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# Development of high accuracy hazardous air pollutants, primary standard gas mixtures

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# Development of High Accuracy Hazardous Air Pollutants Primary Standard Gas Mixtures



UNIVERSITY OF THE
WITWATERSRAND,
JOHANNESBURG

By

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A dissertation submitted to the faculty of Science, University of the Witwatersrand, Johannesburg, in fulfillment of the requirements for the degree of Master of Science

2018

## DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Master of Science at the University of the Witwatersrand, Johannesburg. It has not been submitted before or any degree or examination at any other University. This research has been conducted at National Metrology Institute of South Africa (NMISA) Gas Analysis Laboratory.

_____

Signature of Candidate

_____day of_____20_____in_____

## ABSTARCT

Volatile organic compounds also classified as hazardous air pollutants (HAPs) such as benzene, chloroform, dichloromethane, 1,2-dichloroethane, tetrachloroethylene, trichloroethylene, vinyl chloride and 1,3-butadiene. have been identified to be potential carcinogens and travel longer distances from their point sources from one environmental compartment to the other. Monitoring of HAPs in ambient air has been receiving great attention across the world due to its contribution to emission studies of air pollution. However, to accurately measure these contaminants in the atmosphere standards of high accuracy are needed to ensure good air quality monitoring. Measurements which are accurate have traceability to SI unit because they are comparable internationally and are associated with low uncertainty.

In this study the development of gaseous standard gas mixtures was carried following gravimetric method. The preparation of gaseous mixture is difficult due to the nature and properties of gas. To accurately follow gravimetric preparation, purity analysis of high pure starting materials was performed to obtain the precise composition of the final mixture. Various techniques such as gas chromatography coupled to mass-spectroscopy, thermal conductivity detector and pulsed charged ionisation detector were used.

The development of gases was carried out following direct-step dilution for pure liquid samples using syringe method and multiple-step dilution for pressurized liquid. To carefully understand the behaviour of gases, binary gas mixtures were prepared in nitrogen at 10 µmol/mol, followed by 10 µmol/mol multicomponent of six gas component and 100 nmol/mol eight components to check for matrix interference.

Gas chromatography coupled to flame ionisation detector was used to verify gravimetric concentration and following ABA sequence using one-

point calibration. The sequence was used to monitor instrumental drift, affecting analysis results. No impurities were detected in benzene, chloroform, tetrachloroethylene, trichloroethylene, dichloromethane and 1,2-dichloroethane. Nitrogen impurities were detected in vinyl chloride at 681±4.4 µmol/mol and 1,3-butadiene at 254± 2.1 µmol/mol.

The method of analyses obtained good results with instrumental drift of less than 1.0. Good accuracy of less than 3 % was obtained between the gravimetric and analytical results. Relative expanded uncertainty was different for the binary gas mixtures, benzene was obtained within 3.2 %, tetrachloroethylene 1.9 %, chloroform 2.5 %, vinyl chloride 0.15 %, trichloroethylene 2.3 %, dichloromethane 2.7 %, 1,2-dichloroethane 2.5 % and 1,3 butadiene 0.15 % at coverage factor of K= 2 at 95 % c-onfidence level. Multicomponent development showed no interferences within the mixture during analyses for determining of accuracy of mole-fraction gravimetrically prepared. Percentage difference between the gravimetric and analytical values were within 2.03 % with relative expanded uncertainty ranging between 3.1 to 9.8 % at K=2 at 95 % confidence level.

The developed multicomponent was successfully used to identify and quantify HAPs found in air sample.

## DEDICATION

*This dissertation is dedicated to my younger brother Kgothatso Mashiane*

## PRESENTATIONS IN CONFERENCES

1. Lekoto, G. A., Ntsasa, N., Tshilongo, J. and Chimuka, L. Development of Hazardous Air Pollutants(HAPs) Primary Reference Gas Mixtures. Oral presentation at Test and Measurement Conference held at Saint George Conference Centre, August (2017).
2. Lekoto, G. A., Ntsasa, N., Tshilongo, J. and Chimuka, L. Development of Trichloroethylene and Tetrachloroethylene Primary Reference Gas Mixtures. Poster presentation at National Metrology Institute of South Africa 70/10 Celebrations held at Council for Scientific and Industrial Research Conventional Centre, August (2017).
3. Lekoto, G. A., Ntsasa, N., Tshilongo, J., Lushozi. S., Gorst-Allman, P and Chimuka, L. Gravimetric Preparation of Benzene and Chloroform Primary Reference Gas Mixtures. Oral presentation at National Association of Clean Air conference held at Cedarwoods of Sandton, October (2017).
4. Jozela, M., Tshilongo, J., Ntsasa. N. and Lekoto, G. A. Poster presentation at Asia Pacific Metrology Programme $15^{h}$ (APMP) / TCQM Gas Analysis Working Group Workshop (2017), India.
5. Ntsasa, N., Tshilongo, J., Jozela, M. and Lekoto, G.A. Analysis of selected volatile organic compounds at background level in South Africa, Poster presentation at EGU General Assembly, April 2017.

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## ABBREVIATIONS

| | |
|---|---|
| BIPM | International Bureau of Weights and Measurements |
| GAW | Global Atmospheric Watch |
| GUM | Guide to the Expression of Uncertainty of Measurement |
| HAPs | Hazardous Air Pollutants |
| IARC | International Agency for Research on Cancer |
| KP | Kyoto Protocol |
| MDV | Minimum Dead Volume |
| NRL | National Reference Laboratory |
| NMISA | National Metrology Institute of South Africa |
| SI unit | International System of Units |
| USEPA | United State Environmental Protection Agency |
| VOCs | Volatile Organic Compounds |
| VIM | International Vocabulary of Metrology |
| WHO | World Health Organisation |

# CHAPTER ONE- INTRODUCTION

This section includes general description, impacts and distribution of Hazardous Air Pollutants in the environment. It also highlights the need for high accuracy standard gas mixtures and how it links to metrology. Finally, there is a brief elucidation of the significance of the study.

## 1.1 Background

Air pollution is a broad concept and difficult to define. One acceptable way of defining it is that, air pollutants are substances in the atmosphere that have exceeded their safe mole-fractions causing negative effects to humans, animals, climate, environment and plants (Daly et al., 2007). In the earliest years air pollution was not significant, the first case to get attention was of burning coal. Burning of coal results in smog and carbon dioxide ($CO_2$) released in the atmosphere. In 1373 King Edward passed a law of prohibiting the use of one type of coal, this was the beginning of trying to control air pollution (Hinch, 1969). Currently Volatile Organic Compounds (VOCs) have received great attention in research due to their presence in ambient air and other environmental compartments. There is a wide range of VOCs such as benzene, chloroform, trichlorethylene, etc which have been identified as hazardous air pollutants (HAPs). These compounds are monitored across the world due to negative health impacts to humans and photochemical reactivity to form ozone in the lower atmosphere (Rivett et al., 2004; Oliver et al., 1995; Zhang et al., 2018). Chemical reactions are influenced by air temperature, air humidity and wave radiation. Pollutants become dispersed in the atmosphere by metrological factors such as wind speed, turbulences and atmospheric stability (Mayer, 1999). They can travel longer distances from various point sources which are either anthropogenic or natural (Daly et al., 2007; Kim et al., 2011). The monitoring of these compounds also involve quantification by various laboratories and research groups.

For pollutants to be accurately quantified in food, water and air, reference standards traceable to the International System of Units (SI unit) are required. Traceable standards produce accurate, reliable measurements which are comparable in space and in time. This allows the process of implementing environmental regulations and laws to protect the human health and sustain clean environment to be reliable (Rhoderick et al., 2004; Kim et al., 2016).

## 1.2 Problem Statement

In April 2010, the National Air Quality Act no 39 of 2004 was implemented in South Africa. The Act regulates laws which protects the environment from harmful substances or pollution. The acts states that we must identify substances or mixtures of substances in ambient air which, through ambient concentrations, bioaccumulation, deposition or in any other way, present a threat to health, well-being or the environment or which the Minister reasonably believe present such a threat in section 9 (a) of National standards and in Section 9 (c) it states that in respect of each of those substances or mixtures of substances, establish national standards for emissions from point, non-point or mobile sources. National Metrology Institute of South Africa (NMISA) is the custodian measurement centre of the country, mandated by Department of Trade and Industry to disseminate traceability in SA to the International System of Units (SI unit) by provision of standards . The gas laboratory at NMISA provides primary reference gas mixtures (PRGMs) to the industry with a wide variety of gases such CO, $CO_2$, $O_2$, $H_2S$, ethanol, etc (Van Rensburg, 2007). However, there is no availability of hazardous air pollutants reference gas mixture. This leads to the country not having its own reference gas mixtures of HAPs traceable to SI and not having representative standards which are comparable to other countries. To respond to the National Air Quality, it is therefore an obligation to establish HAPs national standards as a country due to the health threats it pose to the environment.

## 1.3 Rationale

The purpose of the research is to develop hazardous air pollutants in nitrogen primary standard gas mixtures traceable to the SI unit. The aim is to have standards used to attain measurement traceability for air pollution monitoring in South Africa. This is to ensure accuracy of measurements taken are reproducible and are independent of time and place. Compounds which the study will be focused on are benzene, trichloroethylene, tetrachloroethylene, chloroform, vinyl chloride, 1,3-butadiene, dichloromethane and 1,2-dichloroethane. These compounds exist in the atmosphere from various sources, hence the development will be focused on developing lower µmol/mol to nmol/mol. The motivation behind the choice of HAPs is based on the potential toxicity to human health and environment. Also, due to the ongoing research taking place across the world. It has also been identified that other NMIs across the world have previously developed HAPs standards.

A long-term goal of the project is to have HAPs measurements around the country comparable internationally, this will be obtained by participation in Key Comparison held by BIPM taking place in the end of 2018. The developed primary reference mixtures will be compared with other NMIs to confirm the accuracy and international capability of the work.

## 1.4 Hypothesis

It is hypothesized that gravimetric method according to ISO 6142 will sufficiently produce primary standard gas mixtures, which will be internally consistent and uncertainty comparable with previous studies. The developed standards will adequently quantify an unknown air sample.

## 1.5 Aims and Objectives

The main purpose of the study is to develop hazardous air pollutants primary standards gas mixtures which will provide traceability to SI unit to the country. The standards can be used as calibration gases by air monitoring laboratories . The developed standards will be used to identify

pollutants found in air sample collected at a remote area such as Cape Town Global Atmospheric Watch (GAW) Point Station. This is to identify HAPs found in background air. The objectives of the study are:

- To carry out purity analysis of starting materials were impurities associated with the high pure components are quantified. Using various techniques such as gas chromatography coupled to mass spectroscopy, flame ionisation detector, thermal conductivity detector and pulsed discharged ionisation detector.
- To gravimetrically prepare binary standard gas mixtures according to ISO 6142 using the syringe method for liquids.
- To gravimetrically prepare multicomponent standard gas mixtures consisting of six and eight components according to ISO 6142.
- Use ABA sequence, method of analyses to minimise instrumental variations caused by the environmental conditions.
- Check internal consistency of the prepared gas mixtures using gas chromatography-coupled to flame ionisation detector
- Identify and quantify the HAPs found in air sample, using the developed standards.

# CHAPTER TWO - LITERATURE REVIEW

This chapter entails the background information on Hazardous air pollutants and monitoring in ambient air. Each component to be focused on in the study is thoroughly explained in terms of properties, sources and toxicity. Detailed information on the need for high accuracy standard is given. It also includes various techniques previously used for preparation of standard gas mixtures and instrumentation techniques applied in the field of gas analysis.

## 2.1 Background on Hazardous Air Pollutants

In 1990 the Clean Air Act in the United States identified two classes of pollutants; criteria pollutants and hazardous pollutants which are also known as the toxic air pollutants (Cadwell et al., 1998). The criteria pollutants are damaging to public health, example of such compounds are lead (Pb), ozone ($O_3$), carbon monoxide, nitrogen dioxide. Hazardous Air Pollutants (HAPs) are listed among volatile organic compounds (VOCs) (Wood et al., 2008). They contain 189 list of components which were defined by United State Clean Air Act Amendment in 1990 (Francis et al., 2009; Oliver et al., 1996). These compounds are associated with negative health impacts such as cancer, neurological and developmental effect by Environmental Protection Agency (EPA). There is limited monitoring data, thus United States Environmental Protection Agency (USEPA) developed a nationwide database recording annual average mole-fractions (Windham et al., 2006).

HAPs are known to be persistent in the environment and can partition into different compartments of the environment i.e soil, food, air and water. Persistence of components varies depending on the compartments of the environment they are found in. A study carried out by Srivastara in 2007 showed that HAPs have the potential to travel longer distances, crossing

to different compartments and that they would have longer life span depending on the environment. The length of duration impacts on human health and surrounding environment. The longer components remain in the environment, the greater the potential concern (Srivastara et al., 2007). The atmospheric lifetime of these compounds also depend on rections with hydroxyl radical, ozone, photolysis, wet or dry decomposition. Chemical reactions can also form harmful reagents (Chester et al., 2002). The negative health effects, depends on the chemical structure, mole-fraction and time of exposure. Health impacts can either be carcinogenic and non-carcinogenic. Carcinogenic effects include lung cancer and other types of cancer while non-carcinogenic includes skin irritation to life threatening conditions. **Table 2.1** show a list of 33 HAPs causing negative health impacts such as carcinogenic, mutagenic and teragenic toxicity identified between 1996 and 2001. Exposure of these components occurs through ingestion, dermal contact and inhalation.

Table 0.1:HAPS impacting health negatively (Spicer et al., 2002.)

| | | |
|---|---|---|
| Acetaldehyde | Manganese compounds | Propylene Dichloride |
| Formaldehyde | Berylium compounds | Chromium compounds |
| Acrolein | Mercury compounds | Polycyclic Dioxin |
| Hexachlorobenzene | 1,3-Butadiene* | 1,1,2,2-Tetrachloroethene* |
| Chloroform* | Methylene Chloride* | Ethylene Dibromide |
| Acrylonitrile | Cadmium Compounds | Trichloroethylene* |
| Hydrazine | Nickel Compounds | Quinoline |
| Arsenic compounds | Carbon Tetrachloride | 1,3-Dichloropropene |
| Lead compounds | Polycyclic organic matter | Ethylene dichloride* |
| Benzene* | Coke oven emissions | Vinyl chloride* |
| Ethylene oxide* | Propylene dichloride | Hydrazine |

*****compounds studied in this research

## 2.2 Hazardous Air Pollutants of Focus

### 2.2.1 Vinyl Chloride

Vinyl chloride also known as chloroethene is an organochloride compound, colourless at room temperature and stored as compressed liquid. It is flammable with a mild sweet odour. Vinyl chloride introduced in the atmosphere through bacterial degradation of solvents containing chlorine or industrial waste. The primary source of vinyl chloride is poly

vinyl chloride (PVC) which is used in the production of pipes, packaging materials, insulation and bottles. During production of these materials vinyl chloride escapes to the atmosphere and due to its property of being heavier than air, it is transported to other mediums (such as groundwater, landfills and waste water) from the point source. Human exposure of vinyl chloride occurs through inhalation of contaminated air or ingesting contaminated water. Exposure has also been noticed in smoke produced by tobacco. High levels of exposure lead to dizziness, spontaneous abortion or even death. USEPA has identified vinyl chloride as a carcinogen and International Agency for Research on Cancer (IARC) classified it as group 1 human carcinogen, meaning that there is enough evidence that it causes a specific type of cancer. The most common type diagnosed in humans are lung, brain and liver cancer.

### 2.2.2 1,2-Dichloroethane

This is a clear liquid which does not exist naturally in the environment. It is a manufactured chemical, primarily used in the production of vinyl chloride. Its is spread to the atmosphere during its uses, transportation,disposal and storage. The lifetime of 1,2-dichloroethane is approximately five months until it undergoes photochemical reactions in the atmosphere. High exposure lead to problems in kidneys, nervous system, respiratory distress. Environmental Protection Agency(EPA) classified it to be Group 2B carcinogen agent. The most common way of exposure is through inhalation of ambient or working environment air. Other ways of becoming in contact with the chemical, is individuals with habitats closer to waste disposal area or manufacturing industries (ATDR, 2001).

### 2.2.3 Tetrachloroethylene

Tetrachloroethylene also known as Perchloroethylene or tetrachloroethene is a colourless, volatile, non-flammable, sweet odour liquid. It was introduced commercially in the 1900s as dry-cleaning agent and

applications increased to metal degreasing purposes (Roda et al., 2013). With years wide range of applications increased to commercial and domestic activities such as solvents, metal degreasing agents and extraction, etc. (Fabbr et al., 2007). This compound evaporates to the atmosphere during manufacturing of dry cleaning agents. It has been determined that the concentration in the atmosphere is below 1-2 µg\m$^3$. Its behaviour depends on the media which it is found in. When found in air, it undergoes thorough degradation producing phosgene, trichloroacetyl, hydrogen chloride, carbon monoxide and carbon dioxide. Half-life in the air is approximately 3 to 5 months. It evaporates when found in surface water and soil. In deep waters under abiotic and aerobic conditions it is resistant. Under anaerobic conditions it biodegrades to produce dichloroethane, vinyl chloride, ethane and ethane. Higher mole-fractions of tetrachloroethylene are observed at buildings and ground water near the production site. Humans became exposed through inhalation and direct contact. Once exposed to the compound it is mainly distributed to the adipose tissues, smaller proportions reach the liver, brain, lungs and kidneys (WHO, 2006). Exposure results in nausea, confusion, dizziness, headache, and unconsciousness, difficulty in walking and speaking and death. The International Agency for Research on cancer determined that tetrachloroethylene is suspected to cause cancer (Barton, 2014).

### 2.2.4 Trichloroethylene

Trichloroethylene also known as trichloroethene ($C_2HCl_3$) is a volatile chlorinated hydrocarbon, non-flammable, colourless liquid with a sweet odour. This compound does not exist naturally in the environment. It has been introduced in the environment by anthropogenic sources. It has various applications such as typewriter correction, fluids, paint removers, stain removers and rug-cleaning fluids but it is predominately used for metal degreasing and cleaning (Dobosy et al., 2016).

When released into the environment through anthropogenic sources, most of it goes into the atmosphere and only a small proportion goes to the water, groundwater, soil and food. It has low solubility in water but evaporates quickly from surface water. Research has shown that groundwater is contaminated with trichloroethylene and this is because the compound fuse with particles found in water, then eventually settle on the bottom of the sediments. Its mole-fraction varies due to the environmental compartment that it is found in. High mole-fractions are found closer to the sources of emissions, especially indoors where employees use trichloroethylene for various applications. In air, its mole-fraction varies due to strength of the source, wind direction and photodecomposition. Lower mole-fractions are found in food, water and soil. Human exposure can occur when there is dermal contact, inhalation or ingestion of the compound. This lead to negative health impacts such as dizziness, liver damage, impaired immune system and death.

### 2.2.5 Chloroform

Chloroform also known as trichloromethane has been widely studied in different environmental compartments such as water, soil and air because of its contribution to the chlorine-budget in the atmosphere. It is a colourless, non-flammable, sweet odour dense liquid which is volatile under environmental conditions. Introduction in the atmosphere is through natural or anthropogenic sources. Natural sources are volcanic activity, soils and oceans; anthropogenic sources are burning of biomass and industrial production (Hsu, 2003).

This compound has negative impacts on both humans and the environment. Great human exposure occurs when it is found in enclosed environments and water. It can be through inhalation and dermal contact. The most common way of exposure is inhalation due to its high volatility character. Studies have shown that chloroform it is suspected to be a carcinogen and other negative health impacts are cytotoxicity in the liver, kidney and nasal epithelium (Hsu et al., 2009). When found in

environmental compartments such as water and soil it escapes to the atmosphere. In water surroundings, it has the ability of equilibrating with the surrounding because of its low solubility in water and high vapour pressure properties. This results in chloroform partitioning to the atmosphere (McCulloch, 2003). It has an atmospheric life of approximately one year and it follows two paths when found in the atmosphere; it becomes very reactive to hydroxyl radicals leading to its depletion and approximately 16 % travel to the stratosphere, where depletion of the ozone layer occurs (Khalil, 1999; Kolusu et al.,2017).

### 2.2.6 Dichloromethane

Dichloromethane (DCM) also known as methylene chloride is a colourless, mild sweet odour, extremely volatile liquid. It is widely used as a solvent due to its ability to dissolve organic and organometallic substances (Goncalves et al., 2011). It is predominately from natural sources and about 10-15 % is from anthropogenic sources. Most common natural point of source is oceans and common used applications are paint stripper and cleaning agent, other applications as solvents include plastics, solid-phase and liquid phase extractions, food processing insecticides and aerosols (Shestakova et al., 2013). Introduction in the environment is during industrial production of various products, through transportation and storage; waste sites, industrial effluent and water treatment facilities.

### 2.2.7 1,3-Butadiene

1,3-Butadiene is a colourless flammable compressed liquid with a mild gasoline odour released from anthropogenic and natural sources. Anthropogenic sources are by products of waste or emissions from plant refineries, tobacco smoke, rubber production companies, gasoline and auto mobile sources. Natural sources which contribute largely its mole-fraction in the atmosphere is biomass combustion (Laowagul et al., 2009).

This component is highly reactive due to its double bond property. It forms secondary pollutants in the atmosphere. It is involved in atmospheric photochemical reactions leading to toxic aldehyde, peroxyacetyl nitrate and ozone. Its lifetime in the atmosphere is very short due to fast reaction with different reagents such as OH, $O_3$ and $NO_3$. Reactions with OH radical lasts for about 1-2 hours for production of tropospheric ozone. Reactions with $O_3$ and $NO_3$ to produce carbonyl is 11 hours to 2.4 days ( Czader et al., 2014).

The second toxic VOC /HAP is known to be 1,3-butadiene following benzene. United State Environmental Protection Agency (USEPA) classified it to be a suspected carcinogen. Adverse health impacts of are associated with the duration or level of exposure. Most common way of exposure is inhalation. Contact can also occur through dermal exposure which leads to cold sensation. After a short while a burning sensation follows resulting in frost bite. Long term exposure lead to cardiovascular diseases, mutation, cancer which primarily attacks the blood and lymphatic system this results in leukaemia. Other non-cancer health impacts are irritation, inflammation of the respiratory system, decreased growth in foetus and death.

### 2.2.8 Benzene

Benzene is a clear, colourless liquid accompanied by a slight sweet odour. This aromatic hydrocarbon is highly flammable, volatile and has low water solubility. This liquid is introduced in the atmosphere by natural and anthropogenic sources (WHO, 2010). Amounts introduced by natural sources are lower than those contributed by anthropogenic sources. Natural sources are manly from crude oil used for production of petroleum. Anthropogenic sources include oil refineries, rubber production industries, chemical plants, tobacco smoke, shoe manufacturing industries and automobile emissions (Weisel, 2010).

