, the syringe needle was maintained within the loading ring for 20 seconds to achieve complete evaporation of the target analytes, as recommended by the manufacturer. The tube was immediately desorbed.

3 Results and discussion

3.1 Method development

In this study, a list of compounds belonging to different chemical families, presenting different volatilities and chromatographic behaviour, was selected. The compounds

included aromatic compounds, aldehydes, phenolic compounds, sulphur-containing compounds, and terpenes. Chromatographic conditions were evaluated in order to obtain a good separation of all the target compounds within a reasonable analysis time. The final temperature programme was set as described in Section 2.4 (Figure S1 in Supplementary Materials).

Due to the different characteristics of the studied analytes, special attention was given to the evaluation of memory effects since semi-volatile compounds can undergo partial desorption and accumulation in the transfer lines. For this reason, blank chromatograms were acquired after each analysis. The amount of the standards introduced in the sampling tubes was also controlled in order to avoid overloading.

3.1.1 Selection of sorbent tube

In order to check the best sorbent tube for the retention of the studied compounds, two tubes were tested, one containing Tenax TA and the other containing Tenax TA/Carbograph 1TD. Tenax TA is a weak strength and hydrophobic sorbent. It has been used in the determination of non-polar VOCs, slightly polar VOCs, terpenes, aldehydes>C_5, and acids<C_3 [24]. Volatile organic sulphur compounds have also been analysed using cartridges containing this sorbent [7]. It has been found that Tenax TA retains quantitatively, without showing significant breakthrough, VOCs with boiling points above 100^{o}C [12]. Carbograph 1TD is a hydrophobic, medium strength sorbent and is commonly used in the analysis of different VOC groups, such as a wide range of aromatic compounds and chlorinated compounds [13,25,26].

For thermal desorption, the initial conditions were set within the range of conditions recommended by EPA method TO-17 [14]. Tube desorption was carried out at 275^{o}C for 15 min using a flow of 30 mL·min^{-1} in splitless mode. Cold trap desorption was performed at 300^{o}C for 10 min with a split flow of 15 mL·min^{-1}. 25 ng of the studied compounds were loaded in both tubes (n=3 for each tube). No significant differences (p>0.05, t-test) were obtained for most compounds using the two types of sorbent tubes except for 1,2,3-trimethylbenzene (p=0.047), 1,4-diethylbenzene (p=0.035) and

carvone (p=0.042) (Figure S2 in Supplementary Materials). In those cases showing differences, responses were higher when the two-bed tube was used. Wang et al. [18] compared the same two sorbents for a group of 12 VOCs and found found no differences between the two sorbents for the compounds evaluated, except for decane that gave higher responses with the dual bed trap.

Blank (carryover) analyses were also compared and no significant differences were observed between the two types of sorbent tubes. As a result, the dual bed Tenax TA/Carbograph 1TD tube was selected for further experiments.

3.1.2 Selection of the thermal desorption parameters

The sorbent tube and cold trap desorption parameters were evaluated to ensure the best desorption conditions. Tubes containing the dual bed Tenax TA/Carbograph 1TD and loaded with 25 ng of the target compounds were analysed (n=3 in each case).

3.1.2.1 Cold trap desorption

The cold trap conditions were first evaluated to ensure that quantitative desorption from the cold trap is achieved and to avoid memory effects. Temperatures of between 250 and 320^{o}C and times of 3 and 10 min were tested, maintaining the initial conditions for the tube desorption. Blank (carryover) analyses were evaluated after each sample to check whether the compounds were quantitatively desorbed from the cold trap.

For desorption temperature, no differences (p>0.05, ANOVA test) were observed for most analytes at the temperatures evaluated (Figure S3 in Supplementary Materials). The only exception was phenol (p=0.02), which showed a decrease when the cold trap desorption temperature was set at 320^{o}C. In the case of the less volatile compound evaluated (1,4-dioxane), the variability obtained in the results at the lowest temperature (250^{o}C) was significantly greater than at the other temperatures.

No differences (p>0.05, t-test) were observed for the analytes at the different desorption times evaluated (Figure 1), except for benzothiazole (p=0.01) and skatole

(p=0.02). Cold trap desorption at 300°C for 10 min was selected in order to ensure the quantitative desorption of analytes and no carryover.

