

**Final Report:
Analytical Methodology Development and Evaluation**

Author(s): Eric C. Sivret, Bei Wang, Gavin Parcsi, and Richard M. Stuetz



12 December, 2012



DOCUMENT STATUS RECORD

Project Title: SP3: Odour measurement and assessment, evaluation of odour treatment technologies
Client:
Document Title: Final Report: Analytical Methodology Development and Evaluation
Document Number: 2012/4
File Name:

| Issue No. | Date of Issue | Description | Signatures | | |
|-----------|---------------|-------------|------------|---------|----------|
| | | | Authors | Checked | Approved |
| 1 | 02-08-2012 | Draft | E Sivret | | |
| 2 | 12-12-2012 | Final | E Sivret | | |
| | | | | | |
| | | | | | |

Notes

Disclaimer:

1. The Water Research Centre has taken all reasonable steps to ensure that the information contained within this report is accurate at the time of production. In some cases, we have relied upon the information supplied by the client.
2. This report has been prepared in accordance with good professional practice. No other warranty expressed or implied is made as to the professional advice given in this report.
3. The Water Research Centre maintains no responsibility for the misrepresentation of results due to incorrect usage of the information contained within this report.
4. This report should remain together and be read as a whole.
5. This report has been prepared solely for the benefit of the client listed above. No liability is accepted by the Water Research Centre with respect to the use of this report by third parties without prior written approval.

Contact Details:

UNSW Water Research Centre
School of Civil and Environmental Engineering
The University of New South Wales

Name: Dr. Eric C. Sivret
Email: e.sivret@unsw.edu.au

Physical:

Building H22, Vallentine Annexe
Botany Street Gate 11
Kensington.

Postal:

UNSW, Sydney, 2052

Telephone: (02) 9385 5017

Fax: (02) 9313 8624

© Water Research Centre

Font Name: Optima LT Std

Table of Contents

| | |
|---|----|
| Table of Contents | i |
| List of Figures | ii |
| List of Tables | ii |
| 1.0 Overview | 1 |
| 2.0 VOC Analytical Methodology..... | 2 |
| 2.1 Key Parameters and Conditions | 2 |
| 2.2 Analytical Method Development and Calibration | 4 |
| 2.3 Analytical Method Evaluation..... | 6 |
| 2.3.1 Laboratory Evaluation | 6 |
| 2.3.2 Field Evaluation | 9 |
| 3.0 Sulfur Compound Analytical Methodology | 10 |
| 3.1 Key Parameters and Conditions | 10 |
| 3.2 Analytical Method Development and Calibration | 11 |
| 3.3 Method Evaluation | 13 |
| 3.3.1 Laboratory Evaluation | 13 |
| 3.3.2 Field Testing | 17 |
| 4.0 Closure..... | 18 |
| 5.0 References..... | 19 |

List of Tables

| | |
|--|----|
| Table 1 VOC Analytical Methodology Development - Compound List | 5 |
| Table 2 VOC Analytical Methodology Calibration | 5 |
| Table 3 Laboratory Evaluation of VOC Analytical Method | 8 |
| Table 4 Field Evaluation of VOC Analytical Methodology Reproducibility | 9 |
| Table 5 Sulfur Analytical Methodology Development - Compound List | 12 |
| Table 6 Sulfur Analytical Method Calibration | 13 |
| Table 7 Laboratory Evaluation of Sulfur Analytical Method | 16 |
| Table 8 Field Evaluation of Sulfur Analytical Method Reproducibility | 17 |

List of Figures

| | |
|--|----|
| Figure 1 GC-MS System for VOC Analysis | 3 |
| Figure 2 Linearity Evaluation of VOC Analytical Methodology | 7 |
| Figure 3 GC-SCD System for Sulfur Compound Analysis | 11 |
| Figure 4 Linearity Evaluation of Sulfur Analytical Methodology | 15 |

1.0 Overview

One of the key objectives of the SCORE project is the provision of data and knowledge to support odour abatement process selection, design, performance evaluation, and process investigation/diagnosis. A critical first step towards meeting this objective is the development of a comprehensive integrated monitoring and assessment protocol that 1) improves the identification of key groups of odour producing and treatment interfering compounds that are able to be treated by existing abatement technologies, and 2) identifies:

- appropriate sampling techniques;
- when to sample for determining peak loads and average daily loads;
- appropriate analytical techniques to use; and
- limitations and levels of accuracy in the results obtained while following the protocol.

This report details the results of work conducted to develop and assess the analytical techniques component of the comprehensive analytical protocol (component 1). The development of guidance with regards to the second component of the comprehensive integrated monitoring and assessment protocol will be detailed in a subsequent report.

Current methods of sewer gas monitoring include field and laboratory analysis of gaseous emissions using olfactory and chemical analysis (odour concentration, H₂S, volatile organic carbon (VOC), and ammonia measurements) and continuous in-situ monitoring of H₂S, volatile organic carbon (VOC), and ammonia. To date there has been limited application of more intensive analytical monitoring to provide comprehensive knowledge of the compounds present in sewer emissions and their interaction (removal, pass through, or interference) with odour abatement processes, and the need exists for the development and objective evaluation of these analytical methodologies.

Analytical methodology development and evaluation will focus gas chromatography based methods for two compound groups of interest, volatile organic carbon compounds (VOCs – **Section 2**), and sulfur compounds (**Section 3**).

2.0 VOC Analytical Methodology

Gas chromatography coupled with a mass spectrometer detector (GC-MS) allows speciation and quantification of selected VOCs of interest. As existing GC-MS based methodologies such as the United States Environmental Protection Agency's TO-15/TO-17 methods primarily focus on a set range of air toxins and hazardous air pollutants, they are not necessarily appropriate methodologies for identifying and quantifying compounds of interest in sewer emissions (both odorants and interferents). The development and evaluation of an exploratory GC-MS technique (utilising the scan mode to assess all potential compounds instead of a specific list of analytes) is presented in **Sections 2.1 to 2.3**. This exploratory technique is of particular use for investigative work (the core of SP3, or as part of emission characterisation studies used to support odour abatement process design or process troubleshooting). This method, when limited to a prioritised list of key compounds of interest in sewer emissions (dominant odorants and interferents identified as part of SP3), will provide the industry with a cost effective tool for more routine monitoring purposes.