Human exposure is predominately through inhalation, dermal contact is relatively low due to its volatile property. It evaporates quickly before it can be absorbed on the skin. Benzene is listed as one of the most significant HAP due to it's adverse health effects. USEPA identified it to be a suspected carcinogen and International Agency for Research on Cancer (IARC) listed it as group I carcinogen (Zhang et al., 2015). Health effects depend on the level of exposure and amount or mole-fraction exposed to. Low exposure of benzene for a short period results in headache, drowsiness and nausea. Low exposure at high mole-fractions results in death, genetic effects, euphoria followed by headache, nausea and vomiting (Moola et al., 2013).

### 2.3 Ambient Air Monitoring

In 1987 the industry reported 2.7 billion pounds of toxic pollutants emitted in the atmosphere in the United States. Cases of leukaemia and lung cancer have been evident in urban environment of developing and developed countries. These cases have been attributed to carcinogens in the air pollutants in ambient air such as HAPs (benzene, vinyl-chloride, 1,3-butadiene, tetrachloroethylene) and Poly-Aromatic Hydrocarbons (PAHs). The toxic air pollutants or hazardous air pollutants have been defined as components which are harmful to the human health or environment. The reports on high levels of HAPs in the atmosphere which has a link to negative health impacts gave rise to implementation of a law for reduction of pollutants emission in the United States in the 1990s (Tsai, 2016).

South Africa has various air quality stations across the country. **Figure 2.1** indicates various monitoring stations administered by the National Ambient Air Quality Monitoring Network (NAAQMN). The most commonly monitored pollutants are $SO_2$, $NO_x$, $O_3$, and VOCs including benzene, tolouene, ethyl benzene and xylenes. Pollutants such as VOCs have been considered due to their rise in ambient air from industry (DEA, 2012). The

monitoring of VOCs is supported by Act no.39 in 2004 of National Environment Management Act. It was stated that ‘’substances or mixtures of substances in the ambient air which through ambient mole-fractions, bioaccumulation, deposition or in any other way, present a threat to health, well-being or the environmental’’. So far there is limited information or literature review on HAPs in South Africa. The most commonly compound monitored is benzene (Jaars et al., 2014).

To properly monitor pollutants in the atmosphere it was proposed that a National Research Laboratory (NRL) is important in developing national standards which can support decision making and compliance monitoring in South Africa. Act no.39 of 2009 also states that there should be establishment of national standards of harmful substances or mixtures of substances.

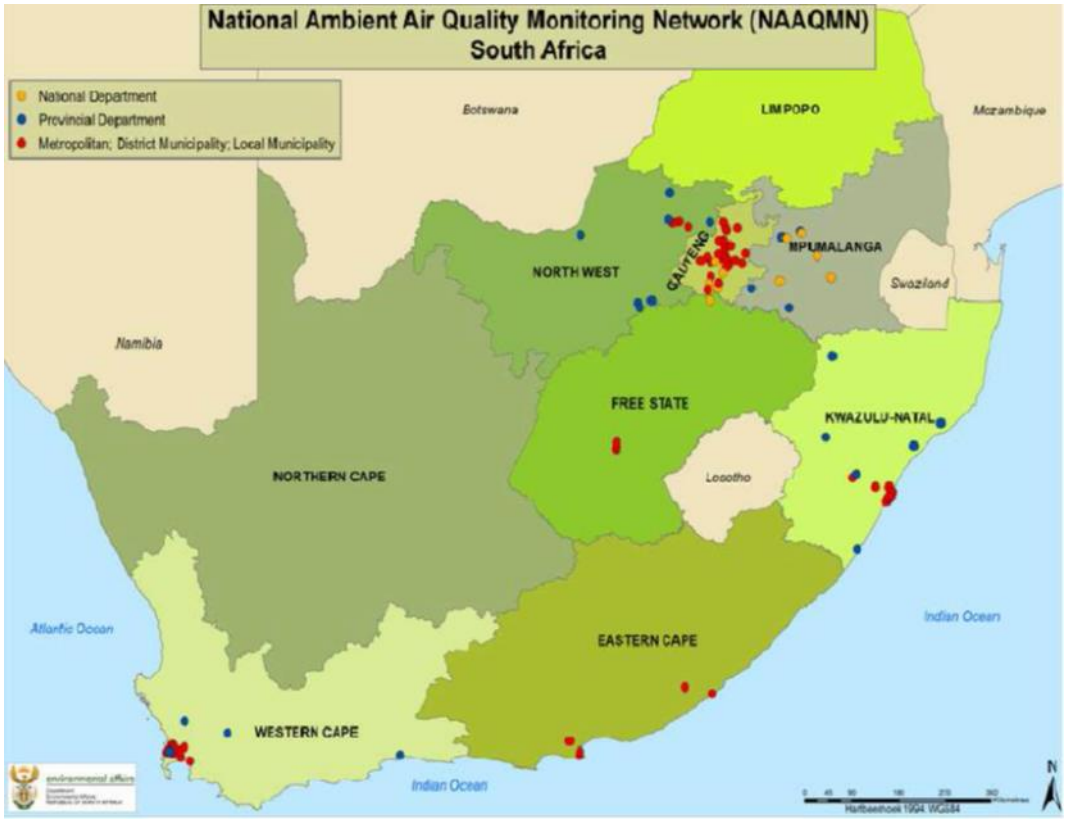



Figure 2. 1: NAAMQN Monitoring Stations in South Africa (DEA, 2012)

## 2.4 Metrological need in Science

Metrology is defined as the science of measurements, according to International Vocabulary in Metrology (VIM). To provide reliable measurements around the world, a uniform system was agreed upon amongst different countries. This led to the creation of The International Bureau of Weights and Measures (BIPM) in Paris in 1975. Its mandate is to ensure that measurements are independent of the place or time taken at. It is a system that is involved in ensuring quality assurance and quality control by proving measurements are associated with a value of composition and uncertainty traceable to International System of Units (length, metre, mole, ampere, seconds, kelvin and candela). This work is carried out by different metrology institutes.

Factors contributing to quality assurance and quality control are; traceability, uncertainty, validation of analytical procedure, use of reference material and laboratory inter-comparison (Slominska et al., 2014).

It is significant to have a National Metrology Institute (NMI) reference materials or standards, for organisations responsible for reporting trends of pollutants mole-fractions. This is because NMIs provide direct traceability measurements associated with lower uncertainty leading to more accurate measurements data (Rhoderick, 2015; World Metrological Organisation, 2013).

### 2.4.1 Significance of Primary Standard Gas Mixtures

A reference material is defined as “material sufficiently homogeneous and stable with reference to specified properties which has been established as fit for its intended use in measurement or in examination of nominal properties” (Slominska et al., 2014). Reference material can be in a form of liquid, solid or gas. A standard gas mixture must contain a known amount of analyte and diluting gas. International Vocabulary of Basic General Terms in Metrology defines a standard as a material measure,

measuring instrument, Reference materials (RM) or measuring system intended to define, realize, conserve or reproduce a unit or one or more values of a quantity to serve as a reference. For standard to be fit for purpose, it must be associated with metrological uncertainty. Standard gas mixtures are classified into non-matrix and matrix reference mixtures. Non-matrix RMs are those which the matrix affects the results obtained and matrix RMs, there is no interference between the analyte and matrix.

The main purpose of using standard gas mixtures is to ensure quality in analytical results. Research studies in science protect the environment and strategies in building a healthier atmosphere or indoor air. This requires proper measurement which can be agreeable in different countries. This problem is solved by using standard gas mixtures. Konieczka, Slominiska and Alink highlighted importance of using standard gas mixtures explained below:

i. Used to calibrate instruments used for analyses of environmental samples. Calibration is important in analytical chemistry because instruments are used to quantify unknown samples using relative measurements.
ii. Validate existing analytical procedures
iii. Used for inter-laboratory comparison, this assist monitoring overall performance of laboratories. Which can assist in improving repeatability and uncertainty of measurements.
iv. When prepared by a metrology institutes, serve as national measurements standard which is a way of disseminating traceability in a country.

### 2.4.2 Traceability to System of International unit

For reference standards to be traceable to SI unit, a primary method must be adopted for development or preparation of the standard. A primary method is associated with highest metrological traceability, it changes abstract definitions of SI unit by giving measurements practical unit

associated with it (Milton, 2001; Walden,2009). The measurements taken has lower uncertainty with units. Most importantly the primary reference prepared using primary method does not need another reference mixture to verify its measurement. These measurements are trusted and are associated with base units of (kilogram, length, mole, kelvin, second, ampere and candela). In gas analysis gravimetric method is chosen as the primary method. This is employed in the development or preparation of gas mixtures. a reference mixture which already has measurements value with statement of uncertainty with unit can be used to dilute to or prepare a new mixture (Milton et al., 2001; Di Meane et al., 2009).

### 2.5 Traditional Preparation Methods of Primary Gas Mixtures

Preparation of gases is generally difficult when compared to solids and liquid. Because the chemistry and physical state of gases is affected by temperature and pressure, hence variation in these factors must be kept minimal; it is not easy to weigh gases accurately and the volume is prone to changes during handling of the mixtures. The best traditional methods of gas preparation are dynamic method and static method. Dynamic method involves continuous flow of gas at a known rate into a system. Static method involves transferring known mass of a gas or liquid in a known volume of a vessel, this can either be cylinder, plastic bag, or flasks.

Dynamic method can generate gases in large volumes, no adsorptions problems due to equilibrium between the gas flowing and the surface wall of the vessel used to prepare the mixture. Control of flow rate of gases must be taken into consideration and the method require expensive equipment's (Slominska et al., 2014; Konieckza et al., 2004; ISO 6142,2015.

Static method comes of cheaper than dynamic method. The method is primary and offers the highest accuracy. Disadvantages are that the mixture is prone to adsorption on the wall of the vessel, variation in

pressure affect mole-fraction and it is prone to leaks (Barratt, 1981; Konieckza et al., 2004). Gravimetric preparation falls under static method and is explained in details in section 2.6.

### 2.6 Gravimetric Preparation Method of Gases

This is a primary method in which by principle each component is defined by mass. In gravimetric preparation, the composition of the final gas mixture is expressed in mole fraction. The uncertainty is expressed at a coverage factor of two, expressed as expanded uncertainty. Further details explained in **Section 2.8**. Preparation can be done from high purity gases or liquids or diluting from an existing primary reference standard. According to ISO 6142 mass of gas to be transferred to a cylinder is calculated using **Equation 2.1** and **2.2** (ISO 6142, 2015)**.**

$$m_j = \frac{y_k \times M_k}{\sum_{i=1}^{q} y_i \times M_i} \times m_\Omega \qquad 2.1$$

$$m_\Omega = \frac{P_{F,\Omega} \times V_{cyl}}{Z_\Omega \times R \times T_F} \times \sum_{i=1}^{q} y_i \times M_i \qquad 2.2$$

Where:

$m_j$ mass of diluent component expressed in g

$M_j$ molar mass of diluent component expressed in g/mol

$y_k$ mole fraction of diluent component

$M_i$ mass of molar mass of component expressed in g/mol

$y_i$ mole fraction of component

$m_{\Omega}$ mass of component in the mixture expressed in g

$P_{F,\Omega}$ final pressure of the mixture expressed in pascals

$V_{cyl}$ volume of cylinder expressed in $m^3$

$Z_{\Omega}$ compressibility factor of the mixture at T and $P_f$

R gas rate constant (8.314 J/mol.k)

$T_F$ Temperature expressed in K

The preparation method involves weighing of two cylinders which are similar, that is having the same material, size, volume and valves (ISO 6142, 2015). One cylinder is chosen as a tare cylinder and the other is a sample cylinder. Tare cylinder only serves in the weighing cycle and components of the gas mixture are added in the sample cylinder. The weighing of cylinders during preparation is carried out according to Borda Method or Substitution Method (Alink, 2000; van Andel et al., 2012)). The tare cylinder and sample cylinder are weighed against each other in a sequence manner. The results of the cycle are the mass difference between the tare and sample cylinders. The method of weighing cylinders against each other is carried out to minimize buoyancy effect and variations caused by air density (Milton, 2011). The buoyancy effect is due to weighing of large volumes of cylinders which results in air variations caused by carbon dioxide composition, temperature, humidity and barometric pressure (Matsumoto et al., 2004).

Addition of components are added following single-step or multiple dilution step to make the final mixture. The weighing cycle is repeated until all components are added. The mass added in to cylinder is obtained from the differences between weighing. Once all components are added, homogenisation within the cylinder is achieved.

There are different ways in which a mixture can be thoroughly be mixed, depending on the size, shape of the vessel used to prepare the mixture and the diffusion character of gases. Diffusion could be used to attain homogeneity, but it is time consuming, as it could take even months.

Rolling the vessel is a much efficient way as it reduces the time taken for mixing. Another method is through convectional current which is generated by running cold and hot water over the end of the cylinder (Barratt, 1981).

### 2.6.1 Direct and Multiple-dilution Step Preparation Methods

The choice of method to use depends on the mass of gas to be added into a cylinder. When the mass is large enough to accurately be weighed provided that the mixture will be within the required uncertainty, direct-step method is preferable. Alternatively, when the desired mole-fraction final mixture is very low, multiple mixtures will be prepared to dilute further. **Figure 2.2** indicate a schematic diagram of the methods.

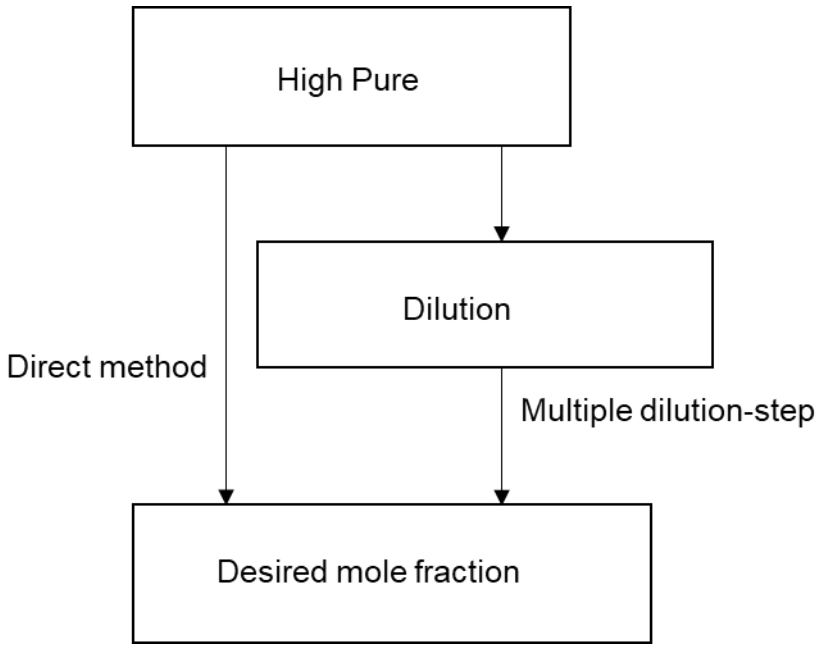



Figure 2. 2: Flow diagram of preparation by direct or multiple dilution (ISO 6142, 2015)

### 2.7.2 Methods of liquid Introduction

#### *2.7.2.1 The Syringe Method*

A gas-tight syringe is used to transfer liquid into an evacuated cylinder which is pressurized by a diluent gas\the matrix gas. The gas-tight syringe is first weighed before and after being filled with liquid. The mass that is transferred into the cylinder is calculated by getting the difference between mass of the syringe after filling with liquid and mass of the syringe after transferring the liquid to the cylinder (ISO 6142, 2015).

#### *2.7.2.2 The Sample Loop Injection Method*

Evacuated sample loops are used to transfer liquid components of the final gas mixture in an evacuated cylinder. Empty evacuated loops are weighed against a similar loop which is used as tare. The liquid contents are transferred to the evacuated loops using a gas-tight syringe. The loops are weighed with reference to the tare loop, and this step is repeated after transferring the liquid components in the cylinder to know how much was transferred into the cylinder. The diluent gas is then added into the cylinder. The cylinder is weighed against tare cylinder and rolled to achieve homogeneity (Grenfall, 2010).

Grenfel et al, 2010 showed a study of preparation of multicomponent containing 22 VOCs in air primary gas mixtures following the sample loop method. The sample liquids were combined in vials, grouped according to similar vapour pressure and transferred to evacuated sample loops. The method of grouping according to vapour pressure was done to avoid differential displacement. It is also essential in calculating the correct gravimetric mole-fraction to be prepared. The loops were connected to minimum dead volume (MDV) nut connector to transfer the sample liquids to the cylinder. MDV was used to minimise loss and adsorption during transfer. Initially DIN 1 nut connecter was used instead of MDV and

sample liquid was trapped in the nut and was not transferred into the cylinder.

## 2.8 Theory of Uncertainty of Measurements

In general, every measurement that is taken is accompanied by doubt. This doubt is called uncertainty and it gives information about the quality of the measurements. According to Guide to the Expression of Uncertainty of Measurement(GUM) uncertainty of measurement is a parameter, associated with the result of measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. The uncertainty of the measurement is expressed numerically (an interval), indicating how long the doubt is and has confidence level which indicates how definite the interval is. There are two approaches that must be followed when estimating the numerical value, Type A and Type B.

Type A - the uncertainty is based on statistical method

Type B - the uncertainty estimates are based on other information such as manufacturer's specification, data from work done previously, calibration reports, published work, and general knowledge.

### 2.8.1 Type A Uncertainty

Type A evaluations are calculated from estimated variance or estimated standard deviation.

After taking a repeated set of measurements, a mean $\bar{x}$ and estimated standard deviation, s is calculated. Estimated standard uncertainty, $u$ of the mean is calculated from:

$$u = \frac{s}{\sqrt{n}} \qquad 2.3$$

Where n is the number of measurements in a set.

### 2.8.2 Type B Uncertainty

There are various ways of calculating the uncertainty value depending the type of information one has. For this approach, it is important to know the probability distribution to be able to carry out the calculation.

Gaussian or normal probability distribution- The set of readings taken fall near average **Figure 2.3**, represent a graph indicating normal distribution.

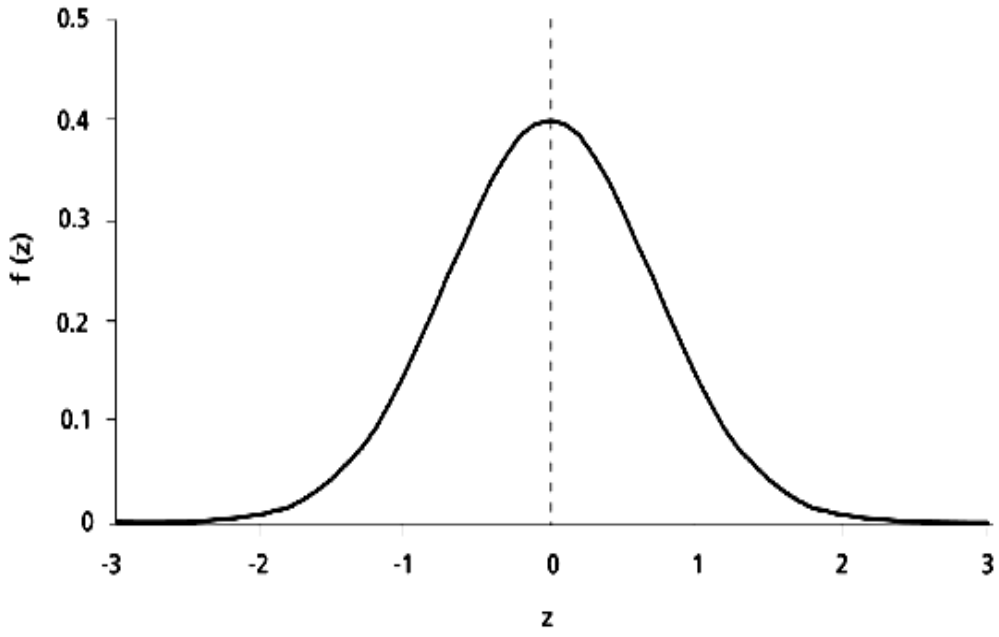



Figure 2. 3: Normal Distribution curve (Eurachem,2012)Rectangular or uniform probability distribution - Represents a set of readings which are evenly distributed. **Figure 2.4** represent a graph indicating rectangular distribution

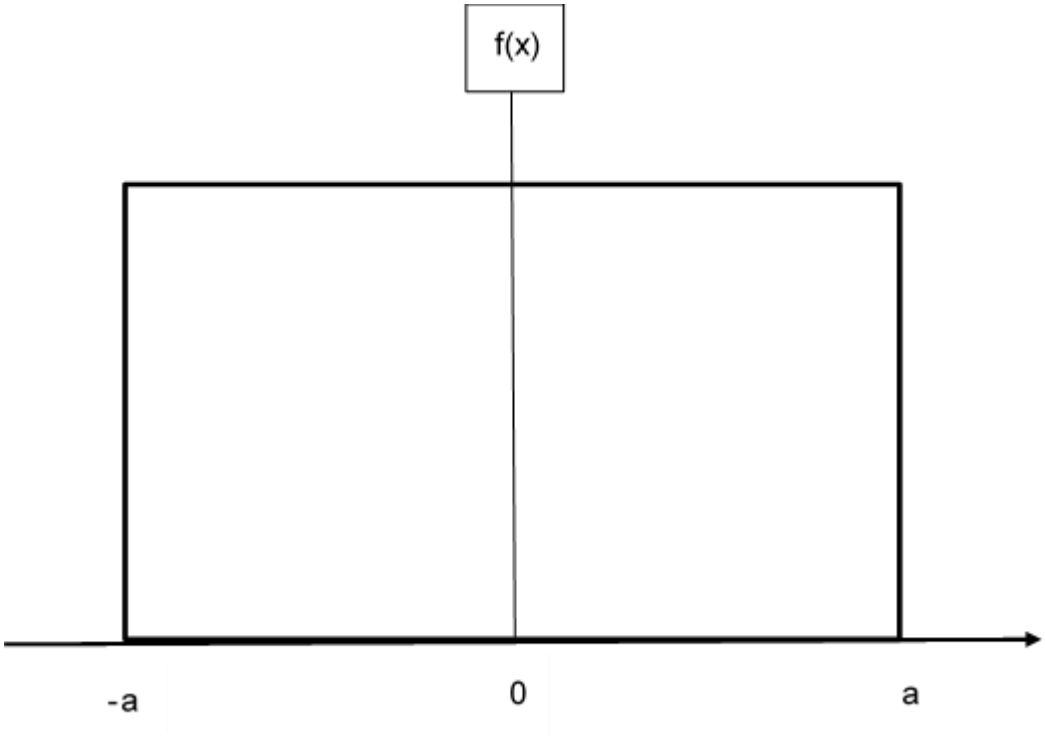



Figure 2. 4: Rectangular Distribution (Eurachem, 201Triangular probability distribution - The probability function take the shape of a triangle, represented by three values. The minimum, maximum and the peak value. **Figure 2.5** represents a graph indicating triangular distribution.