Different split flow rates were also assessed to evaluate the response level of the analytes. Split flows of 5 and 10 mL·min^{-1} were evaluated and a small decrease in the response of all analytes was observed when the split flow was increased. Despite this reduction in sensitivity, a split flow of 10 mL·min^{-1} was selected in order to prevent the saturation of the capillary column in the analysis of samples containing high amounts of the studied compounds.

3.1.2.2 Sorbent tube desorption

The tube desorption conditions were evaluated in order to obtain the highest responses. The cold trap desorption parameters were set at the values selected in the previous section.

Tube desorption times of 5, 10 and 15 min at 275°C were evaluated. Peak areas obtained from standard chromatograms increased for the majority of the studied compounds when desorption time was increased from 5 to 10 min, and did not show significant differences between 10 and 15 min. Blank (carryover) analyses performed after each analysis at the different desorption times tested revealed phenol to be the only compound present in blank chromatograms with relatively large peak areas, which increased with desorption time. This fact could be attributed to the degradation of the sorbents into a wide variety of carbon-containing compounds [27], which increases with desorption time. A tube desorption time of 10 min was selected to avoid excessive phenol peaks in blank analyses.

Different tube desorption temperatures were also evaluated. Analyses at 275, 300 and 320°C were carried out and no significant differences were obtained in terms of peak area (Figure S4 in Supplementary Materials). Blank (carryover) analyses were also performed at each desorption temperature and, as previously observed with tube desorption times, only phenol presented peak areas higher than those obtained in the analysis of blank samples , which increased with the tube desorption temperature

applied. Taking into account these results, a temperature of 275°C was chosen for tube desorption in order to obtain the best blank chromatograms.

Finally, the tube desorption flow was evaluated. Analyses were performed using flows of 30 and 50 mL·min^{-1}. A significant decrease in the signals was observed when the desorption flow was set at 50 mL·min^{-1} for all compounds except for indole and skatole, the least volatile compounds evaluated. This fact indicates that some target analytes are not efficiently retained by the cold trap during primary desorption at high flows and so the desorption flow through the sorbent tube was set at 30 mL·min^{-1}.

3.2 Breakthrough evaluation

Breakthrough data are available for many individual sorbent materials but these data has to be used with care as correspond to synthetic samples with no presence of interferences. Safe sampling volume was evaluated to ensure that no breakthrough takes place. Air from the inlet of a WWTP, at a height ~1 m above the water level, was pumped through two sorption tubes filled with Tenax TA/Carbograph 1TD connected in series. Back tubes were analysed to check for target compounds as a means of investigating whether analytes were quantitatively retained in the front tube. Air volumes up to 3 L were sampled at a flow rate of 35 mL·min^{-1}.

This sampling point was chosen as high levels of VOCs and large relative humidity are expected in this area. Although the two sorbents used are hydrophobic, the effect of the relative humidity was taken into account as a competition for the adsorbent active surface can occur between water and the target compounds, which reduces the sorption capacity of the sorbent [28].

DMDS, toluene, ethylbenzene, xylenes, phenol, and limonene were detected in the back tube in quantities between 8 and 16% (with respect of a total amount determined from the sum of amounts found in the front and the back tubes) when 3 L of air was sampled. These percentages are excessive as typical VOCs recommended breakthrough values are <5% [14,29]. When 1 L of air was sampled, analytes were quantitatively retained in the front tube. A previous study analysing emissions from two sewer sites in Sydney did not

find breakthrough for 2 L samples [18]. A sample volume of 1 L was selected in the present study to prevent breakthrough.

The LODs of the method obtained (Table 2) are below the range of concentrations usually found in contaminated atmospheres, such as WWTPs, petrochemical complexes and industrial areas [6-8,17,25,30,31]. For non-contaminated atmospheres the LODs may not allow the quantification of some of the target compounds [32,33]. However, in this situation, breakthrough volumes will increase significantly and large volumes of samples can be taken, which will lead to a decrease in the LODs. When less contaminated environmental samples have been checked, indoor and outdoor air in the city of Barcelona, the use of a Tenax TA tube showed breakthrough for >10 L sampling volumes [12].

