An efficient method for measuring dissolved VOSCs in wastewater using GC-SCD with static headspace technique

Jing Sun, Shihu Hu, Keshab Raj Sharma, Beatrice Keller-Lehmann, Zhiguo Yuan*

Advanced Water Management Center, The University of Queensland, St. Lucia, 4072, Queensland, Australia

*Corresponding author
Phone: +61 (0)7 3365 4374
Fax: +61 (0)7 3365 4726

Email addresses: j.sun@awmc.uq.edu.au (J. Sun); zhiguo@awmc.uq.edu.au (Z. Yuan)

Abstract
Volatile organic sulfur compounds (VOSCs) are important sources of unpleasant odor in wastewater systems. However, the study of VOSCs is usually hindered by their complicated measurement method and highly reactive nature. In this work, a static headspace method utilising gas chromatography (GC) with a sulfur chemiluminescence detector (SCD) was developed to quantitatively analyze VOSCs in wastewater matrices. The method has low detection limits and requires no pre-concentration treatment. Three typical VOSCs, namely methanethiol (MT), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS), were chosen as examples for this study. The calibration curves of all three compounds covering a wide range from 0.5 ppb to 500 ppb showed good linearity ($R^2>0.999$). The method detection limits (MDL) were 0.08, 0.12 and 0.21 ppb for MT, DMS and DMDS, respectively. The reproducibility (relative standard deviation) was approximately 2%. The recovery ratio of MT, DMS and DMDS in spiked wastewater samples were 83±4%, 103±4%
and 102 ± 3%, respectively. Sample preservation tests showed that VOSCs in wastewater samples could be preserved in vials without headspace under acidified conditions (pH ~1.1) for at least 24 h without significant changes (<1.8 ppb). The analysis of real wastewater samples from both a laboratory-scale sewer system and a full-scale sewer pipe demonstrated the suitability of this method for routine wastewater VOSC measurement.

**Keywords**

Volatile organic sulfur compounds (VOSCs); gas chromatography (GC); sulfur chemiluminescence detector (SCD); static headspace technique; wastewater

### 1. Introduction

Odor problems in wastewater collection and treatment systems have become critical issues to water industry (Stuetz and Frechen 2001). In addition to hydrogen sulfide, volatile organic sulfur compounds (VOSCs), such as methanethiol (MT), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) are believed to be important sources of unpleasant odor in municipal and industrial wastewater (Devai and DeLaune 1999, Hvitved-Jacobsen 2002, Cheng et al. 2005, Sekyiamah et al. 2008, Catalan et al. 2009, Marleni et al. 2012). Because of their malodorous characteristics and low odor thresholds (0.07 - 5.9 ppb) (van Gemert 2011), even a small amount of VOSCs can contribute to significant odor pollution. At higher concentrations (> 0.5 - 20 ppmv), they could cause health problems (Lomans et al. 2002). Some recent studies have focused on VOSC measurement in the air around wastewater treatment plants (WWTPs) (Ras et al. 2008, Sekyiamah et al. 2008, Sheng et al. 2008, Lasaridi et al. 2010). However, it is also worthwhile to monitor VOSC concentrations in the wastewater itself as it can help understand the conversion of VOSCs in wastewater and thus solve the odor problem at the root. Therefore, it is important to have a reliable and efficient method to measure VOSCs in wastewater.
The analyses of VOSCs in wastewater have been mainly carried out by using gas chromatography (GC) with flame photometric detector (FPD) or mass spectrometry (MS) (Van Langenhove et al. 1985, Hwang et al. 1995, Abalos et al. 2002, Cheng et al. 2007, Sheng et al. 2008, Godayol et al. 2011). Since the detection limits of these two detectors are relatively high (10^{-11} gS/s), pre-concentration of VOSCs in wastewater samples is often required before the measurement. One commonly used pre-concentration method is purge-and-trap (Van Langenhove et al. 1985, Hwang et al. 1995, Cheng et al. 2007, Sheng et al. 2008). VOSCs are firstly stripped from the aqueous phase and adsorbed on a sorbent. During the injection, the analytes on sorbent are desorbed thermally and flushed to GC column with an inert gas. However, major disadvantages of this method include expensive equipment, tedious procedure and potential loss of VOSCs from the trap if excessive purge time or flow rates are used (Wylie 1988). Solid phase microextraction (SPME) was an alternative pre-concentration method recently used in wastewater VOSC analysis (Abalos et al. 2002, Godayol et al. 2011). This method involves the use of a thin polymer-coated silica fiber to adsorb VOSCs from the headspace of the wastewater sample. The fiber is then inserted directly into the GC injection port for thermal desorption and analysis. Compared with the purge-and-trap process, SPME is relatively simple and inexpensive. However, the extraction process is time-consuming, normally taking more than half an hour for a sample. Moreover, Lestremau et al. (2004) showed that a large proportion of MT was dimerized to DMDS during the SPME process, resulting in errors in MT and DMDS measurements.

