MEASUREMENT OF DILUTE VOLATILE ORGANIC COMPOUNDS IN AIR

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Master of Engineering in Research

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ABSTRACT

Based on public information and several research papers, air quality and unpleasant industrial related odours have a major impact on the population’s concerns, health and social behaviour and malodorous emissions haven’t been thoroughly investigated in Central Queensland; to address this issue, this project has been created to focus on such emissions. There is a high demand for a more comprehensive method to quantify odour emissions from alumina refineries and other local industries. These odorous compounds are mostly VOC (volatile organic compounds) which have also been associated with cancer and asthma. Most of the VOC in air were present at very dilute concentrations which are often below the detection level of the GCMS (gas chromatograph/ mass spectrometer). Only a couple of research groups have investigated the effect of dilute concentrations of VOC on health but according to McDermott et al., there is growing evidence that these dilute concentrations (usually in parts per billion concentrations) that are not normally measured by conventional monitoring methods are harmful to human health (McDermott et al, 2007). The need to produce a more comprehensive laboratory instrumental set-up which can detect, identify and quantify dilute concentrations of these odour emissions will be a valuable tool for reduction of odour nuisances to an acceptable level by the population.

The focus of the Masters has been on the development of appropriate trapping mechanisms for the pre-concentration of VOC’s prior to injection into the GCMS, as the detection limit for the GCMS on direct injection of samples was limited to 100 ppmv (parts per million by volume) initially before instruments modifications were
developed. The researcher was faced with the challenge to increase the GCMS detection level in order to quantify the odour emissions from the alumina refinery at the start of the study. Upon attachment of a purge and trap sample concentrator, experiments were started with liquid VOCs namely toluene, p-xylene, methyl 1.4 cycohexadiene, ethylbenzene and methyl-disulfide, in order to test the capability of the instrument set-up to detect trace contaminants. The experiments have resulted detection of compounds down to 10 ppbv. Experiments with standard air samples have been a real challenge with the construction of a polyurethane cylindrical calibration mixer in the PELM laboratory. The efficiency recovery of the mixer for preparation of standard air samples were tested with various experiments involving flow rate, collection time and other instrumental parameters. A range of gas concentration standards were made using the calibration mixer. The calibration curves for the detection process were made using these standards at concentration levels down to 1 ppb by volume. Research on appropriate adsorbents used in the secondary trap of the purge and trap apparatus and the thermal tubes were conducted. This project used a system based on thermal desorption tubes loaded with tenax adsorbent to pre-concentrate the gases. The efficiency of recovery of the VOC’s was studied and was found to be reasonably high at these levels.

The method used external standardisation for developing the calibration curve which showed linearity for five orders of magnitude with concentrations ranging from 5 ppm by volume (ppmv) down to a detection of 1 ppbv. Comparison analyses of liquid and gaseous VOC showed recoveries from 98 to 99%. The use of thermal desorption tubes for sample and standard collection proves to be advantageous compared to other existing procedures. Tenax, a kind of adsorbent was used as the
trapping material inside the thermal desorption tubes and in the secondary trap of the purge and trap system.

By the end of the study, a laboratory method for identifying and quantifying VOC in parts per billion concentrations by volume (ppbv) was successfully developed. The application of the method developed enables the scientist to link the relationship between the odour intensity of a certain VOC to its concentration.

This thesis gives an overview of the existing literature for air analysis, experiments that were necessary to identify the correct instrument parameters and laboratory set-up, further experiments for testing the modified laboratory instrumentation for detection of the prepared air standards, procedures for making the calibration standards and the validation of the method developed.
MEASUREMENT OF DILUTE VOLATILE ORGANIC COMPOUNDS IN AIR
# TABLE OF CONTENTS

ABSTRACT ......................................................................................................................... i
STATEMENT OF ORIGINALITY ...................................................................................... xiii
GLOSSARY ........................................................................................................................ xiv

**Chapter 1: Scope and Outline of Thesis** ......................................................................... 1
1.1 Introduction .................................................................................................................. 1
1.2 Scope of the Research Study ....................................................................................... 4
1.3 Aims and Objectives .................................................................................................. 5

**Chapter 2: Overview of Existing Literature** ................................................................. 7
2.1 Introduction .................................................................................................................. 7
2.2 Literature on Air Emissions ....................................................................................... 7
2.2.1 Summary of Existing Methods for Analysis of VOC ........................................... 13
2.3 Preparation of Standards .......................................................................................... 32
2.3.1 External Standardisation Method ....................................................................... 33

**Chapter 3: Methodological Approach** ......................................................................... 37
3.1 Static Gas Standards .................................................................................................. 37
3.2 Summary of the Developed Method ......................................................................... 42
3.3 Instrumentation Set-up ............................................................................................. 44
3.4 Selection of Appropriate Adsorbent ......................................................................... 46

**Chapter 4: Experimentation** ....................................................................................... 49
4.1 Introduction ............................................................................................................... 49
4.2 Parameters of the Instrumental Set-up ................................................................. 49
4.3 Experiments on GCMS Linearity Using Ethanol as Solvent ...................... 52
4.4 Experiments on O.I. purge & Trap Sample Concentrator for Liquid VOC... 52
4.5 Experiments with Standard Air Samples .............................................................. 53
4.6 Experiments at Different Flow Rates ................................................................. 59
4.7 Experiments on Ethylbenzene Standard at 1:10 Split Ratio: .................. 59
4.8 Duplicate Trials for Thermal tubes 2, 3 and 4 ...................................................... 59
4.9 Final Experimental Parameters ......................................................................... 59
4.10 Analysis of Blanks .............................................................................................. 60
4.11 Testing for Memory Effects .............................................................................. 61
4.12 Experiments Showing the Effect of Time .......................................................... 61

Chapter 5: Results and Discussion ........................................................................... 62
5.1 Introduction ............................................................................................................ 62
5.2 Experimental Results on GCMS Linearity Using Ethanol as Solvent........ 62
5.3 Suitability of the GCMS for VOC Analysis ....................................................... 64
5.4 O.I. Analytical Purge & Trap Sample Concentrator Analysis Results ....... 64
5.5 O.I. Analytical Purge & Trap Sample Concentrator Capability .................... 69
5.6 Results of the Experiments with Standard Air Samples ............................. 71
5.7 Discussion for Experiments with VOC in Standard Air Matrix ................. 75
5.8 Results for Experiments at Different Flow Rates ............................................ 78
5.9 Results of Analysis of Ethylbenzene Standard at 1:10 Split Ratio .............. 80
5.10 The Effects of Changing Split Ratio to 1:10 ................................................. 81
5.11 Results of Duplicate Trials for Thermal Tubes 2,3 & 4 .............................. 82
5.12 Using the Final Parameters with Different Thermal Desorption Tubes ...... 85
5.13 Final Results ........................................................................................................ 86
5.14 Validation of Final Results ................................................................. 88
5.15 Results of Blank Analysis ................................................................. 89
5.16 Results for Memory Effects ............................................................... 90
5.17 The Effect of Time ........................................................................ 90
5.18 Discussion on the Effect of Residence Time .................................... 91
5.19 Effective Lower Working Limit ....................................................... 92
5.20 Discussion on Detection Levels and Sample Recovery .................... 92

Chapter 6: Conclusion ............................................................................. 93

6.1 Background of the Original Problem .............................................. 93
6.2 Conclusion Summary ........................................................................ 94
6.3 Recommendations for Further Study ............................................. 95

References ............................................................................................. 97

Appendices ............................................................................................. 101
# LIST OF TABLES AND FIGURES

<table>
<thead>
<tr>
<th>Figure/Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1</td>
<td>Thermal Oxidiser Flow Path in Queensland Alumina</td>
<td>3</td>
</tr>
<tr>
<td>Table 1</td>
<td>VOC Emission in Different locations in the Alcan Gove Refinery</td>
<td>8</td>
</tr>
<tr>
<td>Table 2</td>
<td>Existing EPA Methodologies of Sample Collection for Volatile Organic Compounds using Gas Chromatography</td>
<td>12</td>
</tr>
<tr>
<td>Figure 2</td>
<td>The SPME Device</td>
<td>18</td>
</tr>
<tr>
<td>Figure 3</td>
<td>Schematic Diagram of Standard Gas Generator System</td>
<td>21</td>
</tr>
<tr>
<td>Table 3</td>
<td>Summary of Sampling Procedures Base on Several Studies</td>
<td>23</td>
</tr>
<tr>
<td>Figure 4</td>
<td>Enrichment and Injection of Gaseous Samples using Tenax®</td>
<td>26</td>
</tr>
<tr>
<td>Table 4</td>
<td>Comparison of % Recovery of FSL and SUMMA Canister</td>
<td>28</td>
</tr>
<tr>
<td>Table 5</td>
<td>Comparison of GC Injection Techniques</td>
<td>30</td>
</tr>
<tr>
<td>Figure 5</td>
<td>Calibration Curves for 2-butanone (MEK), 2-pentanone (MPK), 2-hexanone (MnBK), 2-methyl 1,4-pentanone (MiBK).</td>
<td>34</td>
</tr>
<tr>
<td>Figure 6</td>
<td>Piston Type Cylindrical Chamber</td>
<td>40</td>
</tr>
<tr>
<td>Figure 7</td>
<td>Flow Chart for Analysis of Standards and Sample</td>
<td>43</td>
</tr>
<tr>
<td>Figure 8</td>
<td>The Shimadzu GC/MS Series 5050</td>
<td>44</td>
</tr>
<tr>
<td>Figure 9</td>
<td>The Thermal Desorption Accessory as Attach to the Purge &amp; Trap Concentrator</td>
<td>45</td>
</tr>
<tr>
<td>Figure 10</td>
<td>The Calibration Mixer Attached to the Vacuum Pump</td>
<td>46</td>
</tr>
</tbody>
</table>
Table 6: Injection Volumes to Make 10 ppmv of Specified VOC

Table 7: Amount of Compound Injected into the GCMS at 10 ppmv, 1 ppmv and 100 ppbv

Figure 11: Calibration Curves of 50 µl acetone, MPK, toluene at 10, 20 & 50 ml Dilutions in Ethanol

Figure 12: 10 ppmv of acetone, xylene & toluene purge& trap in distilled water

Figure 13: 100 ppbv of acetone, xylene & toluene purge& trap in distilled water

Table 8: Data from purge & trap analysis in distilled water Trial 1

Figure 14: 10 ppmv analysis of toluene, p-xylene, methyl 1,4 cyclohexadiene in distilled water

Figure 15: 10 ppbv analysis of toluene, p-xylene, methyl 1,4 cyclohexadiene in distilled water

Figure 16: Graph of concentration vs. log scale of peak area for toluene by purge & trap

Figure 17: Graph of concentration vs. log scale of peak area for Ethylbenzene by purge & trap

Table 9: Experimental Data for Dimethylsulfide

Figure 18: Graph of dimethylsulfide Amount vs. Log of Peak Areas

Table 10: Experimental Data for p-xylene

Figure 19: Graph of p-xylene amount vs. Log of Peak Area

Table 11: Experimental Data for Toluene

Figure 20: Graph of Toluene Amount vs. Log of Peak Areas

Table 12: Experimental Data for Ethylbenzene

Figure 21: Graph of Ethylbenzene Amount vs. Log of Peak Areas

Table 13: Experimental Data for Methylcyclohexane
Figure 22: Graph of Methylcyclohexane Amount vs. Log of Peak Areas

Table 14: Experimental Data for Methyl 1,4 cyclohexadiene

Figure 23: Graph of Methyl 1,4 cyclohexadiene Amount vs. Log of Peak Areas

Table 15: Experimental Data at Different Flow Rates and Time

Figure 24: Graph of the Log Amount Ethylbenzene vs. Peak Area / amount

Table 16: Experimental Data of Ethylbenzene at Split Ratio 1:10

Figure 25: Graph of the Amount of Ethylbenzene vs. Peak Area Intensities of Ethylbenzene at 1:50 and 1:10 Split Ratio at 50 ml/min for 3L of Standard Air

Table 17: Data for Analysis of Ethylbenzene Standard Tube #2

Figure 26: Ethylbenzene Graph for Trials 1&2 Tube #2 from 1 ppmv to 1 ppbv Ranges

Table 18: Data for Analysis of Ethylbenzene Standard Tube #3

Figure 27: Ethylbenzene Graph for Trials 1&2 Tube #3 from 1 ppmv to 1 ppbv ranges

Table 19: Data for Analysis of Ethylbenzene Standard Tube #4

Figure 28: Ethylbenzene Graph for Trials 1&2 Tube #4 from 1ppmv to 1 ppbv Ranges

Table 20: Experimental Data for Final Analysis of Ethylbenzene Standard Tube #4

Figure 29: Graph of Ethylbenzene Amount vs. Area Peak Intensities from 1 ppbv to 5 ppmv Concentration Ranges

Figure 30: Chromatogram of Analytical Air
Figure 31: Analysis of Tube #4 After 10 ppmv Ethylbenzene Standard Analysis

Table 21: Data for Peak Area Intensities at 20 Minutes & After 3 Hours

Figure 32: Chromatogram of 1 ppbv, Tube #4 Trial 5 for Newly Prepared Standard

Figure 33: Chromatogram of 1 ppbv, Tube #4 Trial 5 After 3 hours of Preparation

Table 22: Data for Analysis of 1 ppbv Ethylbenzene Standard Using Tube #4
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STATEMENT OF ORIGINALITY

I declare that to the best of my knowledge the work presented in this thesis is original except as acknowledged in the text, and that the material has not been submitted, either in whole or in part, for another degree at this or any other university.

Signed: .................................Lilian De Torres

Date:
GLOSSARY

BTV- breakthrough volume; the volume of carrier gas that may be passed through a trap before a particular analyte leaves the other end of the sorbent bed

CAR- Carboxen fibre; a type of sorbent material

CW/DVB- Carbowax/ divinyl benzene fibre; a type of sorbent material

EPA- Environmental Protection Agency; the government agency designed to provide data and technical support for solving environmental problems today and to build scientific knowledge necessary to manage our ecological resources wisely.

DERM- Department of Environment and Resource Management; formerly EPA

GC/FID- gas chromatograph/ flame ionisation detector

GC/MS- gas chromatograph/ mass spectrometer

HRGC- high resolution gas chromatography

KH- Henry’s Law constants; the ratio of a compound’s abundance in the gas phase to that in the aqueous phase at equilibrium

MDL- method detection limit; measures the sensitivity of the procedure done by preparing individual sample (n≥7) and analysing each one once.

MPK- methyl propyl ketone; an aromatic ketone

PA- polyacrylate fibre; a type of sorbent material

PDMS- polydimethyl siloxane fibre; a type of sorbent material

ppm - parts per million; a unit of concentration either by weight or by volume. Because the density of a dilute aqueous solution is close to 1.00 g/ml, we frequently equate 1g of H2O with 1 ml of H2O, although this equivalence is only approximate. Therefore, 1ppm corresponds to 1 µg/ml = 1 mg/L and 1 ppb is 1 ng/mL = 1 µg/L. For gases, ppm usually refers to volume rather than mass.

ppmv- parts per million by volume

ppb - parts per billion; a unit of concentration either by weight or by volume

ppbv- parts per billion by volume

POHC’s- principal organic hazardous constituents
PTFE- polytetrafluoroethylene; commonly known as “Teflon”

PTR- MS- Proton transfer mass spectrometer; the instrument used by AIRLABS personnel to measure air emission

QAL- Queensland Alumina; one of the largest alumina refineries in Australia located in the Gladstone Region

SPME- solid phase microextraction; one of the recently develop method of sample introduction in analysing compounds by GC/MS

SVOC - semi volatile organic compounds; also referred to as extractables, because an extraction technique must be used to separate these compounds from water and soil

TD- thermal desorption; extraction of compounds from an adsorbent with the help of a carrier gas at elevated temperature to refocus the compound into the GC column

VOC - volatile organic compounds; generally have boiling points less than 200°C, vapour pressure greater than 0.1 Torr at 25°C and atmospheric pressure

VOST method- volatile organic sampling train; one of the existing EPA methods for measuring VOC’s in ambient air
Chapter 1
Scope and Outline of Thesis

1.1 Introduction

Volatile organic compounds (VOC) are an issue of major concern for many scientists worldwide, being active in different disciplines such as food, flavour and fragrances, medical, pharmaceutical and forensic sciences, and particularly environmental sciences. The latter is mainly because of the growing awareness of the impact of VOC on both human health and global environment. Both VOC and their degradation products may be important in the epidemiology of respiratory disorders and cancer. VOC contribute to major environmental problems such as global warming, stratospheric ozone depletion, photochemical ozone formation and odour nuisance.