3.3 Method validation

External calibration in the ranges shown in Table 2 was performed. Each concentration level was analysed three times. Linearity was confirmed for all compounds from the evaluation of the residual plots, with determination coefficients (R^2) greater than 0.99. Standards at reduced concentrations were analysed (n=5) to determine the limits of detection (LOD) and quantification (LOQ) of the method, which are summarised in Table 2. The calculated standard deviation for each compound was taken as the standard deviation of the blank, and IUPAC 3σ and 10σ criteria were used to determine LODs and LOQs, respectively. LODs ranged between 0.2 and 2 $\mu g \cdot m^{-3}$ (for a sample volume of 1 L), except for nonanal (LOD=20 $\mu g \cdot m^{-3}$).

For the determination of the precision of the method, desorption analyses (n=3) of 25 ng of the target compounds were performed within the same (intra-day precision) day and between days (inter-day precision). Relative standard deviations (RSD) of between 1 and 12% were obtained for intra-day repeatability and values of between 5 and 19% for inter-day precision (Table 2), which were found to meet EPA standards [14] .

The stability of the sorption tubes loaded with all target compounds was evaluated after 24 h of storage. The results obtained confirm that there were no significant losses of the

target analytes (recoveries >80%). These results agree with a previous study that evaluated stability during storage of 90 VOCs in Tenax TA/Carbograph 1TD tubes [34] in which it was found that there was no significant loss of analytes after 3 and 7 days of storage. All samples evaluated in the present study have been analysed within 24 h of sampling.

3.4 Analysis of air samples

Samples were obtained from the entrance of each plant, the biological treatment inlet and the sludge pre-treatment area. Figure 2 illustrates the total ion chromatogram of an air sample taken at the biological treatment inlet of Castell D'Aro WWTP. It must be taken into account that samples were taken in open areas and that concentration levels in the air are influenced by the dispersion of emission gases into the atmosphere.

Eleven of the target VOCs were detected in samples from WWTPs. Table 3 shows the concentrations found for the target compounds at each sampling point. Toluene, limonene and nonanal were the compounds found at higher levels, with maximum values of 437.9, 232.6 and 382.4 $\mu g \cdot m^{-3}$, respectively. These values agree with previous studies where WWTPs and sludge management areas were evaluated (Table 4).

1,4-dioxane, benzothiazole, carvone, indole, and skatole were not detected in the samples analysed. Other studies confirm that 1,4-dioxane is not usually detected in atmospheres from WWTPs. This compound has only been detected in the air of a petrochemical complex but at a maximum level of 0.9 $\mu g \cdot m^{-3}$ [17], which is below the LOD of the method proposed here. The other four compounds that were not detected were evaluated as they are usually found in water samples from the inlet of the WWTPs evaluated in the present study [35]. However, the determination of their gas-liquid partition coefficients indicates the limited partitioning of these compounds to the air surrounding the plants [30]. Therefore, although indole and skatole have previously been detected in air from some sewage treatment plants [8], calculations made taking into account the levels detected in water samples and their calculated partitioning

coefficients confirm that air levels well below the LODs are to be expected in the air surrounding the WWTPs.

As can be seen from Table 4, the presence of toluene, ethylbenzene and xylene isomers in urban areas is significantly smaller than in areas closed to WWPTs, with maximum values being at least one order of magnitude higher in areas closer to WWPTs. Moreover, the contents of these compounds tend to be larger in the vicinities of sludge management areas.

The odorous compounds evaluated in this study are not usually detected or found at levels well below their OTC values in urban areas. However, in the case of WWTPs, some of these compounds are detected at levels above their respective OTCs. In the present study, toluene, *m*-cresol and nonanal gave concentrations above their OTCs in some samples. *m*-cresol and nonanal were present at concentrations above their odour threshold concentrations in the majority of the samples from the two WWTPs. Other studies (Table 4) also showed levels of toluene, *m*-cresol and nonanal above their OTCs in some WWTP samples. Moreover, a study [6] showed odorous levels of ethylbenzene and xylene isomers in the sludge management area of a WWTP.

