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Characterising Volatile Organic Compounds from Sewer Emissions by Thermal Desorption coupled with Gas-Chromatography-Mass Spectrometry

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An analytical method was developed to characterise volatile organic compounds (VOCs) emitted from sewer networks by actively collecting the samples using sorbent tubes followed by the Thermal Desorber coupled with Gas Chromatography-Mass Spectrometry (TD-GC-MS). The method parameters including sorbent tubes materials, tube desorption temperature, desorption time and cold trap desorption temperature were selected and optimized. Validation of TD-GC-MS method showed good precision, linearity and accuracy. Breakthrough tests showed that there is no significant breakthrough when 5,000 ppm (v/v) stock solution was spiked into sorbent tubes (breakthrough volume <1 %). The method was evaluated by collecting VOCs from two sewer sites in Sydney. The identification of key chemical groups at individual site is important for monitoring odour annoyance and developing design criteria for odour and VOC abatement systems.

1. Introduction

Biochemical reactions under microaerobic and anaerobic conditions during sewage transportation process may cause the formation and subsequent release of a wide variety of volatile organic compounds (VOCs) from sewer networks, therefore is potential source for VOC emissions (Vincent, 2001). The occurrence of VOCs in the sewer gas environments, even at trace concentrations, can be toxic, cause corrosion and result in odour annoyance due to the low odour threshold values for many of these compounds. A better understanding of the composition of sewer VOCs emissions is become critical for managing their release into the atmosphere.

Studies on VOC emissions derived from sewer network is rarely reported compared to wastewater treatment plants (Atasoy et al., 2004, Ras et al., 2008). This is most likely due to insufficient sampling and the analytical limitations for the analysis of VOCs that are present at trace level and over a range of concentrations. From previous studies, sorbent-based sampling methods have been successfully used in the collection of a wide range of VOCs from atmospheric environment or other industrial processes and some standardised protocols have been established to sample and analyse the air-born VOCs (McClenny and Colón, 1998, Ribes et al., 2007), no methodologies were particularly optimised for the determination of VOCs from sewers and wastewater treatment plants (WWTPs) sources.

This study aims to characterise chemical species and corresponding amounts present in the gas phase of sewer networks at some representative sites by developing analytical methodology that actively collects the samples using sorbent tubes followed by Thermal Desorption coupled with Gas

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Chromatography-Mass Spectrometry (TD-GC-MS). Initially three different sorbent materials were tested followed by the optimisation of the methodology in terms of thermal desorption parameters.

2. Materials and Method

2.1 Chemicals and standard preparation

All reagents used were of high purity grade and obtained from Sigma-Aldrich. Methanol was used as a solvent for all standard compounds. Standard solution at different concentration of 12 compounds, considering as representative of VOC emissions from sewer networks were prepared in methanol in order to calibrate the methodology and make comparisons among three different sorbent tubes. 1ul liquid standard were loaded onto stainless steel sorbent tubes (Markes, UK) via a Calibration solution loading Rig (Markes, UK) and flushed with clear air (100 mL/min) after liquid injection, the gas stream was applied for 3min before the tubes was disconnected from the injection port to allow the VOCs to fully evaporate and be retained by the sorbent bed. The tubes were analysed under the same analytical conditions as followed for the field samples.

2.2 Sample Collection and thermal desorption procedures

Gas phase samples were collected to validate developed method on February 2012 from two selected sewer networks sites (S1-S2) operated by the Sydney Water Corporation. Samples were collected using Tenax TA, Carbotrap 300 and Tenax/Carbongraph1TD (Markes, UK) as the adsorbing material. Prior to sampling, the sorbent tubes were conditioned and tested to ensure that the tubes were contaminant free. VOC samples were collected onto sorbent tubes using a calibrated air-sampling pump (SKC) at a constant flowrate of 100 mL/min for 20 min to ensure that the correct sampling volume (2L) was collected. Samples were analysed within 24 hours after the sampling events. A thermal desorber (Unity, Markes, UK) coupled with an Ultra automatic sampler (Markes, UK) was employed to desorb the sample from the sorbent tubes. The sorbent tubes were heated at 275°C for 8 min while high purity helium was passed through the sorbent tubes at the flow rate of 50 mL/min to desorb VOCs and focus them onto cold trap at minus 10 °C by a Peltier cooler. Following the sample transfer, the cold trap was heated to 290 °C at 40 °C/min heat rate for 5 min to desorb the VOCs from the cold trap and then injected into the chromatographic column. A split flow of 20.7 mL/min was applied during tube and traps desorption to prevent column overloading.