Sulfur chemiluminescence detector (SCD) is a relatively new gas chromatographic sulfur-selective detector. It converts the sulfur compounds to sulfur chemiluminescent species and detects the chemiluminescence from the reactions between ozone and sulfur chemiluminescent species (Yan 2002). This detector, coupled with GC, has been applied for detection of sulfur containing compounds in petroleum, atmosphere and food (Di Sanzo et al. 1994, Steely Jeffrey 1994, Galán et al. 1997, López García...
et al. 2002, Rouseff Russell 2002, Nylén et al. 2004). Compared to FPD and MS, SCD is superior on the following aspects:

(1) Excellent sensitivity. The detection limit of SCD can reach $10^{-13}$ gS/s, which is about 2 orders of magnitude lower than FPD and MS (Wardencki and Zygmunt 1991).

(2) High selectivity. The sulfur-selective characteristic of SCD makes it superior to MS, as it can eliminate the signals of many other compounds that may interfere with the detection. Though it is also sulfur selective, FPD has a selectivity (C/S) of about 1 to 4 orders of magnitude lower than SCD (Wardencki 1998).

(3) Easy operation. The operation of SCD is much easier than MS and also simpler than FPD.

The prominent advantages and successful application of SCD in other fields suggest its promising potential for measuring VOSCs in wastewater matrices. Especially for its high sensitivity, the use of SCD might make it possible to eliminate the complicated, time-consuming and error-prone pre-concentration processes. However, to our knowledge, no studies have been reported to date on the use of SCD to detect VOSCs in wastewater.

The purpose of this paper is to develop a method for the measurement of VOSC compounds in wastewater using GC-SCD. The static headspace technique, rather than a pre-concentration process, was used for the transfer of VOSCs from water to the gas phase, which made the measurement fast and simple. Also, it would avoid errors caused by sample loss or contamination during the pre-concentration. The GC was operated above room temperature (28°C), so the cooling system of GC column, which is usually applied to enhance separation of volatile compounds, is not required. The linear ranges, detection limits, reproducibility, and recovery ratios of this method were examined and compared with other VOSC detection methods. Given the highly reactive nature of VOSCs, different sample preservation methods were assessed and an effective method was selected. Finally, this method was applied to measure VOSC
concentrations in real wastewater samples collected from laboratory and real sewer systems.

2. Material and Methods

2.1 The GC-SCD method with static headspace technique

The whole procedure of the VOSC analysis using GC-SCD includes 6 steps as illustrated in Figure 1. The details of all these steps are described in following sections. Figure 1- A schematic diagram of the steps involved in VOSC measurement with the static headspace technique using GC-SCD.

2.2 Standard solution

Methanethiol (MT), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS) were chosen as examples of VOSCs in this work, which are VOSCs typically found in wastewater (Wu et al. 2006, Sheng et al. 2008, Lasaridi et al. 2010). Analytical reagent grade of CH₃SNa, DMS and DMDS (Sigma-Aldrich, Australia) were used to prepare the standard solutions using MilliQ water (Merck Millipore, Germany). As these compounds can be easily oxidized, the MilliQ water was deoxygenated before making the solution by purging it with nitrogen gas (99.99%, BOC, Australia) for at least 1 h. A concentrated stock solution (50 ppm) was firstly prepared, which was further diluted to 5 different levels (0.5-500 ppb) for calibration purpose. All the standard solutions were prepared without headspace to avoid loss of compounds through volatilization.