Air quality protocols and the methods for air quality monitoring are relatively well developed, however little work has been done to directly quantify volatile organic emissions and odour nuisance in industrial regions. The Gladstone Region, Australia’s port city to the world is surrounded by global industrial companies which are the big contributors to greenhouse gas emissions. Global alumina plants like Rio Tinto Yarwun and Queensland Alumina, Boyne Smelter, Cement Australia, NRG Power Plant and an approved proposal for a Liquefied Natural Gas (LNG) plant are amongst the industrial giants that surround the region. Considered to be one of the most progressive industrial regions there are major
downfalls, the primary focus of which is the community health of the people and workers living in the area.

The most common air pollutants in Gladstone which originate from the local industries are volatile organic compounds (VOC). Besides being associated with environment and health hazard, most VOC are odorous compounds and have been the source of many complaints from Gladstone residents. Odours are often associated with major emotions such as anger, fear or unhappiness (Nimmermark, 2004) but more importantly, some odorous compounds have been associated with cancer and asthma (Parra et al., 2008). Odour complaints remain largely under-investigated in Australian industrial regions while other industrial cities across the world have already made major progresses in identification of odorous compounds (Sironi, 2010)). The only attempt to identify odorous chemicals emitted by alumina refineries was undertaken by Foster et al. in 2005, a work commissioned by the Alumina Industry Air Emissions Forum (AIAEF). Although a first step into identification of odorous compounds in alumina refinery, this study didn’t attempt to quantify the amount of chemicals emitted.

In response to complaints related to the apparently high level of chronic lymphoid leukemia in the Gladstone community, the Environmental Protection Agency (EPA) launched the Clean and Healthy Air Project for Gladstone in 2007. Despite efforts already given to the matter by the EPA, the population concerns and complaints about air quality and odour nuisance continue. Evidently, there is a demand from the population that local, impartial, high-quality, and relevant science regarding the effects of air pollution on health is investigated. Such high quality and impartial research was started at the PELM centre located in
Gladstone in 2008. In collaboration with Airlabs Pty Ltd, CQU decided to do a project regarding the development of a highly sensitive technique for air emission analysis which can be use in the Gladstone industries.

**Figure 1: Thermal Oxidiser Flow Path in Queensland Alumina**

Ever since an existing odour problem is found in the digestion/evaporation area of alumina refineries. The odour is caused by the organics that are part of the bauxite, being broken down and then released into the atmosphere. In Queensland Alumina (QAL), the thermal oxidiser is currently in use to minimise these odours through incineration. The methods currently use by AIRLABS Environmental Pty Ltd using the PTR-MS (proton transfer mass spectrometer) target the odorous compounds mainly.

The PELM Centre (Process Engineering & Light Metal Centre) of CQU Australia, Gladstone campus and AIRLABS Environmental Pty Ltd has the expertise and the suite of instruments required for the development of the method.
of characterisation of the VOC. The researcher uses the GCMS (gas chromatograph/mass spectrometer) instrument for separation and detection of compounds. The GCMS was modified by attaching a purge & trap concentrator to increase detection of VOC in parts per billion volume to volume concentration (ppbv). A separate thermal desorber kit had been placed in the purge & trap concentrator making it possible to analyse air standards which were loaded in thermal desorption tubes.

This research discusses the detailed procedures needed to quantify VOC in thermal desorption tubes. Sample collection, external standard calibration, experimental procedures and method validation will be discussed in specific details to provide a comprehensive method of quantifying dilute concentrations of VOC at levels to be expected in alumina refineries.

1.2 Scope of the Research Study

This research describes how a procedure of making external standards to quantify volatile organic compounds in the alumina stack emission was created. It describes how standard and samples are collected in thermal desorption tubes, using Tenax as adsorbent for VOC. It gives the details for setting up laboratory instrumentation for analysing air samples at very dilute concentrations. The Shimadzu 5050 GCMS, purge and trap system and thermal desorption kit connected to each other were used to analyse air standards in lower concentrations (parts per billion by volume). This study attempts to overcome the difficulty of producing air standards of at least 1 ppbv which had been the downfall of many researchers who tried to quantify alumina stack emission. A calibration mixer was constructed in PELM laboratory to produce the standard
compounds in an air matrix. Computations for determination of injection of a precise volume of each VOC to the mixer were shown. It shows how VOC standards were loaded in thermal desorption tubes at constant flow rate with the help of a customised vacuum pump. The next step is the analysis of the standards at different concentrations by the described instrumentation producing a calibration curve that can be used for quantification of each volatile organic compound.

1.3 Aims and Objectives

This research project addresses the development of a sensitive and comprehensive laboratory set-up and method for quantification for very dilute concentration of compounds in the stack emission of alumina refineries in the Gladstone Region. Some alumina manufacturers have made extensive measurements of the composition of the emissions from major emission sources. Complex mixtures of VOCs have been observed from digestion sources, calcinicers and coal- fired boilers (refer to page 7, Table 1). Many of these VOCs are highly odorous and are considered to give rise to the characteristic odours from an alumina refinery. Inorganic gases from combustion sources such as SO$_2$ can also contribute to the refinery odour when emitted from combustion of sulphur fuels but they are present at higher quantifiable concentrations.

The quantification of compounds was done through analyses using a developed thermal desorption GC/MS procedures with compound detection up to the parts per billion range using various sampling enrichment procedures. This method can serve as a reference for quantification of VOC for other industries as well as a reference for further study of odorous stack emissions.
The candidate initially focussed on studying six compounds such as toluene, acetone, p-xylene, methyl 1,4 cyclohexadiene, ethylbenzene and methyldisulfide to developed the method of quantification. These compounds are believed to be emitting strong odours based from Forster’s study and because authentic standards are readily available for these VOCs, they were chosen for the research.
Chapter 2
Overview of Existing Literature

2.1 Introduction

This chapter will give an overview of the past studies done in measuring air emissions. There are studies relating to VOC emissions which provide various techniques, instrumentation and the method done in identification of compounds. Although there is more literature that can be found in qualitative analysis, there is very little literature found in quantifying VOC emissions in stack of alumina plants. Comparison of the different instruments and techniques and the present methods use by DERM (Department of Environment and resource Management) to analyse toxic air compounds will be presented.

2.2 Literature on Air Emissions

A study conducted in 2002 by Pacific Air and Environment on Air Quality Assessment for Alcan Gove Alumina Refinery revealed that the following VOC emissions were observed in the following locations:

- boilers
- calcinicers
- lime kiln
- digestion blowers
- mills vent
- hydrate vacuum
The table below shows the VOC present in the areas mentioned:

<table>
<thead>
<tr>
<th>VOC</th>
<th>Location</th>
<th>Compound Name</th>
</tr>
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<tbody>
<tr>
<td>benzene</td>
<td>3-methyl 2-butanone</td>
<td>phenols</td>
</tr>
<tr>
<td>toluene</td>
<td>acetophenone</td>
<td>2-cyclopentene-1,2 methyl</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>Diethyl phthalate</td>
<td>2-cyclopentene- 1,3,4 dimethyl</td>
</tr>
<tr>
<td>xylene</td>
<td>isophrone</td>
<td>3-hydroxy-3-methyl-2-butanone</td>
</tr>
<tr>
<td>dimethylsulfide</td>
<td>2-methyl naphthalene</td>
<td>4-hydroxy-4-methyl-2-pentanone</td>
</tr>
<tr>
<td>methyl butane</td>
<td>2-picolene</td>
<td>nonane</td>
</tr>
<tr>
<td>2,3- dimethylpentane</td>
<td>pyridine</td>
<td>2-butanone</td>
</tr>
<tr>
<td>methyl cyclopentane</td>
<td>benzyl alcohol</td>
<td>acetaldehyde</td>
</tr>
<tr>
<td>hexane</td>
<td>alkyl phenols</td>
<td>acetone</td>
</tr>
<tr>
<td>acrolein</td>
<td>benzaldehyde</td>
<td>butanal</td>
</tr>
<tr>
<td>butenal</td>
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</table>

(Pacific Air & Environment, 2004)

An emission estimation technique manual was also drafted by the same company for estimating emissions for alumina refining industry (Pacific Air & Environment, 1999). Though these results were based on the total air quality assessment, the primary focus of this research was on stack emissions and some compounds mentioned earlier may not be relevant to this study, as each alumina refinery is
different but it gives an appropriate indication of some compounds that are expected
to be detected.

Alcoa World Alumina in Western Australia has undertaken a comprehensive air
emission programme to characterise and quantify the total emissions produce from
Bayer refining, with particular attention to their odour properties in 2004 (Coffey,
2004). The method they used for identifying VOC (volatile organic compounds) is
the VOST method (volatile organic sampling train) from stationary sources, this
method is one of the existing EPA (Environmental Protection Agency) methodology
for identifying VOC from ambient air. It will be discuss later in this chapter.
Combination of other methodologies had been used to identify all other emissions.

In the paper “Advances in Assessment of Odours in Alumina Refining”, Peter
Forster tentatively identified 80 VOC’s produced from the stack of Worsely
Alumina’s digestion heater and calcinicer. (Forster et al., 2005). He had also given
each compound’s odour description and odour intensities using an olfactometry
detector outlet. However he had not quantified the compounds due to the
unavailability of producing all standard compounds for calibration and some
compounds shows very low peak detection in the instrumentation used. In fact, until
this time no one had been able to quantify the compounds in alumina stack emission.
Optimisation of the methodologies and instrumentation used is required to identify
odorous components using authentic reference standards. In an air quality review for
Wagerup Alumina by CSIRO in 2004, it was concluded that compounds detected in
the samples collected within the Yarloop community; 3 kilometres away from the
refinery were at concentrations well below odour thresholds reported in the literature.
This suggests that the compounds causing the odour complaints in the community
are either not targeted in the sampling and analysis methods used and the detection limits were not adequate to detect compounds having very low odour thresholds. In spite of the number of studies undertaken, it has proven to be difficult to identify and quantify the causes of the community complaints about air pollution from the Wagerup Refinery (CSIRO, 2004).

A chromatogram gives us a single piece of information about the number of components in the sample (the retention time). This limitation has been overcome by linking chromatographic columns directly with ultraviolet, infrared, and mass spectrometers which results in identifying the components of complex mixtures. A chromatogram also provides evidence of the absence of a compound.

As emphasized earlier proper sample collection is one of the most important parts of data analysis. Emission analyses are based on the assumption that a sample obtained at a given point is a representative of the real composition of this emission on site. If this assumption is wrong, then it is a serious problem. If samples are to retain representativeness, gaseous analytes must be non-reactive with filters or any sample container surfaces and that these containers must also be free from contamination with any interfering substance.

Sorbent sampling is a very important and useful technique when used with appropriate control however we should be aware that if improperly done there will be contamination, interferences and recovery efficiency problems. Volatile compounds may also breakthrough before the completion of sample collection and this will eventually cause errors when quantifying. So it is important to take into consideration the breakthrough volume of a certain adsorbent material with regards
to the target compounds or to use a combination of adsorbent materials to prevent the breakthrough of some compounds.

Solid adsorbents are commonly used for collection of volatile and semi-volatile organic compounds (VOC and SVOC). There are three categories of solid sorbents namely organic polymeric sorbents, inorganic sorbents and carbon sorbents. When choosing sorbents for analysis the capture properties and the recovery process must always be considered.

In sample collection of VOC, the elimination of ozone and nitrogen oxides is necessary so that reactions in sample containers will not take place. Ambient air samples are usually collected in electro polished steel canisters about 6 and 15 litres capacity to prevent decomposition of organic compounds. These canisters are evacuated in advance, filled with air or pressurised using inert interior surfaces pumps.

An alternative container for collecting whole air samples are tedlar / teflon bags which must be checked for leaks before usage. Like the canisters these sample bags are also filled with samples using pumps with inert interior surfaces or indirect pumping. Using indirect pumping, the deflated bag is placed in an airtight container which is then evacuated; the bag then fills as it expands in the container.

Condensation of VOC from air into a cryogenic trap is a good alternative to sorbent sampling. It collects and measures a wide range of organic compounds, greatly reduces contamination of the analytes and recoveries are more consistent.

The Department of Environment and Resource Management (DERM) formerly called EPA is a government agency in charge of protecting the State’s land, air and
water resources. Under a mandate of national environmental laws, the agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life.

There are several EPA methods used for analysing VOC in ambient air. For deciding which method is applicable and the modifications required for optimisation producing the best qualitative and quantitative results for this research it is good to have a good understanding of the present existing procedures for analyses, which is summarised below (Keith et al., 1995; U.S. EPA, 1999).

Table 2: Existing EPA Methodologies of Sample Collection for Volatile Organic Compounds Using Gas Chromatography

<table>
<thead>
<tr>
<th>Method</th>
<th>Method of Sample collection</th>
<th>Detectable compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA Method TO-1</td>
<td>Tenax loaded cartridges undergoes thermal desorption in a TD unit and analyse by GC/MS</td>
<td>Volatile non polar organics with boiling points from 80-200°C</td>
</tr>
<tr>
<td>EPA Method TO-2</td>
<td>Carbon molecular sieve (CMS) cartridges undergoes thermal desorption and analyse by GC/MS</td>
<td>Non polar &amp; non reactive organics with boiling points from -15 to 120°C</td>
</tr>
<tr>
<td>EPA Method TO-3</td>
<td>Cryogenic trap with glass beads submerge in liquid N2 or Ar, heated and analyse by GC/FID and/or ECD</td>
<td>Non polar VOC with boiling points from -10 to 200°C</td>
</tr>
<tr>
<td>EPA Method TO 14-A</td>
<td>stainless steel canisters, concentrated with a cryogen trap and analyse by GC/FID/ECD or GC/MS detection</td>
<td>Non polar VOC</td>
</tr>
<tr>
<td>EPA Method TO-15</td>
<td>Canister with sorbent trap, refocused on a second trap and analyse by GC/MS</td>
<td>Polar and non polar VOC</td>
</tr>
<tr>
<td>------------------</td>
<td>--------------------------------------------------------------------------------</td>
<td>------------------------</td>
</tr>
<tr>
<td>EPA Method TO-17</td>
<td>Multi-bed adsorbent tube undergoes thermal desorption and analyse by GC/MS</td>
<td>Polar and non polar VOC</td>
</tr>
</tbody>
</table>

### 2.2.1 Summary of Existing Methods for Analysis of VOC

- **EPA Method TO-1: VOC In Ambient Air Using Tenax and GCMS**

  Method TO-1 is used to collect and determine volatile, non-polar organics (aromatic hydrocarbons, chlorinated hydrocarbons) that can be adsorbed on Tenax and then undergo thermal desorption. This method is useful for compounds having a boiling point range of 80-200 °C.

  Samples are being collected through cartridges containing 1-2 g of Tenax. Tenax is an organic polymeric adsorbent which is widely used in sampling air for organic compounds. It has low affinity for water and a high thermal stability, which permits the thermal desorption of collected volatile materials. The cartridge is purged with an inert gas into a gas chromatograph and detected by a mass spectrometer. Increases in temperature are programmed into the GC and compounds are eluted in the capillary column in order of increasing boiling points. The MS is used for identification and quantification of compounds by mass fragmentation patterns using a programmed library on the basis of each compound’s retention time and mass spectra.
EPA Method TO-2: VOC in Ambient Air by Carbon Molecular Sieves and GCMS

Method TO-2 is used for collection and determination of compounds which are highly volatile and non-polar (examples are vinyl chloride, vinylidene chloride, benzene and toluene) that can be adsorbed on carbon molecular sieve and then thermally desorbed. It is useful for compounds having a boiling point range of -15 to 120 °C.

Samples are drawn into a cartridge containing 0.4 g of a carbon molecular sieve (CMS). The cartridge is flushed with dry air to remove absorbed moisture. The sample is purged with helium while heating the cartridge to 350-400 °C. The desorbed compounds are collected in a cryogenic trap and flash evaporated into the GC and detected by a mass spectrometer. Increases in temperature are programmed into the GC and compounds are eluted in the capillary column according to increasing boiling points. The MS is used for the identification and quantification of compounds by mass fragmentation patterns using an accomplished library on the basis of each compound’s retention time and mass spectra.

EPA Method TO-3: VOC in Ambient Air Using Cryogenic Preconcentration Techniques and Gas chromatography with Flame Ionization and Electron Capture Detection

Method TO-3 involves the in situ collection of VOC having boiling points in the range of -10°C to 200°C in a cryogenic trap constructed of copper tubing packed with glass beads. The collection trap is submerged in either liquid
nitrogen or liquid argon. With the sampling valve in the fill position, an air sample is loaded into the valve by a volume measuring instrument. Meanwhile, the GC column oven is cooled at sub ambient temperature (-50°C) for sample analysis. When sample collection is completed, the valve is switched so that the carrier gas sweeps the VOC in the trap into the head of the cooled GC column. The liquid cryogen is removed and the trap is heated to assist the sample transfer process. Component peaks eluting from the column are identified and quantified using flame ionization and/or electron capture detector.