2.3 VOCs analysis and identification

Sample analysis was performed using a GC-MSD (Agilent 6890N GC, 5973NMSD, Agilent Technologies). The analytical column used for separation was a DB-VRX (30 m × 0.25 mm ×1.4 μm). Helium gas was used as the carrier gas at a flow rate of 1.8 mL/min .The temperature program for the GC was initially held at 50 °C for 2 min and then raised to 220 °C at a rate of 15 °C/min. The mass spectrometer acquired data in scan mode with m/z interval ranging from 35 to 335. The identity of compounds was verified using reference standard, by matching the mass spectra with a mass spectrum library (NIST02 library) available in the GC-MS system.

3. Result and Discussion

3.1 Selection of adsorbent tubes

To determine the most appropriate sorbent material, three types of absorbents (Tenax TA, Carbotrap 300 and Tenax/Carbongraph1TD) were trailed for their capture capacity for VOCs from sewer emissions. All the sorbent materials are described in the literature as general-purpose tubes for capturing a wide range of volatile organics with varied boiling points and hydrophobic characterises. A comparison study has been performed for the three types of sorbent materials by loading the sorbent tubes with 1ul 100 ppmv model VOC standard, respectively. Figure 1 shows a comparison of peak area for chromatograms. Generally, there was no significant difference observed between the three types of sorbent material for most of tested volatiles, with the exception for Decane and Trichloromethane.

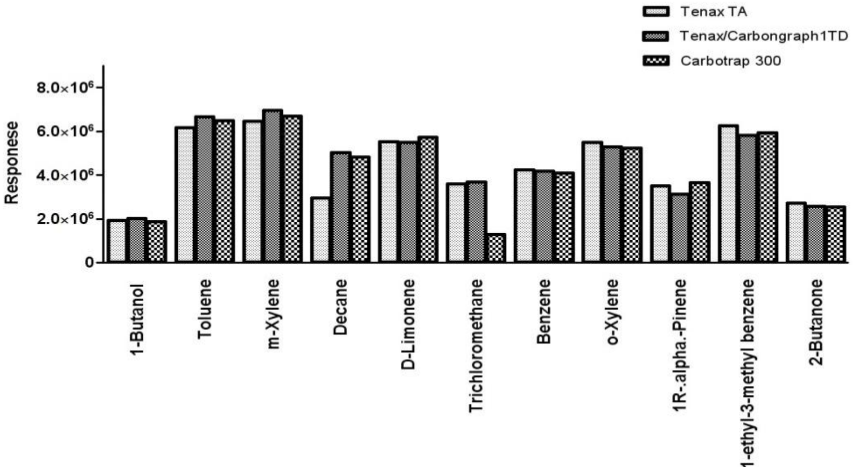

Figure 1: Comparison of capture efficiency between three sorbent materials tested on selected model compounds

An additional study was conducted to investigate the performance under real sampling conditions. A general overview of the chemical species that were captured from sewer emission sampling is shown in Figure 2. As seen in Figure 2, the Carbotrap 300 sorbent material had significantly lower capture efficiency than the two other sorbents most likely due to its mildly hydrophilic nature, which allowed a lower efficiency for collecting samples under humid/moister sewer environment. Both Tenax based sorbent materials shows a good capture capacity for sewer type emissions. Considering the availability and cost of sorbent tube, Tenax TA was chosen for following method development works as well as field sampling studies.

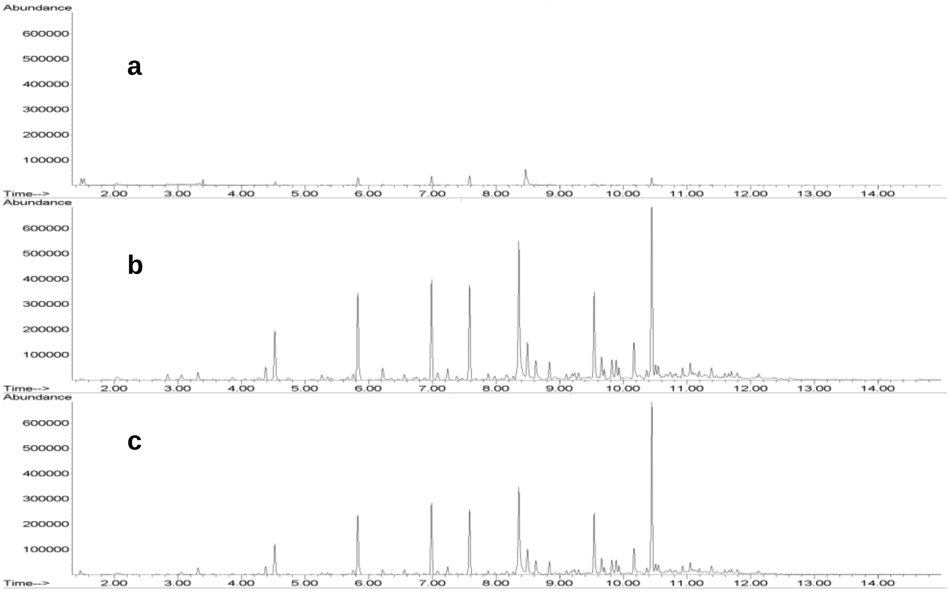

Figure 2: Chromatograms (TICs) of sewer gas from a sewer line obtained using different sorbent materials: (a) Carbotrap 300; (b) Tenax TA + Carbograph 1TD ;(c) Tenax TA