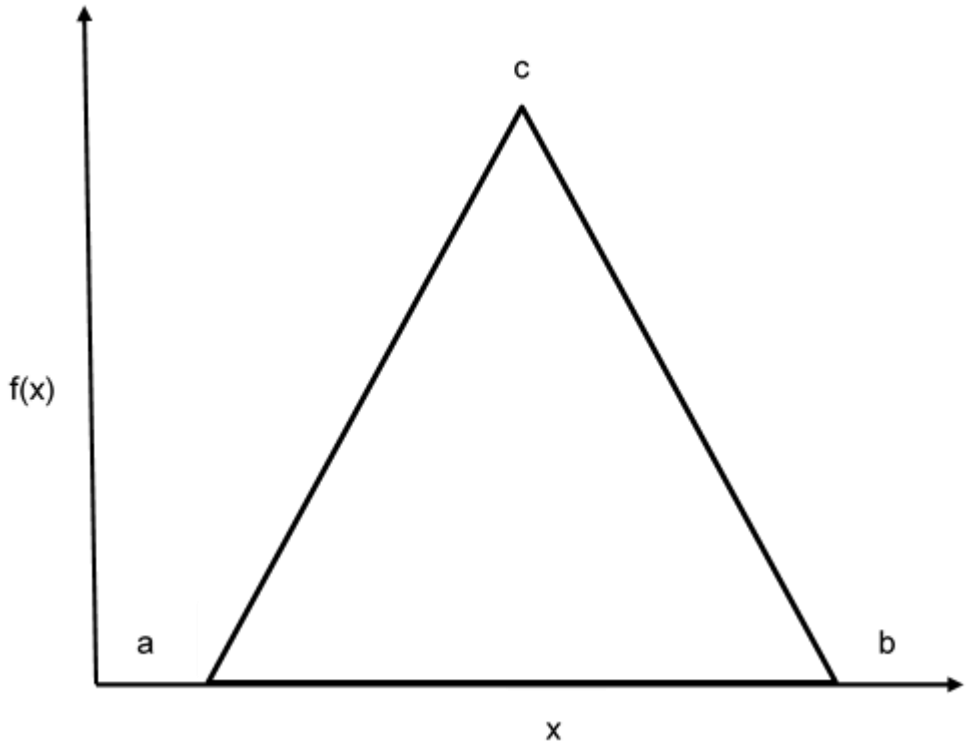


Figure 2. 5: Triangular Distribution (Eurachem,2012)

If there is no scientific knowledge available about the value given, it is important to estimate the interval ($a_-$ $a_+$) at which the value will lie. It can be assumed that the value is equally probable to lie between the interval $a_-$ and $a_+$, this follow rectangular probability distribution. To estimate the uncertainty value:

$$a = \frac{(a_- + a_+)}{2} \qquad 2.4$$

$$\text{then } u = \frac{a}{\sqrt{3}} \qquad 2.5$$

Rectangular probability distribution model is always assumed in case of no prior information about the given values. If information about the value given falls near the centre of the limits, triangular or Gaussian probability distribution models are used.

If triangular distribution is used then,

$$u = \frac{a}{\sqrt{6}} \qquad 2.6$$

Combined uncertainty, $u_c$ is calculated using individual calculations of Type A and Type B evaluations. This is done using root sum of the squares.

$$u_{c=\sqrt{a^2+b^2+c^2}}etc \qquad 2.7$$

Where a, b, c represents standard uncertainty of the measurement taken.

## 2.9 Purity Analysis of Gas Mixtures

One of the crucial steps in preparation of gaseous mixture is purity analysis. This is performed to quantify the impurities found in high pure samples because they contribute to the accuracy of final mole fraction of a mixture. A material is sufficiently pure when the amounts of all impurities associated with it does not go beyond the desired limit of accuracy. It is impossible to get a material which is entirely pure or neat in chemistry. Due to inevitable introduction of other substances before or during purification processes and during transfer or storage. (Deuwer et al., 2004).

According to ISO 6143 (2001) the purpose of purity analysis is to identify and determine the amount of impurities available in the starting material and calculate associated uncertainties. This prevents inaccurate final calculation of mole fraction in a new mixture. Various analytical techniques are used to identify substances at trace levels, which will be found in the final mixture.

## 2.10 Background Knowledge of Instrumentation

### 2.10.1 Gas Chromatography Theory and Operation

Gas chromatography is an analytical separation technique used to analyse chemical samples from different matrices. This includes environmental samples, biological samples, reference standards etc.

Gas chromatography achieves separation through interaction of analytes with mobile phase and stationary phase. The mobile phase has carrier gas and the sample. The carrier gas is usually an inert gas such as helium, argon and nitrogen. The stationary phase is found on the column which known to be the heart of gas chromatography. Due its important function of carrying out separation. This occurs through differential partitioning of sample between the stationary phase and the mobile phase. This

interaction depends on boiling point, polarity and molecular size of sample. The length of the column is also significant because it affects retention time of the analysis.

### 2.10.2 Various Detectors coupled to Gas Chromatography

Different detectors are employed on gas chromatography depending on the type of components being analysed. Thermal Conductivity Detector (TCD) is a universal detector used for determination of permananent and inorganic gases. It detects components in lower µmol/mol. Flame Ionisation Detector (FID) is sensitive to hydrocarbons. Pulsed Discharge Helium Ionisation Detector (PDHID) has greatest sensitivity features. It is able to detect permanent gases which GC-FID cannot and has greater sensitivity than GC-TCD. The limit of detection of components is at pmol/mol level (Roberge, 2004). Electron-Capture Detector is sensitive towards halogenated carbon containing components and is able to measure components in the pmol/mol level. Mass spectrometry(MS) achieves resolution by identifying the fragmented ions of molecules and quantifying the sample. Combination of GC and MS gives higher resolution results because it separates the sample and give detailed information on the structural information. It is commonly used to analyse complex organic and bioorganic components (Hussian et al., 2014; Chauhan et al., 2014).

### 2.10.3 Applications of Gas Chromatography in Gas Analysis Mixtures

Preparation of gaseous standard gas mixtures with direct traceabililty to SI unit is limited to National Metrology Institues. Previously few NMIs developed VOCs/ HAPs standards using gas chromatography coupled to flame ionisation detector with cryogenic preconcentrator. National Institute of Standards and Technology (NIST) developed 5nmol/mol containing thirty VOCs in nitrogen for air monitoring purposes and obtained expanded uncertainty ranging from 1.5 to 10 % for 28 components, and 19 % for two

analytes. Analysis on flame ionisation detector showed standard deviation, ranging from 0-1 %, with the exception of tetrachloride which ranged from 1-2 %. (Rhoderick et al., 2006). Another study for preparation of 1-1000ppb VOCs gas standard mixtures showed expanded uncertainty ranging from 3-10 % at 95 % confidence level (Rhoderick et al., 1988).

# CHAPTER THREE – MATERIALS AND RESEARCH METHODOLOGY

This chapter illustrates precisely how gravimetric method was carried out step by step to achieve the final product of gas mixtures.

## 3.1. Materials

### 3.1.1 Equipment

To carry out gravimetric preparation, specific equipment's were utilised to achieve high accuracy standards.

- Aluminium cylinders with maximum pressure of 200 bar and 300 bar manufactured from Luxfer Gas Cylinder Ltd United Kingdom were used as containers. They were taken to Air Products Pty for

fluorination and passivation processes to eliminate water and other impurities on the interior surface.

- Pfeiffer Turbo Molecular Pump used to evacuate the empty cylinders for preparation. The process is explained in detail in **4.2.1**.
- A filling station from Air and Vacuum Technologies Pty Midrand South Africa used to transfer gas from one cylinder to the other.
- For taking accurate cylinder mass measurements, Mettler Toledo PR10003 with suspension mass pan with resolution of 1mg and automated weighing balance system Mettler Toledo XPE26003LC with resolution of 1mg manufactured by Korean Research Institute of Standard and Science (KRISS) were used. Stainless Mass pieces maintained at National Metrology Institute of South Africa (NMISA) were used calibrate the weighing balances to provide direct link to SI unit, kg.
- To obtain homogeneity in the gas mixture, roller bench was used for rolling the cylinder containing HAPs PSM.
- Gas Tight Syringe supplied by Sigma Aldrich(Pty)Ltd (Johannesburg, South Africa) (50 µl and 100 µl) was used for introduction of liquid components to the cylinders.

### 3.1.2 Chemicals

High pure HAPs starting materials were manufactured from different Sigma Aldrich (Pty)Ltd (Johannesburg, South Africa) with purity of ≥ 99 %. The starting materials to be used are benzene, chloroform, tetrachloroethylene, trichloroethylene, 1,2-dichloroethylene, vinyl chloride,1,3-butadiene and nitrogen. Liquid samples were stored in a carboard, at room temperature with proper ventilation. High pure nitrogen was stored in a build-up cage, which protected the cylinder from the sun or rain to prevent the exterior from rusting. Vinyl chloride and 1,3-butadiene were stored in the laboratory at room temperature.

## 3.2 Experimental Procedure

### 3.2.1 Cleaning of Cylinders

Prior to the evacuation process, the external surface of the aluminium cylinder is cleaned with a paper towel and lacquer thinners to remove particles that might contribute to errors or uncertainty during weighing.

During evacuation process, the aluminium cylinders are connected to the evacuation system containing Pfeiffer turbo molecular pump and rough pump shown in **Figure 3.1**. The cylinders are disconnected after reaching a vacuum of less than $2.5 \times 10^{-7}$ mbar.

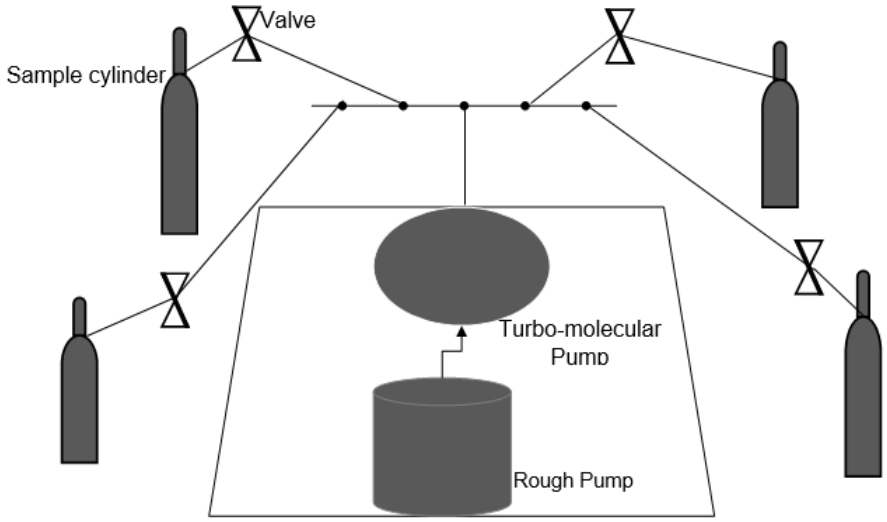



Figure 3. 1: Schematic of cylinders connected to evacuation system

### 3.2.2 Weighing and Filling Process of Gas Cylinder

The evacuated cylinder is weighed against a tare cylinder on a high accuracy mass balance following the Borda Substitution Method to eliminate the buoyancy effect explained in **Section 2.6** (Milton, 2011). A

specific amount of liquid sample is also weighed using Hamilton syringe on a Sartorius balance.

The weighed cylinder is connected to a filling system to add the first component (sample liquid weighed). The filling system shown in **Figure 3.2** comprises a stainless tubing which enables connection to the cylinders, a needle valve to control flow of gases, a pressure display, turbomolecular pump and a rotatory vane fore pump. The cylinder and the filling station are connected by an injection system equipped with a minimum dead volume nut (MDV). On the other end of the filling station, high pure nitrogen gas cylinder is connected. This is introduced in the cylinder after transferring the sample liquid, to add any residual sample liquid in the MDV to the cylinder. To accurately know how much of nitrogen is going into the cylinder, there is a weighing balance close to the filling station.

The filled cylinder is weighed against a tare cylinder and nitrogen gas is added to complete the mixture. The cylinder is weighed again and rolled for a minimum of two hours to ensure homogeneity (Baptista, 2009).




Figure 3.2: Filling system and weighing balance for transfering gas in the cylinder

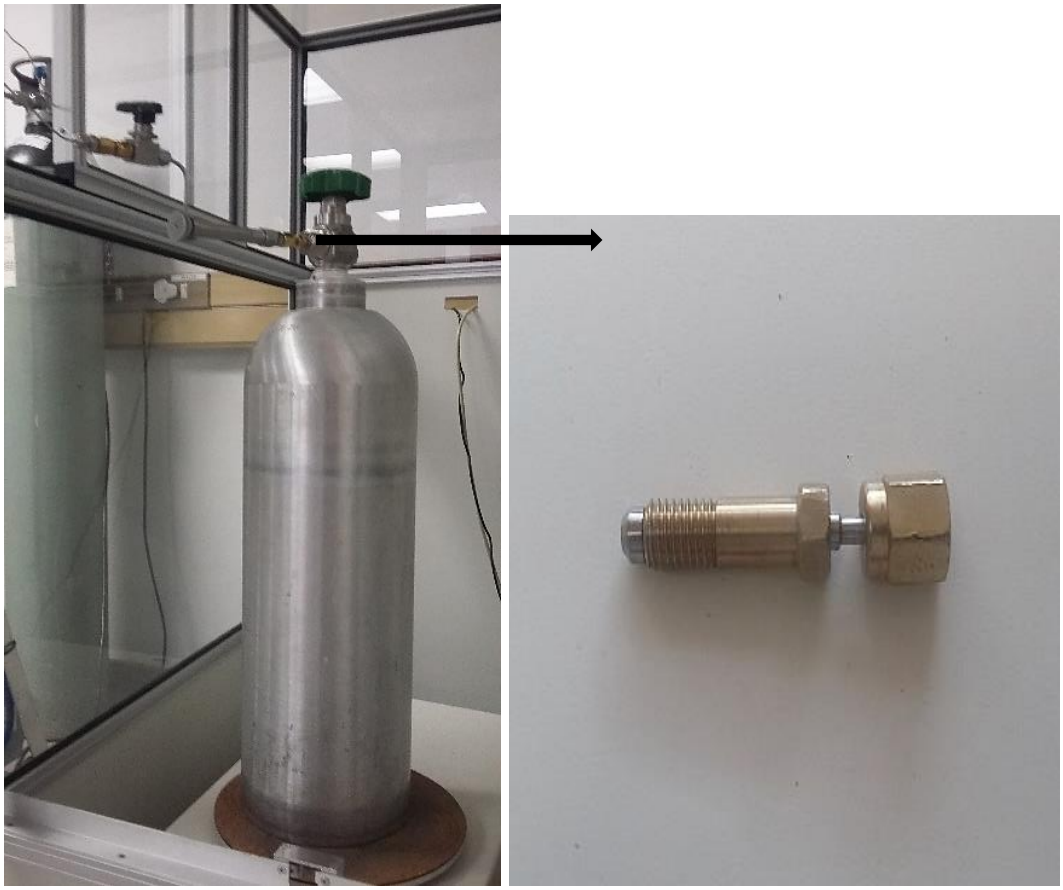


Figure 3.3: Injection system and minimum dead volume for transferring liquid sample to the cylinder

## 3.3 Analysis

### 3.3.1 Purity Assessment of Vinyl Chloride and 1,3 Butadiene

High purity vinyl chloride was stored as compressed liquid contained in an aluminium cylinder. Manufacturer specification indicated that the purity of the material was 99.95 %, no other components were mentioned. Impurities of nitrogen, carbon dioxide, carbon monoxide and oxygen were checked using Gas Chromatography equipped with four detectors namely PDHID, TCD, FID and Nitrogen chemiluminescence detector. Only TCD was used for analysis due to its sensitive property to permanent gases. The cylinder was connected to a pressure regulator, which was supplied to six-port valve injecting to the molecular sieve 5Å column. **Figure 3.4 and 3.5** show the position of the system when the sample was loaded on to the

valve and when the valve was in a loading position to the column. Hydrogen was used as a carrier gas and oven temperature was kept at 150 ℃.

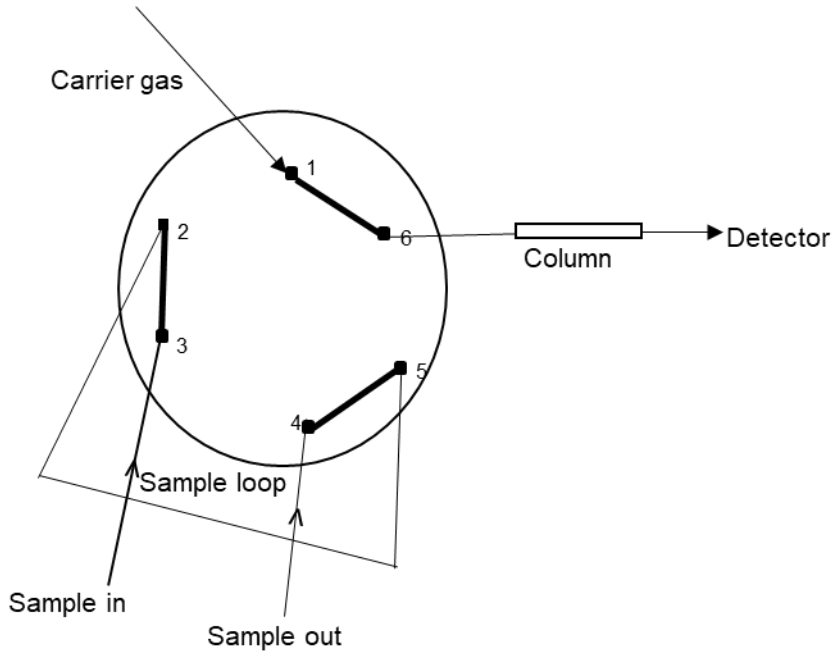



Figure 3. 4: Six-port valve with sample loop in a loading position

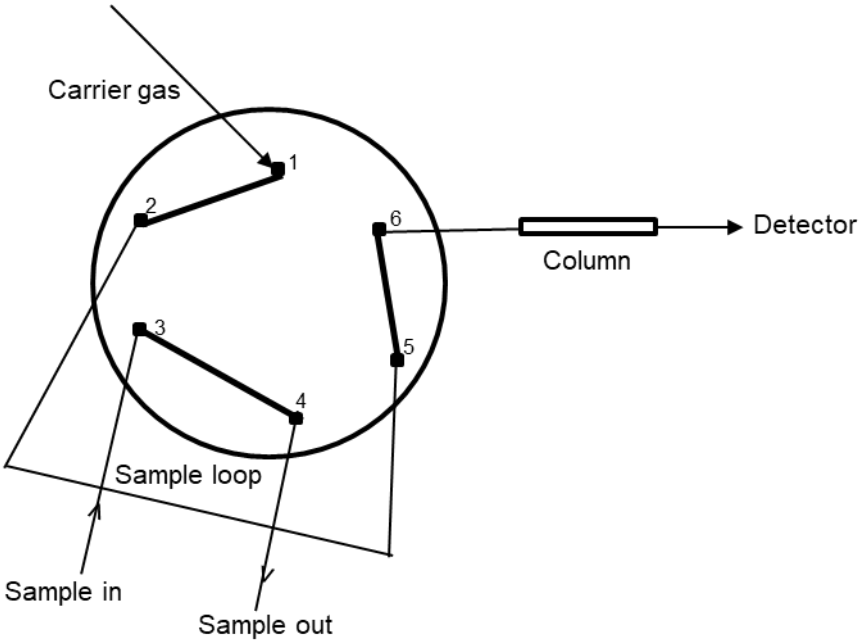



Figure 3. 5: Six-port valve with sample loop in an injecting position to the column

### 3.3.2 Purity Assessment of Liquid samples

High purity samples of benzene, chloroform, tetrachloroethylene, trichloroethylene, 1,2-dichloroethane and dichloromethane were analysed on Agilent Technologies 7809B\5977B GC-MSD. Liquid samples were separated on DB-1 column, length 60 m, internal diameter 0.32 µm and film thickness of 1.2 mm, then introduced to MSD using a transfer line. The GC column oven temperature was kept at 170 ℃, with column flow of 1.5 ml/min. The MSD instrument is equipped with a fore line pump which acquire vacuum of $10^{-2}$ mbar and a turbo pump which acquire vacuum of $10^{-6}$ mbar -$10^{-7}$ mbar. A single quadrupole analyser is used as a mass filter which directs fragmented mass of sample bombarded by electron ionisation energy at 70 Ev to electron multiplier.

### 3.3.3 Analytical Verification of Mole-fraction of Binary Primary Standard Gas Mixtures

To measure the amount of mole-fraction prepared, standards were analysed on Agilent 7802B gas chromatography coupled to flame

ionisation detector using single point calibration following ABA sequence. The gas cylinder containing the standard gas mixture was connected to a pressure regulator which was with the mixture to avoid contamination. The regulator was connected to a flow meter leading to the valve of GC-instrument. Each set of mixture was analysed using different instrumental conditions and on different columns. **Table 3.1** formulate analysis information of each gas mixture.

In ABA sequence, a reference is chosen from the standards and other mixtures are taken as sample. Reference is run alternatively with the sample, A representing the reference and B a sample. This method minimizes the instrumental drift observed during analyses due to environmental conditions. All prepared standards were used to verify each other (chosen to be a reference). During analyses 5 injection were made, the first two injections were taken as to clean the column due to GC-FID response (peak area) was reading either high or low. For the last three injections GC-FID response (peak areas) was used for calculation of composition.

Equation 3.1 calculates the mole-fraction obtained from GC-FID responses

$$C_{unknown} = \frac{Cknown \times A_{unkown}}{A_{known}} \qquad 3.1$$

Where $C_{known}$ is mole-fraction of reference obtained from the gravimetric preparation, $C_{unknown}$ is mole-fraction of sample, $A_{unkown}$ is area of reference obtained from GC-FID response and $A_{known}$ is area of sample obtained from GC-FID response.