2.1 Key Parameters and Conditions

The VOC analytical methodology was developed on gas chromatograph equipped with a mass spectrometer detector, depicted in **Figure 1**. This analytical system consists of a Markes International sample handling system (Ultra 2 automatic sampler, Unity 2 thermal desorber with a U-T11PGC general purpose cold trap) and Agilent Technologies analytical components (7890N GC gas chromatograph equipped with a DB-VRX column for compound separation and a 5975MSD mass spectrometer detector).

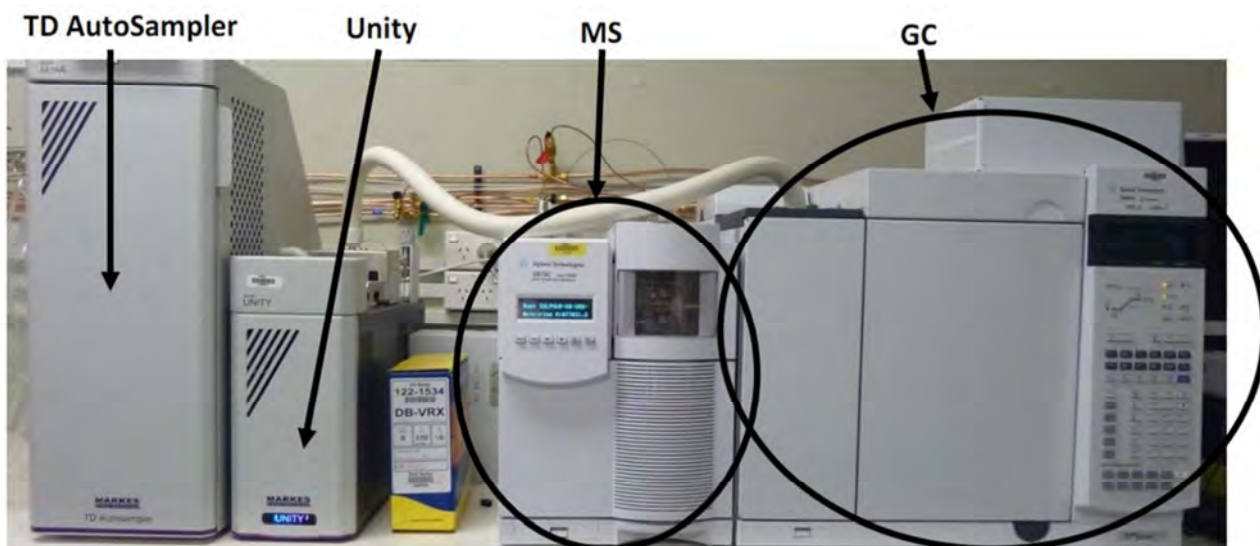


Figure 1 GC-MS System for VOC Analysis

In this system, sorbent tubes delivered by the Ultra 2 automatic sampler VOC are thermally desorbed using the Unity 2 thermal desorber and the sample is collected in the general purpose cold trap prior to sample injection into the gas chromatograph. Separation of the sample components is conducted using a DB-VRX column (with helium as the carrier gas at a flow rate of 1.8 ml/min), with the chromatograph column temperature initially held at 50°C for 2 mins, then raised at a rate of 15°C/min to 220°C, and then held for 3 minutes. The elution from the gas chromatograph is analysed by the mass spectrometer which is operating in a continuous scan mode (33-335 m/z), allowing for identification and quantification of a wide range of compounds present in the sample. The National Institute of Standards and Technology (NIST) NIST02 and NIST11 databases were used for spectra matching and compound identification.

Column Selection

The DB-VRX is a low polarity stationary phase column, 30m x 0.25mm, with a 1.4 µm film thickness. Based on previous column comparison work (Sivret et al. 2010), for typical compounds of interest, polar columns offers significantly better compound separation and identification than non-polar columns. However, while polar columns significantly outperform non-polar ones for this application, the high level of column bleed in these columns limits their practicality due to the increasing calibration demand and complications in direct comparison of successive chromatograms associated with the aging of polar

columns (Sivret et al 2010).

The low polarity DB-VRX column provides a compromise, retaining much of the strengths of the polar and non-polar separation columns, providing a good separation and peak identifiability while still having low bleed and stable retention times (Sivret et al 2010). To provide consistency in compound order between the different methodologies utilised in the laboratory, this column is used for both the VOC and VOSC methodologies outlined in this report.

Sorbent Selection

Based on sample media evaluation work (which will be presented as part of the sample collection technique component of the upcoming comprehensive integrated monitoring and assessment protocol), it was established that sample bags were not suitable for VOC analysis due to the artefacts associated with the bag materials. Utilisation of sorbent tubes was identified as the most appropriate sample collection method.

The sorbent tube evaluation component of the sample media evaluation work has identified Tenax TA (a widely used, inert, hydrophobic, weak sorbent, with target volatile organic compounds in the n-C₇ to n-C₃₀ range) as the optimal sorbent for this application. The following methodology is thus based upon samples collected onto sorbent tubes containing Tenax TA media.

2.2 Analytical Method Development and Calibration

Using initial field samples (range of odour abatement process inlet and outlet sampling points), appropriate oven temperature profiles were developed to maximise component identifiability while minimising run times. Initial method calibration was conducted for a list of compounds prepared based on potential odorants and key compounds that may be observed in sewers. A summary of the VOCs used in method development and calibration is provided as **Table 1**. It should be noted that the list is updated on an ongoing basis and additional compounds are being added to the list based upon the key odorants and interferences identified through the field testing component of SP3.