- **EPA Method TO-14A: VOC in Ambient Air by Canister Sampling and HRGC**

Method TO-14 is used for determination of semi-volatile and volatile organic compounds in ambient air. Pressurised sample canisters can be placed above or below atmospheric pressure and detected at ppb level.

Samples are collected through a sampling train into a pre-evacuated sample SUMMA canister. The canister is then attached to the analytical system. Water vapour is reduced in the gas stream by a Nafion dryer. VOC are then concentrated into a cryogenically cooled trap. The cryogen is then removed and the sample is delivered into a HRGC (high resolution gas chromatograph) with a raised temperature high enough to volatilise the samples and eluted from the column in order of increasing boiling points into your choice of detector.
- **EPA Method TO-15: VOC in Air Collected in Specially Prepared Canisters and Analysed by GC/MS**

The atmosphere is sampled by introduction of air into a specially prepared stainless steel canister. Both sub atmospheric and pressurised sampling modes use an initially evacuated canister. A pump ventilated sampling line is used during sample collection with most commercially available samplers. Pressurised sampling requires an additional pump to provide positive pressure to the sample canister. A sample of air is drawn through a sampling train comprised of components that regulate the rate and duration of sampling into a pre evacuated and passivated canister.

For sample analysis, a known volume of sample is directed from the canister through a solid multisorbent concentrator. A portion of the water vapour in the sample breaks through the concentrator during sampling to a degree dependent on the multisorbent composition, duration of sampling and other factors. Dry purging the sample with helium reduces water content whilst retaining the target compounds. The VOC are then thermally desorbed with the help of a stream of helium gas, focused in a secondary multisorbent trap and then released by thermal desorption and carried into the GC for analysis.

- **EPA Method TO-17: VOC in Ambient Air Using Active Sampling in Sorbent Tubes**

The procedure for this method involves pulling a volume of air through a sorbent packing to collect VOC followed by thermal desorption- capillary GC/MS analysis.
The method involves the selection of an adsorbent or adsorbent mix tailored for a target compound list, data quality objectives and sampling environment. The sorbent tube is dry purge with helium before analysis to remove water vapour and air. It is then thermally desorbed and analytes are refocused on a secondary trap. The analytes are then rapidly desorbed, injected/transfer to a high resolution capillary GC for analysis.

- **Solid Phase Micro extraction (SPME)**

An ideal approach to sample isolation and analysis that will produce an analytical sample that is identical to chemical composition of the matrix, free of solvents and other impurities and can be completed in a few minutes with no intermediate processing of the sample is the solid phase micro extraction.

Solid Phase Micro extraction (SPME) is a new technique for fast solventless extraction of volatile and semi-volatile organic compounds. The technique is relatively independent of the sample matrix; liquids, solids and gas can be sampled readily. This is an equilibrium technique that is done under carefully controlled conditions to obtain accurate quantification. R. Marsili comments that “*the incorporation of an internal standard into the matrix and adherence to specific sampling times will usually result in excellent quantitative correlations*” (Marsili, 2007).
The SPME Device

R. Marsili gives the complete information of the SPME device in both his two books, “Techniques for Analysing Food Aroma” and “Flavour, Fragrance and Odour Analysis”.

“Figure 2 shows the apparatus introduced by Supelco (Bellefonte, PA) for manual injections. Varian 8100 and 8200 CX series GC auto samplers are designed for automated techniques. The manual device is a modified syringe having a spring loaded plunger and a barrel with a detent to allow the plunger to be held in extended position during the extraction phase and during the injection/desorption period. Also contained within the barrel is a modified 24 gauge stainless steel needle, which encloses another length of stainless steel..."
tubing, fitted tightly to a short piece of solid core fused silica fibre. The bottom centimetre of the fused silica fibre is coated with a thin film of any several stationary phases. The film serves as the organic solvent during the absorption of the volatile compounds from the analytical matrix. The needle functions to puncture the septa sealing both the sample container and the GC injection port and to protect the fragile fused silica fibre during storage and use”. (Marsili, 2007)

Solid phase microextraction has been observed in detail in recent years and man applications had been reported. It is a phase distribution theory in which the amount extracted depends on the partition coefficient between the sample solution and the fibre. There is an immediate concern that the fibre volume is small, that the target analytes are often not completely extracted. However, a representative sample is obtained that can be compared with the extraction of a standard solution. The biggest advantage of the method is that no solvent is needed to completely separate the sample from the fibre. The disadvantage is that though the fibre is protected when out of the sample, it is very fragile and can still be damage by a build up of in-volatile materials from the samples. The extraction process can be very slow because it relies on sufficient diffusion to bring the target compounds into the location of the fibre and good reproducibility requires that equilibrium is established (Smith, 2003).

An interesting study of waste gas from a fat refinery by Kleeberg (Kleeberg et al., 2005), uses the SPME technique in identifying odorous emissions. Bags made of polyterephatalic ester (Nalophan ®) were used for sample collection. They tested the properties of the different fibre types (polyacrylate (PA), polydimethylsiloxane
(PDMS), carbowax/divinylbenzene (CAR/DVB), polydimethylsiloxane/divinylbenzene (PDMS/DVB), carbowax/polydimethyl siloxane (CAR/PDMS) by piercing the sample bag with the SPME needle and exposing the fibre to the sample for a given time (3-30 min.) at ambient temperature. The fibre was then retracted into the needle and was introduced to the gas chromatograph injection port and was thermally desorbed for 1-5 minutes, then transferred to the GC column for analysis. The identity of the compounds present was identified by using reference standards, using the mass spectra library and by the description of odour properties and literature comparison. The method had also been use for the determination of compounds present in a fire scene for qualitative analysis (Hook et al., 2002).

Gorlo had done a specific calibration procedure for solid phase micro extraction of organic vapours in air since SPME is an equilibrium method and analytical methodologies based on it require calibration. The most reliable calibration approach would be to subject standard gaseous mixtures of precisely and accurately known analyte concentration to the complete analytical procedure identical to the procedure for a real sample (Gorlo et al., 1997).

The study is based on permeation of vapours of volatile organic compounds through membranes which are mainly PTFE, polyethylene and silicon rubber into a stream of diluting gas. The apparatus for generation of gaseous standard mixtures is compose of purifier, drier, three generators, preliminary mixing chamber, Teflon 3-way valve, thermostatic mixing glass chamber, glass 3-way valve, flow meter, rotameter and suction pump. The membrane of the mixing chamber is pierced with the SPME syringe, the fibre is taken out from the needle and exposed to a standard mixture for a given time and then withdrawn into the needle, in which the tip is immediately
closed by piercing it into a silicone septum to prevent the sample from desorption. The needle is immediately introduced into the gas chromatograph with the fibre extended from the syringe for 20 s and later on transferred to the GC column by the carrier gas.

Another study conducted by Mingyu Jia and Co. uses SPME for the quantification of VOC in indoor air. Calibration curves for the target VOC were determined with selected SPME fibres. A standard gas generating device with a flow through sampling chamber (figure 3) was made to provide a wide range of target VOC concentrations at constant temperatures.

(Figure taken from Jia et al., 2000)

**Figure 3: Schematic Diagram of Standard Gas Generator System**

Standard gases were produced with the use of NIST (National Institute of Standard and Technology) traceable certified permeation tubes. Ultra high purity air was supplied from a Whatman air generator and maintained at 50 psi head pressure. The permeation tubes were supported inside a glass permeation tube holder and maintained with the constant flow of dilution air. The holder was incubated inside a heated, cylindrical oven made of aluminium which is operated with an electronic heat control device. The airflow rate was controlled by two sidetrack mass flow
controllers which can be found on both the primary and dilution hoops in the system. Actual air flow rate was measured using a gas flow calibrator. Wide ranges of concentration for target VOC were generated by adjusting both the airflow rate and the permeation tube incubating temperature. Air samples were collected from the specially constructed sampling chamber downstream from the standard gas generator. (Jia et al., 2000).

Studies showed that the method detection limits (MDL) of the method described were in the lower parts per billion (ppb) ranges. In estimation of the MDL, a stationary source of target VOC standard gas was produced in a 1 litre glass bulb with two stopcocks and half-hole-type septa. 1 µl of a diluted VOC standard solution was placed into the air sampling valve and was left to evaporate for one hour at room temperature. 65 µm PDMS/DVB fibres were exposed for 1 minute and samples was analysed into the GC.

In 2005 Matz developed a new method for on-site measurement of odorous compounds specifically aerosol bound chemical compounds. Odorous compounds in the waste gases produced by the food industry were analysed based on high volume aerosol sampling techniques, enrichment on solid phase micro extraction cartridges and thermal desorption using GCMS. A dehumidifier with a closed sampling path was designed for flow controlled sampling. Quantification is done with the help of a standard generator, which generates a specified amount of sample mixture during sampling time. The compounds were injected with a specially designed thermal desorption injector and a new gas detector array was designed and used as a detector. This kind of detector was also used in the study to measure the odour pattern of industrial emissions in order to create an odour
pattern database. Future work will study if this pattern can be used to characterise a particular industrial source based on measured emissions (Matz et al., 2005).

The table below gives you the advantages and disadvantages of different sampling procedures conducted by different authors which was discussed earlier (the SPME method) and will be discuss on the next pages.

**Table 3: Summary of Sampling Procedures Base on Several Studies**

<table>
<thead>
<tr>
<th>Method</th>
<th>Author</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPME</td>
<td>R. Marsili, Kleeberg, Gorlo, Mingyu, J.</td>
<td>Solvent less; fast extraction</td>
<td>Fibre volume for extracting analytes is small, concerns are raised that the target compounds are not completely extracted. Difficulties in quantification</td>
</tr>
<tr>
<td>Canister</td>
<td>Zielinska, 1995</td>
<td></td>
<td>Hydrocarbons &gt;C10 could not be recovered. Age, history, sample storage temperature &amp; cleaning procedures may affect sample stability</td>
</tr>
<tr>
<td>Canister</td>
<td>Dewulf, 1999</td>
<td>Allows one to analyse a single collected sample several times</td>
<td></td>
</tr>
<tr>
<td>Canister</td>
<td>Colon, 2001</td>
<td></td>
<td>Requires hybrid equipment for its cleaning procedures</td>
</tr>
<tr>
<td>sorbent sampling PDMS</td>
<td>Dewulf, 1999</td>
<td>Low water retention and less interference</td>
<td></td>
</tr>
<tr>
<td>Sorbent sampling/thermal desorption Tenax</td>
<td>Matz, 1996</td>
<td>Hydrophobic material so water is not absorb during injection</td>
<td></td>
</tr>
</tbody>
</table>
Characteristics of an ideal sorbent for sample collection:

- Infinite breakthrough volume particularly for target compounds
- Complete desorption of target compounds at moderate temperature
- No generation of artefacts
- No retention of water vapour

Earlier studies for VOC up to C20, emitted from motor vehicles from 1993 to 1995 by Zielinska reveal that the non-methane hydrocarbon range that can be reliably quantified from canisters extends from C2 to C10 hydrocarbons (Zielinska et al., 1995). Hydrocarbons greater than the C10 range could not be recovered quantitatively using canister sampling technique. The canister’s age, history, sample storage temperature, cleaning procedures, etc., may affect the sample stability during storage. Storage losses in the C5 to C9 region in canisters were assessed and demonstrated to occur.

C8 to C20 range hydrocarbons seem to be more stable in Tenax cartridges upon storage. Tenax cartridges should be capped tightly right after sampling, preferably with clean Swagelock caps with graphite/vesper ferrules, stored in the freezer, packed in metal containers with activated charcoal on the bottom. The use of Nafion dryer lowers the analytes concentration and may introduce contaminants so
the researchers said, it is not recommendable. The canister method alone is not recommended for sampling hydrocarbons in the range of C10-C20.

Dewulf expressed that the most widely applied pre concentration techniques are the sorbent sampling, cryogenic sampling and canister sampling. He said that “the major advantage of canister sampling is that it allows one to analyse a single collected sample several times, which is not the case for a cryogenically collected or adsorbed sample” (Dewulf et al., 1999). However, canister sampling should require hybrid equipment for its cleaning procedures. Colon (Colon et al., 2001), discusses the detailed method in canister sampling where repeated flushing and evacuation at 100°C using an automated canister cleaning system. Before shipping the tubes were pre conditioned for 15 minutes at 350°C in highly purified helium gas for removal of impurities and later sealed with brass Swagelok fittings and teflon ferrules. The canister tubes were individually wrapped with aluminium cans filled with cushioning material to prevent breakage before and after sample collection, when transporting.

The cleaning and shipping procedures for canister sampling done by Colon for analysing VOC in automotive emissions shows that this technique involves high cost procedures which may not be practical (Colon et al., 2001).

PDMS (polydimethylsiloxane) adsorbent is a type of sorbent based on adsorption process (Dewulf et al., 1999). It has low water retention and the degradation products of the polymer are usually not compounds to be detected in the sampling of ambient air. Information about sorption equilibrium of this material is found in the Kovats indices (estimates for gas/polymer equilibrium coefficients).
A study of GCMS analysis of hazardous compound emissions from fire and chemical accidents have been conducted by Matz using Tenax as an adsorbent for sampling combustion environments with high humidity levels (Matz et al., 1996). Because of the low breakthrough volume of water in Tenax, the absolute amount of water adsorbed is kept low and does not absorb injection. The adsorbent tubes are stored in metal cartridges with Teflon seals and Swagelok fittings on both sides (see next figure).

(Figure taken from Matz et al., 1996)

**Figure 4: Enrichment and Injection of Gaseous Samples Using Tenax®**

Internal standards are spiked onto the adsorbent by injection of 5 µl methanolic solution (d6-benzene, d8-toluene, d10-oxylene, d8-naphthalene at 500 ng each) to the glass wool in front of the adsorbent layer. The evaporating compounds are pumped at the rate of 40 ml/min through the adsorbent by a hand pump with a flow restrictor. For sampling, the cartridges are connected to the hand pump and 100 ml of air is sucked through the adsorbent. The glass tube is then taken out of the cartridge and inserted into the thermal desorber and heated for 30 sec. at 240°C in the stop flow
carrier gas supply mode. Then the column flow started to perform the injection and was terminated after 15 sec. by a counter current gas flow and the GCMS run is started (Matz et al., 1996)

In 2001 Jia-Lin Wang and Wei-Li-Chen studied the determination of dissolved volatile organic compounds in aqueous samples. They use an automated purge and trap chromatographic system with full automation capability using self developed hardware and software. The use of a small bore multi-bed carbon based sorbent trap avoided the use of cryogen for pre concentration and at the same time eliminated water interference. The use of a multi sorbent bed quantitatively captured a large range of volatile organic compounds at ambient temperature. Flash heating for fast desorption and accurate plumbing for minimising dead volume resulted in a high resolution chromatographic separation at temperatures above ambient which eliminated cryogenic cooling. A method for validating the system’s linearity for extremely volatile compounds was developed (Wang et al., 2001).

Nobuo Ochiai uses a three-stage cryogenic trapping pre concentration system for the analysis of volatile sulphur compounds in breath by GCMS. The breath sample was collected in a fused silica lined canister and introduced into the three stage cryogenic trapping pre concentration system. To eliminate the adsorption of the sulphur volatiles onto the interior surface of the sample paths in the three stage cryogenic trapping pre concentration system, a fused silica lined stainless steel tube was also used for all sample paths. After purging the sample using high purity nitrogen, the breath sample was pumped from the canister at the rate of 100 ml/min. The sample were concentrated in a glass bead cryogenic trap, heated at 20°C and transferred by helium to a secondary Tenax® trap held at -30°C. The sample is then back flushed
while heating to focus on a capillary focusing trap for fast injection onto the analytical column (Ochai et al., 2001).

Analysis of the canisters for sampling was also examined in the mentioned study. The effect of the condensed water from the canister for the recoveries of VSC (volatile sulphur compounds) and VOC (volatile organic compounds) from the high humidity sample was observed by spiking 0.2 ml of water prior to the loading of the standard gas mixture in fused silica canisters and SUMMA canisters. The recoveries of the test mixture from the canisters and Henry’s Law constants (KH) are shown in the table below (Ochiai et al., 2001).