Table 3. 1: Analytical parameter on gas chromatography coupled to flame ionisation detector

| Column | Component | Flow (ml/min) | Oven Temperature (℃) |
|---|---|---|---|
| Rxi-624 Sil MS (60 m x 0.35 µm x0.18 µm) | Benzene | 2 | 110 |
| | Trichloroethylene | 1.9 | 180 |
| | Tetrachloroethylene | 1.9 | 60 |
| | Chloroform | 2.3 | 160 |
| | Dichloromethane | 3 | 160 |
| | 1,2-dichloroethane | 3 | 160 |
| Agilent DB-624 (60 m x 0.35 µm x0.18 µm) | Vinyl chloride | 2 | 160 |
| | 1,3-butadiene | 1.5 | 170 |

### *3.2.2.1 Analysis of six HAPs-multicomponent primary gas mixture on GC-FID*

Analysis of the developed primary gas standard mixtures was carried on three different columns on GC-FID to achieve good resolution. Agilent HP-Innowax (60 m x 0.25 mm x 0.5 mm), DB 624 (60 m 0.32 mm x 0.5 mm) and CP-Sil 5CB (30 m x 0.15 mm x 2 mm) columns were used under various analytical conditions highlighted in **Table 3.2**. hydrogen was used as carrier gas and nitrogen as make-up gas. FID conditions kept at temperature 300 ℃, air at 300 mL/min, hydrogen at 35 mL/min and nitrogen at 20 mL/min.

Table 3. 2:Analysis parameters for Multicomponent Mixtures

| Column | Parameters |
|---|---|
| HP-Innowax | 80 ℃ with 3 min hold time, 110 ℃ at rate 18 min/C and 1 min hold time |
| DB-624 | 60℃ with 5 min hold time, 80℃ at rate 2 min/C and 12 min hold time |
| CP-Sil 5CB | 60 ℃ with 5 min hold time, 110 ℃ at rate 10 min/C and 12 min hold time |

### *3.2.2.2 Analysis of 8-HAPS multicomponent primary standard gas mixtures*

0.100 µmol/mol primary gas mixtures were analysed on Entech model 7200 pre-concentrator coupled to Agilent GC-FID. The pre-concentrator used External Cold Trap Dehydration (CTD) principle with helium as carrier gas and liquid nitrogen as a coolant. Firstly, the system was checked for leaks and the sample introduced to the pre-concentrator via

stainless steel tubing. Conditions for the pre-concentrator are in **Table 3.3**, the sample was then focused to the GC with spitless injection. Hydrogen as carrier gas, CP-Sil 5CB (30 m x 0.15 mm x 2 mm). Oven temperature kept at 45℃, 60℃ at 5 min/ C and 130℃ at 10 min/C.

Table 3. 3: Pre-concentrator Trapping Conditions

| | Trap Temperature(℃) | M1 Preheat(℃) | M1->M(℃) | M3 Precool(℃) | M2 Preheat(℃) | M2->M3(℃) | Inject(℃) | Bake out(℃) |
|---|---|---|---|---|---|---|---|---|
| Module 1 Trap | -40 | 10 | 10 | | | | | 150 |
| Module 1 Bulkhead | 10 | | 60 | | | | | 150 |
| Module 2 | -40 | | -40 | | -40 | 230 | | 220 |
| Module 2 Bulkhead | 30 | | | | 40 | | | 150 |
| Module 3 | | | | -150 | | -150 | 80 | |

### 3.4 Sampling of Ambient Air

Grab sampling method was used for collection of ambient air. An evacuated 5.0 L aluminium cylinder was used to collect ambient air at Cape Point GAW station shown in **Figure 3.6**. The cylinder was transported to NMISA in Pretoria, were it was stored at room temperature in a horizontal position.




Figure 3. 6: Cape Point Gaw station, located in Cape Town, South Africa. Representing background air sample

### 3.5 Measurement Accuracy

Accuracy is defined as the closeness of measurement to the actual or true value. In terms of this project the gravimetric mole-fraction was compared with the verified mole-fraction to determine the degree of success of gravimetric preparation method of the gas mixtures (Beloufa et al., 2017).

Accuracy is expressed as % difference shown in equation 4.2

$$\%\text{difference} = \frac{|\text{grav}_c - \text{ver}_c|}{\text{grav}_c} \times 100 \qquad 4.2$$

Where:

$grav_c$ is mole-fraction obtained from gravimetric preparation

$ver_c$ is calculated mole-fraction obtained from GC analysis

### 3.6 Measurement Precision

Precision is defined as closeness of independent measurement result to each other. This was obtained from %relative standard deviation from the analysis made from GC (Belouafa et al., 2017; Magnusson et al., 2014).

$$\%\ \text{RSD} = \frac{\sigma}{\bar{x}} \times 100 \qquad 4.3$$

Where:

$\sigma$ is standard deviation

$\bar{x}$ is average

### 3.8 Internal Consistency Tests

Internal consistency is a measure based on correlation of various substances. This is performed to check behaviour of samples relative to the reference

Internal consistency information is obtained by comparing sensitivity ratios of the reference gas mixture and sample gas mixture.

$$\text{sensitivity} = \frac{\bar{x}}{\text{grav}_c} \qquad 4.5$$

$$\text{sensitivity ratio} = \frac{\text{sensitivity(sample)}}{\text{sensitivity(reference)}} \qquad 4.6$$

Where $\bar{x}$ is average response from instrument and $\text{grav}_c$ is mole-fraction obtained from gravimetric preparation.

In general sensitivity ratio of reference is 1.0. In an ideal situation consistency in comparison with other of components of the same mole-fraction or composition is equal to 1.0. However, any difference in mole-fraction and composition will deviate from 1.0. (Marebane, 2017).

# CHAPTER FOUR – Development of Binary Gas Mixtures

Chapter 4 presents the results obtained during gravimetric preparation of each component, from purity assessments of high pure to obtaining a value with an associated uncertainty and behaviour of gases in the cylinder is monitored.

## 4.1 Purity Assessment Results

In gravimetric preparation of primary standards gas mixtures, identification of impurities or confirmation of purity of high pure starting materials is essential. Impurities contributes to final mole fraction or mole-fraction of final gas mixtures (ISO 143, 2001). Various tests are taken to eliminate inaccurate mole fraction or mole-fraction amounts. The manufacturer specification of materials gives roughly a range of mole-fraction of expected impurities; hence purity analysis is taken to give an approximation of the amount found in the high pure starting materials. Grenfel ( 2010) purchased high pure components from commercial suppliers and used gas chromatography to obtain correction factor of final molefraction from purity analysis.

### 4.1.1 Purity Assessment of Pressurised Gases

Vinyl chloride and 1,3 butadiene are pressurized gas at room temperature, contained in a 1.0 L cylinders. The manufacturer specification stated to be ≥ 99.95 % of vinyl chloride and ≥ 99.60 % of 1,3-butadiene. No information of impurities found in these pure components were mentioned. The matrix of the primary standard gas mixtures is nitrogen; hence it is crucial to quantity it because it will contribute to the mole-fraction and uncertainty of the final mixture. A standard of nitrogen in argon was used to quantify nitrogen in the pure gases. For analysis of nitrogen TCD detector was chosen due to its high sensitivity to permanent gases, but different analytical conditions were employed, explained in **Chapter 2**. **Figure 4.1**

and **4.2** depict a peaks of nitrogen observed in vinyl chloride and 1,3-butadiene.

Other constituents of air, such as CO and $CO_2$ were checked in the high pure mixtures using GC-TCD. This is because nitrogen high pure, which is used as diluent gas contains these component, hence their presence will lead to incorrect estimation the mole fraction of the final mixture. No peaks were observed in the components in high pure vinyl chloride and 1,3-butadiene.

It was assumed that these components might be existing at trace level, however CO and $CO_2$ at lower concentrations have low sensitivity of thermal conductivity detector (Marebane, 2017). Vans Rensburg (2007) showed the analysis of permant gases on FID equipped with methaniser which uses Nickel catalyst in the presence to convert the components into methane. Hence for further investigations GC-FID in the presence of mechanizer was used and no identification of carbon dioxide and carbon monoxide was found. **Table 4.1** and **4.2** show the overall quantifies impurities found in vinyl chloride and 1,3-butadiene.

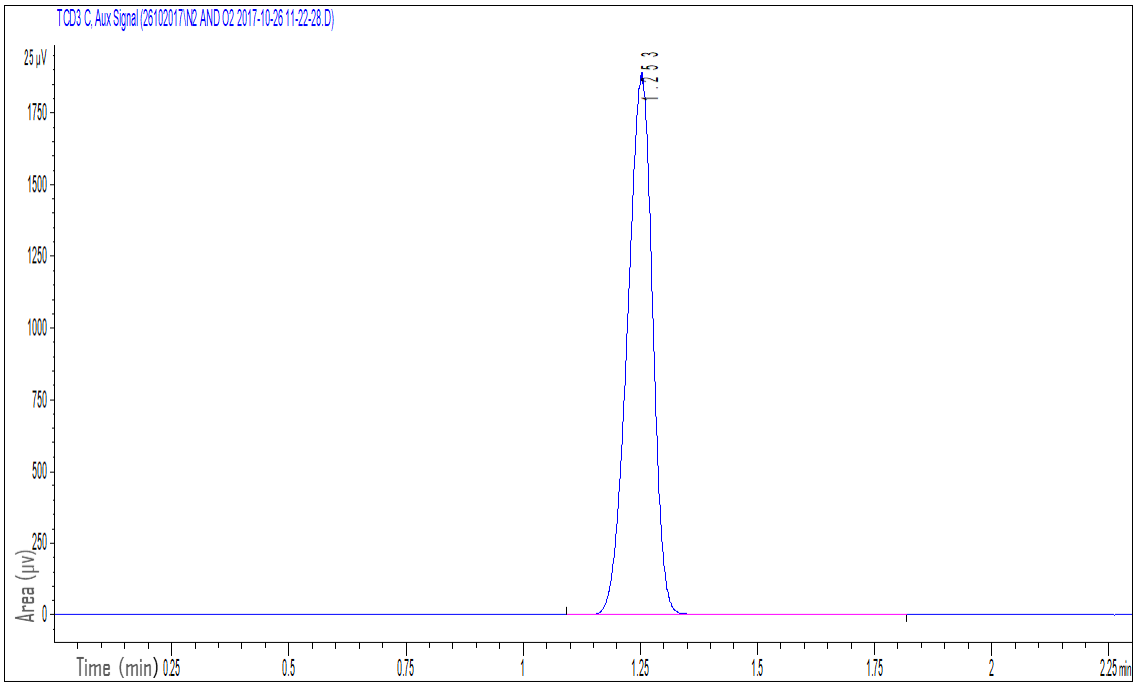



Figure 4. 1: Nitrogen impurity in high pure vinyl chloride

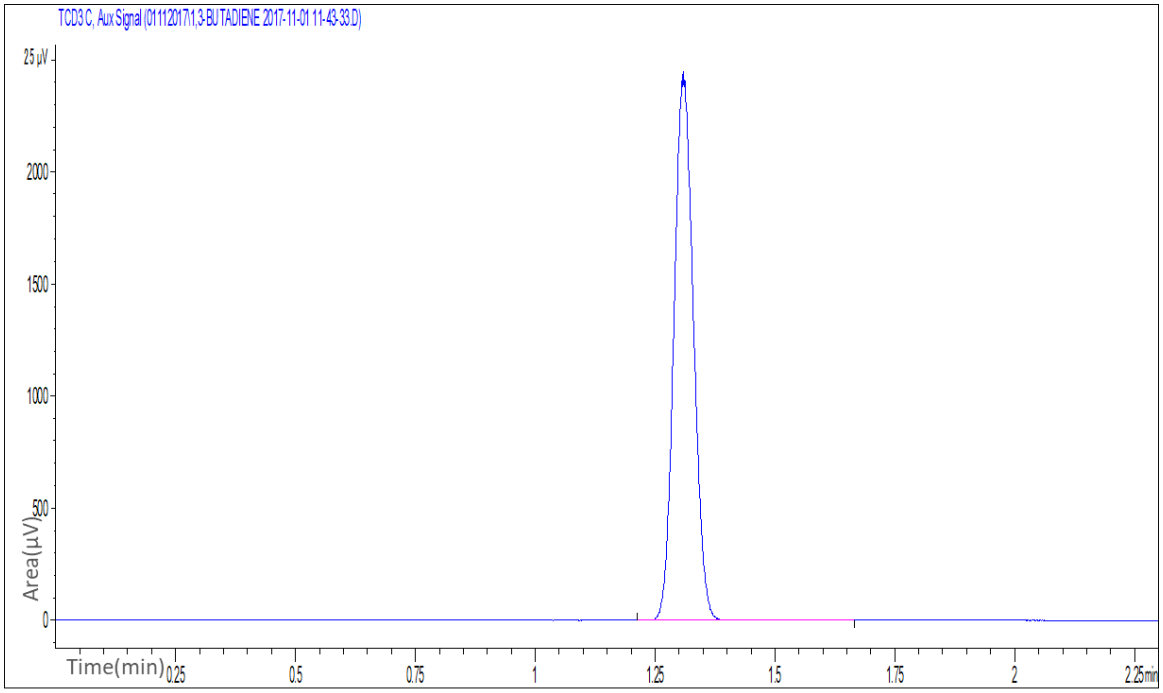



Figure 4. 2: Nitrogen peak in high pure 1,3-butadiene

Table 4. 1: Purity Table of Vinyl Chloride

| Component | Analysis Value | Distribution | Mole fraction (µmol/mol) | Standard Uncertainty (µmol/mol) | Expanded Uncertainty |
|---|---|---|---|---|---|
| Nitrogen | 254.4 | Normal | 254.4 | 2.1 | 4.2 |
| | | Total impurities | 254.4 | | |
| | | | **0.9997** | **2.100** | **4.2** |
| Vinyl Chloride | | **% mol/mol** | **99.9745600000** | **0.00021** | **0.00042** |

Table 4. 2: Purity Table of 1,3-Butadiene

| Component | Analysis Value | Distribution | Mole fraction (µmol/mol) | Standard Uncertainty (µmol/mol) | Expanded Uncertainty |
|---|---|---|---|---|---|
| Nitrogen | 681 | Normal | 681 | 45 | 90 |
| | | Total impurities | 681 | | |
| | | | 0.9993 | 45 | 90 |
| **1,3-Butadiene** | | **% mol/mol** | **99.9319000000** | **0.00450** | **0.009** |

### 4.1.2 Purity Assessment of Liquid Samples

To identify components found in high pure liquid samples, GC-MS was used during analyses. MS is the best technique to be used due to the ability to identify finger-print of unknown molecules. After analysis National Institute of Standards and Technology (NIST) software data base was used to identify the analysed component. Components are more likely to be identified correctly if the database gives more than 80 % comparability with the spectrum of the sample.

The manufacturer specification indicated that benzene is ≥ 99.70 %, no other organic components were stated. **Figure 4.3** and **4.4** shows results of benzene analysis by GC-MS. The chromatogram only shows one peak, which NIST software identified to be benzene. The comparability percentage of the sample spectrum and NIST was 93.31 %.

Water content was indicated to be 0.03 % using Karl Fischer by the manufacturer's specification. Moisture is a common impurity in liquid samples. It is important to know how much is in the high pure sample initially before preparation. That is because high pure nitrogen also contains moisture. Determining moisture assist in calculating the final composition or mole-fraction of the final mixture. The most common way of determining mole-fraction of moisture is through Karl Fisher. ISO 6142 (2015) states that manufacturer specification can be used to estimate the mole-fraction of given impurities or components. It also mentions that the quality of results is not compromised when choosing method of quantification.

According to ISO 6142 to estimate mole-fraction of impurity from the manufacture specification, the given value should be divided by 2. To calculate uncertainty of the mixture, the mole-fraction is divided by $\sqrt{3}$ assuming rectangular distribution.

The total mole-fraction of benzene was found to be 99.99 %. As stated in the manufacturer specification, the value is above 99.70 %, hence there is good correlation between the results. For other high pure components, no

impurities were identified. Results are shown on **Appendix A1.** Purity information on other components is shown in **A3** to **A8**. National Metrology Institute of Japan (CERI) performed impurity analysis on GC-FID of high pure liquids and obtained more than 99.90 % within uncertainty of 0.1% (CCQM K22, 2005). In this study lower uncertainity of purity analysis of high pure was obtained within 0.056 % was obtained using GC-MS, which is similar to uncertainty obtained by NIST using GC-MS of 0.60 % (CCQM K22, 2005).

Table 4. 3: Purity Table of Benzene

| Component | Manufacture specification | Distribution | Mole-fraction (µmol/mol) | Standard Uncertainty (µmol/mol) | Standard Uncertainty (µmol/mol) |
|---|---|---|---|---|---|
| $H_2O$ | ≤ 0.001 | Type B Rectangular | $5x10^{-4}$ | $2.9x10^{-4}$ | $5.8x10^{-4}$ |
| | | Total Impurities | $5x10^{-4}$ | | |
| Benzene | | %mol/mol | 99.95 | 0.029 | 0.058 |

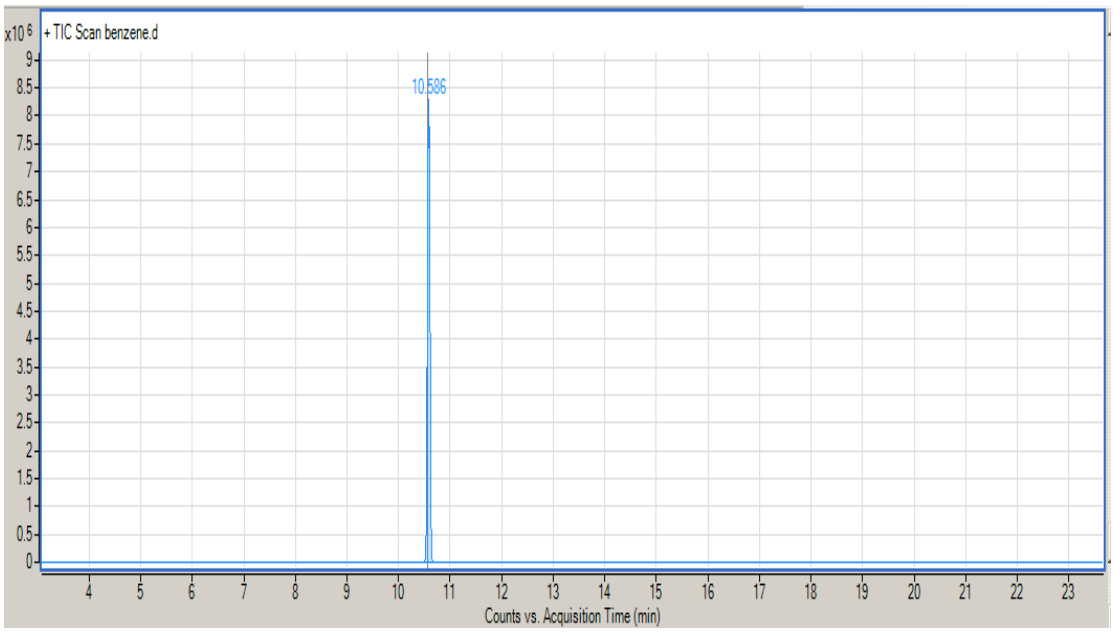



Figure 4. 3: Pure benzene chromatogram

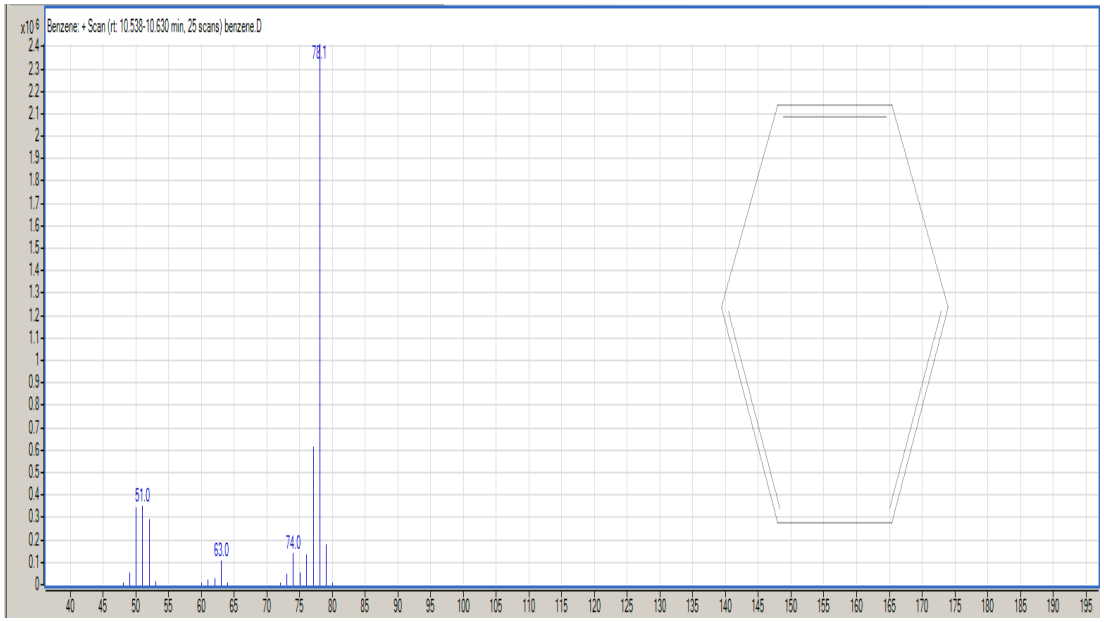



Figure 4. 4: Ion chromatogram of pure benzene

### 4.2.3 Purity Assessment of Nitrogen

High pure Build in Purifier 99.99 % was purchased from Air Product company. Nitrogen is used as a diluent gas in all the gas mixtures, hence it is crucial to quantify the impurities found in the mixture to know the uncertainties contribution of each component to the final mixture. The impurity analysis of nitrogen was performed in the Gas Analysis Lab at NMISA by other analysists. Argon was quantified using GC-PDHID. Rectangular distribution was assumed using the manufacturer specification for mole-fraction of other impurities following ISO 142 (2015). **Table 4.4** indicates the impurity table of nitrogen.