3.2 Optimisation of thermal desorption parameters

An appropriate tube desorption time and temperature were determined for the analysis methodology to ensure that all volatiles that were retained by the sorbent tubes were completely desorbed in order to reach good recoveries and avoid carryover. Desorption temperature were set from 250 °C to 310 °C to determine the optimal desorption condition using Tenax TA.

Figure 3a (tube desorption temperature) shows the dependence of the analyte recovery on desorption temperature. It was observed that the recovery increased with enhanced temperature up to 275 °C and clearly decreased from this point for most of target compounds. Thus, the optimal desorption temperature was chosen as 275 °C. The desorption time was set from 2 min to 10 min to determine the optimal desorption condition using Tenax TA. The plots of peak response for the model VOCs versus desorption time is shown in Figure 3b, which shows that tube desorption time was not significantly affecting the peak area but with time greater than 8min resulted in relatively greater mass responses except for one target compound, hexane. This maybe because hexane exhibiting a lower boiling point tend is decomposed under extend desorption times. The optimum tube desorption time were selected to be 8 min.

The cold trap heating temperature and time were optimised under the initial developed tube desorption method. Various temperatures between 240 to 325 °C and time between 3 min to 8 min were tested to check analyst recoveries and carry-over effect. By analysing blank after each cold trap desorption, tested compounds are all completely or closely desorbed under all the time settings. Therefore, an intermediate time of 5 min was chosen for trap heating. The desorption temperature was selected according to Figure 3c, which shows that the most of the compounds had their greatest recovery between the range of 290 and 310 °C therefore 290 °C was chosen to ensure a better desorption as well as a longer life-span for cold trap as very high heating temperature may destroy the trap resin life.

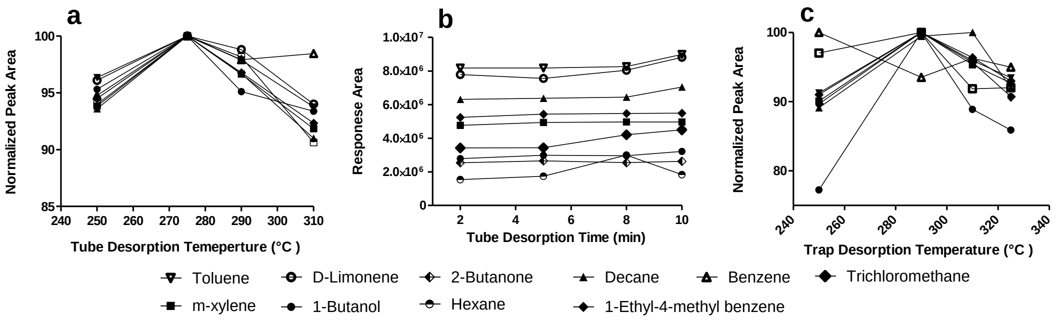

Figure 3: a) Analyte Response on tube desorption time; b) Dependence of analyte recovery on tube desorption temperature, the peak area has been normalized to maximum value for each individual compound; c) Dependence of analyte recovery on trap desorption temperature

3.3 Method performance evaluation

In the optimised thermal desorption conditions, extensive validation was conducted for the analytical methodology. Table 1 provides method detection limit, precision, response factor values for all the target analysts in chromatographic elute order. The method detection limit was measured by subsequent dilutions of the working standard when a signal-to-noise ratio is established at 3. The MDL value ranges from 0.43 to 8.05 ng in absolute mass and when those values are converted into concentration MDL using approximate sample collection volumes (2 L), they corresponded to 0.06-1.37 pptv. The precision study was conducted by performing seven replicate measurements of sorbent tubes, which were spiked with the same amount of working solution (with 500ppmv roughly representing about 400 ng for each analyst). All the tested VOCs showed reproducibility less than 10 %. The linearity was also assessed with the correlation coefficient (R^2)>0.995, almost all the VOCs exhibited linearity ranges from 2 to 3 orders of magnitude.