In 1999 Manura compared the sensitivity of the headspace technique; purge and trap thermal desorption and direct thermal extraction for volatile organic compounds. In selecting a method of analyses, the selection of a sample collection method and gas chromatography introduction technique depends on a large number of variables. Manura presented a table of variables to be considered when selecting an analysis technique and a table of comparison of the different GC injection techniques. These tables are presented in the next pages (Manura et al., 1999):

<table>
<thead>
<tr>
<th>Compound</th>
<th>Recovery (%)</th>
<th>Recovery (%)</th>
<th>KH (mol/atm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>96</td>
<td>96</td>
<td>0.39</td>
</tr>
<tr>
<td>Chloroform</td>
<td>98</td>
<td>100</td>
<td>0.92</td>
</tr>
<tr>
<td>1,2-Dichloroethane</td>
<td>96</td>
<td>103</td>
<td>0.92</td>
</tr>
<tr>
<td>Benzene</td>
<td>97</td>
<td>102</td>
<td>0.18</td>
</tr>
<tr>
<td>Toluene</td>
<td>93</td>
<td>108</td>
<td>0.15</td>
</tr>
<tr>
<td>1,3 Butadiene</td>
<td>98</td>
<td>102</td>
<td>0.014</td>
</tr>
<tr>
<td>Ethanol</td>
<td>54</td>
<td>42</td>
<td>190</td>
</tr>
<tr>
<td>Isopropanol</td>
<td>38</td>
<td>56</td>
<td>130</td>
</tr>
<tr>
<td>Isobutanol</td>
<td>43</td>
<td>76</td>
<td>110</td>
</tr>
<tr>
<td>Acetone</td>
<td>86</td>
<td>82</td>
<td>26</td>
</tr>
<tr>
<td>Methyl Ethyl Ketone</td>
<td>98</td>
<td>99</td>
<td>2.2</td>
</tr>
<tr>
<td>Methyl Isobutyl</td>
<td>99</td>
<td>99</td>
<td>2.2</td>
</tr>
<tr>
<td>Compound</td>
<td>Value 1</td>
<td>Value 2</td>
<td>Value 3</td>
</tr>
<tr>
<td>------------------------</td>
<td>---------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>97</td>
<td>96</td>
<td>6.5</td>
</tr>
<tr>
<td>Butyl acetate</td>
<td>102</td>
<td>104</td>
<td>3.5</td>
</tr>
<tr>
<td>Diethyl ether</td>
<td>98</td>
<td>92</td>
<td>1.2</td>
</tr>
<tr>
<td>Methyl t-butyl ether</td>
<td>100</td>
<td>100</td>
<td>1.6</td>
</tr>
<tr>
<td>Acrylonitrile</td>
<td>94</td>
<td>94</td>
<td>7.3</td>
</tr>
<tr>
<td>Methanethiol</td>
<td>97</td>
<td>ND</td>
<td>0.39</td>
</tr>
<tr>
<td>Ethanethiol</td>
<td>99</td>
<td>ND</td>
<td>0.28</td>
</tr>
<tr>
<td>Propanethiol</td>
<td>101</td>
<td>ND</td>
<td>0.25</td>
</tr>
<tr>
<td>Butanethiol</td>
<td>102</td>
<td>ND</td>
<td>0.22</td>
</tr>
</tbody>
</table>

(Table Taken from Ochai et al., 2001)

### Variables for Consideration in Selection of Analysis Technique

- Sample matrix (gas, liquid or solid)
- Amount of sample available for analysis
- Concentration of volatiles in sample matrix
- Detection limit of GC detector
- Amount of water in the sample
- Solvents or major interfering compounds
- Thermal stability of analytes
- Lowest range of volatiles desired in analysis
- Highest range of volatiles desired in analysis
- Number of samples to be analysed
- Sample preparation time
- Use and disposal of solvents
- Cost of analysis
Table 5: Comparison of GC Injection Techniques

Due to the low concentrations of analytes, there are samples that can not normally be analyse using solvent desorption. Thermal desorption (TD) is a solvent-free desorption method which works excellently using gas chromatography. TD gives the advantage of lower detection limits, since the sample can be completely transferred to the chromatographic column, thus avoiding the existence of a solvent peak, which can be mistaken as analyte peaks. It also prevents analyte losses by minimizing sample manipulation and risk of contamination due to solvents. One of the main disadvantages of TD is the initial cost of the equipment. This technique is commonly used for volatile chemical analysis to determine VOC in several studies of urban and industrial air, indoor and workplace atmospheres and those influenced by waste emissions (Ras et al., 2008).

A method for thermal desorption for analysis of polar compounds in workplace air was developed using pumped and diffusive sampling. Volatile organic compounds
such as esters, alcohols, ketones and aldehydes are analysed using adsorption tubes filled with solid adsorbents such as Carbosieve SIII, Carboxen 569, Carbopack B and Tenax TA. Analysis was performed by thermal desorption of the analytes from the adsorbent tubes followed by gas chromatography- flame ionisation detection (GC-FID). The method developed can easily be used with both active and passive sampling (Hallama et al., 1998).

Another study for the performance evaluation of adsorbent tube sampling method using a short path thermal desorption for VOC was developed by Peng and Batterman. The study provides a comprehensive performance evaluation of an adsorbent sampling and analysis method using thermal desorption. The evaluation includes an assessment of blank emissions, artefact formation, method detection limit, reproducibility, linearity, desorption efficiency, storage stability and water management effectiveness (Peng, Chiung-Yu et al., 2000).

Later studies conducted by Forster regarding assessment of odours from alumina refining reveals that a combination of cryogenic trapping and adsorbent tube techniques facilitates capture of the widest range of volatiles in odour samples to identify the odorous substances. The samples were collected in Nalophan sampling bags and evaluated using the GC/ MS/ODP (odour detection port) for analysis using three techniques (Forster, 2005). These were:

- Direct injection- samples injected using a gas tight syringe into a split/splitless inlet on the GC. Tested up to 100 ml injection volumes.

- Cryogenic pre concentration- up to 5 L of the odour sample is passed through a U tube immersed in liquid nitrogen at 100 ml/min. The condensed material
was warmed to room temperature and 100 ml of the concentrated headspace gases were injected into the split/splitless inlet of the GC.

- Adsorbent tube pre concentration- up to 6 L of the odour sample was pumped through Tenax and air toxics tubes and thermally desorbed onto the GC column.

The adsorbent tube pre concentration gave significant increases in MS response and odour intensities compared to the direct injection techniques and a moderate increase in responses compared with the cryotrapping technique.

Although the study had identified most of the compounds in the stack emission and their corresponding odour intensities it fails to quantify the absolute concentrations of the odour samples. Optimisations of the methods are needed to quantify the compounds; no attempt had been done to produce calibration standards that will help to identify absolute concentrations. This is one issue that research in this thesis tries to achieve.

2.3 Preparation of Standards

An important step in quantitative analysis is the conversion of the size of the chromatographic peak into some measure relating to the quantity of the particular compound of interest. Normally this involves chromatographically analysing known amounts of materials and measuring their peak sizes. Then depending on the method used, the composition of the unknown is identified by relating the unknown peaks to be known amounts through peak size. The external standardisation method is the preferred way of preparing standards for the purpose of this research, although in
some cases internal standardisation is necessary. A precise discussion of this method is detailed below.

### 2.3.1 External Standardisation Method

External standardisation involves the preparation of standards that are within the same range of concentrations as the unknowns in the same matrix as the unknown. These standards are then analysed chromatographically under the same conditions as the unknown samples. The relationship between peak size and the composition of one or more components can then be determined, and unknowns are then compared graphically to the standards for analysis.

Standards can be prepared with all the compounds of interest in each standard mixture and the range of composition of the standard mixture must cover the entire range expected in the unknown. The peak area or height is then plotted against its concentration in the matrix. Two conditions should be satisfied in the preparation of the calibration curves namely: 1) any curves should lie in a straight line and 2) they pass through the origin. These conditions imply that under the conditions of analysis and over the concentration range covered, the column has not been overloaded, the detector have not been overloaded, the instrument are responding linearly and there is no compound adsorption in the injection port, column, detector and associated plumbing.

Figure 5 shows a calibration curve for four methyl ketones in an air matrix in which peak heights were used as the size measurement. Five concentration ranges of standards were used and all four components were present in each standard. It should be noted that although a sample blank (with no component of interest present) give a low or zero signal when none is injected, the 0, 0 point is
not plotted. Data points obtained from the calibration curve must come solely from the standards, and these standards should have the expected range of concentration of the real sample components (Grob, 2004). The calibration curve in figure 5 (next page) shows the evidence of linear relationship between analyte and signal.

(Figure taken from Grob R., 2004)

**Figure 5: Calibration Curves for 2-butanone (MEK), 2-pentanone (MPK), 2-hexanone (MnBK), 2-methyl 1,4-pentanone (MiBK).**

Caution should be exercise when injecting samples in a chromatographic column. In any given system, as the amount of component doubles, the peak size will not double; instead there is tendency of column overloading, distorting peak shape and the detector capacity exceeded. So it is always a safe measure to operate using a smaller sample size or by diluting the sample.
Failure of the calibration curve to extrapolate through the origin indicates that there are adsorption problems and/or sample degradation. Problems like these can be avoided by proper sample handling and proper choice of columns. When the two conditions for generating a calibration curve have been met in any given analytical system it is not necessary to regenerate these curves by running ranges of concentration standard frequently.

One of the limitations with external standardisation is that the sample size of the standards and unknowns must be known accurately. The analyst should attempt to make standards and samples similar in concentration when presented to the instrument. This part of the quantification process is time consuming and also the sensitivity of the detector must remain constant from run to run in order to compare results with the calibration curve (Mc Nair, 1969). If there is a slight variation in sample size, the peak size must be corrected to unit sample size for standards before the calibration curve is plotted and for unknowns before the calculation is made. Sample size needs to be entered into the calculations.

An important source of error in the measurement of sample at ppbv level is the reproducibility of conditions. In the system that follows, where a constant volume is injected it is necessary to make up a series of standards of different concentrations. This means that doubling of the sample size results in doubling of the absolute amounts of each component injected into the chromatograph. But it doesn’t mean that the response received from the chromatographic system will also double in the presence of the doubling of amount in the matrix. Sample sizes for all standards and unknowns should be kept the same within the errors of volume measurement.
There are two methods in the preparation of gas standards namely: 1) static gas standards and 2) dynamic gas standards. For the purpose of this research the static gas standard method is used in preparing the primary standards for generating calibration curves because it is simpler.
Chapter 3
Methodological Approach

3.1 Static Gas Standards

All static methods involve mixing of known amounts of gases together in a container. Depending on what kind of equipment is available these amount may be measured by volume or pressure. Challenges are encountered with these mixtures as the concentration of several components approaches concentration ranges from 1 to 100 ppm by volume. Even for gases which are not reactive in nature, reaction and adsorption becomes a real problem.

Pre-treated cylinders have shown promise of overcoming reaction and adsorption of some reaction gases. Assuming that a mixture stays constant in such cylinders in time, the true concentration must still be known. If in case, the mixture does not remain constant, the situation is impossible.

Standards are available today in small pressurised cans that are extremely convenient to use with a gas sampling valve for injection. However laboratories must consider the costs involved in buying these standards and again the reliability of supplier and verification of these standards are a must.

In general laboratory preparation of standard mixtures can be made. The static methods are used only for low concentrations in a matrix gas. Fixed volume containers made from inert materials, capable of being sealed, and having a resealable septum can be used. The volume of the container is obtained by direct measurement of the chamber boundaries. The usual size is on the order of 20 to 40 L, which allows the removal of enough useful gas without causing excessive dilution by
the replacement gas (Lodge, 1988). Means must be provided to facilitate the mixing of the mixture to provide homogeneity; examples are putting a fan blade or a blower inside the container. The container is then continuously flushed with the matrix gas until such time that it can be assumed that the container has matrix gas only. The container is then sealed and a small volume is withdrawn through the septum for GC analysis to ensure that the matrix inside the container is free of any components that is to be added within the error of the needed standard. Failure to perform this simple check can result in many problems and wasted effort.

For gases, a gastight syringe is flushed thoroughly with the component to be added, filled with the needed amount of pure component, and then emptied into the container through the septum. The resulting concentration is the ratio of their volumes.

\[
\%A = \frac{\text{volume } A \text{ added}}{\text{container volume}} \times 100 \quad \text{equation 1}
\]

\[
\text{ppmv } A = \frac{\text{volume } A \text{ added}}{\text{container volume}} \times 10^6 \quad \text{equation 2}
\]

Concentrations are expressed in volume or mole % or parts per million by volume (ppmv), which is the usual method of presenting gas concentrations.

The two major sources of error of this technique come from inadequate mixing and the lack of assurance regarding whether the syringe volume used contained 100% of the desired component. It is very hard to determine when both conditions have been satisfied so one must be extremely overcautious.
A method of preparation that is the one being considered in this research is by injecting a known volume of each of the target volatile in liquid into a fixed container using a micro litre syringe normally used for liquid sample injection into the GC. The density and molecular weight of each target component are needed in the computation:

\[
ppmv_A = \frac{volume_A \times density_A \times 24.25 \times 10^6}{MW_A \times container\ volume}
\]

Where:

- \(volume_A = \mu l\) of A added as a liquid
- \(density_A = \) density of A (g/ml or mg/µl)
- \(24.45 = molar\ volume\ at\ 25°C\ (L/mol\ or\ mL/mmol)\)
- \(and\ 760\ Torr\ (101\ kPa)\)
- \(MW_A =\) molecular weight of A (g/mol of A mg/mmol)
- \(container\ volume =\) volume of container (ml)

It is advisable that the liquid syringe should touch against the side of the container to obtain the final amount of injected liquid off the needle prior to its withdrawal from the container. Contents of the container should be thoroughly mixed to ensure complete liquid evaporation and mixture homogeneity. If the temperature and pressure inside the container differs from 25°C and 760 Torr, then either the container volume must be corrected to these conditions or the molar volume must be corrected to the conditions of the matrix gas. Differences of 3°C or 7 Torr cause a 1% error. The important point to remember is that the volume of the vapour must be at the same temperature and pressure as the matrix gas for computation of a volume ratio such as volume percent or volume part per million.
Figure 6, below is a piston type cylindrical chamber, similar to the one being constructed at PELM laboratory. Calibration mixture is prepared by introducing the contaminant through the inlet as the piston is raised. The inlet is then closed and at least 15 minutes are allowed for mixing.

![Figure 6: Piston Type Cylindrical Chamber](image)

One of the disadvantages of a fixed volume container is that the sample is depleted as withdrawals are made. This dilution will cause a dilution of the standard air, either from small leaks in the container or as the syringe is withdrawn from the sample under reduced pressure. Adsorption with time can cause problems with vapours; the best practice is to prepare the standard with intermittent mixing over a period of 15-30 minutes. The standard should be used in duplicate or triplicate and discard the standard afterwards. These static standards should be used no longer than 1 hour after preparation.
The use of lubricant greases and sealants should be avoided since they tend to absorb the trace contaminants. The use of rubber & plastic tubing, other than PTFE should be avoided as well if that is possible at all. Compressed air should be of the highest quality and a purification process should be done to remove any unwanted contaminants from the system.

Once preparation of the standards finishes then loadings of the standard mixture into thermal desorption tubes should be given emphasis, if pumped sampling will be use to load the standard sample, a defined uniform volume of the standard gas will be sucked through each desorption tube and should be done carefully (Hallama, 1998). The standard and the emission samples are then analyse and run as separate injections at different times; it is a good idea to have the standard and sample analysis run alternately to reduce the effect of any changes in the operating conditions (Raymond, 2007).

The most important thing to remember here is sample amount injected for both standard and unknown sample should be as constant as possible, since every aspect of analysis is dependent on the sample injection amount. It is also necessary that the analysis condition for the standard sample be strictly identical with the analysis conditions for the unknown sample (Shimadzu, 2000).

For the standard the calculation steps are: 1) for each peak to be calculated calculate the amount of component injected from the volume injected and the known composition of the standard; then 2) divide the peak area by the corresponding component weight to obtain the absolute response factor (ARF):

$$\text{ARF} = \frac{A1}{W1} \quad \text{equation 4}$$
For the sample, the calculation step is 1) for each peak, divide the measured area by the absolute response factor to obtain the absolute amount of that component injected:

\[ W_i = \frac{A_i}{ARF} \]

equation 5

3.2 Summary of the Developed Method

The method involves the analyses of standards by using thermal desorption tubes loaded by Tenax and analysed by thermal desorption /GCMS.

Standards were loaded into thermal desorption tubes with 50ml/minute approximate flow rate for one hour. Concentration ranges of standards were 10 ppmv, 5 ppmv, 1ppmv, 100 ppbv, 10 ppbv and 1 ppbv respectively. Though five different aromatic compounds were analysed in the beginning (methylhexane, methyl cyclohexene, 1, 4 methyl cyclohexadiene, p-xylene, ethylbenzene and toluene), in the end the researcher preferred to do the preparation for six concentration ranges of only one compound. The researcher chooses ethylbenzene for standard preparation. Each of the six concentration ranges for the ethylbenzene standard were analysed five times in the same desorption tube. A fresh standard was prepared in every analysis. Duplicate analyses were also performed for five orders of magnitude using three desorption tubes. The data gathered from the analyses of ethylbenzene standards were used to make the calibration curve that is needed for quantification.

Each loaded thermal desorption tube was attached to the purge and trap and a heater block was clamped into the air tube. The purge and trap unit pre purges the air tube at ambient temperature to remove both oxygen and moisture accumulated during sample loading. The tube then heats, causing adsorbed compounds to release from the matrix (thermal desorption) concentrator’s trap. When the sample concentrator’s
trap receives the GC signal, the concentrator’s trap rapidly heats. VOC released from the trap are transferred as a discrete plug to the GC column for separation and analysis. Both standards and samples are subjected to the same analytical procedure throughout. Figure 7 describes the flowchart for loading and analysis of standards and samples.