Table 4. 4: Purity Table of Nitrogen

| Component | Analysis Value | Distribution | Mole fraction (µmol/mol) | Standard Uncertainty (µmol/mol) | Expanded Uncertainty |
|---|---|---|---|---|---|
| Ar | 55.20222439 | Normal | 55.20222 | 2.760 | 5.520 |
| CO | <0.01348 | Type B rectangular | 0.00674 | 0.004 | 0.007783 |
| $CO_2$ | <0.0228 | Type B rectangular | 0.01140 | 0.007 | 0.013 |
| $CH_4$ | <0.009447 | Type B rectangular | 0.00472 | 0.003 | 0.005 |
| $C_2H_6$ | <0.01414 | Type B rectangular | 0.00707 | 0.004 | 0.008 |
| $O_2$ | <0.00233 | Type B rectangular | 0.00117 | 0.001 | 0.001 |
| $H_2O$ | <0.02 | Type B rectangular | 0.01000 | 0.006 | 0.012 |
| $H_2$ | <0.018 | Type B rectangular | 0.00900 | 0.005 | 0.010 |
| | | **Total impurities** | 55.252 | | |
| | | | **0.9999** | **2.760** | **5.520** |
| **$N_2$** | | **% mol/mol** | **99.9944747677** | **0.00028** | **0.001** |

### 4.2 Traceability of Gravimetric Results

The main aim of preparation of the standards is that they must be traceable to the SI unit. For preparation of standard gas mixtures, units were expressed in µmol/mol thus traceable to mole. During the development, various equipment's are calibrated at National metrology Institute of South Africa laboratories to attain direct link to traceability of different SI units. Weighing balances for measuring mass of cylinders, gas and syringes are calibrated using mass pieces for traceability to kg, shown in **Figure 4.5**. This principle followed is explained by Bièrea and Taylor (1997) Temperature and humidity are monitored during the experiments because they have an impact on how the gaseous mixtures behave. The temperature probes and humidity monitors are calibrated to obtain traceability to Kelvin. Gravimetric method was chosen for the project because it is a primary method (Milton et al., 2001). The measurement results must also have uncertainty associated with it, to show the spread of the measurement (Brown et al., 2017).

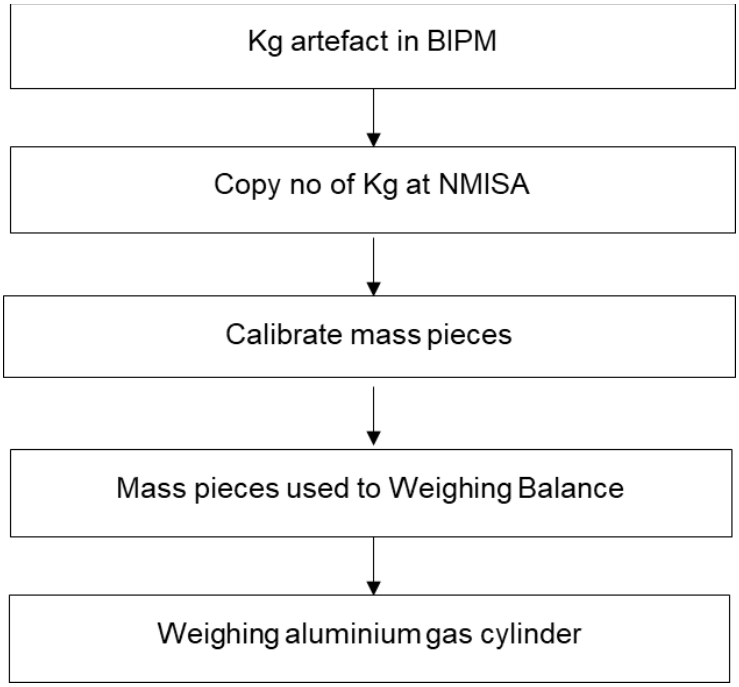



Figure 4. 5: Traceability Chain from kg

### 4.2.1 Uncertainty Associated with the Development of Primary Standard Gas Mixtures

There are various sources which contribute to gravimetric uncertainties and it is important to take them into consideration to make the correct estimation. The main contributors of the final uncertainty of the final mixture are, the weighing process, purity and molar masses of the chemical components (Goncalo et al., 2009). **Figure 4.6** indicates a fishbone of uncertainties contributed to the final products of all the developed primary reference gas mixtures.

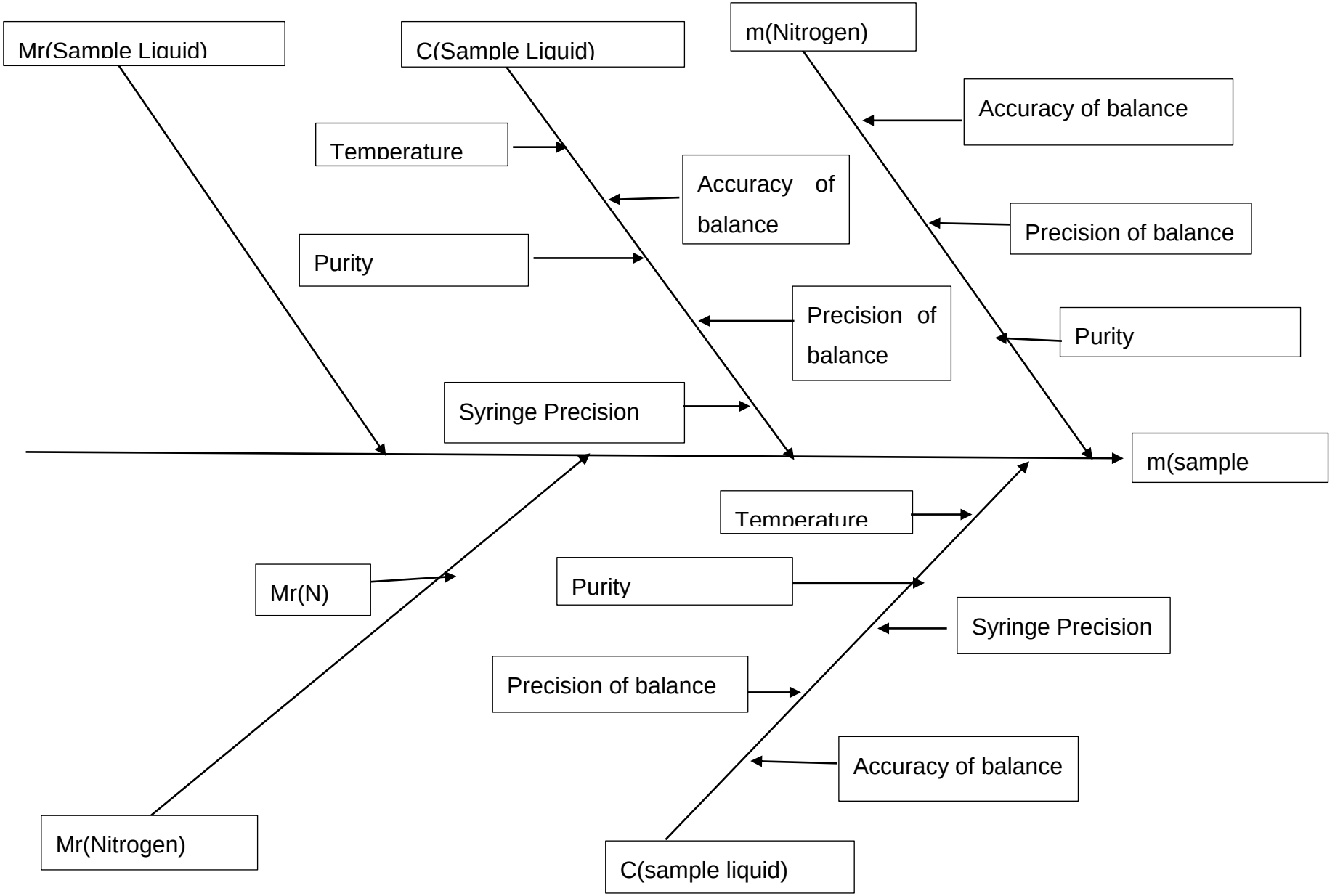



Figure 4. 6: Gravimetric Uncertainty Sources

Uncertainties attributed to the balance: instrument is subjected to drift and this is affected by changes in temperature and time. To minimise this impact, the weighing room kept at a constant temperature (air conditioner). Putting a cylinder in a different location on the pan contribute to uncertainties, this controlled by placing the cylinder in the centre on the pan. Buoyancy effect, which is cancelled out by using a tare cylinder having the same shape and size as the sample cylinder (CCQM K22, 2005; ISO 1642, 2001).

Uncertainties could come from mechanical handling of the cylinder this is attributed to any loss of paint or metal on the surface of the cylinder, but its uncertainty contribution is negligible, thread of the cylinder valve losing metal also is negligible, particles or dust could adsorb on the external surface of the cylinder this uncertainty contribution is negligible. Buoyancy effect this is mostly affected after filling with nitrogen gas because the temperature of the cylinder goes higher. To eliminate this effect the cylinder, attain thermal equilibrium by being placed in the weighing room for a minimum of two hours before it could be weighed. The volume of the cylinder changes as components are being added into the cylinder, its uncertainty contribution is negligible. This was proven by measuring diameter of the cylinder after adding a component by (Korea Research Institute of Science and Standards (KRISS) laboratory (Kato et al., 2005).

### 4.2.2 Uncertainty obtained from Analytical Results

Analytical or verification uncertainty will be used interchangeably as they both mean the same entity. The results are obtained from analysis on gas chromatograph coupled gas flame ionisation. The includes response of gas mixtures towards flame ionisation detector and gravimetric mole-fraction. It was derived from model **Equation 4.1**.

$$C_{unknown} = \frac{C_{known}}{Area_{known}} Area_{unknown} \quad 4.1$$

Where $C_{unknown}$ is concentration or amount of substance for sample, $C_{known}$ is concentration or amount of substance of reference, $Area_{unknown}$ is sample response from GC-FID and $Area_{unknown}$ is reference response from GC-FID.

To calculate analytical uncertainty from the above equation, sensitivity coefficient of each parameter is obtained from **Equation 4.2**, following assumptions made in **Table 4.5**.

Sensitivity coefficient is used to convert the individual parameters uncertainties into combined uncertainty which is reported as analytical uncertainty shown in **Equation 4.3**.

Table 5. 5: Assumptions of Sensitivity Coefficient

| Equation Parameter | Changes made $\Delta y$ |
|---|---|
| C | 0.01 |
| 1/C or $C^2$ | 0.001 |
| $1/C^2$ or $C^3$ | 0.0001 |

$$C_i \approx \frac{\Delta f}{\Delta y} \quad 4.2$$

**Table 4.1** values are used to calculate changes made in y. where $c_i$ is sensitivity coefficient and $\Delta f$ is changes made in y.

$$u_c(x) = \sqrt{u^2(x)} = \sqrt{\sum_{i=1}^{N} [c_i . u(y_i]^2} \qquad 4.3$$

### 4.3 Development of Benzene primary Standard Gas Mixture

#### 4.3.1 Gravimetric Results

Four benzene standard gas mixtures were prepared by gravimetric method aluminium cylinders with nitrogen as a diluent gas at mole-fractions of 9-10µmol/mol. The four mixtures were identified respectively by their unique codes; PSM-B1, PSM-B2, PSM-B3 and PSM-B4. Aluminium cylinder was chosen due to its inert property towards benzene and nitrogen, hence it will not undergo chemical reactions with the final mixture. **Table 4.6** show the final mole fraction of the prepared gases. The results show all the mole fraction and uncertainties of the individual gases contained in the cylinder, this was accomplished by considering composition of components obtained during purity analysis and the mass of benzene and nitrogen added during gravimetric preparation including their uncertainties. **Table 4.7 to 4.10** represents results of all standards taken as references to verify the gravimetric concentration of other samples. When PSM-B1 was taken as reference, PSM-B2, PSM-B3 and PSM-B4 were taken as samples. This exercise was performed to verify the accuracy of preparing gravimetric standards. The tables represent gravimetric concentration ($X_{grav)}$, expanded gravimetric uncertainty at coverage factor of K=2 at 95 % ($U_{grav}$), analytical concentration which is obtained from gas-chromatography coupled to flame ionisation detector response ($X_{analy}$), analytical expanded uncertainty ($U_{analy}$) and overall

combined expanded uncertainty of gravimetric results and relative expanded uncertainty determined at K=2 at 95 % confidence level.

Table 4. 6: Final Composition of Gravimetric Mixture of Benzene

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-B1 | | PSM-B2 | | PSM-B3 | | PSM-B4 | |
| | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $N_2$ | **999936.0484** | **2.7** | **999936.0994** | **2.7** | **999936.8388** | **2.7** | **999936.6909** | **2.7** |
| Ar | 53.90 | 2.6 | 53.90 | 2.6 | 53.90 | 2.6 | 53.90 | 2.6 |
| benzene | **10.00** | **0.081** | **9.949** | **0.081** | **9.209** | **0.081** | **9.358** | **0.081** |
| $H_2O$ | 0.011 | 0.0058 | 0.011 | 0.0058 | 0.011 | 0.0058 | 0.011 | 0.0058 |
| $CO_2$ | 0.0097 | 0.0012 | 0.0097 | 0.0012 | 0.0097 | 0.0012 | 0.0097 | 0.0012 |
| $H_2$ | 0.0090 | 0.0052 | 0.0090 | 0.0052 | 0.0090 | 0.0052 | 0.0090 | 0.0052 |
| CO | 0.0068 | 0.0040 | 0.0068 | 0.0040 | 0.0068 | 0.0040 | 0.0068 | 0.0040 |
| $C_2H_6$ | 0.0063 | 0.0034 | 0.0063 | 0.0034 | 0.0063 | 0.0034 | 0.0063 | 0.0034 |

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-B1 | | PSM-B2 | | PSM-B3 | | PSM-B4 | |
| | $X_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) |
| $O_2$ | 0.00499 | 0.0029 | 0.00499 | 0.0029 | 0.00499 | 0.0029 | 0.00499 | 0.0029 |
| $CH_4$ | 0.0043 | 0.0025 | 0.0043 | 0.0025 | 0.0043 | 0.0025 | 0.0043 | 0.0025 |

To calibrate the instrument for analysis, one-point calibration was used because the mole-fractions range between the standards is within 1 %. To take further pre-cautions on monitoring that the instrumental performance is optimal, instrumental drift was observed during analyses. When PSM-B1 was chosen as reference instrumental drift ranged between 0.086 to 0.29 %, PSM-B2 results ranged between 0 to 0.17 %, B3 is 0.079-0.29 % and PSM- PSM-B4 is between 0-0.31 %. The drift in all analyses indicated to be less than 1 %, indicating that analyses method developed for benzene is not affected by environmental conditions.

Relative standard deviation is calculated from **Equation 3.3**. This indicates measurement repeatability of each analyses. **Figure 4.7** indicates that that the overall benzene measurements have highest repeatability of 0.54 %, which is when PSM- B2 was taken as reference.

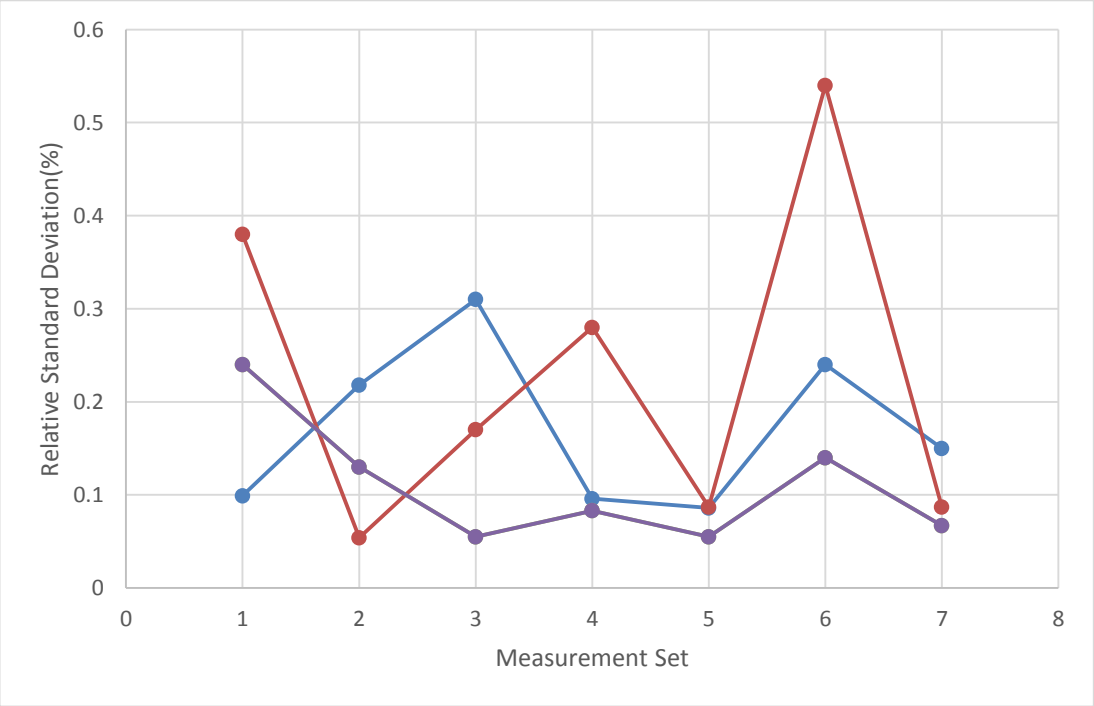



Figure 4. 7: Measurement Repeatability of Benzene Standards. blue:PSM-B1, red: PSM-B2 and purple:PSM-4

To check accuracy of gravimetric preparation, percentage difference was calculated between the analytical mole-fraction and gravimetric mole-fraction. When PSM-B1 was taken as reference, the highest percentage difference obtained is 3.0 %, for PSM-B2 the highest percentage difference is 1.4 %, for PSM-B3 it is 1.5 % and for PSM-B4 it is 1.3 %. The criteria for accepting a sample mixture is having percentage difference within 3.0 %.

The overall development of benzene primary reference gas standard mixtures showed good precision, measurement repeatability and expanded gravimetric combined uncertainty is within 2 % with K=2 at 95 % confidence level.

Table 4. 7: When PSM-B1 was taken as reference

| Gas Mixture | $X_{grav}$ (mol/mol) | $U_{grav}$ | $X_{analy}$ (mol/mol) | $U_{analy}$ | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-B3 | 9.949 | 0.17 | 9.911 | 0.20 | 0.22 | 2.3 |
| PSM-B2 | 9.209 | 0.17 | 8.937 | 0.18 | 0.20 | 2.4 |
| PSM-B4 | 9.358 | 0.17 | 9.226 | 0.19 | 0.21 | 2.3 |

Table 4. 8: When PSM-B2 was taken as reference

| Gas Mixture | $X_{grav}$ (mol/mol) | $U_{grav}$ | $X_{analy}$ (mol/mol) | $U_{analy}$ | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-B3 | 9.209 | 0.17 | 9.138 | 0.19 | 0.21 | 2.3 |
| PSM-B1 | 10.00 | 0.17 | 9.981 | 0.20 | 0.22 | 2.2 |
| PSM-B4 | 9.358 | 0.17 | 9.229 | 0.19 | 0.21 | 2.3 |

Table 4. 9: When PSM-B3 was taken as reference

| Gas Mixture | $X_{grav}$ (mol/mol) | $U_{grav}$ | $X_{analy}$ (mol/mol) | $U_{analy}$ | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-B2 | 9.949 | 0.17 | 10.10 | 0.20 | 0.22 | 2.2 |
| PSM-B1 | 10.00 | 0.17 | 10.14 | 0.18 | 0.20 | 2.0 |
| PSM-B4 | 9.358 | 0.17 | 9.371 | 0.17 | 0.19 | 2.1 |

Table 4. 10: When PSM-B4 was taken as reference

| Gas Mixture | $X_{grav}$ (mol/mol) | $U_{grav}$ | $X_{analy}$ (mol/mol) | $U_{analy}$ | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-B3 | 10.00 | 0.17 | 10.13 | 0.20 | 0.22 | 2.2 |
| PSM-B2 | 9.949 | 0.17 | 9.909 | 0.20 | 0.22 | 2.3 |
| PSM-B4 | 9.209 | 0.17 | 9.219 | 0.27 | 0.29 | 3.2 |

### 4.3.2 Internal Consistency Studies

Internal Consistency graph shows how a standard mixture is comparable to the reference. It is significant when developing standard gas mixtures to ensure that they will be able to show good internal consistency with other components because they indicate how well they will be able to quantify unknown mixtures. The graph is constructed from sensitivity ratio obtained from sensitivity of the refence gas mixture and sample gas mixture. Sensitivity is the response of a gas mixture to a detector. Similar components having similar mole-fractions are expected to have similar sensitivity.

To monitor behaviour of each standard gas mixture prepared, internal consistency was checked by choosing a reference amongst the standard. To avoid bias, all the standands were chosen to be reference to observe how other prepared standards will behave. In **Figure 4.8** PSM-B3 was taken as reference. It is observed that other sample mixtures are comparable to PSM-B3. This is an expected baviour because all gas mixtures have similar mole-fraction obtained from the gravimetric values. Hence, they are expected to show similar response towards GC-FID. It is however observed the mixtures don't fall exactly at 1.0 as the reference mixture, because they do not have the exact mole-fractions as the reference mixture. The mixtures fall within sensitivity ratio of 0.02. When other standards were taken as references, the deviation from 1.0 is quite small. All mixtures have overall range of sensitivity ratio within 0.03 indicated in **Figure 4.9** and **4.10**.