Table 1 VOC Analytical Methodology Development - Compound List

| Family | Compound |
|-------------------------|--------------------------|
| Butyl Compounds | 1-butanol |
| | 2-butanone |
| | 3-methyl-2-butanone |
| Aromatics | Benzene |
| | Toluene |
| | m-xylene |
| | o-xylene |
| | p-xylene |
| | 1-ethyl-2-methyl benzene |
| Alkane | 1-ethyl-3-methyl benzene |
| | 1-ethyl-4-methyl benzene |
| Chlorinated Hydrocarbon | Decane |
| Terpenes | Trichloromethane |
| | D-limonene |
| | 1R- α -pinene |

Pure liquid standards were obtained for the compounds assessed. A known quantity of each standard was injected onto Tenax TA sorbent tubes and analysed using the method outlined in **Section 2.1**. Five samples (with differing analyte masses) were analysed for each compound. Compound retention times (**Table 2**) were combined with the MSD results to confirm compound identity. A linear regression of the magnitude of the detector response vs. the analyte masses injected onto the sorbent tubes was conducted to determine the response factor (**Table 2**) to allow quantitative analysis.

Table 2 VOC Analytical Methodology Calibration

| Compound | CAS No. | Retention Time (min) | Response Factor (Area/ng Analyte) |
|--------------------------|-----------|----------------------|-----------------------------------|
| Trichloromethane | 67-66-3 | 4.18 | 15992 |
| 2-butanone | 78-93-3 | 4.61 | 13541 |
| 1-butanol | 71-36-3 | 5.42 | 13827 |
| 3-methyl-2-butanone | 563-80-4 | 5.57 | 19449 |
| Benzene | 71-43-2 | 5.69 | 20032 |
| Toluene | 108-88-3 | 7.30 | 38336 |
| m-xylene | 108-38-3 | 8.78 | 40263 |
| p-xylene | 106-42-3 | 8.80 | 43596 |
| o-xylene | 95-47-6 | 9.11 | 38920 |
| 1R- α -pinene | 7785-70-8 | 9.51 | 26559 |
| 1-ethyl-3-methyl benzene | 620-14-4 | 9.82 | 42258 |
| 1-ethyl-4-methyl benzene | 622-96-8 | 9.85 | 46141 |
| Decane | 124-18-5 | 10.00 | 27073 |
| 1-ethyl-2-methyl benzene | 611-14-3 | 10.05 | 41428 |
| D-limonene | 5989-27-5 | 10.52 | 29806 |

2.3 Analytical Method Evaluation

Two evaluations were conducted on the developed analytical method. The first evaluation, under laboratory conditions, focused on assessing fundamental aspects of the methodology including linearity, reproducibility, and method limits of detection. A field evaluation was then conducted using the method to assess the useability of the method under field conditions.

2.3.1 Laboratory Evaluation

The laboratory evaluation was conducted for three important analytical aspects; response linearity, method reproducibility, and method limits of detection. Response linearity and method reproducibility are critical measures of analytical method quality. For situations where specific odorants or interferents are not detected, method detection limits provide upper bounds on concentrations. For odorants, a useful test of method suitability is to compare the odorant's limit of detection to its odour threshold to assess method sensitivity.

Response linearity was evaluated through the analysis of a series of five samples containing varying concentrations of the compounds identified in

Table 1 across concentration ranges expected to be encountered in field conditions (**Figure 2**). The identified linear ranges and linear fit quality are presented in **Table 3**. The MSD response was linear for the specific compound concentration ranges studied. **Method reproducibility** for each compound studied was analysed through the analysis of a series of 7 replicate samples. As seen in the results presented in **Table 3**, the relative standard deviations varied from 1.3% to 13.7% over the compound range studied, but generally were on the order of 7-9%.

Method detection limits (MDL) were determined using compound standards, with the mass of analyte being sequentially decreased until the response from the detector fell below the limit of quantification (10 times the baseline noise) and the limit of detection (3 times the baseline noise). For the range of compounds studied, the method detection limits (**Table 3**) ranged from 0.02 – 4.03 $\mu\text{g}/\text{m}^3$, and were typically less than 1.75 $\mu\text{g}/\text{m}^3$. The method detection limits were below the reported odour threshold values for the compounds studied

(in many cases several orders of magnitude lower), and are sufficiently sensitive for this application.