Figure 7: Flow Chart for Analysis of Standards and Sample
3.3 Instrumentation Set-up

The Shimadzu GCMS series 5050 was the main equipment use in the research.

![Image of Shimadzu GC/MS Series 5050](image)

Figure 8: The Shimadzu GC/MS Series 5050

Earlier experiments reveal that the existing GCMS can detect compounds in 1000 ppmv. There is a need for instrument modification because this is not the instrument detection expectation for this research.

By means of the purge and trap system attachment coupled with an air desorber kit, the instrument was able to do air analysis with detection in lower parts per billion (ppbv). The original set-up for the purge and trap unit is for liquid sample loading.
The researcher made some instrument modifications for it to have the capability of analysing samples from a gaseous matrix.

During analyses of gas standards, the sparge vessel for loading liquid samples and its assembly were taken out and it was replaced by an adsorbent kit with glass desorption tubes loaded with Tenax adsorbent. A heater block assembly was clipped into the tubes; when the instrument receives the GC signal, the heater block will then heat up causing captured VOC in the glass tube to be released and thermally desorbed in a secondary Tenax trap inside the purge and trap system.

Figure 9: The Thermal Desorption Accessory as Attach to the Purge & Trap Concentrator
A calibration mixer was also constructed in the PELM laboratory with a vacuum pump attachment to aid in the loading of compounds in thermal desorption tubes. This was used for data accumulation in the creation of the calibration curve.

Figure 10: The Calibration Mixer Attached to the Vacuum Pump

3.4 Selection of Appropriate Adsorbent

The adsorbent used to capture target VOC combined with thermal desorption should meet the following criteria for valid determination of VOC:

1. High enrichment of the target compounds

2. High level and fast desorption of analytes

3. Surface must be homogenous and inert to minimise artefact formation, irreversible adsorption and catalytic effects during sampling, storage and desorption.

4. Low affinity to water to avoid interferences during GCMS analysis
5. Low adsorption ability for inorganic constituents of air

6. High thermal stability

7. Multiple usability

Although there are a wide range of adsorbents that is commercially available, the researcher decided to use the Tenax (poly-2, 6 -diphenyl -p- phenylene oxide) adsorbent. Tenax is capable of adsorbing a fairly wide range of organic compounds and is especially good with aromatics. It can be heated to relatively high temperatures for desorption and is long lasting.

Tenax showed low water trapping of generally less than 2 to 3 mg water/gram of adsorbent under the highest humidity conditions while other adsorbents like Carboxen 569 and Carbosieve S111 exhibited substantially higher water trapping capacity, with up to 400 mg of water/gram of adsorbent under the highest humidity conditions. (Helmig, 1995, Gawlowski et al., 1999).

Adsorbents use in thermal desorption tubes can be a combination of different kinds. EPA Method TO-17 had presented the different compounds that can be capture on each kind of adsorbent and a study using Carbotrap, Carbopopack X and Carboxen 569 to capture aromatics, alcohol, alkanes, chlorides, esters, ketones, amides, terpenes and isocyanates using the method was done by Ribes et al. (Ribes et al., 2006).

Sunesson, Anna-Lena conducted an evaluation of eight adsorbents for sampling and analysis of microbial volatiles. Tenax, Tenax GR (with 23% graphitised carbon), Chromosorb 102, Carbotrap C, Carbopack B, Anasorb 227, Anasorb 747 and Porasil
were among the adsorbents tested. These adsorbents were tested at 20% and 85% relative humidities at an atmosphere of 50 µg/m³. The criteria for evaluation were:

1) recovery of the test substance, which is dependent on both the adsorption and desorption efficiency of the adsorbent for the specific compound, compared with reference standard compounds in methanol; 2) background disturbance; 3) relative standard deviation. Among the adsorbents tested, Tenax showed the highest % recovery for volatiles like dimethyl sulphide at 103% recovery, toluene at 111% recovery, furfural at 102%, 3- octanone at 101% recovery. Only 2- propanol showed a 46% recovery using Tenax. Carbotrap C is comparable to Tenax for 1-octen-3-ol and compounds with higher boiling points, but obviously has lower adsorption properties than Tenax for the most volatile compounds. Tenax, the most used adsorbent for sampling low amounts of organic compounds in air for analysis using thermal desorption, is known to be inert, thermally stable, unaffected by water, has high storage stability and a low background, but has a low breakthrough volume for compounds under C₆. Tenax is considered to be the adsorbent showing the overall best properties for sampling complex mixtures of volatiles (Sunesson et al., 1995).
CHAPTER 4  
Experimentation  

4.1 Introduction  
This chapter describes all the experimental procedures done in the research from the beginning until the researcher developed the modified instrumental set-up and procedures for quantification. Computations for compound volume injections were discussed. The procedures for loading of samples and standards, calibration and quantification were shown. The final instrumental parameters used in the preparation and analyses of standards were presented.  

4.2 Parameters of the Instrumental Set-up  
For the GCMS method, the injection and interface temperature were set to 200°C in order to vaporise the VOC once it enters the head of the column. The boiling points of the target compounds must be considered in choosing an injection temperature. The injection temperature is advisable to be well above the boiling points of all compounds of interest but never so high that will cause compound deterioration. Ethylbenzene is the standard that had been chosen for experimental study; the compound has a boiling point of 136°C; all other odorous compounds that have been tested have boiling points between of 35 to 140°C therefore 200°C injection and interface temperature is considered a safe parameter. Split injection was used as the control mode to avoid column overloading. The split ratio of 1:50 was used initially for examining detection limits but later on was changed to 1:10 to increase detection levels. To achieve better separation of compounds and to decrease analysis time temperature was programmed from 50°C up to 180°C at a ramping rate. The MS
parameter was set to scan mode to detect the presence of impurities in the system. The mass range (m/z) values were set from 30 to 350.

For the purge & trap system, the sample was pre heated at 1 minute to allow a heated sample to equilibrate to a preset temperature before purging begins. To remove oxygen and excess moisture accumulated during standard preparation the pre purge state was set to 3 minutes. This state also reduces the moisture transferred to the trap. The “purge” state is the extraction state where ultra purity helium passes through the sample at a specified time and temperature and volatiles are adsorbed in the secondary Tenax trap for subsequent desorption to the GC column. The purge was set to 20°C at 11 minutes. During “desorb”, the system trap heats rapidly to the set temperature of 180°C within 4 minutes, transferring volatile compounds to the GC injection port. The last stage which is “bake” was set to 180°C at 20 minutes. This is a clean-up state which back flushes the trap under heat and reverse flow of helium remove and vent any components that was not transferred to the GC column.

The following analytical conditions were used as the final standard parameters for used in analysing the external standards and emission sample using the GCMS.

GCMS Method:

<table>
<thead>
<tr>
<th>PARAMETER</th>
<th>VALUE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection Initial Temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Interface Temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Control Mode</td>
<td>Split injection</td>
</tr>
<tr>
<td>Column Inlet Pressure</td>
<td>100 KPa</td>
</tr>
<tr>
<td>Column Flow</td>
<td>1.7 ml/min</td>
</tr>
<tr>
<td>Linear Velocity</td>
<td>47.4 ml/min</td>
</tr>
<tr>
<td>Split Ratio</td>
<td>10</td>
</tr>
<tr>
<td>-------------</td>
<td>----</td>
</tr>
<tr>
<td>Total Flow</td>
<td>21.7 ml/min</td>
</tr>
</tbody>
</table>

GC Oven Temperature Program

<table>
<thead>
<tr>
<th>Rate</th>
<th>Temperature (°C)</th>
<th>Duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>_</td>
<td>50.0</td>
<td>5.00</td>
</tr>
<tr>
<td>20.0</td>
<td>80.0</td>
<td>3.00</td>
</tr>
<tr>
<td>30.0</td>
<td>120.0</td>
<td>3.00</td>
</tr>
<tr>
<td>40.0</td>
<td>180.0</td>
<td>3.00</td>
</tr>
</tbody>
</table>

MS Parameters:

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<th>Acquisition Mode</th>
<th>Scan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interface Temperature</td>
<td>200 °C</td>
</tr>
<tr>
<td>End Time of scanning</td>
<td>18 min.</td>
</tr>
<tr>
<td>Start m/z</td>
<td>30.00</td>
</tr>
<tr>
<td>End m/z</td>
<td>350.00</td>
</tr>
</tbody>
</table>

Purge & Trap System Analytical Conditions:

<table>
<thead>
<tr>
<th>Instrument State</th>
<th>Temperature (°C)</th>
<th>Time (min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre heat</td>
<td>_</td>
<td>1</td>
</tr>
<tr>
<td>Pre purge</td>
<td>_</td>
<td>3</td>
</tr>
<tr>
<td>Purge set</td>
<td>20</td>
<td>11</td>
</tr>
<tr>
<td>Desorb</td>
<td>180</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Bake</td>
<td>Valve Oven</td>
</tr>
<tr>
<td>-------------------------</td>
<td>------</td>
<td>------------</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

4.3 **Experiments on GCMS Linearity Using Ethanol as Solvent**

The first experiments were conducted to test the GCMS capability to detect liquid aromatic and aliphatic hydrocarbons. Standard mixtures of acetone, methylpropylketone and toluene in ethanol were directly injected to the GCMS at 5000 ppmv (parts per million by volume), 2500 ppmv and 1000 ppmv. Results of the experiments were discussed in section 5.2.

4.4 **Experiments on O.I. Purge & Trap Sample Concentrator for Liquid VOC**

The purge and trap sample concentrator was connected to the GCMS to increase detection levels. Experiment was conducted to know the capability of the O.I. analytical purge & trap sample concentrator to detect trace contaminants. Three liquid VOC were tested namely; toluene, acetone and xylene. Decreasing volume of each VOC was diluted in distilled water to test the sensitivity of the purge & trap sample concentrator. Note that in using the purge and trap apparatus alcohols cannot be used as a solvent because it will produce peaks that will swamp all the other trace contaminants; instead distilled water is used as the solvent. The inside trap of the concentrator consisted of activated charcoal/ Tenax and silica gel but these trap materials are not suitable for thermal desorption, and so the trap has been changed to Tenax alone. Mixtures of standard solutions were prepared with concentrations of...
500 ppmv, 100 ppmv (5 µl VOC/ 50 ml solution), 20 ppmv, 10 ppmv (1 µl VOC/ 100 ml solution), 1 ppmv, 100 ppbv and 10 ppbv each of toluene, acetone and xylene in distilled water.

Another set of experiments was done on compounds like toluene, p-xylene, methyl 1,4 cyclohexadiene, ethylbenzene and methyldisulfide to see their response using the purge & trap sample concentrator. Different concentrations were prepared in distilled water. Duplicate experiments were conducted. Results of the experiments were discussed in section 5.5.

4.5 Experiments with Standard Air Samples

After all instrumentation modifications the modified set-up was tested for its ability to recover gas mixtures. A calibration mixer was made up of polyurethane cylindrical container with a piston for loading analytical air was constructed in the PELM laboratory to aid in making air mixtures fortified with standards at known concentrations. The following procedures were used for injecting standards into the mixer and for preparation of the calibration curve:

1. The calibration mixer was emptied by means of pushing the piston handle until all remaining air inside the cylinder has gone out through a small opening at the opposite side.

2. The valve of the analytical air cylinder was opened; then the air regulator was also opened until a sound of air coming through can be heard as the piston slowly goes back to its original position as the cylinder is filled up with analytical air.
3. When the piston handle is already near its original position, the piston was adjusted by rotating the handle clockwise or counter-clockwise so that the screws can fit into the holes at the bottom part of the mixer. The plastic caps (3 pieces) were put to closed the system.

4. The air regulator and the valve of the analytical air bottle were turned off.

5. The liquid volatile was carefully injected by means of a GC microlitre syringe through a rubber septa into the teflon dish inside the cylinder.

6. The fan regulator was turned on and a 15 minutes wait time allows the volatile to evaporate and mix completely with air inside the cylinder.

7. The fan regulator was then turned off and the researcher waited for further 5 minutes to settle the condition inside the cylinder.

8. The polyethylene bag was connected into one end of the cylinder. The black plastic caps were unscrewed and the handle of the cylinder was pushed until all analytical air inside the cylinder was transferred into the plastic bag.

9. The bag was then connected to the adsorbent tube, and the sampling end of the adsorbent tube was connected to the vacuum pump. The vacuum pump was turned on and the correct time was recorded.

10. The flow rate was adjusted to stabilise at 50 ml/minute using the adjustment screw located beside the flow rate monitor.

11. Air collection was stopped after an hour by turning the vacuum pump off.
12. The adsorbent tube was disconnected from the vacuum pump and was immediately put in its container with teflon seals on both sides.

13. The loaded adsorbent tube was connected into the purge & trap unit and then analysed using the analytical conditions specified in section 4.2.

14. The whole procedures were repeated for 6 concentration ranges. The data points obtained from the six concentration ranges were plotted (concentration or amount vs. peak area). The resulting graph served as the standard calibration curve.

In the final experiment the method described above was repeated five times for each standard concentration for method validation. Preparation of fresh standard was done in every trial. After every standard analysis, the adsorbent tubes are analysed again to check for memory effects.

The required volume of compound to be injected into the calibration mixer is determined by the formula:

\[
ppmv \ A = \frac{volume \ A \times density \ A \times 24.25 \times 10^6}{MW_A \times container \ volume}
\]

Where: 

\[
ppmv \ A \ = \ \text{parts per million by volume concentration of the resulting mixture}
\]

\[
volume \ A = \ \text{volume of A added as a liquid (µl)}
\]

\[
density \ A = \ \text{density of A (g/ml or mg/µl)}
\]

\[
24.45 = \ \text{molar volume at 25°C (L/mol or ml/mmol)}
\]
and 760 Torr (101 kPa)

\[ MW_A = \text{molecular weight of A (g/mol of A mg/mmol)} \]

\[ \text{container volume} = \text{volume of container (ml)} \]

Six odorous gases which comprise alumina stack emission were chosen namely:

- Dimethyl sulfide
- Methyl cyclohexane
- para xylene
- Toluene
- Ethyl benzene
- Methyl 1,4 cyclohexadiene

Conditions for temperature and pressure apply and need to be 25°C at 101 kPa of the gases inside the cylindrical container to be use. If it is not possible to maintain temperature and pressure conditions at this state then temperature and pressure correction factors are introduced in the equation.

The cylindrical container should be flushed first with pure medical air until all that is inside the container are just medical air and analyse afterwards before injecting any standard component to assure that there are no contaminants inside the system that might interfere during the analyses of the standards.

The measured boundary of the polyurethane cylindrical container used was 22.4 litres. Based on the known density and molecular weight of each compound mentioned, the volume of each compound to be injected inside the cylindrical
container can be computed for each desired concentration. If the desired range of concentration of these contaminants in the real sample is in the mid ppmv and lower ppbv range in volume, standards should be prepared in 10 ppmv, 1 ppmv and 100 ppbv. The next table shows the desired volume of each liquid VOC to be injected inside the cylindrical container in order to make a 10 ppmv standard mixture. 1 ppmv and 100 ppbv mixture can be made by dilution of the 10 ppmv mixture in ethanol before injecting uniform amounts in the cylindrical container.

The split ratio used in the GCMS at this stage was 1:50.

Table 6: Injection Volumes to Make 10 ppm Volume Concentration of Specified VOC

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular weight (g/mol)</th>
<th>Density (g/ml)</th>
<th>Volume of compound injected (µL) to make 10 ppmv</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethyl sulfide</td>
<td>62.13</td>
<td>0.840</td>
<td>0.6832</td>
</tr>
<tr>
<td>Methyl cyclohexane</td>
<td>98.19</td>
<td>0.77</td>
<td>1.178</td>
</tr>
<tr>
<td>p xylene</td>
<td>106.16</td>
<td>0.864</td>
<td>1.135</td>
</tr>
<tr>
<td>toluene</td>
<td>92.14</td>
<td>0.865</td>
<td>0.984</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>106.17</td>
<td>0.8665</td>
<td>1.132</td>
</tr>
<tr>
<td>1 methyl, 1,4 cyclohexadiene</td>
<td>94.15</td>
<td>0.838</td>
<td>1.038</td>
</tr>
</tbody>
</table>

The thermal glass tubes used were OI Analytical glass tubes with Tenax adsorbent size 4.5” L x 6 mm O.D.

The data of the chromatogram for 1 ppmv analyses of the six compounds mentioned were shown in the appendix (appendix 1-6). From the volume of each
compound mentioned in Table 7 we can then compute for the actual amount that is injected into the GCMS. An example of this computation is given below.