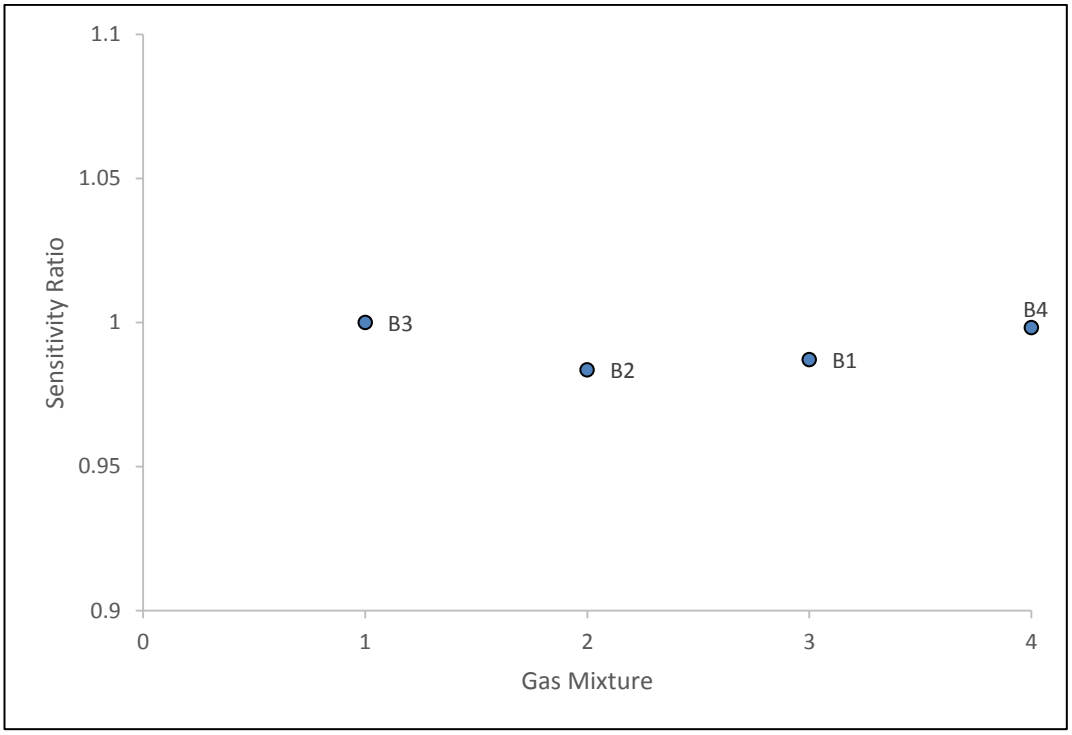



Figure 4. 8: Internal Consistency graph of PSM-B3

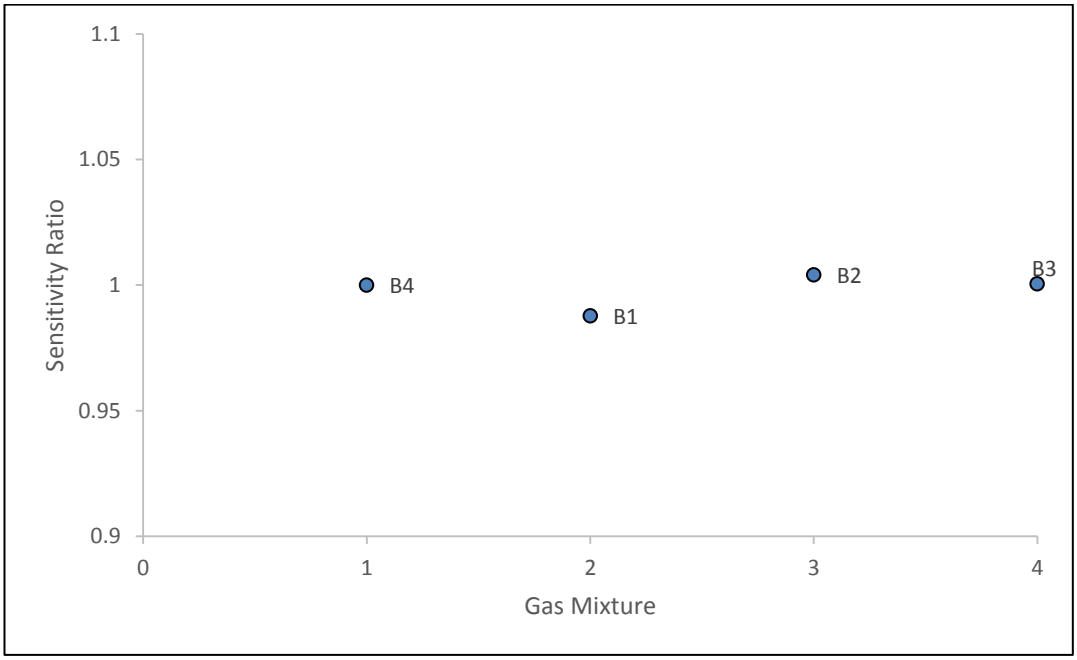



Figure 4. 9: Internal Consistency graph of when PSM-B4 was chosen as reference gas mixture.

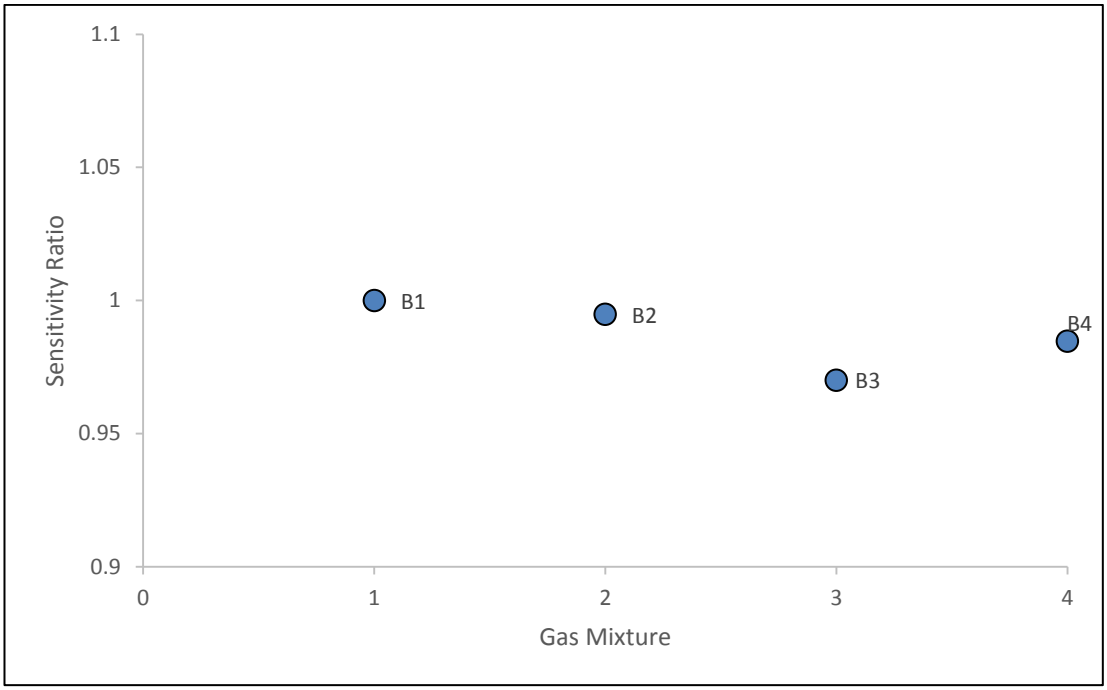



Figure 4. 10: Internal Consistency graph of when PSM-B1 was chosen as reference gas mixture.

## 4.4 Development of binary primary reference gas mixture of 1,3-butadiene

### 4.4.1 Gravimetric Results

High pure 1,3-butadiene is contained in a cylinder as liquified gas. Due to its nature, and mass to be added during preparation it was feasible to have initial gravimetric mole-fraction of 1.0 %. The prepared primary standards were verified and used to diluted further to 10µmol/mol in nitrogen. The results discussed in this section only cover 1.0 % amount-of-substance mixtures. **Table 4.11** show gravimetric mole-fractions of 1,3-butadiene in nitrogen.

For gravimetric verification, when PSM-BT1 was used as a standard instrumental drift of ≤ 0.12 was achieved, when PSM-BT2 was used as reference ≤ 0.50 was achieved and when BT3 was used as refence ≤ 0.083 was achieved. The results are good because they are less than 1.0. Good instrumental drift is accounted for in the repeatability of

measurements. For PSM-BT1 and PSM-BT2 is % RSD is ≤ 0.11 and PSM-BT3 is ≤ 0.16.

The analytical results also show that the gravimetric mole-fraction agrees well with the verification values. When PSM-BT1 was chosen as reference the highest percentage difference is 0.065 %, PSM-BT2 chosen as reference the highest percentage difference is 0.59 % and for PSM-BT3 percentage difference is 0.48 %. The results discussed are shown in **Table 4.12** to **4.14** and **Figure 4.11**.

The overall gravimetric expanded uncertainty (U) values are higher than of benzene. This is due to great dilution factor from high pure component (99 %) to 1.0 % (Traple et al., 2014). Another source of uncertainty is weight and dilution factor. The higher the dilution factor and weight to be transferred the higher the uncertainty.

The relative expanded uncertainty of show capability of gravimetric preparation of 1,3-butadiene at 1.0 % and method of analysis to be within 0.2 %.

Table 4. 11: Gravimetric Results of 1,3-Butadiene

| | Standard Gas Mixtures | | | | | |
|---|---|---|---|---|---|---|
| Component | PSM-BT1 | | PSM-BT2 | | PSM-BT3 | |
| | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $N_2$ | 990041.64 | 2.779 | 990039.07 | 2.779 | 990016.0064 | 2.779 |
| Ar | 53.3624 | 2.673 | 53.3623 | 2.6730 | 53.3610 | 2.673 |
| $C_4H_6$ | 9966.06 | 0.3506 | 9968.6529 | 0.35052 | 9991.86 | 0.3520 |
| $H_2O$ | 0.00990027 | 0.0058 | 0.009900 | 0.005638 | 0.0099 | 0.005692 |
| $CO_2$ | 0.0097499 | 0.0012 | 0.009652 | 0.001118 | 0.009652 | 0.0011 |
| $H_2$ | 0.00891024 | 0.005148 | 0.008910 | 0.005148 | 0.008910 | 0.008910 |
| CO | 0.00678169 | 0.003920 | 0.006781 | 0.003921 | 0.006782 | 0.003920 |
| $C_2H_6$ | 0.006237 | 0.003604 | 0.006237 | 0.003603 | 0.006237 | 0.003604 |

| | | | | | | |
|---|---|---|---|---|---|---|
| $O_2$ | 0.004950 | 0.028611 | 0.004950 | 0.002861 | 0.004950 | 0.002861 |
| $CH_4$ | 0.004247 | 0.002455 | 0.00424 | 0.002455 | 0.004247 | 0.002455 |

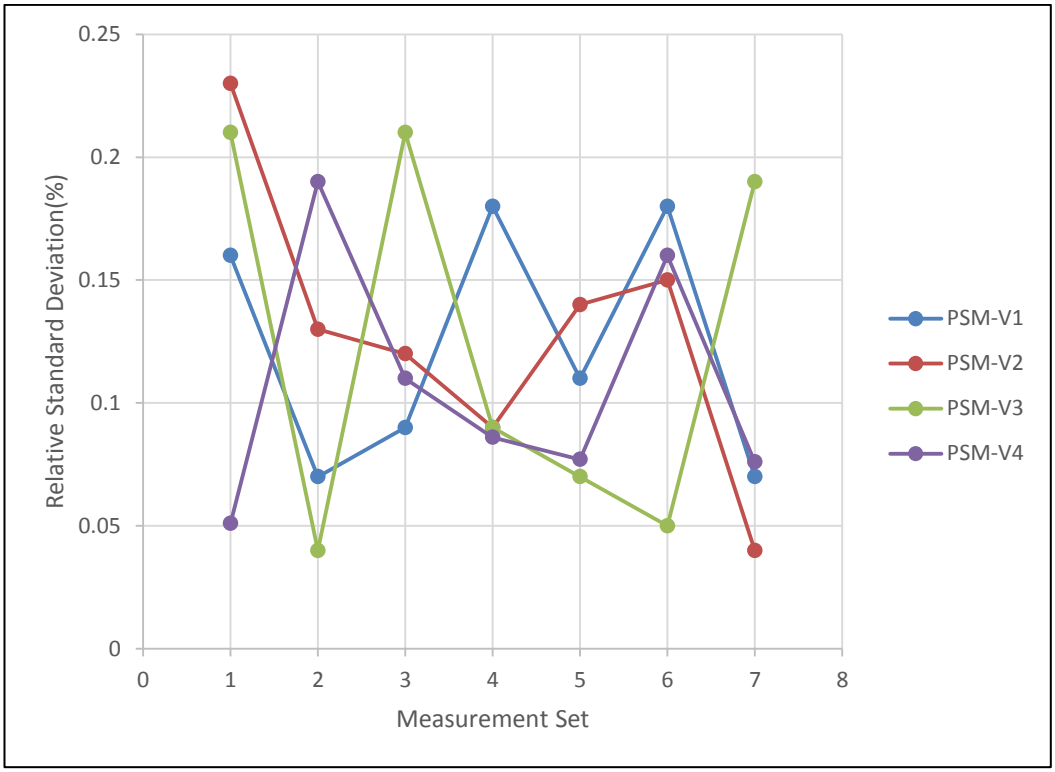



Figure 4. 11: Repeatability Measurements of Vinyl chloride

Table 4. 12: When PSM-BT1 was taken as reference

| Gas Mixture | $X_{grav}$ (mol/mol) | $U_{grav}$ (mol/mol) | $X_{analy}$ (mol/mol) | $U_{analy}$ (mol/mol) | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-BT2 | 9968.54 | 0.70 | 9974.99 | 9.24 | 9.26 | 0.10 |
| PSM-BT3 | 9991.86 | 0.70 | 9968.86 | 13.54 | 13.56 | 0.14 |

Table 4. 13: When PSM-BT2 was taken as reference

| Gas Mixture | $X_{grav}$ (mol/mol) | $U_{grav}$ (mol/mol) | $X_{analy}$ (mol/mol) | $U_{analy}$ (mol/mol) | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-BT3 | 9991.86 | 0.70 | 9933.63 | 14.88 | 14.89 | 0.15 |
| PSM-BT1 | 9966.54 | 0.70 | 9959.79 | 10.70 | 10.73 | 0.11 |

Table 4. 14: When PSM-BT3 was taken as reference

| Gas Mixture | $X_{grav}$ (mol/mol) | $U_{grav}$ (mol/mol) | $X_{analy}$ (mol/mol) | $U_{analy}$ (mol/mol) | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-B1 | 9966.06 | 0.70 | 9969.56 | 14.82 | 14.82 | 0.15 |
| PSM-B2 | 9968.54 | 0.70 | 9990.90 | 9.16 | 9.19 | 0.10 |

### 4.4.2 Internal Consistency Studies

Internal consistency of all three standard gas mixtures is good. When PSM-BT1 was used as reference sensitivity ratio of sample mixtures was within 0.01. When PSM-BT2 was used as reference the mixtures were within 0.007 and when PSM-BT3 was used as reference the mixtures were within 0.005.

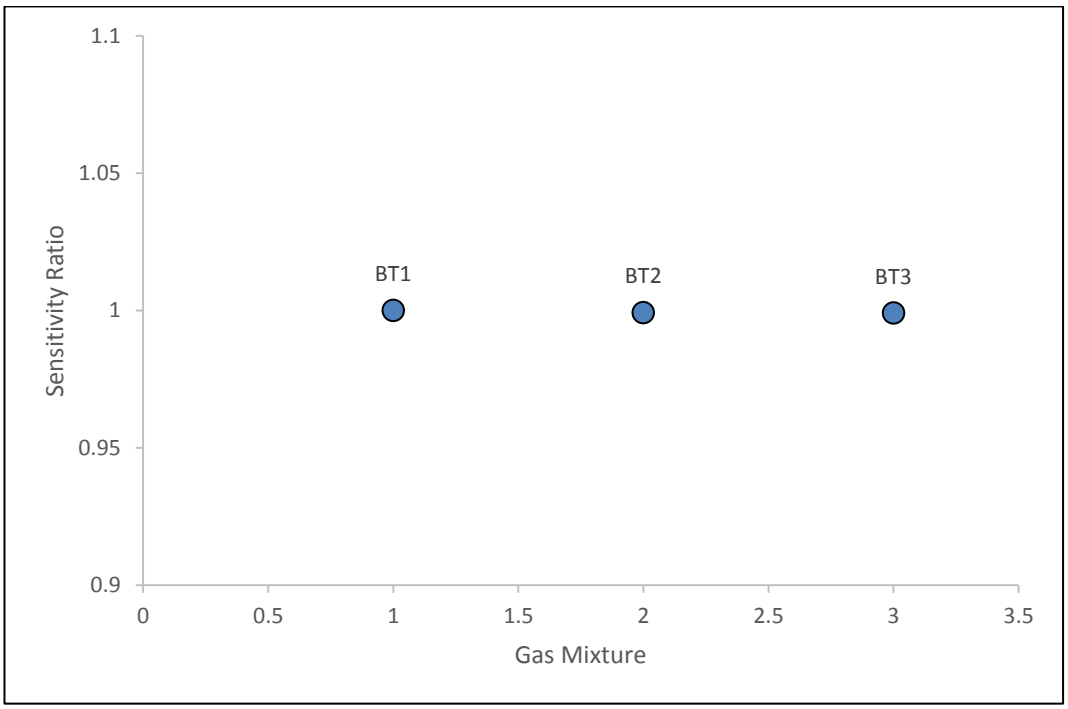



Figure 4. 12: PSM- BT1 as reference

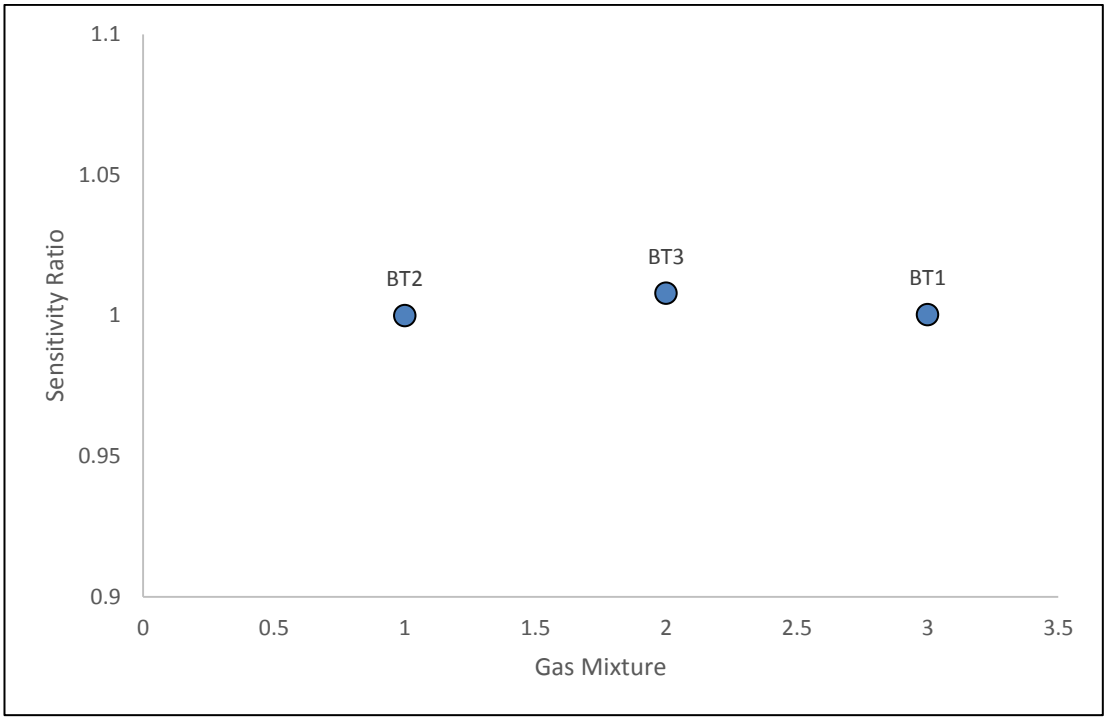



Figure 4. 13: PSM-BT2 as reference

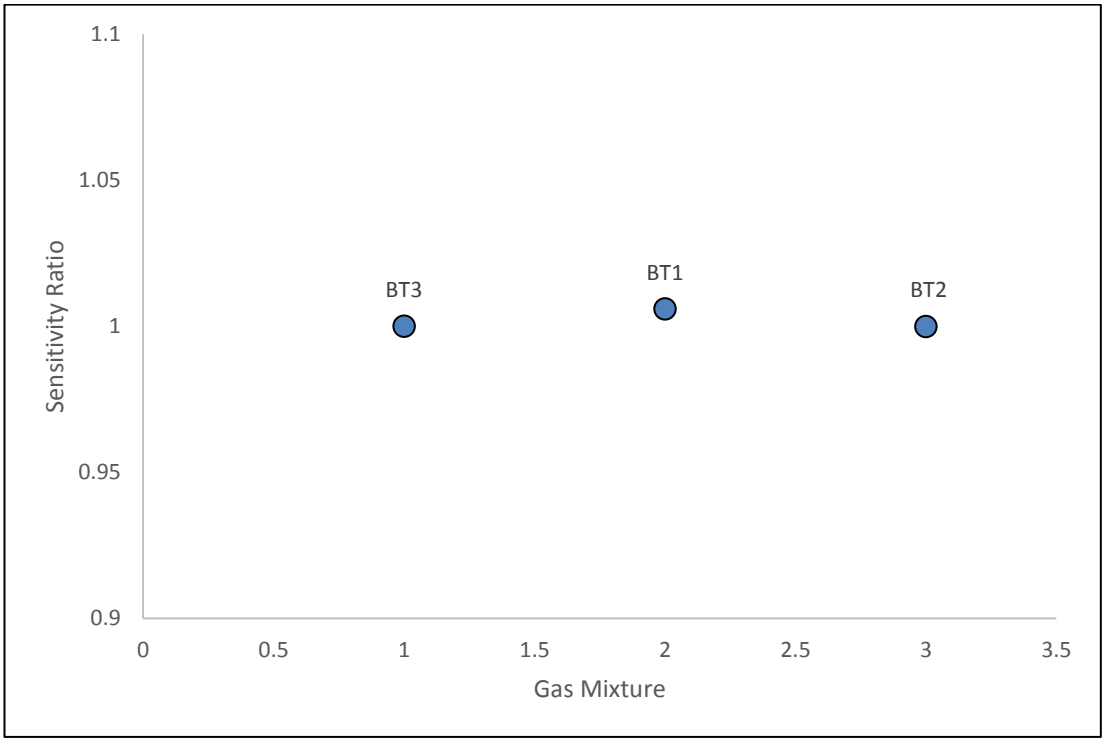



Figure 4. 14: PSM-BT3 as reference

All the 1.0 % primary standards gas mixtures showed good results. The gravimetric mole-fractions agree with the verified mole-fraction and the behaviour of the mixtures showed to be consistent with one another. The binary development of 1,3-butadiene was successful. One standard was used to dilute to four gas mixtures of 200 µmol/mol. After verification of 200 µmol/mol, dilution of 10 µmol/mol was performed. The gravimetric results and verification results were represented at the confidence level of 95 % at K=2.

## 4.5 Development of binary primary standard gas mixture of chloroform

### 4.5.1 Gravimetric Results

Chloroform was diluted from high pure liquid compound; hence it was feasible to prepare 10 µmol/mol in direct-step method. Composition of binary mixture obtained from gravimetric preparation show similarities with previously discussed mixtures in terms of uncertainty of argon and nitrogen **Tabulated in 4.15**. Both are higher than other substances in the mixtures, this is attributed to higher amount-of-substance found in the high pure nitrogen.