4. Conclusions

In this study, we show that thermal desorption followed by GC-MS analysis is an effective procedure for the determination of 16 volatile organic compounds including odour-causing compounds belonging to four different chemical families and ozone precursors. A two-sorbent bed containing Tenax TA/Carbograph 1TD showed the best performance in the concentration of the analytes. Tube and cold trap desorption parameters have been evaluated and the developed method has been validated. Appropriate method detection limits, ranging between 0.2 and 2.0 $\mu g \cdot m^{-3}$, were obtained for the target compounds, excluding nonanal which presented a higher value. The developed method has been applied to the analysis of air samples from two WWTPs. Toluene, limonene and nonanal were the compounds found at the highest concentrations, while 1,4-dioxane, benzothiazole, carvone, indole, and skatole were not

detected at all. Only toluene, *m*-cresol and nonanal were detected at concentration levels above their respective odour threshold concentrations in some samples.

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Figure 1. Peak areas obtained in the analysis of 25 ng of the studied compounds at different cold trap desorption times. Tube desorption conditions: 15 min at 275°C and a flow of 30 mL·min^{-1}. Cold trap desorption conditions: 300°C and a split flow of 15 mL·min^{-1}.

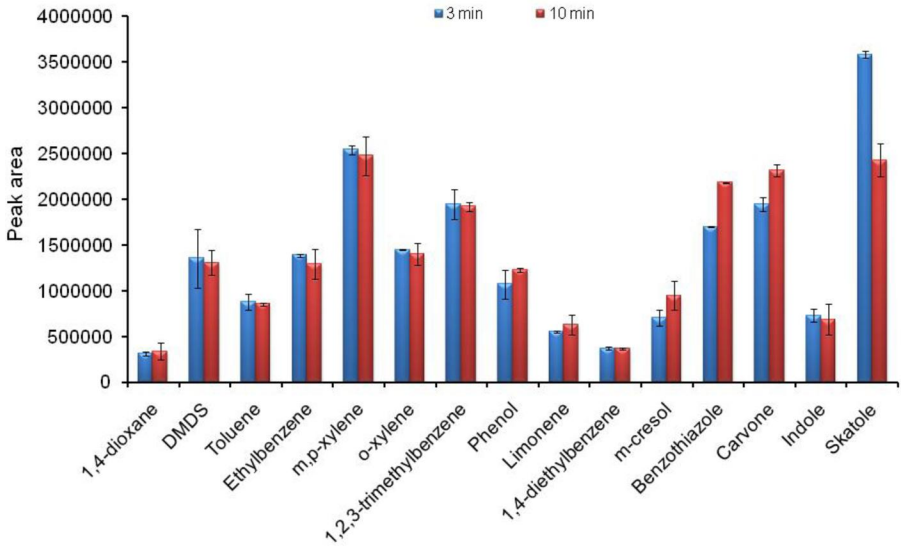

Figure 2. Total ion chromatogram (TIC) of an air sample taken at the biological treatment inlet of Castell D'Aro WWTP. 1. DMDS; 2. toluene; 3. ethylbenzene; 4. *m*,*p*-xylene; 5. *o*-xylene; 6. phenol; 7. limonene; 8. 1,4-diethylbenzene; 9. *m*-cresol; 10. nonanal.