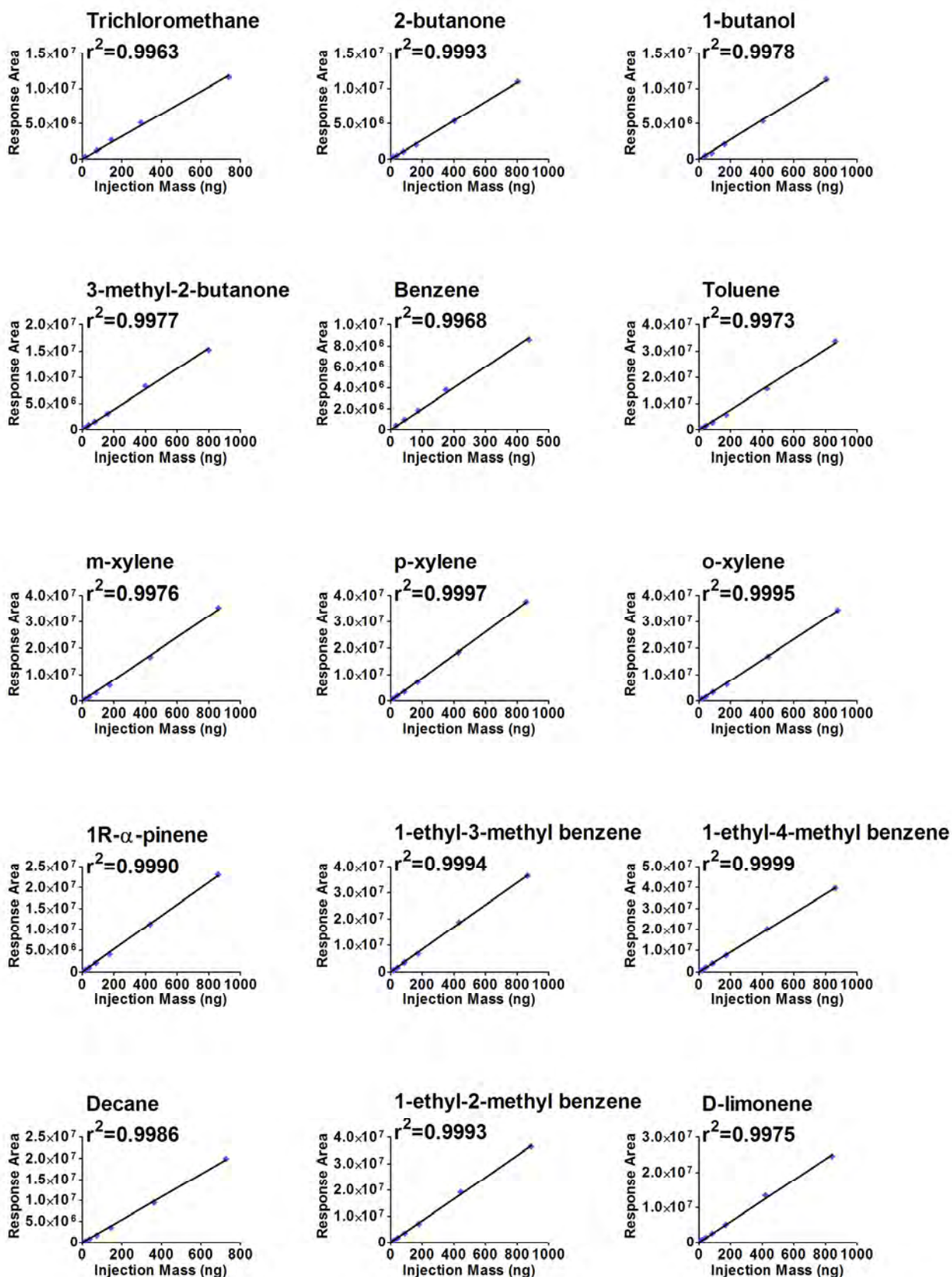


Figure 2 Linearity Evaluation of VOC Analytical Methodology

Table 3 Laboratory Evaluation of VOC Analytical Method

| Compound | CAS No. | Linear Range (ng) | Linear Fit Quality (R ²) | Relative Standard Deviation (%) ¹ | Method Detection Limit (ng) | Method Detection Limit (µg/m ³) ² | Odour Threshold Value (µg/m ³) ³ |
|--------------------------|-----------|-------------------|--------------------------------------|--|-----------------------------|--|---|
| Trichloromethane | 67-66-3 | 14.8 - 740 | 0.9963 | 3.6 | 2.96 | 1.48 | 500 – 1,350,000 |
| 2-butanone | 78-93-3 | 16.1 - 805 | 0.9993 | 7.2 | 8.05 | 4.03 | 290 – 250,000 |
| 1-butanol | 71-36-3 | 40.3 - 806 | 0.9978 | 8.3 | 8.06 | 4.03 | 10 – 250,000 |
| 3-methyl-2-butanone | 563-80-4 | 17.2 - 862 | 0.9977 | 2.5 | 1.60 | 0.80 | 15,000 – 17,000 |
| Benzene | 71-43-2 | 17.5 - 437 | 0.9968 | 1.3 | 1.75 | 0.87 | 1,500 – 380,000 |
| Toluene | 108-88-3 | 17.2 - 862 | 0.9973 | 9.7 | 0.43 | 0.22 | 600 – 590,000 |
| m-xylene | 108-38-3 | 17.2 - 862 | 0.9976 | 8.8 | 0.86 | 0.43 | 52 – 86,000 |
| p-xylene | 106-42-3 | 17.1 - 857 | 0.9997 | 3.7 | 0.86 | 0.43 | 520 – 9,100 |
| o-xylene | 95-47-6 | 17.5 - 876 | 0.9995 | 8.1 | 0.88 | 0.44 | 77 – 23,600 |
| 1R- α -pinene | 7785-70-8 | 17.2 - 858 | 0.9990 | 5.0 | 0.86 | 0.43 | 23 – 105,000 |
| 1-ethyl-3-methyl benzene | 620-14-4 | 17.3 - 865 | 0.9994 | 8.7 | 1.73 | 0.87 | NA |
| 1-ethyl-4-methyl benzene | 622-96-8 | 17.2 - 861 | 0.9999 | 13.7 | 0.86 | 0.43 | NA |
| Decane | 124-18-5 | 14.5 - 726 | 0.9986 | 7.7 | 1.45 | 0.73 | 11 300 |
| 1-ethyl-2-methyl benzene | 611-14-3 | 17.7 - 887 | 0.9993 | 9.3 | 0.89 | 0.44 | NA |
| D-limonene | 5989-27-5 | 16.8 - 841 | 0.9975 | 10.0 | 0.63 | 0.32 | 56 – 55,000 |

¹Based on a series of 7 replicate samples analysed

²For a 2 L sample volume

³van Gemert, L.J. (2003). *Odour Thresholds: Compilations of Odour Threshold Values in Air, Water and Other Media*. Oliemans Punter & Partners BV, The Netherlands.

NA – No OTV available

2.3.2 Field Evaluation

Evaluation of the application of the analytical methodology under field conditions was conducted as the final evaluation stage. The evaluation consisted of the collection of six simultaneous samples from two emission sources representing typical emission sources encountered during the monitoring campaign. The inlet of one of the activated carbon odour abatement processes (SWC-AC-1) was selected as the site representing typical emission concentrations and compound distribution, while the second site (SWC-S-2) was selected to represent a higher strength emission site.