2.3 Sample preparation

A 12 ml glass headspace vial (Labco Limited, United Kingdom) was used to prepare samples for GC-SCD analysis. The vial was firstly purged with nitrogen gas for 10 min to remove oxygen. Subsequently, 3ml of standard solution or filtered wastewater
sample (0.22 µm membrane) was injected into the vial. The possible adsorption of VOSCs on the membrane filter was investigated by comparing response areas with and without sample filtration, and the results showed insignificant difference (Figure S1, Supplementary Information). To further reduce the risk of adsorption, the filter was used to filter an initial 3 ml of the same wastewater without collecting the filtrate. If there was any adsorption, the VOSCs on membrane surface would be saturated.

Wastewater usually contains a high concentration of H\(_2\)S. Its peak could create a large tail on the chromatogram, which could affect the detection of MT as the MT peak would appear on the tail of the H\(_2\)S peak. In order to solve this problem, two different buffers, namely a boric buffer (pH=8.1 ± 0.1) and a phosphate buffer (pH=7.6 ± 0.1), each with two different strengths at 0.05 M and 0.15 M, were tested. Three milliliters of buffer was added to the headspace vial and their effect on reducing the spread of the H\(_2\)S peak were investigated.

As the vial was sealed and gas inside would not be released when injecting sample or buffer, it resulted in overpressure in the vial. The overpressure would not change the partial pressure of the VOSCs in the headspace, which is determined by the amount of VOSCs in the liquid sample at equilibrium conditions (according to Henry’s Law). However, the relative concentration of VOSCs (ppmv) in the headspace would vary with the overall pressure in the vial headspace, which could affect the detection limits of the method. The addition of 6 ml liquid into the vial would result in relatively high concentrations of VOSCs (Figure S2) so that relatively low detection limits could be achieved.

The vial was then mixed using a vortex mixer for 2 min to ensure that the gas-liquid equilibrium was reached (There were no increase of GC response areas of all three compounds for mixing time longer than 2 min). At last, 300 µL of headspace gas was drawn with a gas-tight syringe (SGE Analytical Science, Australia) and injected into
the GC for analysis.

2.4 Instrumentation

The analysis was performed on an Agilent 7890A GC (Agilent Technologies, Santa Clara, California) coupled with an Agilent 355 SCD. The GC uses a capillary column (30 m × 320 μm × 5 μm, Zebron™, Phenomenex) for VOSC separation and helium as a carrier gas. The injection was operated in pulsed splitless mode. In order to optimize GC separation of targeted compounds in both standard solutions and wastewater samples, the injection temperatures ranging from 80°C to 120°C were tested. Also different GC oven temperature programs were performed (temperature starting at 28°C, 40°C and 50°C respectively; total retention time varying from 8.5 min to 11.6 min). The SCD was operated according to the manufacturer’s guidelines. The burner was operated at 800°C. The hydrogen and air flow rates were maintained at 42 ml/min and 62 ml/min, respectively, and the pressure in the reaction cell was at ~8 Torr.

2.5 Sample preservation method

As GC-SCD is normally unavailable in field and VOSCs are highly reactive, it is critical to preserve wastewater samples prior to their analysis for VOSCs. In this study, two different preservation methods were evaluated. One method was to store the headspace of the wastewater sample in a separate glass vial (hereinafter referred to as “separated headspace method”). 4ml gas was drawn from the aforementioned 12ml headspace vial containing wastewater sample and injected into a separate 4ml glass vial containing CaCl₂ (0.5 g) and ascorbic acid (0.3 g). These two compounds were used to remove moisture and oxygen in the VOSCs-containing air and prevent the oxidation of VOSCs (Tangerman 1986, Inomata et al. 1999). The vial with gas only was covered with aluminum foil to avoid light and then stored at ~4°C.