Table 4. 15: Gravimetric Results of Chloroform

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-C1 | | PSM-C2 | | PSM-C3 | | PSM-C4 | |
| | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $N_2$ | 999936.20 | 2.7 | 999935.94 | 2.7 | 999936.06 | 2.7 | 999936.0754 | 2.7 |
| Ar | 53.899469 | 2.71 | 53.90 | 2.7 | 53.90 | 2.6 | 53.90 | 2.6 |
| chloroform | 9.847 | 0.064 | 10.10 | 0.073 | 9.985 | 0.068 | 9.973 | 0.062 |
| $H_2O$ | 0.0099999 | 0.0058 | 0.009999 | 0.0057 | 0.009999 | 0.0058 | 0.009999 | 0.0058 |
| $CO_2$ | 0.0097499 | 0.0012 | 0.009749 | 0.0012 | 0.0098 | 0.0012 | 0.009749 | 0.0012 |
| $H_2$ | 0.0089999 | 0.0052 | 0.008999 | 0.0052 | 0.008999 | 0.0052 | 0.00899 | 0.0052 |
| CO | 0.0068499 | 0.0040 | 0.006850 | 0.0040 | 0.006849 | 0.0040 | 0.006849 | 0.0040 |

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-C1 | | PSM-C2 | | PSM-C3 | | PSM-C4 | |
| | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $C_2H_6$ | 0.0062999 | 0.0037 | 0.0063 | 0.0037 | 0.0062999 | 0.0037 | 0.006299 | 0.0037 |
| $O_2$ | 0.0049999 | 0.0029 | 0.004999 | 0.0029 | 0.004999 | 0.0029 | 0.00499 | 0.0029 |
| $CH_4$ | 0.0042899 | 0.0024 | 0.004289 | 0.0025 | 0.004289 | 0.0025 | 0.004289 | 0.0025 |
| AMYLENE | 0.0005170 | 0.00026 | 0.000530 | 0.00027 | 0.0005242 | 0.00027 | 0.0005236 | 0.00027 |

Each mixture was chosen as reference cylinder in order to monitor behaviour of individual gas mixture. **Table 4.16** represents results PSM-C1 chosen as reference. Instrumental drift was less than 1.0, indicating that GC-instrument was not affected by environmental condition variations. PSM-C4 shows higher verification uncertainty when compared to PSM-C2 and PSM-C1 and higher percentage difference of 7.4 %.

Table 4. 16: Reference PSM-C1 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-C1 | 0.099 | | | |
| PSM-C2 | 0.218 | 10.21 | 0.073 | 1.00 |
| PSM-C1 | 0.31 | | | |
| PSM-C3 | 0.096 | 9.285 | 0.068 | 0.93 |
| PSM-C1 | 0.086 | | | |
| PSM-C4 | 0.24 | 10.13 | 0.12 | 1.01 |
| PSM-C1 | 0.15 | | | |

Table 4. 17: Accuracy Results of PSM-C1

| Sample | $X_{grav}$ | $X_{analy}$ | Percentage | Relative |
|---|---|---|---|---|

| Name | (µmol/mol) | (µmol/mol) | Difference | Expanded Uncertainty (%) |
|---|---|---|---|---|
| PSM-C2 | 10.10 | 10.21 | 1.1 | 2.1 |
| PSM-C4 | 9.973 | 9.285 | 7.4 | 2.2 |
| PSM-C3 | 9.985 | 10.12 | 1.3 | 2.7 |

When PSM-C2 was chosen as reference, instrumental drift of less than 0.2 was achieved. Accuracy of gas mixtures is represented in **Table 4.18**, PSM-C4 and PSM-C1 have high percentage difference of above 3 %.

Table 4. 18: Reference PSM-C2 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $U_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-C2 | 0.099 | | | |
| PSM-C3 | 0.218 | 9.943 | 0.099 | |
| PSM-C2 | 0.31 | | | 0.287 |
| PSM-C1 | 0.096 | 9.448 | 0.089 | |
| PSM-C2 | 0.086 | | | 0.086 |
| PSM-C4 | 0.24 | 9.153 | 0.092 | |
| PSM-C2 | 0.15 | | | 0.259 |

Table 4. 19: Accuracy Results of PSM-C2

| Sample Name | $X_{grav}$ (µmol/mol) | $Y_{analy}$ (µmol/mol) | Percentage Difference | Relative Expanded Uncertainty (%) |
|---|---|---|---|---|
| PSM-C3 | 9.985 | 9.943 | 0.42 | 2.4 |
| PSM-C1 | 9.847 | 9.448 | 4.2 | 2.4 |
| PSM-C4 | 9.973 | 9.153 | 9.0 | 2.5 |

When PSM-C3 was chosen as reference in **Table 4.20**, good instrumental conditions were attained. PSM-C4 has percentage difference of above 3 %, compromising its accuracy.

Table 4. 20: Reference C3 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-C3 | 0.099 | | | |
| PSM-C4 | 0.218 | 9.088 | 0.099 | |
| PSM-C3 | 0.31 | | | 0.287 |
| PSM-C2 | 0.096 | 10.12 | 0.089 | |
| PSM-C3 | 0.086 | | | 0.086 |
| PSM-C1 | 0.24 | 9.690 | | |
| PSM-C3 | 0.15 | | 0.092 | 0.259 |

Table 4. 21: Accuracy Results of PSM-C3

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | Percentage Difference (%) | Relative Expanded Uncertainty (%) |
|---|---|---|---|---|
| PSM-C4 | 9.973 | 9.088 | 8.87 | 2.4 |
| PSM-C2 | 10.10 | 10.12 | 0.20 | 2.3 |
| PSM-C1 | 9.847 | 9.690 | 1.59 | 2.3 |

When all mixtures were chosen as reference mixtures, C4 showed high percentage difference. This indicates that errors could have occurred during gravimetric preparation. Faults are attributed to gravimetric preparation because in all cases instrumental drift is below 1.0. Indicating less disruptions from the environment. In all cases C4 reads lower than gravimetric mole-fraction. Liquid sample could have been lost during preparation, when transferring from the syringe into the cylinder or more nitrogen was added during preparation. Due to inconsistency in gravimetric and analytical amount-of-substance, PSM-C4 was not chosen as reference.

### 4.5.2 Internal Consistency Studies

To further monitor behaviour of the prepared gas mixtures, internal consistency graphs were plotted. When PSM-C1 was chosen as reference the gas mixtures showed good correlation with it. The mixtures showed to be within the ratio of 0.07, represented in **Figure 4.15**. When PSM-C2 was chosen as reference the gas mixtures in **Figure 4.16**, the ratio is between 0.08. In **Figure 4.17** PSM-C3 was chosen as reference. Gas mixtures are within 0.8 ratio. It is noted that in all the sensitivity graphs,

PSM-C4 has the highest ratio. This correlates with results observed in the verification section.

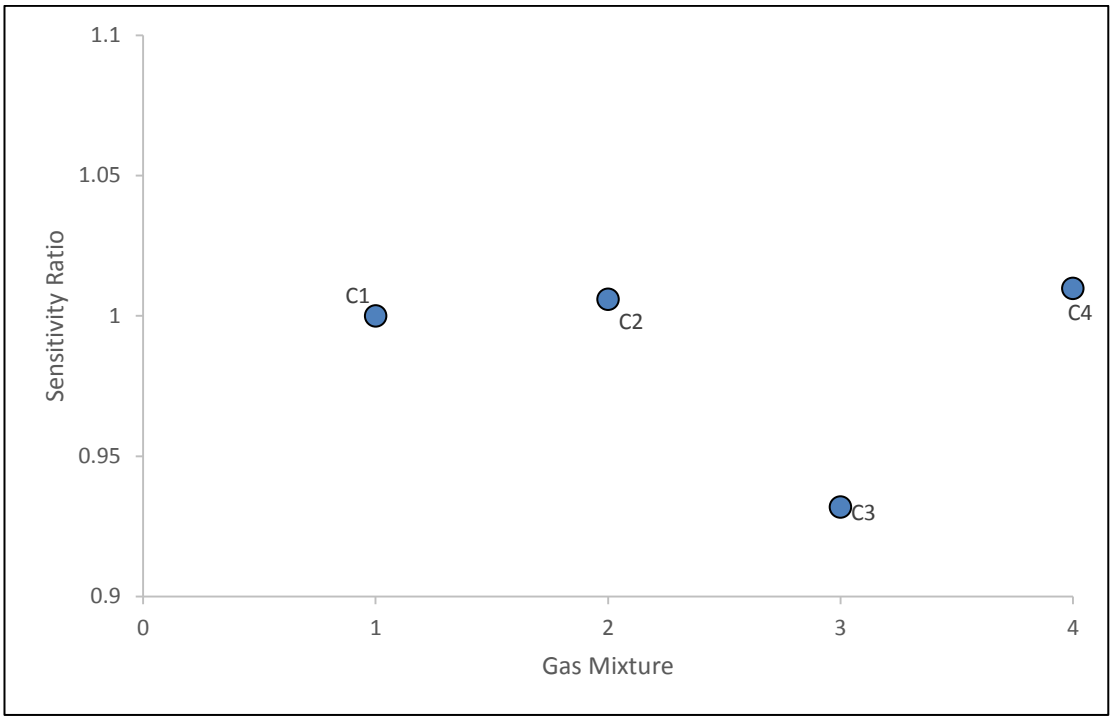



Figure 4. 3: Internal Consistency graph of when PSM-C1 was chosen as reference gas mixture

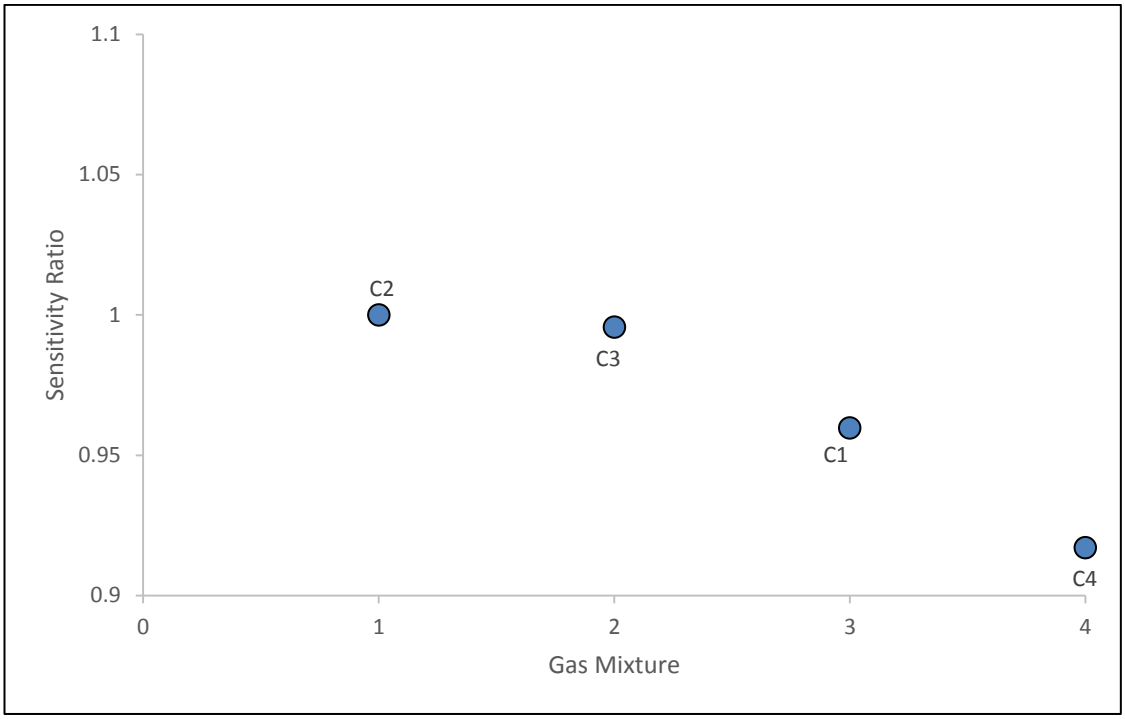



Figure 4. 4: Internal Consistency graph of when PSM-C2 was chosen as reference gas mixture

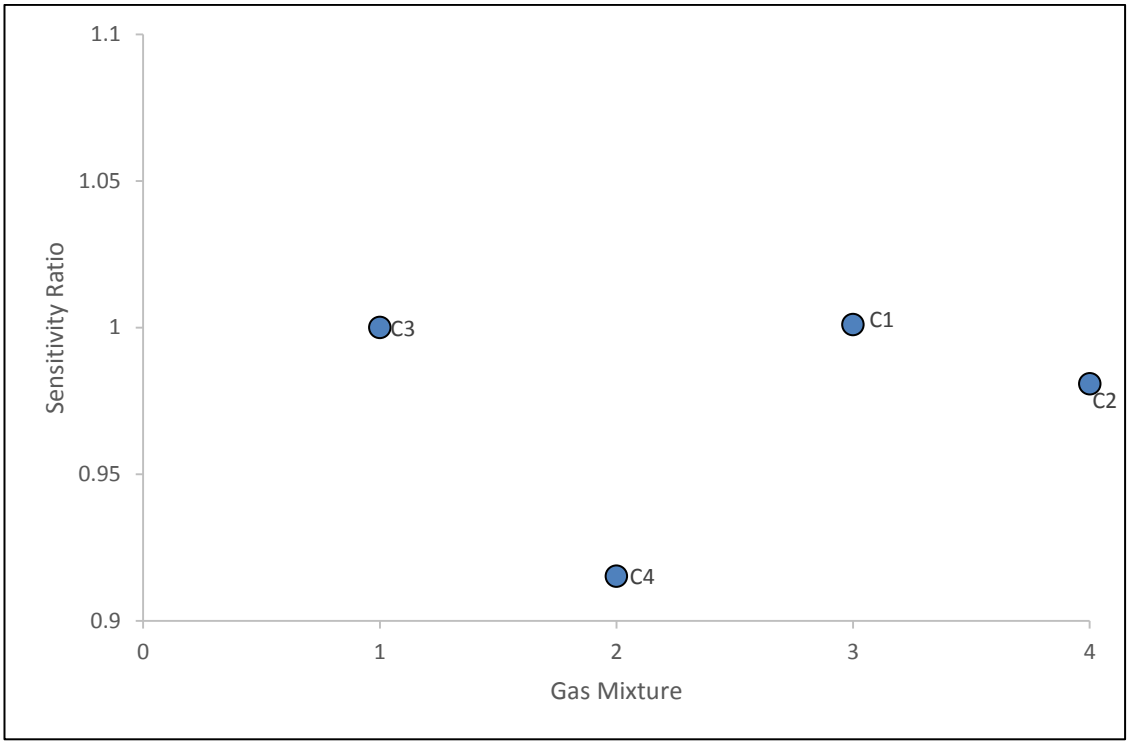



Figure 4.5: Internal Consistency graph of when PSM-C3 was chosen as reference gas mixture

## 4.6 Development of binary reference standard gas mixture of trichloroethylene

### 4.6.1 Gravimetric Results

**Table 4.22** represents gravimetric results of trichloroethylene. It is observed that mole-fractions of argon in each gas mixture is the same beside in PSM-T1. This is because different high pure nitrogen was used as diluents. This trend is also observed in other impurities as well.

For gravimetric mole-fraction verification, one-point calibration was used following ABA sequence. When PSM-T1 was taken as reference instrumental drift of ≤ 1.0 was achieved and repeatability of ≤ 1.7 was obtained shown in **Table 4.23**. PSM-T4 show gravimetric verification of 9.466 µmol/mol with percentage difference of 5.6 % in **Table 4.24**. Other sample reads ≤ 2.5 % percentage difference. When PSM-T4 was chosen as reference repeatability of less than 5.5 % was achieved in **Table 4.25**. PSM-T1 showed gravimetric verification of 9.966 µmol/mol with percentage difference of 0.38 % while other samples showed ≤ 2 % in

**Table 4.6**. The results of PSM-T1 were achieved at percentage difference of 2.54. This indicates that accurate results for analysis method of trichloroethylene could be achieved at instrumental drift of ≤ 3. When other standards were chosen as references there was great variations, hence the best developed standard gas mixtures were PSM-T1 and PSM-T4. Table 5.27-5.28 indicate the uncertainities achieved for each trichloroethylene. The overall results range between 1.8-2.3 % expanded relative uncertainity.

Table 4. 22: Gravimetric Results of Trichloroethylene

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-T1 | | PSM-T2 | | PSM-T3 | | PSM-T4 | |
| | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $N_2$ | 999934.745 | 2.8 | 999936.04 | 2.7 | 999936.04 | 2.7 | 999936.04 | 2.7 |
| Ar | 55.20 | 2.8 | 53.90 | 2.71 | 53.90 | 2.71 | 53.90 | 2.71 |
| $C_2HCl_3$ | 10.00 | 0.058 | 10.00 | 0.064 | 9.999 | 0.064 | 9.999 | 0.064 |
| $H_2O$ | 0.0100 | 0.0058 | 0.0100 | 0.0058 | 0.0100 | 0.0058 | 0.0100 | 0.0058 |
| $CO_2$ | 0.0113998 9 | 0.0070 | 0.0097499 | 0.0012 | 0.0098 | 0.0012 | 0.0098 | 0.0012 |
| $H_2$ | 0.0100499 1 | 0.0060 | 0.0089999 | 0.0052 | 0.0090 | 0.0052 | 0.0090 | 0.0052 |

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-T1 | | PSM-T2 | | PSM-T3 | | PSM-T4 | |
| | $Y_{grav}$ (µmol/mo) | $U_{grav}$ (µmol/mo) | $Y_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mo) | $U_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) |
| $O_2$ | 0.0011699 | 0.0010 | 0.0049999 | 0.0029 | 0.0049999 | 0.0029 | 0.050 | 0.0029 |
| $CH_4$ | 0.0047199 | 0.0030 | 0.0042899 | 0.0028 | 0.0042899 | 0.0025 | 0.0043 | 0.0024799 |
| HeavyMetalsPb | 0.0000500 | 0.0000029 | 0.0000500 | 0.0000029 | 0.0000500 | 0.0000029 | 0.0000500 | 0.0000029 |
| $O_2$ | 0.0011699 | 0.0010 | 0.0049999 | 0.0029 | 0.0049999 | 0.0029 | 0.050 | 0.0029 |
| CO | 0.0067399 | 0.0040 | 0.0068499 | 0.0040 | 0.0069 | 0.0040 | 0.0069 | 0.0040 |
| $C_2H_6$ | 0.0070699 | 0.0040 | 0.0062999 | 0.0037 | 0.0062 | 0.0037 | 0.0062 | 0.0037 |

Table 4. 23 : Reference PSM-T1 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-T1 | 1.7 | | | |
| PSM-T4 | 0.24 | 9.466 | 0.092 | |
| PSM-T1 | 0.49 | | | 1.0 |
| PSM-T3 | 0.77 | 9.753 | 0.074 | |
| PSM-T1 | 0.16 | | | 0.27 |
| PSM-T2 | 0.58 | 9.935 | | |
| PSM-T1 | 0.14 | | 0.075 | 1.0 |

Table 4. 24 : Comparison of concentration from T1

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| T4 | 9.999 | 9.466 | 5.6 |
| T3 | 9.999 | 9.753 | 2.5 |
| T2 | 10.00 | 9.935 | 0.65 |

Table 4. 25: Reference PSM-T4 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-T4 | 0.52 | | | |
| PSM-T1 | 0.21 | 10.48 | 0.077 | |
| PSM-T4 | 0.22 | | | 2.54 |
| PSM-T2 | 0.47 | 10.20 | 0.070 | |
| PSM-T4 | 0.41 | | | 0.27 |
| PSM-T3 | 0.34 | 10.07 | | |
| PSM-T4 | 0.50 | | 0.068 | 1.0 |

Table 4. 26: PSM-T4 Gravimetric vs Analytical mole-fraction

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-T1 | 10.00 | 9.966 | 0.38 |
| PSM-T2 | 10.00 | 10.20 | 2.0 |
| PSM-T3 | 9.999 | 10.07 | 0.71 |

Table 4. 27: When PSM-T1 was taken as reference

| Gas Mixture | $X_{grav}$ (µmol/mol) | $U_{grav}$ | $X_{analy}$ (µmol/mol) | $U_{analy}$ | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-T4 | 9.999 | 0.12 | 9.466 | 0.19 | 0.22 | 2.3 |
| PSM-T3 | 9.999 | 0.12 | 9.753 | 0.15 | 0.19 | 1.9 |
| PSM-T2 | 10.00 | 0.12 | 9.935 | 0.15 | 0.19 | 1.9 |

Table 4. 28: When PSM-T2 was taken as reference

| Gas Mixture | $X_{grav}$ (µmol/mol) | $U_{grav}$ | $X_{analy}$ (µmol/mol) | $U_{analy}$ | U | RU (%) |
|---|---|---|---|---|---|---|
| PSM-T1 | 10.00 | 0.12 | 9.966 | 0.15 | 0.19 | 1.9 |
| PSM-T2 | 10.00 | 0.12 | 10.20 | 0.14 | 0.18 | 1.8 |
| PSM-T3 | 9.999 | 0.12 | 10.07 | 0.14 | 0.18 | 1.8 |

### 4.6.2 Internal Consistency Studies

For internal consistency results of the prepared gas mixtures, when PSM-T1 was used as reference in **Figure 4.18**, the sample mixtures showed that sensitivity ratio is within 0.06. **Figure 4.19** and **4.20**, PSM-T3 and PSM-T4 have same sensitivity ratio for the sample mixtures of within 0.05. The internal consistency of all mixtures is good, indicating similar behaviour within the cylinder.