All samples were collected onto Tenax TA sorbent tubes and transported to the laboratory for analysis using the analytical methodology presented and evaluated in **Sections 2.1 to 2.3**. Specific compound concentrations were determined for each sample and the relative standard deviation between the 6 samples was calculated. The standard deviations for each of the sites compared to the standard deviation under laboratory conditions utilising pure standards are compared in **Table 4**.

Table 4 Field Evaluation of VOC Analytical Methodology Reproducibility

| Compound | SWC-AC-1 | | SWC-S-2 | | Lab Evaluation RSD (%) |
|--------------------------|------------------------------------|---------|------------------------------------|---------|------------------------|
| | Concentration (mg/m ³) | RSD (%) | Concentration (mg/m ³) | RSD (%) | |
| Trichloromethane | 226 | 2.8 | 851 | 8.9 | 3.6 |
| 2-butanone | nd | NA | nd | NA | 7.2 |
| 1-butanol | nd | NA | nd | NA | 8.3 |
| 3-methyl-2-butanone | nd | NA | nd | NA | 2.5 |
| Benzene | 5.5 | 6.3 | 2.6 | 17.0 | 1.3 |
| Toluene | 112 | 4.3 | 73.3 | 7.8 | 9.7 |
| m,p-xylene | 106 | 2.5 | 215 | 5.8 | 9.7 / 8.8 |
| o-xylene | 50.8 | 2.1 | 83.9 | 6.6 | 8.1 |
| 1R- α -pinene | 3.0 | 9.6 | 73.3 | 12.0 | 5.0 |
| 1-ethyl-3-methyl benzene | nd | NA | nd | NA | 8.7 |
| 1-ethyl-4-methyl benzene | 19.7 | 2.7 | 21.0 | 6.5 | 13.7 |
| Decane | 14.4 | 2.1 | 11.8 | 14.7 | 7.7 |
| 1-ethyl-2-methyl benzene | 10.1 | 2.8 | 12.6 | 10.7 | 9.3 |
| D-limonene | 110 | 2.4 | 195 | 7.7 | 10.0 |

nd – not detect, below method detection limit

NA – not applicable

As seen in **Table 4**, the relative standard deviations varied from 2.1% to 17% under field conditions, although there was no consistent pattern, with some compounds having lower variability under field conditions and others greater variability.

3.0 Sulfur Compound Analytical Methodology

Gas chromatography coupled with a sulfur chemiluminescence detector (GC-SCD) allows quantification of sulfur containing compounds. The sulfur chemiluminescence detector has a high level of sensitivity to sulfur compounds, allowing for detection of these compounds at levels comparable to their odour thresholds (which are typically very low as these compounds are highly odorous). As the sulfur chemiluminescence detector does not directly identify the compounds being detected, retention time matching using compound standards is required. The development and evaluation of the GC-SCD technique is presented in **Sections 3.1 to 3.3**. As the method assesses a portfolio of highly odorous sulfur compounds that can be found in sewers (and other emission sources such as biosolids), this technique is of particular value for investigative work to gain process/mechanism understanding, and as part of emission characterisation studies used to support odour abatement process design or troubleshooting.

3.1 Key Parameters and Conditions

The sulfur analytical methodology was developed on a gas chromatograph equipped with a sulfur chemiluminescence detector, depicted in **Figure 3**. This analytical system consists of a Markes International sample handling system (CIA 8 Air Server, Unity 2 thermal desorber with a U-T6SUL specialised sulfur cold trap) and Agilent Technologies analytical components (7890N GC gas chromatograph equipped with a DB-VRX column for compound separation and a 355 Sulfur Chemiluminescence Detector).

In this system, gas samples are extracted from the sample bags by the Air Server and are collected in the specialised sulfur cold trap prior to sample injection into the gas chromatograph. Separation of the sample components is conducted using a DB-VRX column (with helium as the carrier gas at a flow rate of 1 ml/min), with the chromatograph column temperature initially held at 37°C for 3 mins, then raised at a rate of 15°C/min to 225°C, and then held for 2 minutes. The elution from the gas chromatograph is analysed by the sulfur chemiluminescence detector, allowing quantification of the sulfur compounds present in the sample.