*For Dimethylsulfide at 10 ppmv:*

Density is 0.778 g/ml

\[
0.778 \text{ g/ml} \times 0.7 \mu l = 5.46 \times 10^{-4} \text{ g} = 546 \mu g
\]

amount injected into mixer at 10 ppmv

Since the mixture was collected at 50 ml/min in one hour only 3 litres of air was sucked by the vacuum pump to the thermal glass tubes so

\[
(546 \mu g \text{ dimethylsulfide}) \times 3/22.4 \text{ litres} = 73.12 \mu g
\]

amount collected in tubes

At a split ratio of 1:50 only 2% of the amount collected in thermal tubes was fed in the GCMS so:

\[
73.12 \times 2\% = 1.46 \mu g \text{ dimethylsulfide}
\]

actual amount injected into the GCMS

Table 7 shows the amount injected into the GCMS at different concentration for dimethylsulfide, methylcyclohexane, P-xylene, toluene, ethylbenzene and methyl 1,4 cyclohexadiene.

**Table 7: Amount of Compound Injected into the GCMS at 10 ppmv, 1 ppmv and 100 ppbv**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Amt injected in mixer (µg)</th>
<th>Amt injected in GCMS (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10 ppmv</td>
<td>1 ppmv</td>
</tr>
<tr>
<td>dimethylsulfide</td>
<td>546</td>
<td>54.6</td>
</tr>
<tr>
<td>methylcyclohexane</td>
<td>924</td>
<td>92.4</td>
</tr>
<tr>
<td>p-xylene</td>
<td>950</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>toluene</td>
<td>865</td>
<td>86.5</td>
</tr>
<tr>
<td>ethylbenzene</td>
<td>953</td>
<td>95.3</td>
</tr>
<tr>
<td>methyl 1,4-cyclohexadiene</td>
<td>838</td>
<td>83.8</td>
</tr>
</tbody>
</table>

### 4.6 Experiments at Different Flow Rates

To further analyse if differing flow rates and time for collection of standards had an effect on the recovery of VOC, the researcher experimented on ethylbenzene standard at 1000 ppbv and 100 ppbv at the same split ratio of 1:50 at 20 minutes mixing time.

### 4.7 Experiments on Ethylbenzene Standard at 1:10 Split Ratio:

Further experiments were carried out to increase the detection level of the whole laboratory set-up. A split ratio of 1:10 was used and all the instrumental parameters remained the same.

### 4.8 Duplicate Trials for thermal tubes 2, 3 and 4

Duplicate analyses for five orders of magnitude were done using thermal glass tubes #’s 2, 3 and 4. The results of such experiments were shown in section 5.11.

### 4.9 Final Experimental Parameters

The following final experimental parameters were used to carry out standard loading and analyses.

1) Calibration mixer
The standard compound injected in the calibration mixer is 1.1 µl of ethylbenzene for each concentration range mixed with analytical air inside the calibration mixer. The concentration ranges were 10 ppmv, 5 ppmv, 1 ppmv, 100 ppbv, 10 ppbv and 1 ppbv respectively. Five trials for each range were conducted. The mixing time from the injection of ethylbenzene up to the withdrawal of the homogeneous mixture to the polyethylene plastic bag is 20 minutes. The standard mix was extracted from the polyethylene bag at a flow rate of 50 ml/min in 1 hour to the “O.I. Analytical”, 6mm OD, 4.5” length Tenax thermal desorption glass tubes.

2) Purge & Trap sample Concentrator

The conditions set in section 4.2 were the final parameters used in the sample concentrator. The Tenax tube loaded with standard was attached to the concentrator. The start button of the concentrator when pressed will start the standard extraction from the Tenax adsorbent glass tubes to the secondary Tenax trap inside the sample concentrator and later on refocusses the compound to the GC column.

3) GCMS Method

The final GCMS parameters were given in section 4.2.

4.10 Analysis of Blanks

In order to see if there is contamination in the system, after analysis of 10 ppmv standard, the polyethylene bag is filled with analytical air, loaded into thermal glass tubes at 50 ml/min for one hour and analysed.
4.11 Testing for Memory Effects

After every standard analysis, the same desorption tube needed to be analysed again to check for any compound leftover. Randomly the researcher conducted a repeat analysis of the desorption tube after a standard analysis to make sure that all compounds were thermally desorbed into the GCMS.

4.12 Experiments Showing the Effect of Time

To know whether time had an effect on concentration, the polyethylene bag with 1 ppbv concentration in trial 5 was subjected to the same sample loading and analysis procedures after three hours.
CHAPTER 5
Results and Discussion

5.1 Introduction
This chapter will show all experimental results and address in detail the explanation of results. It will provide analytical figure of merit for each data presented. Method validation is given based on experimental findings.

5.2 Experimental Results on GCMS Linearity Using Ethanol as Solvent
The following calibration curve and data chromatogram were obtained from direct injection to the GCMS of standard mixtures of acetone, methylpropylketone and toluene at 5000ppmv, 2500 ppmv and 1000 ppmv respectively.

![Calibration Curves](image)

Figure 11: Calibration Curves of 50 µl acetone, MPK, toluene at 10, 20 & 50 ml Dilutions in Ethanol
The first information that was obtained from the experiment is the retention time of the compounds identified from their chromatographs.

Retention time for ethanol = 1.214 minutes

Retention time for acetone = 1.289 minutes

Retention time for MPK = 2.420 minutes

Retention time for toluene = 3.836 minutes

The reportable sensitivity range of the Shimadzu GCMS 5050 series using the autoinjector is about 5000 ppm by volume. Though the actual sensitivity of the compounds tested is 1000 ppm by volume, the chromatograph peaks obtained at this level is already very hard to measure.

The calibration of the data using the GCMS software shows the linearity of the procedures done with linear regression square coefficients ($R^2$) values $\geq 0.99$. The calibration was done based on the TIC (total ion count) of the compounds. The experiments can also be repeated for testing other aromatic compounds. The average relative % of error lies in the accuracy of measurements in the preparation of standard compounds. The average relative % error of the procedure done is +/- 3% relative which is calculated thru the comparison of the experimental area of the chromatogram obtained from each compound.

This experiment concludes that sample enrichment procedures will be needed to proceed with experiments for detecting much lower level of concentrations.
5.3 **Suitability of the GCMS for VOC Analysis**

In the results of the above mentioned experiments on the detection levels of 3 odorous compounds suggest that using the GCMS as the sole instrument for this project is not feasible. Though the analyses provide a better separation of compounds due to temperature programming based on retention times (ethanol RT= 1.214 min., acetone RT= 1.289 min., MPK RT= 2.42 min. and toluene RT= 3.836 min.), it doesn’t reach the levels necessary for the analysis of actual VOC samples. Compounds like acetone, methylpropylketone and toluene with initial volume concentration of 2500 parts per million (ppmv) were injected at 1 µl to the GC column and the detection were shown in Figure 12 which was at its detection level. There is a need to pre-concentrate compounds and to modify the existing instrument so that lower concentration levels up to parts per billion can later on be detected.

5.4 **O.I. Analytical Purge & Trap Sample Concentrator Analysis Results for Liquid VOCs**

At 100 ppbv the compounds acetone, p-xylene and toluene showed very good detection and at 10 ppbv the peaks were still evident. The data for 10 ppmv and 100 ppbv analyses were shown next page.
Figure 12: 10 ppmv of acetone, xylene & toluene purge & trap in distilled water
Figure 13: 100 ppbv of acetone, xylene & toluene purge & trap in distilled water

Toluene, p-xylene, methyl 1,4 cyclohexadiene, ethylbenzene and methyldisulfide in distilled water responses to the purge and trap sample concentrator were shown in the following set of data.
Table 8: Data from purge & trap analysis in distilled water Trial 1

<table>
<thead>
<tr>
<th>concentration of compounds</th>
<th>Peak Area Intensities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>toluene</td>
</tr>
<tr>
<td>10ppbv</td>
<td>280827</td>
</tr>
<tr>
<td>1ppmv</td>
<td>7233244</td>
</tr>
<tr>
<td>10ppmv</td>
<td>1.05E+08</td>
</tr>
<tr>
<td>100ppmv</td>
<td>8.87E+08</td>
</tr>
</tbody>
</table>

Figure 14: 10 ppmv analysis of toluene, p-xylene, methyl 1,4 cyclohexadiene in distilled water

Figure 15: 10 ppbv analysis of toluene, p-xylene, methyl 1,4 cyclohexadiene in distilled water
The graphs below showed data for three trials for compounds like toluene and ethylbenzene in log scale.

![Toluene Chart](image)

**Figure 16:** Graph of concentration vs. log scale of peak area for toluene by purge & trap

![Ethylbenzene Chart](image)

**Figure 17:** Graph of concentration vs. log scale of peak area for ethylbenzene by purge & trap
Though the existing OI analytical purge and trap sample concentrator shows good results in detecting compounds in parts per billion ranges the original instrument set-up can only load liquid samples. There was a need to modify the instrument for its applicability of loading gas samples. One modification that the researcher had done is the installation of an air tube desorber connected in the purge and trap unit. The whole sample valve assembly for loading liquid sample was taken out and an air tube desorber assembly coupled with an external heater were installed in the purge and trap unit.

5.5 O.I. Analytical Purge & Trap Sample Concentrator Capability

There are a few modifications that needed to be done with the sample concentrator. The first was to change the existing inside trap material to “Tenax”. The original trap was made of a combination of adsorbent materials consisting of charcoal, Tenax and silica gel. Since the process of pre-concentration involves thermal desorption, the original combination adsorbent are not suitable because their high surface activity can lead to sample degradation at high temperatures (Ras et al., 2008). A particular problem with activated charcoal, and especially silica gel is their tendency to adsorb water, which must be dealt with if it is not to be transferred to the gas chromatograph. Relative humidity has a big effect in collecting emission samples on site. It can interfere with analysis procedure which will make identification and quantification of compounds harder for the analyst. In alumina stack emissions, the real matrix is more often at 95% relative humidity, therefore it is very important to choose the right adsorbent that will capture the target compounds to the adsorbent bed with minimal moisture as absorption.
Possible measures to minimise the amount of water absorbed are by collecting small sample volumes, minimising the amount of adsorbent in the sampling tube, moderately heating the adsorbent tube during sampling and dry purging the sample tube before thermal desorption (Analytical Chemistry, 1995). Though these steps are easy to follow, the analyst has no control of how sample collection was done in site; the best thing to do is to decide a better adsorbent that can give the best analysis result.

Tenax (poly-2, 6-diphenyl-p-phenylene oxide) is an adsorbent capable of sorbing wide range of organic volatiles. It is especially good with aromatics; it can be heated to relatively high temperatures for thermal desorption and is long lasting. It is not suitable for very volatile hydrocarbons (pentane and below) or for small alcohols, which is frequently an advantage. In a certain study for water trapping capacity for solid adsorbents (Analytical Chemistry, 1995), “Tenax” and Carbotrap showed the lowest trapping capacity of generally less than 2-3 mg H₂O/g of adsorbent under the highest humidity conditions while Carboxen 569 and Carbosieve exhibited substantially higher water trapping capacity, with up to 400 mg H₂O/g of adsorbent under the highest humidity conditions tested.

The researcher had chosen “Tenax” as the adsorbent for the thermal glass tubes for the reasons stated above. The target compounds in the alumina emission were the odorous aromatics and the solvent that was used to make the standards was ethanol which means that it was expected that not 100% of ethanol can be captured into the Tenax adsorbent bed; it will not present any problems since ethanol is not one of the target compounds, its main usage was to act as the solvent in standard preparation.
Figures 12 and 13 of section 5.4, shows that very good separation and level of detection were achieved by acetone, toluene and xylene from 10 ppmv and 100 ppbv standard preparations in distilled water. These results also confirmed that changing the original inside trapping material of the purge & trap unit improved the capturing properties of these odorous compounds.

In similar duplicate experiments of standard preparations for toluene, p-xylene, methyl 1,4 cyclohexadiene, ethylbenzene and methyldisulfide in distilled water it was confirmed that the purge & trap unit was operating in good condition with all the compounds present being adequately separated and clearly detected at 10 parts per billion by volume (ppbv) in the modified instrument set-up. The next step is finding a way for the purge & trap unit to load gas samples. This was the part where thermal desorption glass tubes were introduced and procedures for making standard VOCs in air were done.

5.6 Results of the Experiments with Standard Air Samples

The results of the peak areas for the first trial were given by the following table. A graph of the compound amount in µg vs. log peak areas is shown below.

Table 9: Experimental Data for Dimethylsulfide

<table>
<thead>
<tr>
<th>dimethylsulfide</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.014625 µg= 100ppbv</td>
<td>291446</td>
</tr>
<tr>
<td>0.14625 µg= 1ppmv</td>
<td>2129046</td>
</tr>
<tr>
<td>1.46 µg=10ppmv</td>
<td>109189237</td>
</tr>
</tbody>
</table>
Figure 18: Graph of dimethylsulfide Amount vs. Log of Peak Areas

Table 10: Experimental Data for p-xylene

<table>
<thead>
<tr>
<th>p-xylene</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.025446 µg=100 ppbv</td>
<td>312790</td>
</tr>
<tr>
<td>0.25446 µg=1 ppmv</td>
<td>1965100</td>
</tr>
<tr>
<td>2.54 µg=10 ppmv</td>
<td>59295676</td>
</tr>
</tbody>
</table>

Figure 19: Graph of p-xylene Amount vs. Log of Peak Areas
Table 11: Experimental Data for Toluene

<table>
<thead>
<tr>
<th>Toluene amount (µg)</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02317 µg = 100 ppbv</td>
<td>435862</td>
</tr>
<tr>
<td>0.2317 µg = 1 ppmv</td>
<td>6416632</td>
</tr>
<tr>
<td>2.32 µg = 10 ppmv</td>
<td>105815611</td>
</tr>
</tbody>
</table>

Figure 20: Graph of Toluene Amount vs. Log of Peak Areas

Table 12: Experimental Data for Ethylbenzene

<table>
<thead>
<tr>
<th>Ethylbenzene amount (µg)</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02553 µg = 100 ppbv</td>
<td>566511</td>
</tr>
<tr>
<td>0.2553 µg = 1 ppmv</td>
<td>3946690</td>
</tr>
<tr>
<td>2.55 µg = 10 ppmv</td>
<td>38682659</td>
</tr>
</tbody>
</table>

Figure 21: Graph of Ethylbenzene Amount vs. Log of Peak Areas
Table 13: Experimental Data for Methylcyclohexane

<table>
<thead>
<tr>
<th>methylcyclohexane</th>
<th>Peak Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02475 µg = 100 ppbv</td>
<td>733497</td>
</tr>
<tr>
<td>0.2475 µg = 1 ppmv</td>
<td>12330017</td>
</tr>
<tr>
<td>2.475 µg = 10 ppmv</td>
<td>22886997</td>
</tr>
</tbody>
</table>

Figure 22: Graph of Methylcyclohexane Amount vs. Log of Peak Areas

Table 14: Experimental Data for Methyl 1, 4 cyclohexadiene

<table>
<thead>
<tr>
<th>methyl 1,4cyclohexadiene</th>
<th>run 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 ppbv</td>
<td>410188</td>
</tr>
<tr>
<td>1 ppmv</td>
<td>4493651</td>
</tr>
<tr>
<td>10 ppmv</td>
<td>65814658</td>
</tr>
</tbody>
</table>

Figure 23: Graph of Methyl 1, 4 cyclohexadiene Amount vs. Log of Peak Areas
The results showed that at 1:50 split ratio of the compounds studied at a 100 parts per billion by volume compounds were still detected in the present instrument set-up. Though the detection level is very good at this stage, there was a need to adjust some parameters so that the detection level can still be lower. The aim of this study is to get a good detection for a 1 nanogram (ng) of VOC.

5.7 Discussion for Experiments with VOC in Standard Air Matrix

The preparation of standard VOC in a gas matrix was the most challenging part of the whole research due to the lower concentration needed for standards (1ppbv etc.). Many laboratories buy VOC standards in aerosol containers for each VOC concentration from specified suppliers, but most of the ranges of standards needed for this research were not available. The 1ppmv and 10 ppmv standards available commercially were very costly. When quantification of a large number of compounds is needed, the approach of buying commercially available standards is not always practical. In the study conducted by Forster et al. in 2005, he didn’t attempt to quantify compounds in Worsely Alumina Refinery, Western Australia (WA). When asked, he said it was very hard to quantify compounds because of the unavailability of air standards that will be used as the basis for quantifying the compounds. So this research tries to overcome the difficulty of producing standard compounds in air by introducing a detailed procedure of making the standard VOC in air by means of a custom made standard mixer.