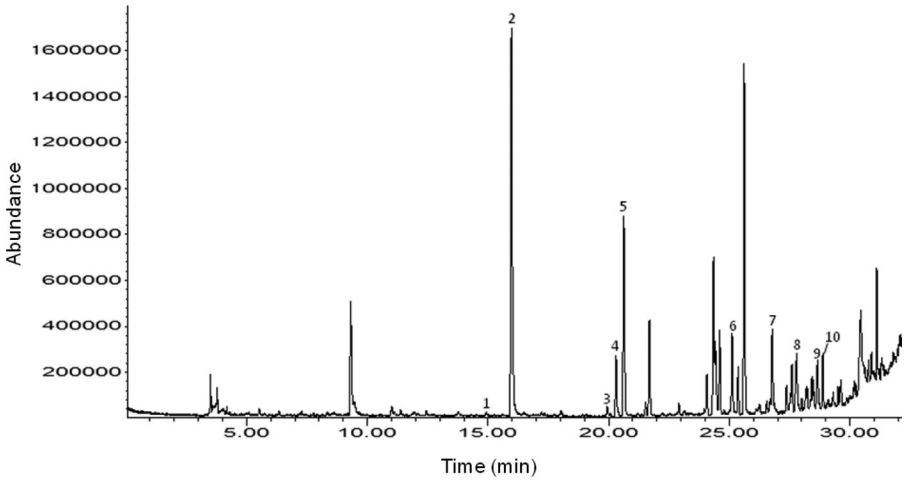

Table 1. Target compounds in chromatographic elution order with their retention times, odour threshold concentrations (OTC) and *m/z* ratios. n.a.: not available.

Compound	OTC ($\mu g \cdot m^{-3}$) [a]	Retention time (min)	m/z [b]	Boiling point (^{o}C)
1,4-dioxane	n.a.	13.2	57, 58, 88	101
DMDS	303	14.9	45, 79, 94	110
Toluene	80	16.0	91, 92	111
Ethylbenzene	400	20.3	91, 106	136
m-xylene	850	20.7	91, 105, 106	139
p-xylene	570	20.7	91, 105, 106	138
o-xylene	850	21.7	91, 105, 106	144
Phenol	39, 46	25.1	66, 94	182
1,2,3-trimethylbenzene	n.a.	26.8	105, 120	175
Limonene	55000	26.9	68, 93	178
1,4-diethylbenzene	n.a.	27.8	105, 119	183
m-cresol	0.57	28.3	79, 107, 108	203
Nonanal	13.3	28.9	81, 98, 143	195
Benzothiazole	n.a.	32.1	108, 135	227
Carvone *(2-methyl-5-(1-methylethenyl)-2-cyclohexenone)*	85, 150	32.2	82, 108, 151	231
Indole	7.1	33.1	90, 117	253
Skatole *(3-methylindole)*	0.35, 0.5	34.4	130, 131	265

[a] Compendium data from [6] and [36].

[b] Quantifier ion in bold.

Table 2. Quality parameters obtained in standard analysis. nd: not determined.

Compound	Working range[1] (μg·m^{-3})	a (S_a) (·10^5)	b (S_b) (·10^5)	R^2	LOD (μg·m^{-3})[2]	Intra-day precision[3] (RSD,%)	Inter-day precision[3] (RSD,%)
1,4-dioxane	4 - 100	0.6 (0.4)	0.098 (0.005)	0.994	1	3	9
DMDS	1.0 - 100	0.06 (0.12)	0.037 (0.002)	0.995	0.3	3	11
Toluene	1.3 - 300	6 (5)	1.479 (0.008)	0.992	0.4	4	6
Ethylbenzene	3 - 100	5 (5)	1.858 (0.008)	0.995	0.9	1	5
m,p-xylene	1.0 - 100	8 (9)	3.09 (0.01)	0.995	0.3	3	5
o-xylene	1.0 - 100	2 (4)	1.507 (0.006)	0.995	0.3	3	7
1,2,3-trimethylbenzene	0.7 - 100	6 (5)	1.865 (0.005)	0.997	0.2	3	8
Phenol	7 - 100	0.6 (3.4)	1.062 (0.004)	0.994	2	6	15
Limonene	1.0 - 300	0.04 (1.27)	0.42 (0.02)	0.994	0.3	12	19
1,4-diethylbenzene	1.0 - 100	2 (5)	1.62 (0.08)	0.991	0.3	3	10
m-cresol	7 - 100	5 (3)	0.83 (0.03)	0.996	2	2	7
Nonanal	67 - 300	1.3 (0.1)	0.028 (0.001)	0.996	20	nd	nd
Benzothiazole	1.7 - 100	3 (5)	1.51 (0.06)	0.994	0.5	2	11
Carvone	1.0 - 100	0.9 (8.8)	2.2 (0.1)	0.990	0.3	1	6
Indole	1.0 - 100	7 (8)	1.73 (0.09)	0.992	0.3	3	12
Skatole	1.0 - 100	7 (8)	2.76 (0.09)	0.996	0.3	11	18

a = intercept
S_a= standard deviation of the intercept
b = slope
S_b = standard deviation of the slope
R^2 = determination coefficient
LOD = limit of detection

[1] The lowest calibration level was fixed at the determined LOQs
[2] Method LODs determined for a sample volume of 1 L
[3] n=3, 25 ng.