The second method was to acidify the wastewater samples (hereinafter referred to as “acidification method”) since VOSCs were found more stable in acidified wastewater
This method was carried out in the following steps. A 40 ml glass vial, capped with butyl rubber septa, was firstly flush by nitrogen gas for 10 min to remove oxygen. The vial was then filled to the top with 37.5 ml wastewater sample filtered through a 0.22 µm membrane, and 2.5 ml HCl (3 M) so that the pH was adjusted to ~1.1. The vial was covered with aluminum foil to avoid exposure to light and stored at ~4°C. Before doing the analysis, the sample was heated in a water bath (20°C) for 10 min and the pH of sample was raised to ~7.0 by adding 2.4 ml NaOH (3M) into the bottle, with an equivalent volume of the HCl and wastewater mixture withdrawn. The dilution effects of HCl and NaOH addition were considered while calculating the VOSC concentrations in wastewater. Then, 3 ml of sample was taken from the bottle and the normal static headspace technique and GC-SCD analysis was performed as previously described (Section 2.1).

The capabilities of sample preservation by these two methods were evaluated by monitoring the change of MT, DMS and DMDS concentrations in wastewater after different time intervals. The wastewater used for the test was obtained from an anaerobic sewer reactor mimicking a rising main sewer as will be further described in Section 2.6. In each test, several samples were taken at the same time and one of them was measured immediately. Then, samples stored directly in headspace vials and preserved by separated headspace method were measured after 8 h, while samples preserved by acidification method were analyzed after 24 h and 48 h. Spiked wastewater samples were also tested for the effect of acidification method at a high concentration range using the same method as described before.

2.6 Real wastewater sample analysis

Real wastewater samples from both a laboratory-scale sewer system and a real sewer pipe were tested to evaluate the application potential of the method developed in this study. The laboratory sewer reactor used was a cylindrical gas-tight reactor, which mimicked a section of a rising main sewer pipe under anaerobic conditions (Guisasola (Cheng et al. 2007)).
et al. 2008). The reactor was fed intermittently (6 pumping events per day) with municipal wastewater collected weekly from a local sewage pump station in Brisbane (Queensland, Australia). The wastewater was stored in a cold room (4°C) to minimize the biotransformation and was heated up to 20°C before being pumped to the reactor. Further details of the reactor and its operation can be found in Zhang et al. (2009). The reactor was under the steady state at the time of conducting the tests described below. Batch tests were applied to investigate the change of VOSC concentrations in the reactor. At the beginning of each test, the reactor was filled with fresh wastewater. Then samples were collected every 30 min for VOSC measurement during 6-hour experiments.

Field samples were obtained from a rising main sewer pipe (C016) in the Gold Coast area (Queensland, Australia). The C016 rising main had an internal pipe diameter of 300 mm (surface area to volume ratio, A/V = 13.3 m⁻¹), a total daily flow of ~700 m³, with 33 pump events (typically 4–6 min in duration) per day. Samples were collected at two locations: (1) wet well of the C016 pump station; (2) a sampling point at 1100m downstream of the pump station. Hourly samples were taken from 10:00 am until 2:00 pm and preserved using the acidification method described in Section 2.5. All samples were measured immediately after being delivered to the laboratory. Inorganic sulfide and soluble methane concentrations were also measured using ion chromatography (IC) with UV and conductivity detector (Dionex ICS-2000) (Jiang et al. 2009) and GC with a flame ionization detector (FID) (PerkinElmer, Inc.) (Guisasola et al. 2008), respectively.
3 Results and Discussion

3.1 Optimizing analytical conditions

The boric buffer (pH=8.1 ± 0.1) with the strength of 0.15 M was proven to achieve the best effect of reducing H$_2$S peak on the chromatogram (Figure 2). Since the acid disassociation constant ($pK_a$) of H$_2$S is around 7.0 (20°C), pH 8.1 would ensure over 90% of the total dissolved sulfide being in the form of HS$^-$. This would greatly decrease the H$_2$S concentration in the headspace of the vial and thus improves separation of the H$_2$S and MT peaks. While the addition of 3 ml boric buffer of 0.15 M to a 3 ml sample is effective in separating the H$_2$S and MT peaks for the municipal wastewater we tested, specific tests may be needed to determine a suitable buffer concentration for wastewater samples with different sulfide and MT concentrations or pH levels, to achieve satisfactory separation of H$_2$S and MT peaks.