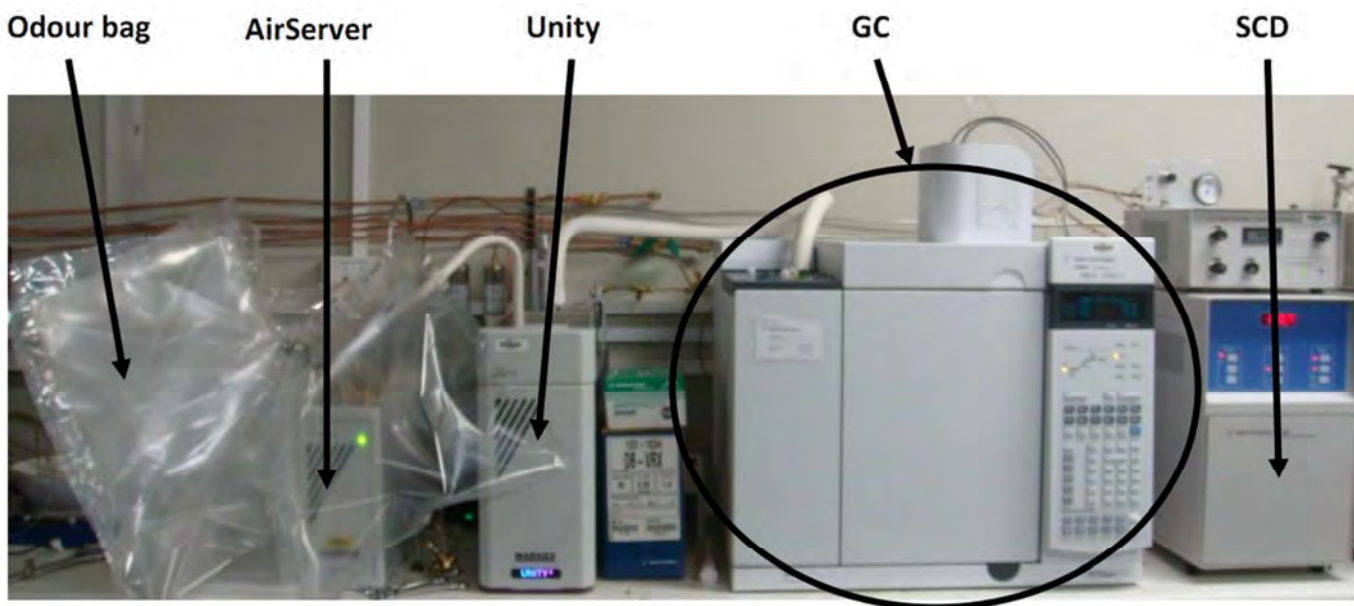


Figure 3 GC-SCD System for Sulfur Compound Analysis

The DB-VRX column utilised in this method is identical to that used for the VOC analytical method; a low polarity stationary phase column, 30m x 0.25mm, with a 1.4 μm film thickness. Selection rationale for this column has been discussed previously in **Section 2.1**.

A range of sample bag materials are available for collection of gas samples (including Tedlar, Mylar and Nalophan). Method development was conducted utilising Nalophan bags. However, as standard storage time in the bags prior to analysis was minimised (standards were made fresh immediately prior to analysis), bag specific influences are not expected to be significant. The impact of bag material on sulfur compound loss and degradation increases with sample storage time and will be evaluated and presented as part of the sample collection technique component of the upcoming comprehensive integrated monitoring and assessment protocol.

3.2 Analytical Method Development and Calibration

Using initial field samples (range of odour abatement process inlet and outlet sampling points), appropriate oven temperature profiles were developed to maximise component identifiability while minimising run times. Method calibration was conducted for a list of compounds prepared based on potential odorants and key compounds that may be observed in sewers, and was expanded to identify dominant peaks obtained during the analysis of field samples. A summary of the sulfur compounds used in method development and calibration

is provided as **Table 5**. It should be noted that the list is updated on an ongoing basis and additional compounds will be added if additional sulfur compound peaks are observed in the chromatograms during the field testing component of SP3.

Table 5 Sulfur Analytical Methodology Development - Compound List

| Family | Compound |
|------------------------|-------------------------|
| Basic Sulfur Compounds | Hydrogen sulfide |
| Thiols | Methyl mercaptan |
| | Ethyl mercaptan |
| | 2-methyl-2-propanethiol |
| | 1-butanethiol |
| Sulfides | Dimethyl sulfide |
| | Carbon disulfide |
| | Ethyl methyl sulfide |
| | Dimethyl disulfide |
| | Diethyl disulfide |
| | Dimethyl trisulfide |

Pure standards were obtained for the compounds assessed. Where gas standards were available, sample bags were filled directly from the gas standard cylinders. Liquid standards were converted to a gas standard in accordance with the Odour Emission Ability (OEA) methodology. This methodology utilises a dynamic injection technique in which a known quantity of liquid standard is injected into a plug of glass wool through which nitrogen gas flows. The evaporating compounds are dispersed into the nitrogen gas which is captured in a sample bag. Specific details of the OEA methodology are provided in a separate OEA methodology report.

The prepared standards were then analysed using the method outlined in **Section 3.1**. Five samples (with differing analyte masses) were analysed for each compound. Compound retention times (**Table 6**) were utilised for compound identification in field samples. A linear regression of the magnitude of the detector response vs. the analyte masses was conducted to determine the response factor (**Table 6**) to allow quantitative analysis.

Table 6 Sulfur Analytical Method Calibration

| Compound | CAS No. | Retention Time (min) | Response Factor (Area/ng Analyte) |
|-------------------------|-----------|----------------------|-----------------------------------|
| Hydrogen sulfide | 7783-06-4 | 1.94 | 490 |
| Methyl mercaptan | 74-93-1 | 2.41 | 1189 |
| Ethyl mercaptan | 75-08-1 | 3.40 | 1169 |
| Dimethyl sulfide | 75-18-3 | 3.70 | 1893 |
| Carbon disulfide | 75-15-0 | 4.01 | 966 |
| 2-methyl-2-propanethiol | 75-66-1 | 5.07 | 1246 |
| 1-butanethiol | 109-79-5 | 5.47 | 1543 |
| Ethyl methyl sulfide | 624-89-5 | 7.32 | 739 |
| Dimethyl disulfide | 624-92-0 | 7.95 | 2933 |
| Diethyl disulfide | 110-81-6 | 10.72 | 2469 |
| Dimethyl trisulfide | 3658-80-8 | 11.47 | 2234 |

3.3 Method Evaluation

Two evaluations were conducted on the developed analytical method, similar to those conducted for the VOC method. The first evaluation, under laboratory conditions, focused on assessing fundamental aspects of the methodology including linearity, reproducibility, and method limits of detection. A field evaluation was then conducted using the method to assess the useability of the method under field conditions.

3.3.1 Laboratory Evaluation

As with the VOC analytical method, the laboratory evaluation of the sulfur analytical method was conducted for response linearity, method reproducibility, and method limits of detection. Odorant limits of detection were compared with the method limits of detection to assess the suitability of the analytical methodology.

Response linearity was evaluated through the analysis of a series of five samples containing varying concentrations of the compounds identified in **Table 5** across concentration ranges expected to be encountered in field conditions (**Figure 4**). The identified linear ranges and linear fit quality are presented in **Table 7**. The SCD response was linear for the specific compound concentration ranges studied. **Method reproducibility** for each compound studied was assessed through the analysis of a series of 3 replicate samples for hydrogen sulfide and methyl mercaptan, and a series of 5 replicate samples for all other compounds. As seen in **Table 7**, the relative standard deviations varied from 1.8% to 6.1% over the

compound range studied, but generally were on the order of 3-3.5%.