The standard mixer was made up of polyurethane tubing with a height of 790 mm and inside diameter of 190 mm. From these dimensions the volume of the cylindrical container was 22.4 X 10^6 mm^3, which was also equivalent to the volume of analytical
air that it can hold. The picture of the mixer was shown in figure 10 section 3.3. One end of the mixer was attached to a tube connected to the gas cylinder bottle of analytical air. A pressure release valve was also connected at the bottom of the cylinder; to make sure that the pressure inside the cylinder when it’s filled with air is always atmospheric. Certain liquid VOC is injected with a microlitre GC syringe into a silicon rubber septum in the mixer depending on what concentration is needed when liquid is mixed with analytical air. The volume of the liquid injected is computed by the equation in page 54, section 4.5. The detailed procedures for loading liquid VOC in the calibration mixer were presented in section 4.5.

In the next step, the researcher tested six different odorous compounds. 10 ppmv, 1 ppmv and 100 ppmv of standard VOC in air were made by injecting the liquid compound in the mixer. A small fan was attached inside the mixer to homogeneously mix the VOC and analytical air for 20 minutes. The resulting standard mix was transferred into a polyethylene plastic bag. The polyethylene bag is then connected to the O.I. analytical thermal desorption glass tubes with Tenax adsorbent and a vacuum pump is connected by a piece of plastic tubing sucking the air to the glass tube at a constant flow rate of 50 ml/min for 1 hour. The same procedure was repeated for each concentration range to make up the data point curves that was presented in figures 18 to 23. The results of the peak areas obtained from analysing dimethylsulfide, p-xylene, toluene, ethylbenzene, methylcyclohexane and methyl 1,4 cyclohexadiene showed linear relationship up to 3 orders of magnitude based on the graph of each compound’s amount vs. log scale of peak areas. Concentrations of 10 ppmv, 1 ppmv and 100 ppbv showed very good instrument detection. At this point there was a need to further increase the detection level of the instrument to lower
parts per billion. In doing so, different flow rates for standard collection to the thermal tubes were tested to see the effect of varying flow rates to the results of peak areas recorded.

Ethylbenzene was chosen as a suitable candidate for evaluating the method. 1000 ppbv and 100 ppbv concentrations were tested at varying flow rates. Table 15 section 5.8 gives the result of the experiments. The average retention time for ethylbenzene was 6.3 minutes, this were shown in the chromatograph for all the experiments conducted. For 1000 ppbv at flow rates of 50 ml/min in 6 minutes and 30 ml/min in 10 minutes the peak area obtained for a longer collection time (10 minutes) was higher. Results of the peak areas were 351,120 and 327,508 respectively. The difference of their peak areas were 23,612; it is not considered to be significant but considering the fact that each result represents only the same amount of ethylbenzene (0.0134 µg) peak area results should almost be the same. Therefore the time of collection for loading standards has considerable effect in the recovery process. The longer the collection time, the better will be the area recovery in the analysis.

In the second set of data for 100 ppbv concentration, same standard collection time of 60 minutes was used at 100 and 50 ml/min respectively. The results of the peak area intensities were almost half of the other (113,2265 & 566,511). Though not expected to be exact, this was the response expected since the sample amounts injected in each run were 0.05105 µg and 0.02553 µg were half of the other. This means that flow rate has a minimal effect on the recovery of the standards in thermal desorption tubes. In the end the researcher chooses 50 ml/min as the flow rate that will be used in the process because the recovery at this flow was indeed very good and still very slightly higher (by 757) when the flow rate is 100 ml/min. Another consideration for choosing the flow rate was the avoidance of the standard breaking
through the surface of the Tenax adsorbent so a very controlled flow of 50 ml/min within an hour was used. This must also be the same flow rate to use during sample collection.

At 100 ppbv at 30 ml/min in 20 minutes, about 5 nanogram of standard was detectable giving a peak intensity of 121,222. The aim is to detect 1 nanogram of standard. In the final experiments the split ratio was increased to 1:10 which means 10% of the sample amount in the tube was fed into the GC column; increasing the split ratio will lead to further increased in compound detection.

5.8 Results of Experiments at Different Flow Rates

The result of the peak areas obtained from the experiment on VOC recovery at different flow rates was given in the table below.

Table 15: Experimental Data at Different Flow Rates and Time

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Flow rate (ml/min)</th>
<th>Time (min)</th>
<th>Peak Intensity</th>
<th>Tube #</th>
<th>RT (min)</th>
<th>vol. air (ml)</th>
<th>amt. EB (ug)</th>
<th>log amt</th>
<th>Peak int/amt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 ppbv</td>
<td>50</td>
<td>6</td>
<td>327508</td>
<td>2</td>
<td>6.304</td>
<td>300</td>
<td>0.0134</td>
<td>-1.8729</td>
<td>24440895</td>
</tr>
<tr>
<td>1000 ppbv</td>
<td>30</td>
<td>10</td>
<td>351120</td>
<td>2</td>
<td>6.299</td>
<td>300</td>
<td>0.0134</td>
<td>-1.8729</td>
<td>26202985</td>
</tr>
<tr>
<td>1000 ppbv</td>
<td>50</td>
<td>60</td>
<td>3806338</td>
<td>2</td>
<td>6.304</td>
<td>3000</td>
<td>0.2553</td>
<td>-0.5929</td>
<td>14909275</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>50</td>
<td>300</td>
<td>2233478</td>
<td>2</td>
<td>6.25</td>
<td>15000</td>
<td>0.1278</td>
<td>-0.8935</td>
<td>17476354</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>100</td>
<td>60</td>
<td>1132265</td>
<td>1</td>
<td>6.279</td>
<td>6000</td>
<td>0.0511</td>
<td>-1.2920</td>
<td>22179530</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>50</td>
<td>60</td>
<td>566511</td>
<td>6.29</td>
<td>3000</td>
<td>0.0255</td>
<td>-1.5929</td>
<td>22190012</td>
<td></td>
</tr>
<tr>
<td>100 ppbv</td>
<td>30</td>
<td>20</td>
<td>121222</td>
<td>1</td>
<td>6.284</td>
<td>600</td>
<td>0.0051</td>
<td>-2.2920</td>
<td>23745739</td>
</tr>
</tbody>
</table>

- indicates experimental data
Figure 24: Graph of the Log Amount Ethylbenzene vs. Peak area/amount

The results of the experiments confirmed that ethylbenzene standard was detected at a retention time of 6.3 minutes. At a concentration of 1000 parts per billion by volume (ppbv), the peak intensity obtained was higher at 30 ml/min flow rate and 10 minute collection time (351120) as compared to the peak intensity obtained at 50 ml/min in 6 minutes (327508). The difference of the two peak intensities are not much (23612). The graph showed an insignificant difference of the peak area/amount.

In the second set of the data for a 100 ppbv concentration at the same collection time of 60 minutes at different flow rate of 100 and 50 ml/min respectively, the area intensities obtained is almost half of the other (1132265 & 566511). The findings just correspond to the real amount of the standard ethylbenzene injected into the GC column which was also half of the other (0.05105 and 0.02553).
5.9 Results on Analyses of Ethylbenzene Standard at 1:10 Split Ratio

The results of the analyses of ethylbenzene standard at 1:10 split ratio were shown in the table below:

**Table 16: Experimental Data of Ethylbenzene at Split Ratio 1:10**

<table>
<thead>
<tr>
<th>concentration</th>
<th>Flow rate (ml/min)</th>
<th>Time (min)</th>
<th>Peak Intensity</th>
<th>Tube #</th>
<th>RT (min)</th>
<th>vol. air (ml)</th>
<th>amt. EB (ug)</th>
<th>log amt</th>
<th>Peak int/amt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 ppbv</td>
<td>50</td>
<td>6</td>
<td>2130100</td>
<td>1</td>
<td>6.34</td>
<td>300</td>
<td>0.1276</td>
<td>-0.8941</td>
<td>16693574</td>
</tr>
<tr>
<td>1000 ppbv</td>
<td>30</td>
<td>10</td>
<td>2091042</td>
<td>1</td>
<td>6.342</td>
<td>300</td>
<td>0.1276</td>
<td>-0.8941</td>
<td>16387476</td>
</tr>
<tr>
<td>1000 ppbv</td>
<td>50</td>
<td>60</td>
<td>24355025</td>
<td>1</td>
<td>6.48</td>
<td>300</td>
<td>1.2763</td>
<td>0.1060</td>
<td>19082524</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>50</td>
<td>300</td>
<td>9387751</td>
<td>1</td>
<td>6.351</td>
<td>15000</td>
<td>0.6382</td>
<td>-0.1950</td>
<td>14709732</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>100</td>
<td>60</td>
<td>16225366</td>
<td>1</td>
<td>6.346</td>
<td>6000</td>
<td>0.2553</td>
<td>-0.5929</td>
<td>63554117</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>50</td>
<td>60</td>
<td>4080468</td>
<td>1</td>
<td>6.341</td>
<td>300</td>
<td>0.1276</td>
<td>-0.8941</td>
<td>31978589</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>30</td>
<td>20</td>
<td>565941</td>
<td>1</td>
<td>6.352</td>
<td>600</td>
<td>0.0255</td>
<td>-1.5929</td>
<td>22167685</td>
</tr>
<tr>
<td>10 ppbv</td>
<td>50</td>
<td>60</td>
<td>1000289</td>
<td>1</td>
<td>6.344</td>
<td>300</td>
<td>0.0128</td>
<td>-1.8941</td>
<td>78392555</td>
</tr>
<tr>
<td>10 ppbv</td>
<td>50</td>
<td>20</td>
<td>147428</td>
<td>1</td>
<td>6.347</td>
<td>1000</td>
<td>0.0043</td>
<td>-2.3716</td>
<td>34688941</td>
</tr>
<tr>
<td>2 ppbv</td>
<td>50</td>
<td>60</td>
<td>601457</td>
<td>1</td>
<td>6.343</td>
<td>300</td>
<td>0.0026</td>
<td>-2.5929</td>
<td>235588328</td>
</tr>
<tr>
<td>1 ppbv</td>
<td>50</td>
<td>60</td>
<td>241848</td>
<td>1</td>
<td>6.344</td>
<td>300</td>
<td>0.0013</td>
<td>-2.8941</td>
<td>189536050</td>
</tr>
<tr>
<td>10 ppmv</td>
<td>50</td>
<td>60</td>
<td>242612055</td>
<td>1</td>
<td>6.404</td>
<td>300</td>
<td>12.76</td>
<td>1.1058</td>
<td>19013484</td>
</tr>
</tbody>
</table>

- indicates experimental data

The results showed a slight difference of peak intensities obtained at 1000 ppbv concentration when carried out at 50 ml/min and 30 ml/min for 6 and 10 minutes respectively (2130100 & 2091042) for the same amount of ethylbenzene (0.1276 µg).

This confirms that flow rate of 50 ml/min is the optimum flow rate required for the research because of slightly higher standard recovery as compared to the 30 ml/min flow rate recovery. The lowest concentration level detected by the experiment was at 1 ppbv equivalent to 1.28 ng (nanogram) of ethylbenzene standard. This was considered a very good detection level. Therefore increasing the experimental
conditions split ratio to 1:10 had a significant effect on recovery and detection. 1:10 was the split ratio used for the final experiment. The figure below showed that the recovery at 1:10 split ratio had improved detection as compared to 1:50 split ratio.

![Graph of the Amount of Ethylbenzene vs. Peak Area Intensities of Ethylbenzene at 1:50 and 1:10 Split Ratio at 50 ml/min for 3L of Standard Air](image)

**Figure 25: Graph of the Amount of Ethylbenzene vs. Peak Area Intensities of Ethylbenzene at 1:50 and 1:10 Split Ratio at 50 ml/min for 3L of Standard Air**

### 5.10 The Effects of Changing Split Ratio to 1:10

In the final experiments the split ratio was increased to 1:10 which means 10% of the sample amount in the tube was fed into the GC column; increasing the split ratio will lead to further increased in compound detection.

The split ratio of standard entering the GC column was changed from 1:50 to 1:10 to further increase the detection level of the ethylbenzene standard. Table 16 in section 5.9 gives the results. This time ethylbenzene standard shows very good detection from 10 ppmv to 1 ppbv within six concentrations ranges using the same thermal
desorption tube. At 1 ppbv, equivalent to 1.28 nanogram of ethylbenzene standard, the signal level with a peak area of 241848 was still very good. This shows that increasing the split ratio to 1:10 can increase the recovery and detection level significantly. This was represented in the graph shown in figure 25 where 1:10 split ratio showed a wider range of recovery and ethylbenzene detection as compared to a 1:50 split ratio. A split ratio of 1:10 was safe enough not to cause any breakthrough of ethylbenzene from the Tenax adsorbent. Increasing the split ratio further might cause column overloading, so 1:10 was used as the final split ratio for the experiment.

5.11 Results of Duplicate Trials for Thermal Tubes 2, 3 and 4

The graphs of the log of ethylbenzene amount vs. log of peak area intensities from 1 ppmv to 1 ppbv recovery were also shown.

Table 17: Data for Analysis of Ethylbenzene Standard Tube #2

<table>
<thead>
<tr>
<th>concentration</th>
<th>amt. ethylbenzene (µg)</th>
<th>Peak Area Trial 1</th>
<th>Peak Area Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppmv</td>
<td>12.76</td>
<td>216937455</td>
<td>226235323</td>
</tr>
<tr>
<td>1 ppmv</td>
<td>1.2763</td>
<td>37009273</td>
<td>42114490</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>0.1276</td>
<td>9519510</td>
<td>11877194</td>
</tr>
<tr>
<td>10 ppbv</td>
<td>0.01276</td>
<td>8159354</td>
<td>3840432</td>
</tr>
<tr>
<td>1 ppbv</td>
<td>0.00128</td>
<td>2844964</td>
<td>3664816</td>
</tr>
</tbody>
</table>
Figure 26: Ethylbenzene Graph for Trials 1&2 Tube #2 from 1 ppmv to 1 ppbv Ranges

Table 18: Data for Analysis of Ethylbenzene Standard Tube #3

<table>
<thead>
<tr>
<th>concentration</th>
<th>amt. ethylbenzene (µg)</th>
<th>Peak Area Trial 1</th>
<th>Peak Area Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppmv</td>
<td>12.76</td>
<td>153769789</td>
<td>151907725</td>
</tr>
<tr>
<td>1 ppmv</td>
<td>1.276</td>
<td>32363905</td>
<td>29897653</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>0.1276</td>
<td>6591350</td>
<td>10259321</td>
</tr>
<tr>
<td>10 ppbv</td>
<td>0.01276</td>
<td>2854555</td>
<td>3894365</td>
</tr>
<tr>
<td>1 ppbv</td>
<td>0.00128</td>
<td>2351129</td>
<td>4359054</td>
</tr>
</tbody>
</table>
Figure 27: Ethylbenzene Graph for Trials 1&2 Tube #3 from 1 ppmv to 1 ppbv ranges

Table 19: Data for Analysis of Ethylbenzene Standard Tube #4

<table>
<thead>
<tr>
<th>concentration</th>
<th>amt. ethylbenzene (µg)</th>
<th>Peak Area Trial 1</th>
<th>Peak Area Trial 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppmv</td>
<td>12.76</td>
<td>120656721</td>
<td>132292612</td>
</tr>
<tr>
<td>1 ppmv</td>
<td>1.2763</td>
<td>20162862</td>
<td>15601671</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>0.1276</td>
<td>6570674</td>
<td>6849648</td>
</tr>
<tr>
<td>10 ppbv</td>
<td>0.01276</td>
<td>3031161</td>
<td>3057589</td>
</tr>
<tr>
<td>1 ppbv</td>
<td>0.00128</td>
<td>2103094</td>
<td>2131679</td>
</tr>
</tbody>
</table>
The results showed a linear curve at 4 orders of magnitude for every set of data. Reproducibility of data was established based on the graphical representations for the duplicate trials of the same tube, even though a fresh set of standard mixture of ethylbenzene was made for each set of trial.

### 5.12 Using the Final Parameters with Different Thermal Desorption Tubes

In order to clearly see the response of different thermal desorption tubes at concentration ranges 10 ppmv to 1 ppbv at 5 orders of magnitude, duplicate trials were made for each thermal glass tubes (tubes 2, 3 and 4). A fresh standard was made in each of the trials for each of the concentration ranges. There was some variability between the responses recorded for tube #2 for the two trials (trials 1 & 2), tube #3 (trials 1&2) and tube #4 (trials 1&2). These differences were probably due to the preparation of fresh standard for every trial in each range of concentration. Care
needs to be taken in measurement and manipulation when injecting the standards in the calibration mixer during preparation. However these differences were considered insignificant as shown in the graphical representations (Figures 26 to 28). These results also showed good repeatability of duplicate experiments using the same desorption tube. It is advisable to use the same thermal desorption glass tube in preparation of standard and loading of real sample to minimise error in quantifying. It is also advisable to analyse the standard first and the sample next for each concentration range.

5.13 Final Results

The traces of the chromatograms and mass spectra for the final analyses were shown in the appendix (Appendix 7-35). The tabulated results and graphical representations for the five trials were shown in this section.