Table 3. Minimum and maximum concentrations found (μg·m^{-3}) at sampled sections from Castell d'Aro and Tarragona WWTPs. <LOQ: below limit of quantification, n.d.: not detected.

	Influent		Biologic treatment influent		Sludge pre-treatment	
Compound	Castell d'Aro (n=3)	Reus (n=3)	Castell d'Aro (n=1)	Reus (n=3)	Castell d'Aro (n=3)	Reus (n=1)
1,4-dioxane	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
DMDS	1.4 – 17.8	<LOQ - 1.7	1.9	3.5 - 5.1	3.2 – 11.2	4.2
Toluene	60.2 – 308.8	8.3 - 26.5	213.3	19.7 - 21.8	134.9 – 437.9	9.3
Ethylbenzene	8.1 – 19.4	3.1 - 5.0	25.4	3.4 - 3.6	<LOQ –3.6	4.6
m,p-xylene	11.6 – 31.0	4.0 - 6.8	44.4	4.2 - 4.9	3.7 – 5.1	4.0
o-xylene	6.2 – 16.1	2.7 - 5.4	37.5	5.3 - 6.3	2.3 – 3.4	2.5
Phenol	n.d. – <LOQ	n.d. - 18.9	<LOQ	<LOQ	n.d. – <LOQ	6.1
1,2,3-trimethylbenzene	11.7 – 18.9	4.4 - 6.4	27.5	4.5 - 5.1	3.8 – 4.3	3.8
Limonene	42.2– 232.6	11.9 - 34.8	2.9	2.9 - 5.1	<LOQ – 5.7	1.6
1,4-diethylbenzene	2.0 – 3.5	1.4 - 3.8	4.6	2.0 - 2.3	n.d.	1.4
m-cresol	n.d. – 11.9	n.d. - 8.7	<LOQ	12.0 - 13.8	10.7 – 13.3	8.5
Nonanal	<LOQ – 132.5	<LOQ - 382.4	n.d.	<LOQ - 74.3	n.d. – 78.8	<LOQ
Benzothiazole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Carvone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Indole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Skatole	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 4. Comparison of concentrations found (µg·m^{-3}) in diferent studies. <LOQ: below limit of quantification, n.d.: not detected. The number in brackets for each column corresponds to the reference number.

	WWTPs and sludge management areas					Urban areas			Present
	[6]	[7]	[8]	[18]	[33] [b]	[22]	[13]	[17]	study
DMDS	0.6 - 119.6	1.0 - 857.8	2.0 - 39.3	--	212.6	--	--	--	<LOQ - 17.8
Toluene	10.0 – 1356.9		24.7 - 191.8	61.1 -111.3	509.2	3.8 - 90.5	0.4 - 45.2	2.2 - 12.1	8.3 - 437.9
Ethylbenzene	1.2 - 409.2		11.5 - 26.7	--	14.7	0.2 - 28.3	0.1 - 7.4	1.4 - 13.6	<LOQ - 19.4
m,p-xylene	2.6 - 1254.7		45.6 -169.7 [a]	105.7 - 183.7	47.2	0.2 - 20.0	0.2 - 25.6	0.8 - 3.3	3.7 - 44.4
o-xylene	2.6 - 935.4			45.7 - 70.6	--	0.2 - 13.9	nd - 5.6	0.4 - 1.7	2.5 - 37.5
Phenol	--		--	--	--	nd - 2.6	--	--	nd - 18.9
1,2,3-trimethylbenzene	--		--	--	--	0.1 - 3.3	--	nd - 0.8	3.8 - 27.5
Limonene	--		--	110.0 - 191.1	114.6	--	--	--	<LOQ - 232.6
1,4-diethylbenzene	--		--	--	--	--	--	nd - 0.3	nd - 4.6
m-cresol	--		nd - 24.5	--	--	--	--	--	nd - 13.3
Nonanal	--		--	--	19.8	nd - 5.6	--	--	nd - 382.4

[a] All xylene isomers determined together

[b] only maximum values detected are given