Method detection limits (MDL) were determined using compound standards, with the mass of analyte being sequentially decreased until the response from the detector fell below the limit of quantification (10 times the baseline noise) and the limit of detection (3 times the baseline noise). For the range of compounds studied, the method detection limits (**Table 3**) ranged from 0.18 – 10.4 $\mu\text{g}/\text{m}^3$, and were typically less than 2.54 $\mu\text{g}/\text{m}^3$. The method detection limits were generally within the reported OTV ranges for the compounds studied, and (with the exception of the mercaptans) were of a similar order of magnitude as the lowest reported OTVs.

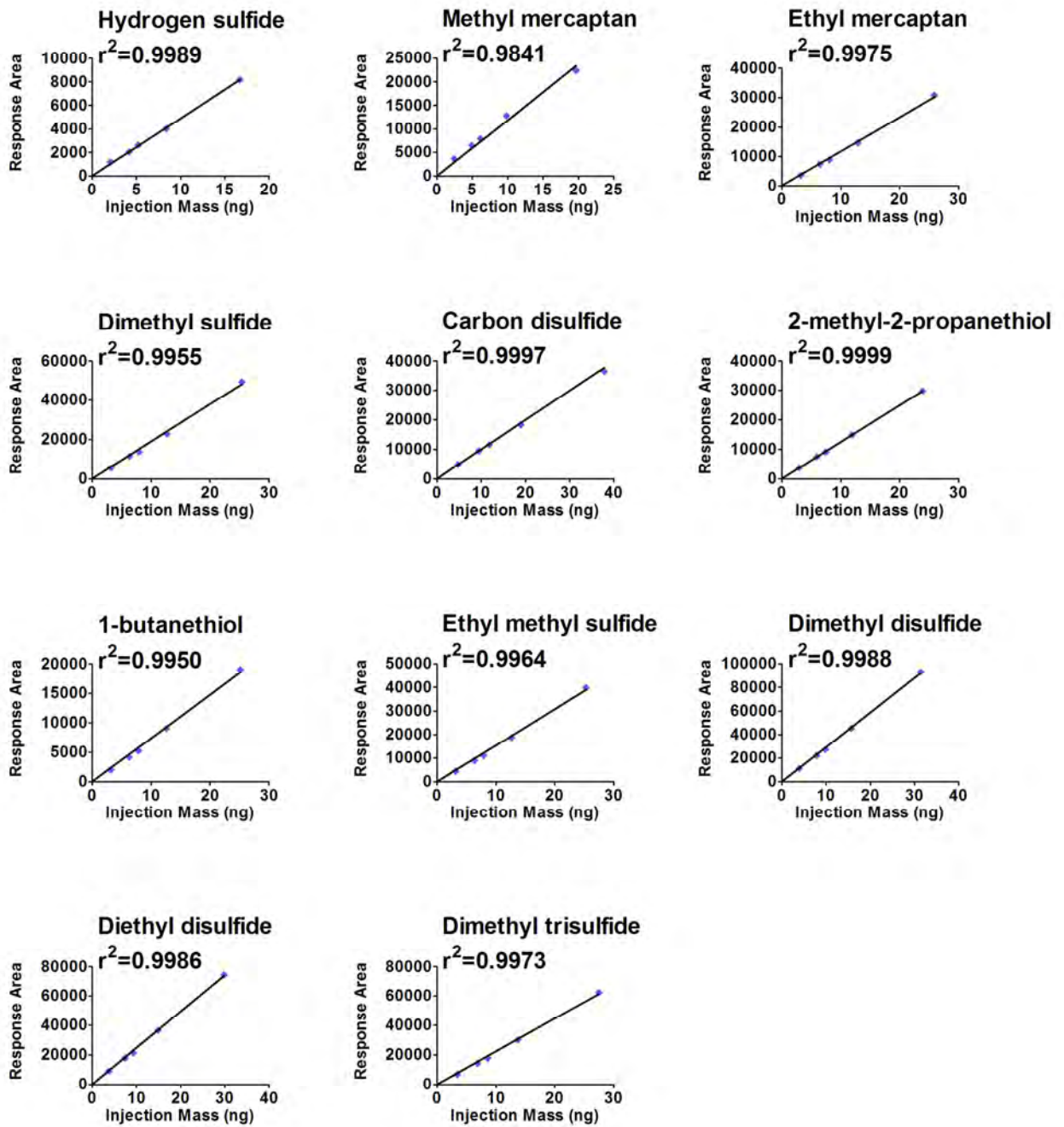


Figure 4 Linearity Evaluation of Sulfur Analytical Methodology

Table 7 Laboratory Evaluation of Sulfur Analytical Method

| Compound | CAS No. | Linear Range (ng) | Linear Fit Quality (R ²) | Relative Standard Deviation (%) ¹ | Method Detection Limit (ng) | Method Detection Limit (µg/m ³) ² | Odour Threshold Value (µg/m ³) ³ |
|-------------------------|-----------|-------------------|--------------------------------------|--|-----------------------------|--|---|
| Hydrogen sulfide | 7783-06-4 | 2.1 - 16.7 | 0.9989 | 6.1 | 0.522 | 10.4 | 0.21 – 270 |
| Methyl mercaptan | 74-93-1 | 2.5 - 19.6 | 0.9841 | 2.5 | 0.082 | 1.63 | 0.0003 – 38 |
| Ethyl mercaptan | 75-08-1 | 3.2 - 25.9 | 0.9975 | 3.1 | 0.270 | 5.40 | 0.046 – 21 |
| Dimethyl sulfide | 75-18-3 | 3.2 - 25.4 | 0.9955 | 3.1 | 0.079 | 1.59 | 0.3 – 160 |
| Carbon disulfide | 75-15-0 | 4.7 – 37.8 | 0.9997 | 3.3 | 0.144 | 2.88 | 70 – 180 |
| 2-methyl-2-propanethiol | 75-66-1 | 3.0 - 23.8 | 0.9999 | 3.0 | 0.127 | 2.54 | 0.09 – 3.3 |
| 1-butanethiol | 109-79-5 | 3.1 - 25.1 | 0.9950 | 1.8 | 0.292 | 5.84 | 1.5 – 3.0 |
| Ethyl methyl sulfide | 624-89-5 | 3.2 - 25.3 | 0.9964 | 5.0 | 0.101 | 2.02 | 62 |
| Dimethyl disulfide | 624-92-0 | 3.9 - 31.4 | 0.9988 | 3.5 | 0.011 | 0.21 | 1.1 – 78 |
| Diethyl disulfide | 110-81-6 | 3.7 - 29.8 | 0.9986 | 3.0 | 0.009 | 0.18 | 0.3 – 23 |
| Dimethyl trisulfide | 3658-80-8 | 3.4 - 27.4 | 0.9973 | 4.8 | 0.018 | 0.36 | 0.06 – 7.5 |