The desorption efficiency was also evaluated by re-analysing the sorbent tube just after it was analysed and the test was done by loading a 1ul high concentration VOC solution (10,000 ppmv). The desorption was demonstrated to be efficient for all the target VOCs with desorption percentage over 99 %; The retention efficiency was also examined in the laboratory by combining the two Tenax TA tubes into series and loading a 2 ul 5000 ppmv VOCs solution via a calibration rig system flushed with dry air (100 mL/min). The front and back tube were all analysed and the results demonstrated that no significant breakthrough was observed (< 1 %).

Table 1: Selected method performance evaluation parameters

Compound	Retention Time (min)	Response Factor (Area/ng Analyte)	MDL (ng)	MDL (pptv)	RSD (%)
Trichloromethane	4.177	15539	2.96	0.30	3.8
2-butanone	4.611	13541	8.05	1.37	7.2
1-butanol	5.421	13827	8.06	1.33	8.3
Benzene	5.685	20032	1.75	0.27	1.3
Toluene	7.304	38336	0.43	0.06	9.7
m,p-xylene	8.775	40263	0.86	0.10	8.8
o-xylene	9.109	38920	0.88	0.10	8.1
1R-α-Pinene	9.506	26559	0.86	0.08	5.0
1-ethyl-4-methyl benzene	9.82	42258	1.73	0.18	8.7
Decane	10.003	27073	1.45	0.12	7.7
1-ethyl-2-methyl benzene	10.051	41428	0.89	0.09	9.3
D-limonene	10.515	29806	0.63	0.06	10.0

Repeatability, expressed as relative standard deviation (RSD %) for the analysis of 100ppmv of VOCs standards (n=7)

3.4 Field Samples validation

In order to evaluate the performance of developed analytical method, gas emission samples were collected from two sewer sites in February 2012. Samples were collected simultaneously for 20 min at a flow of 100 mL/min with six replicates at both sites and no breakthrough of target analyst was observed. Table 2 presents averaged concentration of target VOCs and their precision as well as total concentration of measured VOCs.

Table 2: Concentration (µg/m^3) of target VOCs measured in two sewer sites

Compound	*S1* Sewer upstream of a siphon		*S2* *Sewer line*	
	Concentration	*Precision*	*Concentration*	*Precision*
Trichloromethane	202.00	11.3	654.25	8.8
2-butanone	nd	-	nd	-
1-butanol	nd	-	nd	-
Benzene	5.52	4.2	8.85	14.1
Toluene	111.33	4.6	61.15	8.1
m,p-xylene	105.66	2.7	183.70	7.0
o-xylene	45.71	2.8	70.61	6.8
1R-α-Pinene	2.41	8.8	160.60	11.8
1-ethyl-4-methyl benzene	18.90	3.9	22.85	9.2
Decane	14.36	4.0	141.88	7.7
1-ethyl-2-methyl benzene	10.21	3.9	10.63	8.8
D-limonene	110.03	2.1	191.15	8.1
Total VOCs concentration	626.13		1505.68	

Precision, expressed as relative standard deviation (RSD %) for the analysis of 100ppmv of VOCs standards (n=6)

Among all the targeted volatiles, 2-butanone and 1-butanol could not be detected in the sewer emissions while the other 10 compounds were all detected with a wide concentration range from 2.41 to 654.25 µg/m^3 depends on the site. The total VOC concentration in the two sites were different with S2 (1505 µg/m^3) having a higher concentration than S1 (626.13 µg/m^3). The difference can be associated with sewage source as S2 were located near industrial complex where trade waste is discharged into the sewer catchment. Similarly, the reproducibility test at both sites showed a slightly different result although they showed a very acceptable precision (<15 %). The difference may be caused by different sample collection conditions such as humidity, temperature, wind/sewage fluid velocity as they were proved to have a significant influence on precision of methodology (Wu et al., 2006). The field validation tests demonstrated that the sampling and analytical method described in this study was promising for measuring VOCs emission from sewer networks.

4. Conclusion

In this study, an analytical method has been developed to optimise the determination of VOCs in the sewer gas emission by TD-GC/MS. The thermal desorption method with selected Tenax TA tubes has been optimised to acquire better recoveries of target analysts. The method presented high precision and good linearity for all the compounds being tested, which shows it is a suitable and promising method to measure VOCs at a trace level (pptv). Method performance evaluation carried out on real samples collected from two sewer sites showed good reproducibility for most of VOCs being detected. The analysis methodology will enable further characterisation of sewer VOC emissions in terms of composition. Potentially，this will enable the identification of marker compound and/or groups, which will helps to monitor odour annoyance efficiently and develop design criteria for odour and VOC treatment system in order to prevent the dispersion of odorous compounds from such wastewater systems.

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