Figure 2- The effect of boric different buffers on the separation of H$_2$S and MT peaks on the chromatogram.

For GC parameters, the GC injector temperature was finalized to 120°C. The oven temperature was programmed at 28°C for 5 min then increased at a rate of 20°C/min to 160°C with the total retention time of 11.6 min. Under the analytical conditions described above, optimized GC-SCD performance could be achieved, judged based on the separation and magnitudes of the peaks. Figure 3 shows examples of chromatograms of both standard solutions and wastewater samples. The peaks of all three targeted compounds (MT, DMS and DMDS) were in good sharp shapes. They were well separated in the wastewater samples and were not interfered by other compounds. As shown in Figure 3(B), the small peak next to the DMS peak is an ethanthiol peak. Though these two peaks are very close, there was no overlapping between the two peaks in all wastewater samples tested. The DMS concentration measured would thus not be affected by the presence of ethanthiol in municipal wastewater.
Figure 3- (A) Chromatogram of MT, DMS and DMDS in standard solution at 100 ppb of each compound; (B) Chromatogram of MT, DMS and DMDS in a wastewater sample.

3.2 Calibration curve

The calibration curves for MT, DMS and DMDS were constructed in the concentration range of 0.5 - 500 ppb (Figure 4). This range covered the possible concentration range of these substances in wastewater (see Section 3.5). All the three calibration curves presented good linearity with correlation coefficients over 0.999. The calibration results indicate that this method covers a broad linear dynamic range (4 orders of magnitude).

Figure 4- Calibration curves of MT, DMS and DMDS (0.5 - 500 ppb)

3.3 Method detection limits

Method detection limit (MDL) is defined as the lowest concentration of a substance that can be determined by a given method with 99% confidence that the concentration is higher than zero (US EPA 2010). In this study, the MDL is determined based on analyzing 8 samples at the concentration of 0.5 ppb. The MDL was calculated as follows (US EPA 2003):

\[ \text{MDL} = S \times t \]

where S is the standard deviation of the 8 samples at the concentration of 0.5 ppb; t is the one-sided student’s t value (2.998) for a 99% confidence interval with 7 degrees of freedom. The method detection limits of MT, DMS and DMDS of this method were determined as 0.08, 0.12 and 0.21 ppb, respectively. The detection limits of this method may be further decreased by optimizing the liquid volume injected into the
vial or reducing the buffer solution volume by for example increasing the buffer
solution concentration.

3.4 Reproducibility
The reproducibility was determined by repetitive measurement of 5 separately
prepared spiked wastewater samples at the concentration of 50 ppb. The relative
standard deviations (RSD) of MT, DMS and DMDS calculated based on the 5
measurements were 2.3%, 2.2% and 2.1%, respectively.

3.5 Recovery ratios
The recovery ratios of MT, DMS and DMDS in wastewater were tested by spiking a
pre-known amount of these compounds into a VOSC-free wastewater matrix and
calculating the relative difference between measured concentrations and real
concentrations. The VOSC-free wastewater was obtained by purging with nitrogen for
20 min to remove any preexisting VOSC.s. The result was obtained based on 5 tests
for each compound with concentration ranging from 5 ppb to 500 ppb. The recovery
ratios of MT, DMS and DMDS were 83±4%, 103±4% and 102±3%, respectively.
The recovery ratio for MT is relatively low, but still reasonable. The underlying
reason for this recovery is not clear, which may be due to wastewater matrix effect.
Further research is needed to identify the reason and to improve the recovery.