Table 20: Experimental Data for Final Analysis of Ethylbenzene Standard Tube #4

<table>
<thead>
<tr>
<th>concentration</th>
<th>amt. ethylbenzene (µg)</th>
<th>Peak Area T1</th>
<th>Peak Area T2</th>
<th>Peak Area T3</th>
<th>Peak Area T4</th>
<th>Peak Area T5</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 ppmv</td>
<td>12.76</td>
<td>120656721</td>
<td>132292612</td>
<td>133156733</td>
<td>97253167</td>
<td>87500264</td>
</tr>
<tr>
<td>5 ppmv</td>
<td>6.38</td>
<td>33367978</td>
<td>37570487</td>
<td>38100880</td>
<td>32638663</td>
<td>38817499</td>
</tr>
<tr>
<td>1 ppmv</td>
<td>1.2763</td>
<td>20162862</td>
<td>15601671</td>
<td>17701379</td>
<td>11667824</td>
<td>12230438</td>
</tr>
<tr>
<td>100 ppbv</td>
<td>0.1276</td>
<td>6570674</td>
<td>6849648</td>
<td>7774617</td>
<td>5129306</td>
<td>4831904</td>
</tr>
<tr>
<td>10 ppbv</td>
<td>0.01276</td>
<td>3031161</td>
<td>3057589</td>
<td>4925520</td>
<td>1793276</td>
<td>3138607</td>
</tr>
<tr>
<td>1 ppbv</td>
<td>0.00128</td>
<td>2103094</td>
<td>2131679</td>
<td>1988716</td>
<td>1417171</td>
<td>1656430</td>
</tr>
</tbody>
</table>
The graph above represents only the concentration ranging from 5 ppmv down to 1 ppbv because these lower concentrations were the working range of concern for this study.

Due to manufacturing differences no two thermal desorption tubes are alike. In the results it shows that using the same thermal glass tube (tube #4) to analyse newly prepared standards for each set of trials (trials 1 to 5) still give differences in peak intensity responses. It is very important that the analyst should be consistent in the preparation of liquid standard which was injected into the calibration mixer containing analytical air. To minimise error it is recommended to load the standard first and analyse it, then analyse the tube for a second time to check for any compound leftover; then load the sample in the same tube at the same analytical
condition as the standard and analyse the sample straightaway. All of the five trials confirmed that a linear calibration curve is possible using the method.

5.14 Validation of Final Results

Thermal desorption glass tube #4 was chosen as the final tube for the 5 trials that were carried out. Newly prepared standard for each set of trials and for each concentration range were independently used. In liquid experiments, it was always recommended to take the same aliquot for conducting trials of the same concentration range, in an air matrix the stability of the standard air mixture inside the mixing chamber is not assured for a longer amount of time. In order to have assurance that a certain concentration range was accurately prepared, each standard was prepared at a different time; only the 10 ppmv standards came from the same aliquot in liquid form and all succeeding dilutions were done at different times. This therefore contributed to a large standard deviation. The linear regression square coefficients ($R^2$) of the multi point calibration for 5 orders of magnitude starting from 5 ppmv for the five trials of ethylbenzene standards were as follows:

Trial 1 $R^2 = 0.8664$

Trial 2 $R^2 = 0.9471$

Trial 3 $R^2 = 0.9471$

Trial 4 $R^2 = 0.9801$

Trial 5 $R^2 = 0.9931$

The results suggest that these trials gave an average correlation coefficient, $R^2$ values $\geq 0.9$ from the working range of 5ppmv to 1 ppbv and since these results were all experimental, they were acceptable range for linearity. Peaks for these trials all exhibited a Gaussian shape (see appendix 7-35).
The relative standard deviation of trials at 10 ppmv was 18.2%. At the lowest level of 1 ppbv, the relative standard deviation was 16.73%. This gives an average relative standard deviation of 20% for all trials conducted. Ethylbenzene standard showed repeatability ≤25%. The EPA performance criteria for repeatability must be ≤25%; therefore the method used was acceptable. Comparison of data from the analyses of ethylbenzene standard in distilled water and ethylbenzene in air at 1:50 split ratio showed sample recovery of more than 99%.

5.15 Results on Blank Analysis

The data for the analysis of blank was shown below

![Chromatogram of Analytical Air](image)

**Figure 30: Chromatogram of Analytical Air**

The chromatogram shows that there was no detection of ethylbenzene in the bag and in the thermal glass tubes after analysis of the standard. There was no measurable signal for ethylbenzene adsorption that had occurred in the walls of the polyethylene plastic bag and all the standard ethylbenzene was thermally desorbed from the glass desorption tubes while doing the analysis for 10 ppmv standards. There was a presence of peak eluted at around 16 minutes and this presence should be recorded and later on be identified as a background (figure 30).
5.16 Results for Memory Effects

Figure 31 shows that in the repeat analysis of the same desorption tube, there was no measurable signal of ethylbenzene left.

![Chromatogram (Zoom)](image)

**Figure 31: Analysis of Tube #4 After 10 ppmv Ethylbenzene Standard Analysis**

Results showed that the standard ethylbenzene had been completely desorbed from the glass tubes with Tenax adsorbent during the analysis of standard.

5.17 The Effect of Time

The data below shows the analysis of newly prepared 1 ppbv standard and analysis of the same standard after 3 hours residence time in the polyethylene plastic bag.

**Table 21: Data for Peak Area Intensities at 20 Minutes & After 3 Hours**

<table>
<thead>
<tr>
<th>1ppbv</th>
<th>Fresh standard</th>
<th>After 3 hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak Intensities</td>
<td>1656430</td>
<td>2128990</td>
</tr>
</tbody>
</table>
Figure 32: Chromatogram of 1 ppbv, Tube #4 Trial 5 for Newly Prepared Standard

Figure 33: Chromatogram of 1 ppbv, Tube #4 Trial 5 After 3 Hours of Preparation

5.18 Discussion on the Effect of Residence Time

The results show that there were more compounds detected in the bag after 3 hours preparation. The peak area of ethylbenzene was increased. These changes may be due to some compounds desorbed from the walls of the polyethylene bag and contaminants coming from ambient air outside the bag due to small container leaks over time. By the time the researcher puts on the seals around the bag, there is still some risk of contaminating the standard air inside the bag. There was a new peak eluting at 9.592 minutes identified as cyclotetrasiloxane, octamethyl identified by the NIST library programmed in the software after analysis of the air after 3 hours of
preparation. This means that standards that were prepared using the method can only be used for a very limited time. The stability of the concentration inside the polyethylene bag will not be reliable after a longer period of time. In fact some literature in the preparation of air standards using a rigid container suggests that prepared air standards can only be used after 1 hour of preparation. After an hour all standard air prepared should be discarded.

5.19 Effective Lower Working Limit

At the lowest concentration range of 1 ppbv (1.3 ng) of ethylbenzene, the result of the five trials conducted using tube #4 is given by the table below:

Table 22: Data for Analysis of 1ppbv Ethylbenzene Standard Using Tube #4

<table>
<thead>
<tr>
<th>Tube #4</th>
<th>T1</th>
<th>T2</th>
<th>T3</th>
<th>T4</th>
<th>T5</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ppbv</td>
<td>2103094</td>
<td>2131679</td>
<td>1988716</td>
<td>1417171</td>
<td>1656430</td>
</tr>
</tbody>
</table>

5.20 Discussion on Detection Levels and Sample Recovery

At the lowest level of detection which is at 1 ppbv, the relative standard deviation was at 16.73% for 5 trials. More experiments will be needed to know the method detection limit (MDL) of the procedure.

Data for liquid and gaseous matrix recoveries for ethylbenzene standards were shown in Tables 5 and 11 respectively. The recoveries at 10 ppmv and 1ppmv were observed by comparing the ratios of the amount of ethylbenzene over the peak area intensities obtained from analyses. Results showed that at 10 ppmv in gas, recovery was 99% and at 1 ppmv in gas, recovery was 98%.
CHAPTER 6
Conclusion

6.1 Background of the Original Problem

Air quality protocols and the methods for air quality monitoring are relatively well developed, however little work has been done to directly quantify volatile organic emissions and odour nuisance in industrial regions. The Gladstone region is home to several giant industries such as Queensland Alumina Limited (the world largest alumina refinery), Rio Tinto refinery, NRG – Gladstone Power Station (the largest coal-fired power station in Queensland) and contribute to the 170 million metric tonnes of equivalent CO$_2$ discharged in the atmosphere (Australian government department of climate change web site, 2006 figure) by the Queensland state. As well as being a major contributor to green house gas emissions, the emissions of the Gladstone based industries also produce air pollutants such as VOC, although no comprehensive regional inventory of VOC exists. An attempt of such research was started by Coffey and Ioppolo-Amanios in 2004, Foster in 2005 and Donoghue in 2007, all located in Western Australia. Coffey used a contractor to collect air samples; Foster & Donoghue identified odorous chemicals but didn’t quantify or investigate very small concentrations. Odorous compounds have been the source of many complaints from the Gladstone residents. Odour complaints remain largely under-investigated in Australian industrial regions while other industrial cities across the world have already made major progresses in identification of odorous compounds.

This research addresses the development of procedure for quantification of very dilute concentration of odorous VOC which are often difficult to quantify.
6.2 Conclusion Summary

A sensitive laboratory method has been developed to quantify very dilute concentration of odorous volatile organic compounds from stack emission of alumina refineries that involves chromatographic separation of standard compounds on a GCMS instrument. The preparation of standard compounds which had been a limiting factor for previous research had been overcome by the construction of a mixing chamber connected to a custom made vacuum pump which transferred the VOC gas standard to Tenax filled sorbent tubes. The technique uses a purge and trap sample concentrator connected to the GCMS where sorbent tubes were thermally desorbed and analysed. Ethyl benzene, one of the odorous VOC was chosen as the standard for testing. Ethylbenzene standard eluted at 6.3 minutes producing a Gaussian curve for all analyses. Identification of ethylbenzene standard was confirmed by the mass spectrum produced which was compared to the NIST mass spectra library of compounds programmed in the GCMS software. External method of standardisation was used to prepare the calibration curve for five orders of magnitude. Standard concentrations prepared were from 5 ppmv, 1 ppmv, 100 ppbv, 10 ppbv and 1 ppbv respectively. Each concentration range were tested for five trials and showed linearity for five orders of magnitude with $R^2$ values $\geq 0.9$. The standard deviation for all trials was 20%; this satisfies the EPA performance criteria for repeatability of $\leq 25%$. Analysis of 1 ppbv ethylbenzene equivalent to 1.28 nanogram showed a sensitive detection on the laboratory instrumentation and procedures used.

Based on experimental results, it was concluded that the laboratory instrumentation using the customised calibration mixer, Tenax sorbent tube purge and trap thermal desorption system, GCMS method is a sensitive and comprehensive procedure of
quantifying odorous VOC (volatile organic compounds) down to a concentration of 1 ppbv in alumina refineries.

6.3 Recommendations for Further Study

The developed method is a great reference for use in quantifying stack emission samples which can lead to developing proper control of reducing odour emissions in alumina refineries. It is always better to further explore experimental procedures that can lead to enhancement of the present one; therefore the following recommendations are suggested:

- Experimentation on the combination of adsorbent materials in thermal desorption tubes to provide information on the widest range of VOC in the emission that can be capture on these adsorbents. At present the Tenax adsorbent is the only adsorbent that has been tested. Tenax has proven ability to capture aromatic VOC. It is also hydrophobic which doesn’t permit water to interfere with the VOC during analysis. However there might be some compounds that cannot be captured by Tenax. Using the combination of various adsorbent materials inside each desorption tubes, it is assumed that all compounds of interest can be captured, analyse and detected with the existing procedures.

- The need to use another method of calibration which is the internal standardisation method used by the EPA (Environmental Protection Agency) can compare the advantage of this procedure against the external method of standardisation, that was used in this study. One of the limitations of external standardisation is that the sample size of the standard and unknowns must be known accurately and must be kept the same within the errors of volume
measurement which makes the method time consuming thus the researcher must be careful and discreet in measurement and injection of smaller volume (<1 µl) of compounds in the preparation of standards.

- The use of glass material in comparison to the original cylindrical polyurethane container of the calibration mixer can lead to better VOC recovery and better instrument sensitivity.

- The construction of an olfactometry detector unit for testing the intensity and character of the odorous compounds in the emission samples can confirm the magnitude of odour contribution of each compound to the total odour of the emission.

Time constraints were one of the factors considered to do additional experiments. Longer time is needed to work on instrumentation improvements (e.g. modification of the calibration mixer). Continuation of this research to a PhD study can lead to additional improvement; however the main procedure that was presented in this study is in itself a significant contribution to alumina industries in Gladstone.
References


Ochiai, N. and Masahiko, T., Daishima, S., Cardin, D., (2001), ‘Analysis of volatile sulphur compounds in breath by GCMS using a three stage cryogenic trapping pre
concentration system’, *Journal of Chromatography B*: Biomedical Sciences and Applications, Vol.72, pages 67-75.


Appendices

Appendix 1: Chromatographic Data of Dimethylsulfide in air at 1ppmv Using Thermal Tube #3
Appendix 2: Chromatographic Data of Methylcyclohexane in air at 1ppmv Using Thermal Tube #1
Appendix 3: Chromatographic Data of Para-Xylene in air at 1ppmv Using Thermal Tube #1
Appendix 4: Chromatographic Data of Toluene in air at 1ppmv Using Thermal Tube #1
Appendix 5: Chromatographic Data of Ethylbenzene in air at 1ppmv Using Thermal Tube #1
Appendix 6: Chromatographic Data of Methyl 1,4 cyclohexadiene in air at 1ppmv Using Thermal Tube #1
Appendix 7: Chromatographic Data of Ethylbenzene in air at 10ppmv tube #4 Trial 1
Appendix 8: Chromatographic Data of Ethylbenzene in air at 5 ppmv tube #4
Trial 1
Appendix 9: Chromatographic Data of Ethylbenzene in air at 1 ppmv tube #4
Trial 1
Appendix 10: Chromatographic Data of Ethylbenzene in air at 100 ppbv tube #4 Trial 1
Appendix 11: Chromatographic Data of Ethylbenzene in air at 10 ppbv tube #4 Trial 1
Appendix 12: Chromatographic Data of Ethylbenzene in air at 1 ppbv tube #4 
Trial 1
Appendix 13: Chromatographic Data of Ethylbenzene in air at 10 ppmv tube #4
Trial 2
Appendix 14: Chromatographic Data of Ethylbenzene in air at 5 ppmv tube #4 Trial 2
Appendix 15: Chromatographic Data of Ethylbenzene in air at 1 ppmv tube #4
Trial 2
Appendix 16: Chromatographic Data of Ethylbenzene in air at 100 ppbv tube #4 Trial 2
Appendix 17: Chromatographic Data of Ethylbenzene in air at 10 ppbv tube #4 Trial 2
Appendix 18: Chromatographic Data of Ethylbenzene in air at 1 ppbv tube #4
Trial 2
Appendix 19: Chromatographic Data of Ethylbenzene in air at 10 ppmv tube #4 Trial 3
Appendix 20: Chromatographic Data of Ethylbenzene in air at 5 ppmv tube #4
Trial 3
Appendix 21: Chromatographic Data of Ethylbenzene in air at 1 ppmv tube #4
Trial 3
Appendix 22: Chromatographic Data of Ethylbenzene in air at 100 ppbv tube #4 Trial 3
Appendix 23: Chromatographic Data of Ethylbenzene in air at 10 ppbv tube #4
Trial 3
Appendix 24: Chromatographic Data of Ethylbenzene in air at 1 ppbv tube #4
Trial 3
Appendix 25: Chromatographic Data of Ethylbenzene in air at 10 ppmv tube #4 Trial 4
Appendix 26: Chromatographic Data of Ethylbenzene in air at 5 ppmv tube #4 Trial 4
Appendix 27: Chromatographic Data of Ethylbenzene in air at 1 ppmv tube #4
Trial 4
Appendix 28: Chromatographic Data of Ethylbenzene in air at 10 ppbv tube #4
Trial 4
Appendix 29: Chromatographic Data of Ethylbenzene in air at 1 ppbv tube #4
Trial 4
Appendix 30: Chromatographic Data of Ethylbenzene in air at 10 ppmv tube #4 Trial 5
Appendix 31: Chromatographic Data of Ethylbenzene in air at 5 ppmv tube #4 Trial 5
Appendix 32: Chromatographic Data of Ethylbenzene in air at 1 ppmv tube #4 Trial 5
Appendix 33: Chromatographic Data of Ethylbenzene in air at 100 ppbv tube #4 Trial 5
Appendix 34: Chromatographic Data of Ethylbenzene in air at 10 ppbv tube #4
Trial 5
Appendix 35: Chromatographic Data of Ethylbenzene in air at 1 ppbv tube #4
Trial 5