¹Based on a series of 3 replicate samples analysed for hydrogen sulfide and methyl mercaptan. A series of 5 replicate samples were analysed for all other compounds

²For a 50 ml injection volume

³van Gemert, L.J. (2003). *Odour Thresholds: Compilations of Odour Threshold Values in Air, Water and Other Media*. Oliemans Punter & Partners BV, The Netherlands.

3.3.2 Field Testing

Evaluation of the application of the analytical methodology under field conditions was conducted as the final evaluation stage. The evaluation consisted of the collection of six simultaneous samples from three emission sources representing typical emission sources encountered during the monitoring campaign. The inlet, post-heater, and outlet of one of the activated carbon odour abatement processes (SWC-AC-1) was used as a site representing typical emission concentrations and compound distribution.

All samples were collected onto Nalophan sample bags and transported to the laboratory for analysis using the analytical methodology presented and evaluated in **Sections 3.1 to 3.3**. Specific compound concentrations were determined for each sample and the relative standard deviation between the 6 samples was calculated. The standard deviations for each of the sites compared to the standard deviation under laboratory conditions utilising pure standards are compared in **Table 8**.

Table 8 Field Evaluation of Sulfur Analytical Method Reproducibility

| Compound | SWC-AC-1-In ¹ | | SWC-AC-1-PH | | SWC-AC-1-Out ¹ | | Lab Evaluation RSD (%) |
|-------------------------|----------------------------|---------|----------------------------|---------|----------------------------|---------|------------------------|
| | Conc. (mg/m ³) | RSD (%) | Conc. (mg/m ³) | RSD (%) | Conc. (mg/m ³) | RSD (%) | |
| Hydrogen sulfide | 4677 | 4.4 | 4041 | 4.6 | 20.0 | 6.3 | 6.1 |
| Methyl mercaptan | 1094 | 7.8 | 857 | 3.6 | 6.5 | 5.8 | 2.5 |
| Ethyl mercaptan | nd | NA | nd | NA | nd | NA | 3.1 |
| Dimethyl sulfide | 71.1 | 4.9 | 66.9 | 3.5 | 80.5 | 2.3 | 3.1 |
| Carbon disulfide | 11.6 | 9.5 | 9.7 | 13.5 | 10.0 | 2.5 | 3.3 |
| 2-methyl-2-propanethiol | nd | NA | 23.0 | 7.2 | nd | NA | 3.0 |
| 1-butanethiol | 33.2 | 12.0 | nd | NA | nd | NA | 1.8 |
| Ethyl methyl sulfide | nd | NA | nd | NA | nd | NA | 5.0 |
| Dimethyl disulfide | 16.8 | 15.1 | 12.4 | 6.5 | 203 | 2.3 | 3.5 |
| Diethyl disulfide | nd | NA | nd | NA | nd | NA | 3.0 |
| Dimethyl trisulfide | 10.5 | 13.8 | 9.8 | 7.2 | 4.4 | 12.6 | 4.8 |

nd – not detect, below method detection limit

NA – not applicable

¹Results based on 5 samples due to leakage from one of the sample bags

Based on the results presented in **Table 8**, the relative standard deviations varied from 3.6% to 15%, higher than those observed under laboratory conditions.

4.0 Closure

The analytical techniques to be used as part of the comprehensive analytical protocol have been developed, consisting of a GC-MS based methodology for VOCs and a GC-SCD based methodology for sulfur compounds. Results of the method evaluations (both laboratory and field based) demonstrated that the methods were highly linear in nature and of sufficient sensitivity for sewer and odour abatement process monitoring applications (VOC MDLs ranging from 0.02 – 4.03 $\mu\text{g}/\text{m}^3$ and sulfur compound MDLs ranging from 0.18 – 10.4 $\mu\text{g}/\text{m}^3$).

For VOCs, the MDLs were below the reported odour threshold values for the compounds studied, while for sulfur compounds the MDLs were generally within the reported OTV ranges for the compounds studied, and (with the exception of the mercaptans) were of a similar order of magnitude as the lowest reported OTVs. With regards to method reproducibility, while there was relatively low variability in laboratory conditions. Variability under field conditions typically ranged between 1.3 and 17% although there was no consistent pattern, with some compounds having lower variability under field conditions and others greater variability.

The developed analytical methodologies provide the foundation for the development of the integrated monitoring protocol and are a critical step towards addressing existing knowledge gaps and providing information leading to improved odour abatement process selection, design, operation, and performance evaluation.

5.0 References

Sivret, E. C., Parcsi, G., and Stuetz, R. M. (2010). Sampling and Analysis Methodology Concerns for Volatile Organo-Sulfur Compounds (VOSCs). *Air & Waste Management Association 103rd Annual Conference & Exhibition*, Calgary, Canada.

van Gemert, L.J. (2003). Odour Thresholds: Compilations of Odour Threshold Values in Air, Water and Other Media. Oliemans Punter & Partners BV, The Netherlands.