3.6 Sample preservation
The effect of two sample preservation methods, i.e. the separated headspace method
and the acidification method, are shown in Figure 5. The initial concentrations of
VOSC.s in different tests varied to a certain extent since these experiments were
carried out using different batches of real wastewater. The MT concentration in
wastewater samples stored directly in headspace vials or preserved by the separated
headspace method decreased 11.9 - 13.5 ppb after 8h. DMS and DMDS
concentrations decreased by 0.2 - 0.5 ppb during the same period. With the
acidification method, wastewater samples could be preserved for 24 h without
significant changes in composition (MT concentration decreased by 1.8 ppb, DMS by
0.4 ppb and DMDS by 0.2 ppb). After 48h, MT concentration decreased by 7.2 ppb.
In addition, there were no significant variations of DMS and DMDS concentrations
after 48 h. In the high concentration range (spiked wastewater tests), with the
acidification method, the concentration of three compounds decreased slightly (<1%)
after 48h preservation. These results suggest that MT in the wastewater could be
preserved using the acidification method for at least 24h while DMS and DMDS
could be preserved for at least 48 h.

Figure 5-Variation of MT (A), DMS (B) and DMDS (C) in the wastewater samples
with difference preservation methods. “Headspace vial”, “Separated headspace” and
“Acidification I” refer to real wastewater samples preserved in a headspace vial
directly, by the separated headspace method and by the acidification method,
respectively. “Acidification II” refers to the spiked wastewater sample preserved by
the acidification method.

3.7 Comparison with other methods
A comparison of this method and other reported methods for wastewater VOSC
measurement is listed in Table 1. As this method does not require the pre-
concentration processes, the analytical time is reduced by at least 40 min for the
measurement of each sample. In addition, the complication of sample handling is
avoided. The calibration range of this method covers 4 orders of magnitude, which is
comparable to results of other methods. The higher correlation coefficients (R²) and
relatively lower RDS values obtained indicate a better precision of measurement. The
detection limits of this method are lower than or comparable to those obtained using
purge-and-trap pre-concentration, although they are about 10 times higher than those
achieved by the SPME pre-concentration method. The recovery ratios are also
comparable to results obtained using GC system with pre-concentration processes.

Table 1. A comparison of different methods for wastewater VOSC measurement.

3.8 Application of the method to real wastewater samples

3.8.1 Laboratory reactor study

Time series of MT, DMS and DMDS concentrations in the lab-scale anaerobic sewer reactor obtained in two separate batch tests are presented in Figure 6. The MT concentration increased from about 45 ppb to a peak value of 77 - 103 ppb in the first hour and then decreased gradually to around 10 ppb after five hours. In contrast, DMS and DMDS concentrations were at relatively low levels (0.5 - 2 ppb) during the entire test period in both cases. The results indicate that MT could be produced and subsequently degraded under anaerobic sewer conditions. This trend of MT transformation was also observed in other anaerobic systems such as anaerobic digestion and fresh water sediments (Lomans et al. 1999, Du and Parker 2012). The production might be due to the cleavage of sulfur containing amino acids or methylation of sulfide, while the degradation likely resulted from the activity of methanogens and/or sulfide reducing bacteria (Lomans et al. 2001, Higgins et al. 2006).

Figure 6- Time series of MT, DMS and DMDS concentrations in the lab-scale anaerobic sewer reactor obtained in two separated tests (A) and (B).

3.8.2 Field study

The concentration profiles of VOSCs, dissolved sulfide and methane concentrations measured in the field study are shown in Figure 7. In the pump station, concentrations of all the three VOSCs remained at low levels. Most values were lower than 2 ppb, with MT concentrations being the exception, which increased from below 2 ppb slightly to 5-6 ppb after 12:00 pm. The MT concentration at the pump station in this study is similar to what reported by Lasaridi et al. (2010). They measured the MT concentration in the air above the sewage in a pump station in the range of 160 – 487
µg/m³, which indicated that the concentration in the sewage at that pump station could be around 0.8 – 2.4 ppb (calculated by Henry’s Law assuming gas-liquid equilibrium).

To our knowledge, the DMS and DMDS concentrations at wastewater pump stations have not been reported yet. In agreement with previous studies (Guisasola et al. 2008, Foley et al. 2009), the dissolved sulfide and methane concentrations were low, constant below 1 ppm.

Figure 7- Presence of VOSCs, H₂S and CH₄ in the CO16 rising main sewer: in the pump station (A, B) and at 1100 m downstream (C, D).

At the sampling point in the rising main sewer (1100 m downstream of the pump station), the MT concentration varied between 18.6 to 72.8 ppb, which was much higher than DMS and DMDS concentrations between 0.7 - 3 ppb. The MT concentration is in the range of 11 - 322 ppb reported by Hwang (1995), who measured the concentration in the influent of a WWTP. DMS and DMDS concentrations in this study are lower than Hwang’s results with 3 - 27 ppb for DMS and 30 - 79 ppb for DMDS, respectively. However, our result of DMDS concentration is close to what reported by Godayol et al. (2011), who measured the DMDS concentration in the influent of a WWTP with concentrations in the range of 0 - 5 ppb.

The VOSC concentrations are indeed expected to be dependent of wastewater composition and the sewage retention time in sewers.

The concentrations of MT and DMS in the wastewater samples obtained in the main at 1100 m downstream of the pump station were constantly higher than those obtained from the pump station. This suggests MT and DMS were produced in this anaerobic sewer line. We hypothesize that the increase is dependent of the hydraulic retention time (HRT) of the sewage in the pipe. From the pump operation data, we calculated that the HRT at 10:00 am to 11:00 am was about 1.5 h while the HRT at 12:00 pm to 2:00 pm was around 3 h. The longer HRT around the midday was likely responsible
for the higher increase in MT and DMS concentrations in this period. Figure 8A-D plotted the correlation between MT and DMS concentration and sulfide or methane concentration based on linear regression. Both MT and DMS concentrations showed high correlation with sulfide and methane concentrations ($R^2 = 0.84-0.94$). This could also support that HRT plays important role for MT and DMS concentrations in rising main sewers, since sulfide and methane concentrations in rising main sewer are known to be highly correlated with HRT (Sharma et al. 2008, Guisasola et al. 2009).

In contrast to the cases of MT and DMS, the DMDS concentration did not vary significantly between the two locations. The correlation between DMDS and sulfide or methane concentration was low ($R^2 = 0.04-0.21$, Figure 8 E-F). So the production of DMDS in rising main sewers might follow a mechanism different from that of MT and DMS. More research needs to be conducted before clearly understanding the transformation of VOSCs in sewer systems.

The VOSCs concentrations measured in real wastewater samples from both our laboratory sewer reactor and field sites were in the detection range (0.5-500 ppb) of this GC-SCD method. This range also covered the VOSC concentrations in sewage sampled from WWTPs, pump stations and drainage systems reported by other researchers (Hwang et al. 1995, Cheng et al. 2005, Sheng et al. 2008, Godayol et al. 2011). Therefore, we suggest this GC-SCD method with static headspace technique is suitable for routine wastewater VOSCs measurement.

4. Conclusions
The following conclusions are drawn regarding the suitability of the GC-SCD method for VOSC measurement in wastewater:

(1) VOSCs in the wastewater can be measured by GC-SCD with the static headspace technique.

(2) This method is simple and rapid as pre-concentration of samples is not required.

(3) The calibration curves obtained by this method present good linearity (>0.999).

The detection limit is lower than 1.0 ppb.

(4) The recovery ratio tests and real wastewater sample analysis demonstrate that this method is suitable for routine VOSCs measurement in wastewater.

(5) VOSCs in wastewater samples can be preserved for at least 24 hours by acidification of wastewater samples (pH ~1.1).

Acknowledgements

Funding support was received from the Australian Research Council, DC Water (USA), Gold Coast City Council, Melbourne Water Corporation, South East Water and Western Australia Water Corporation through Industry Linkage Project LP130100361. Ms. Jing Sun receives the University of Queensland International Tuition Award (UQIRTA) and China Scholarship Council (CSC) scholarship.

References


Inomata, Y., Matsunaga, K., Murai, Y., Osada, K. and Iwasaka, Y. (1999) Simultaneous measurement of volatile sulfur compounds using ascorbic acid for


List of tables and figures

Figure 1- A schematic diagram of the steps involved in VOSC measurement with the static headspace technique using GC-SCD.

Figure 2- The effect of different buffers on the separation of H₂S and MT peaks on the chromatogram.
Figure 3- (A) Chromatogram of MT, DMS and DMDS in standard solution at 100 ppb of each compound; (B) Chromatogram of MT, DMS and DMDS in a wastewater sample.
Figure 4 - Calibration curves of MT, DMS and DMDS (0.5 - 500 ppb)
Figure 5-Variation of MT (A), DMS (B) and DMDS (C) in the wastewater samples with difference preservation methods. “Headspace vial”, “Separated headspace” and “Acidification I” refer to real wastewater samples preserved in a headspace vial directly, by the separated headspace method and by the acidification method, respectively. “Acidification II” refers to the spiked wastewater sample preserved by the acidification method.

Figure 6- Time series of MT, DMS and DMDS concentrations in the lab-scale anaerobic sewer reactor obtained in two separated tests (A) and (B).
Figure 7- Presence of VOSCs, H$_2$S and CH$_4$ in the CO16 rising main sewer: in the pump station (A, B) and at 1100 m downstream (C, D).
Figure 8. Correlation analysis between MT and sulfide concentrations (A), MT and methane concentrations (B), DMS and sulfide concentrations (C), DMS and Methane concentrations (D), DMDS and sulfide concentrations (E) and DMDS and Methane concentrations (F).
Table 1. A comparison of different methods for wastewater VOSC measurement.

<table>
<thead>
<tr>
<th>No.</th>
<th>Compounds measured</th>
<th>Apparatus</th>
<th>Pre-concentration</th>
<th>Analytical time per sample</th>
<th>Calibration range</th>
<th>R²</th>
<th>RSD (%)</th>
<th>Detection limits</th>
<th>Recovery (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MT; DMS; DMDS</td>
<td>GC-SCD</td>
<td>No</td>
<td>17 min</td>
<td>0.5 - 500 ppb</td>
<td></td>
<td>0.9995 - 0.9998</td>
<td>2.1% - 2.3%</td>
<td>0.08 - 0.21 ppb</td>
<td>83%-103%</td>
</tr>
<tr>
<td>2</td>
<td>MT; DMS; DMDS</td>
<td>GC-MS</td>
<td>Purge-and-trap</td>
<td>58 min</td>
<td>5 - 500 ppb</td>
<td></td>
<td>0.993 - 0.998</td>
<td>0 - 8%</td>
<td>1.2 - 4.8 ppb</td>
<td>81% - 100%</td>
</tr>
<tr>
<td>3</td>
<td>DMS; EMS²; THIO³; DES²; DMDS</td>
<td>GC-MS</td>
<td>Purge-and-trap</td>
<td>70 min</td>
<td>0.0044 - 10.6 ppb</td>
<td></td>
<td>0.995 - 0.997</td>
<td>4.08% - 6.12%</td>
<td>0.006-0.035ppb</td>
<td>N.A.</td>
</tr>
<tr>
<td>4</td>
<td>DMDS</td>
<td>GC-MS</td>
<td>HS-SPME</td>
<td>72 min</td>
<td>0.1 - 100 ppb</td>
<td></td>
<td>0.9719</td>
<td>14%</td>
<td>0.03 ppb</td>
<td>86%</td>
</tr>
<tr>
<td>5</td>
<td>H₂S; CS₂; MT; DMS; DMDS</td>
<td>GC-FPD</td>
<td>Purge-and-trap</td>
<td>&gt;72 min</td>
<td>N.A.</td>
<td></td>
<td>N.A.</td>
<td>15%</td>
<td>ppt level</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

³ EMS: ethylmethyl sulfide; ² THIO: thiophene; ³ DES: diethyl sulphide; ⁴ N.A: Data not available