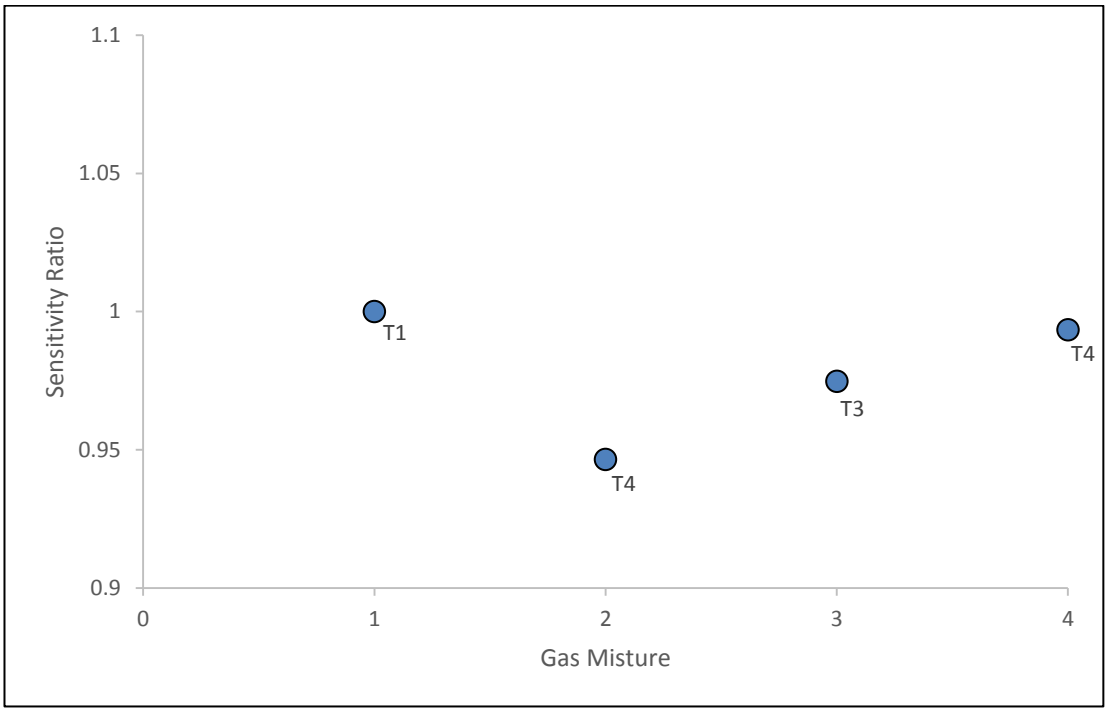



Figure 4. 6: Internal Consistency graph of when PSM-T1 was chosen as reference gas mixture

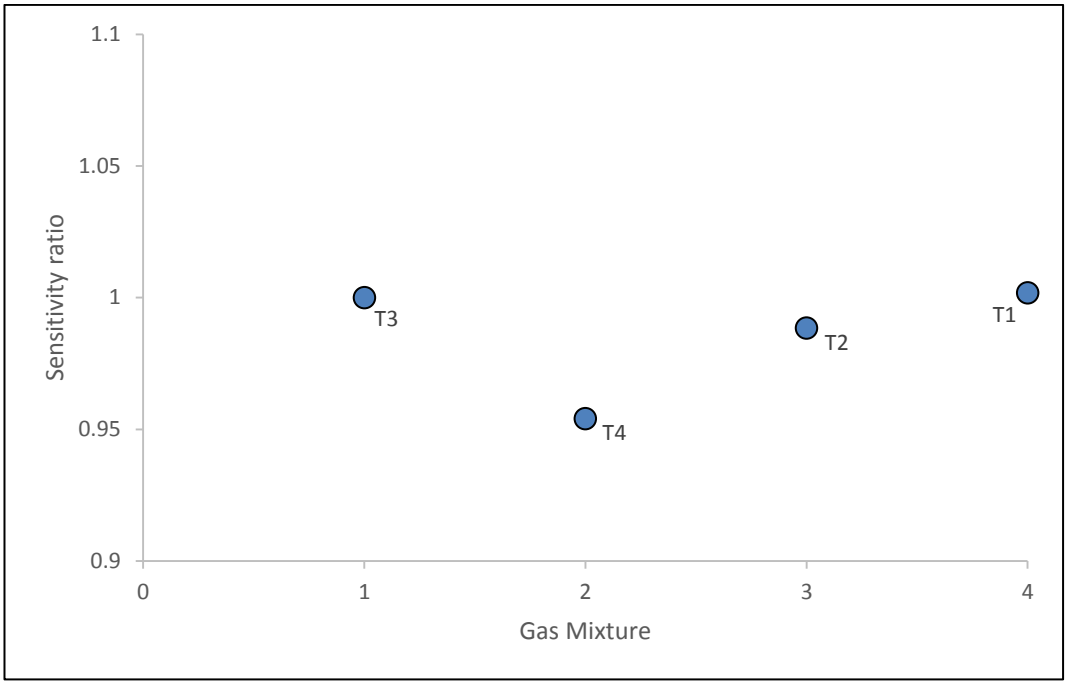



Figure 4. 7: Internal Consistency graph of when PSM-T3 was chosen as reference gas mixture

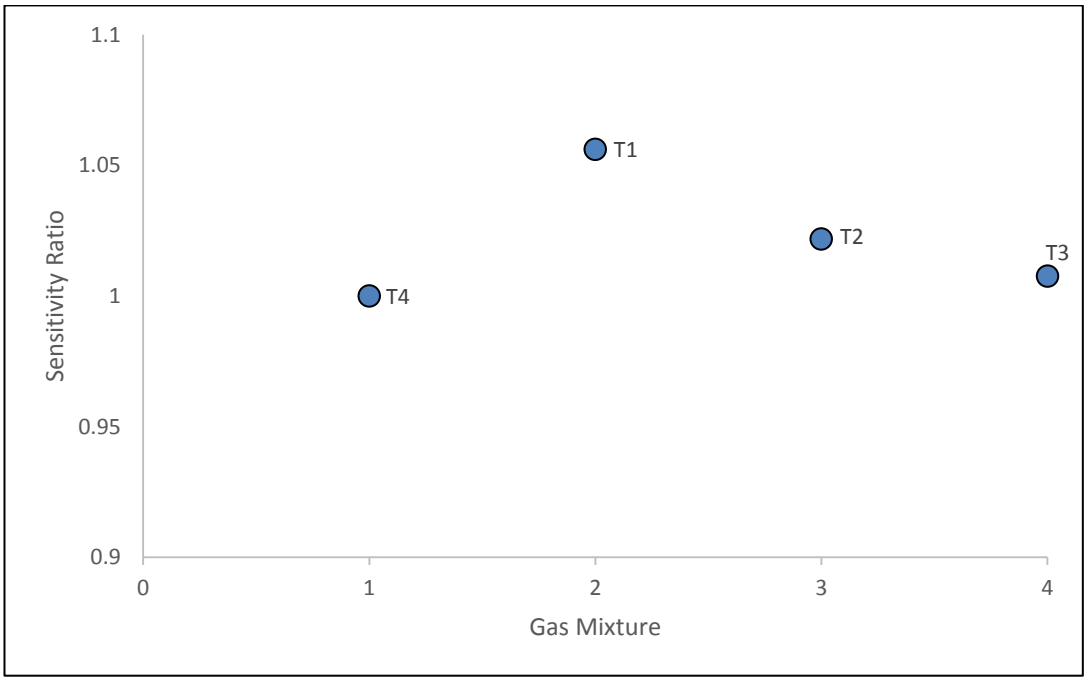



Figure 4. 8: Internal Consistency graph of when PSM-T4 was chosen as reference gas mixture

## 4.7 Development of binary primary reference gas mixture of vinyl chloride

### 4.7.1 Gravimetric Results

Vinyl chloride primary standard gas mixture was developed from a series of dilution. The first level of amount-of-substance prepared was 1.0 %, which was diluted to 200 µmol/mol, and 200 µmol/mol was used to dilute further to 10 µmol/mol. The 1.0 % gas mixtures were analysed using GC-FID and the optimal standard was used to prepare 200 µmol/mol. Analysis results of 1.0 % and gravimetric results are shown in A3 and A4. Gravimetric results composition of 200 µmol/mol are shown in **Table 4.29**.

The results discussed in this section are of 200 µmol/mol. Similar to 1,3-butadiene, uncertainty of the mixtures decreases with concentration. That is because as the mixtures became diluted, even the impurities associated with the mixture decreases hence leading to lower uncertainties and mole-fraction

Table 4. 29: Composition of Vinyl Chloride

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-V1 | | PSM-V2 | | PSM-V3 | | PSM-V4 | |
| | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $N_2$ | 999742.8 | 2.5 | 999746.4 | 2.5 | 999747.48 | 2.5 | 999746.3 | 2.5 |
| Ar | 53.89 | 2.5 | 53.89 | 2.44 | 53.89 | 2.5 | 53.89 | 2.5 |
| $C_2H_3Cl$ | 203.2 | 0.0087 | 199.7 | 0.0087 | 198.6 | 0.0087 | 199.7 | 0.0087 |
| $H_2O$ | 0.009998 | 0.0052 | 0.009998 | 0.0052 | 0.009998 | 0.0052 | 0.009998 | 0.0052 |
| $CO_2$ | 0.009748 | 0.0010 | 0.009748 | 0.0010 | 0.009748 | 0.0010 | 0.009748 | 0.0010 |
| $H_2$ | 0.008998 | 0.0047 | 0.008998 | 0.0047 | 0.008998 | 0.0047 | 0.008998 | 0.0047 |
| CO | 0.006849 | 0.0036 | 0.006849 | 0.0036 | 0.006849 | 0.0036 | 0.006849 | 0.0036 |

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-V1 | | PSM-V2 | | PSM-V3 | | PSM-V4 | |
| | $Y_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $Y_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $O_2$ | 0.0049999 | 0.00276 | 0.004999 | 0.0027 | 0.004999 | 0.0027 | 0.004999 | 0.0027 |
| $CH_4$ | 0.004289 | 0.0023 | 0.004289 | 0.0023 | 0.004289 | 0.0023 | 0.004289 | 0.0023 |
| $C_2H_6$ | 0.006299 | 0.0032 | 0.006299 | 0.0032 | 0.006299 | 0.0032 | 0.006299 | 0.0032 |

For analytical verification of gravimetric amount-of substance, when PSM-V1 was chosen as reference in **Table 2.30** and **2.31**, the performance of the instrument was not impacted by environmental conditions. The instrumental drift is ≤ 0.21, repeatability of the standard is good falls within 0.16 %. the highest percentage difference obtained between the gravimetric mole-fraction and the verified mole-fraction is 1.3 %. When PSM-V2 was chosen as reference in **Table 2.32** and **2.33**, the instrumental drift was within 0.21, repeatability of the measurements was 0.18 % and the highest percentage difference was 1. 7%. Instrumental conditions for PSM-V3 as reference are good with instrumental drift within 0.15, repeatability of measurement results is ≤ 0.21 % and the highest percentage difference is 2.1 % in **Table 2.34** and **2.35**. Lastly for PSM-V4 as reference **Table 2.36** and **2.37**, instrumental drift is ≤0.43, repeatability of measurement results is within 0.09 % and the highest percentage difference obtained is 2.2 %. All the standards were analysed under good environmental conditions as the overall instrumental drift of the analyses was below 0.5 %. Repeatability of the measurements was very low and hence accuracy of the gravimetric results is also indicated by low percentage difference.

The overall method of analyses was developed with good repeatability which is within 0.3 % and accuracy within 3 %. Relative uncertainty achieved to prepare 20 µmol/mol is within 0.5 % at coverage factor of K=2 at 95 % confidence level shown in **Table 2.38** to **2.40**. All standards are deemed to be good reference gas mixtures, with PSM-V1 showing the optimal accuracy to quantify other gas mixture at lower percentage difference when compared to other gas mixtures.

Table 4. 30: Reference PSM- V1 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $U_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-V1 | 0.16 | | | |
| PSM-V4 | 0.07 | 198.9 | 0.13 | |
| PSM-V1 | 0.09 | | | 0.16 |
| PSM-V2 | 0.18 | 202.3 | 0.23 | |
| PSM-V1 | 0.11 | | | 0.016 |
| PSM-V3 | 0.18 | 199.5 | 0.14 | |
| PSM-V1 | 0.07 | | | 0.21 |

Table 4. 31: PSM-V1 comparison of gravimetric and analytical amount-of-substance

| Sample Name | $X_{analy}$ (µmol/mol) | $Y_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-V4 | 199.7 | 198.9 | 0.40 |
| PSM-V2 | 199.7 | 202.3 | 1.3 |
| PSM-V3 | 198.6 | 199.5 | 0.45 |

Table 4. 32: Reference PSM-V2 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-V2 | 0.23 | | | |
| PSM-V4 | 0.13 | 196.3 | 0.25 | |
| PSM-V2 | 0.12 | | | 0.41 |
| PSM-V1 | 0.09 | 199.7 | 0.16 | |
| PSM-V2 | 0.14 | | | 0.033 |
| PSM-V3 | 0.15 | 199.4 | 0.14 | |
| PSM-V2 | 0.04 | | | 0.14 |

Table 4. 33: PSM-V2 comparison of gravimetric and analytical amount-of-substance

| Sample Name | $X_{grav}$ (µmol/mol) | $Y_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-V4 | 199.7 | 196.3 | 1.7 |
| PSM-V1 | 203.2 | 199.7 | 1.7 |
| PSM-V3 | 198.6 | 199.4 | 0.40 |

Table 4. 34: Reference V3 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $U_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-V3 | 0.21 | | | |
| PSM-V4 | 0.04 | 198.8 | 0.17 | |
| PSM-V3 | 0.21 | | | 0.09 |
| PSM-V1 | 0.09 | 199.3 | 0.17 | |
| PSM-V3 | 0.07 | | | 0.15 |
| PSM-V2 | 0.05 | 195.6 | 0.25 | |
| PSM-V3 | 0.19 | | | 0.09 |

Table 4. 35: PSM-V3 comparison of gravimetric and analytical amount-of-substance

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-V4 | 199.7 | 198.8 | 0.45 |
| PSM-V1 | 203.2 | 199.3 | 1.9 |
| PSM-V2 | 199.7 | 195.6 | 2.1 |

Table 4. 36: Reference PSM-V4 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-V4 | 0.051 | | | |
| PSM-V3 | 0.19 | 203.0 | 0.29 | |
| PSM-V4 | 0.11 | | | 0.43 |
| PSM-V2 | 0.086 | 203.3 | 0.14 | |
| PSM-V4 | 0.077 | | | 0.014 |
| PSM-V1 | 0.16 | 203.9 | 0.17 | |
| PSM-V4 | 0.076 | | | 0.22 |

Table 4. 37: PSM-V4 comparison of gravimetric and analytical amount-of-substance

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-V3 | 198.6 | 203.0 | 2.2 |
| PSM-V2 | 199.7 | 203.3 | 1.8 |
| PSM-V1 | 203.2 | 203.9 | 0.34 |

Table 4. 38: Uncertainty evaluation for PSM-V1 reference

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|
| PSM-4 | 0.018 | 0.26 | 0.26 | 0.13 |
| PSM-2 | 0.018 | 0.46 | 0.46 | 0.23 |
| PSM-3 | 0.018 | 0.28 | 0.28 | 0.14 |

Table 4. 39: Uncertainty evaluation for PSM-V2 reference

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|
| PSM-4 | 0.018 | 0.50 | 0.50 | 0.25 |
| PSM-1 | 0.018 | 0.32 | 0.32 | 0.16 |
| PSM-3 | 0.018 | 0.28 | 0.28 | 0.14 |

Table 4. 40: Uncertainty evaluation for PSM-V3 reference

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|
| PSM-4 | 0.018 | 0.34 | 0.34 | 0.17 |
| PSM-1 | 0.018 | 0.34 | 0.34 | 0.17 |
| PSM-2 | 0.018 | 0.50 | 0.50 | 0.26 |

Table 4. 41: Uncertainty evaluation for PSM-V4 reference

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|
| PSM- | 0.018 | 0.26 | 0.26 | 0.13 |
| PSM- | 0.018 | 0.46 | 0.46 | 0.23 |
| PSM- | 0.018 | 0.28 | 0.28 | 0.14 |

### 4.7.2 Internal Consistency Studies

For internal consistency of the developed primary gas mixtures, **Figure 4.21-4.24** represents PSM-V1, PSM-V2, PSM-V3 and PSM-V4 chosen as references. For all the mentioned references, the results indicate that sensitivity ratio of mixtures falls within 0.02. when V4 was used as reference sensitivity ratio of mixtures was within 0.03. The results indicate good internal consistency and indicate that mixtures behave similar relative to each other.

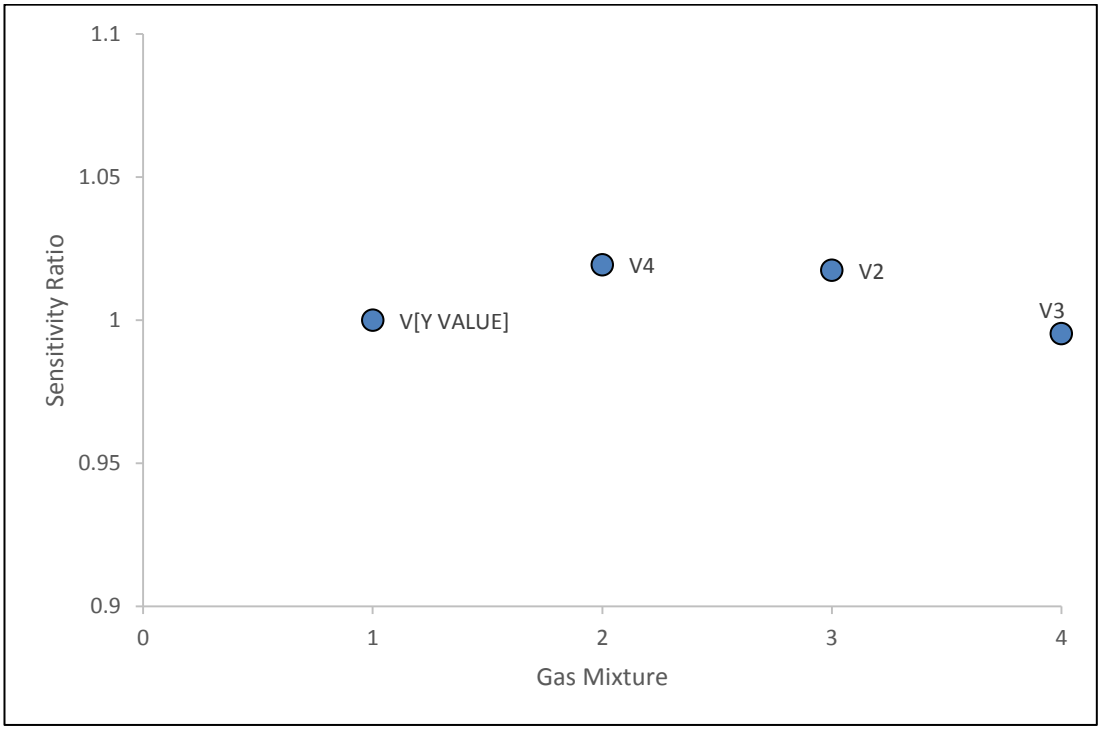



Figure 4. 9: PSM-V1 as reference

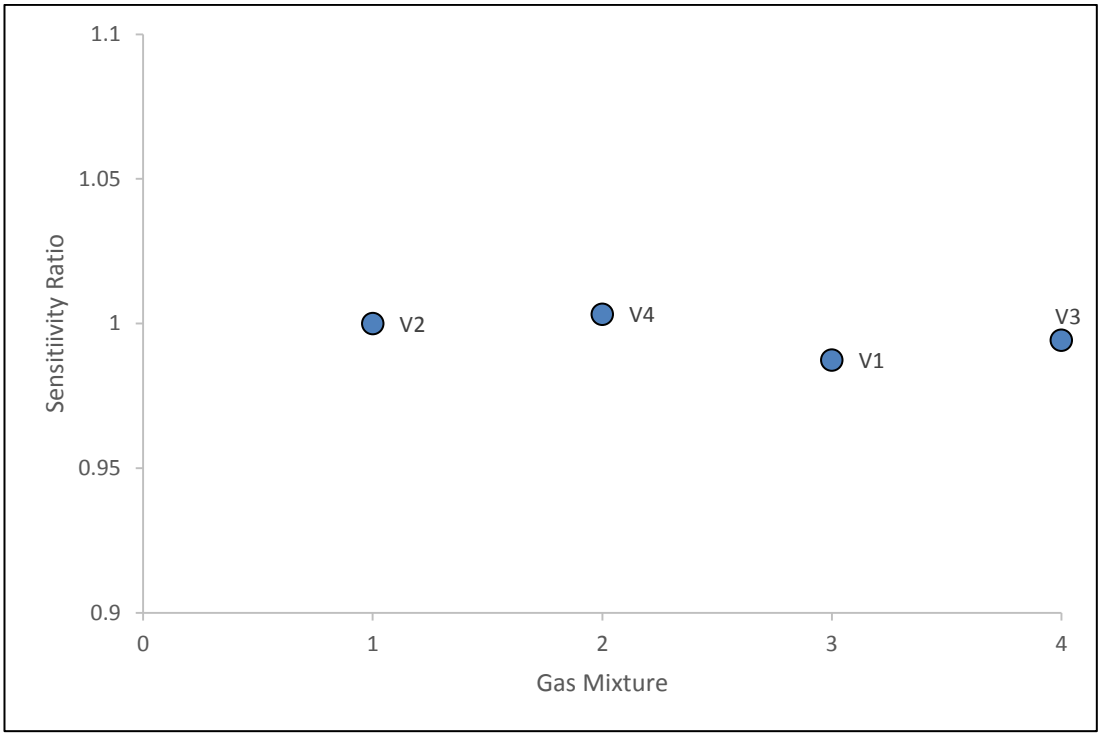



Figure 4. 10: PSM-V2 as reference

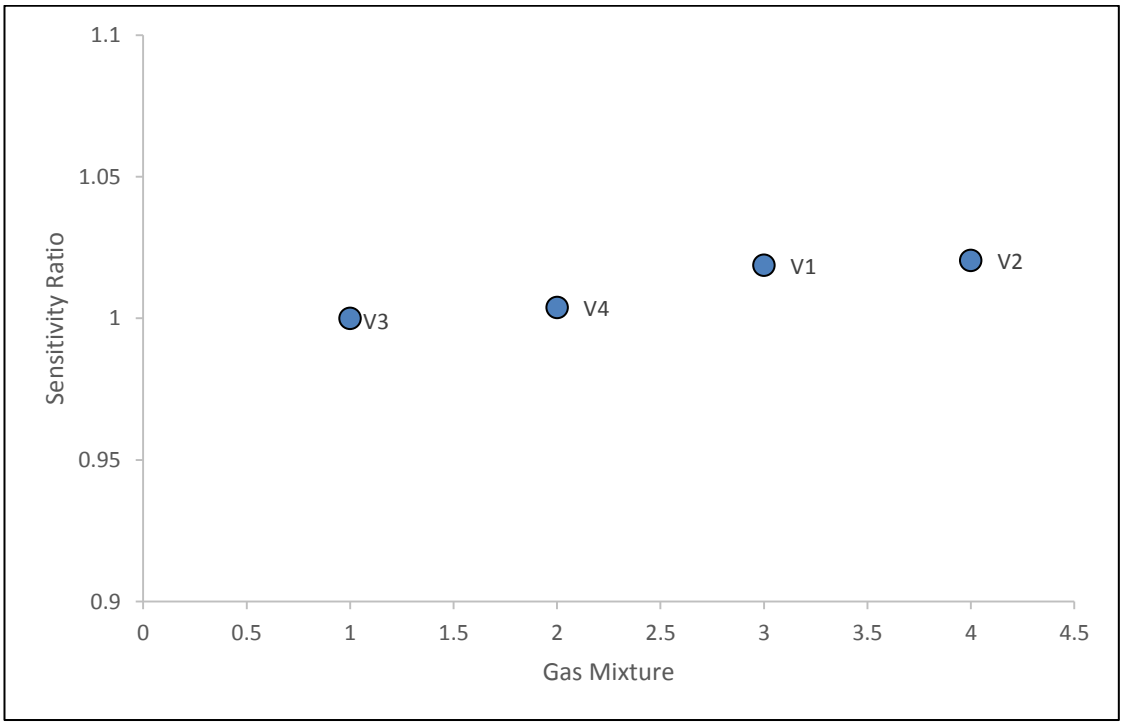



Figure 4. 11: PSM-V3 as reference

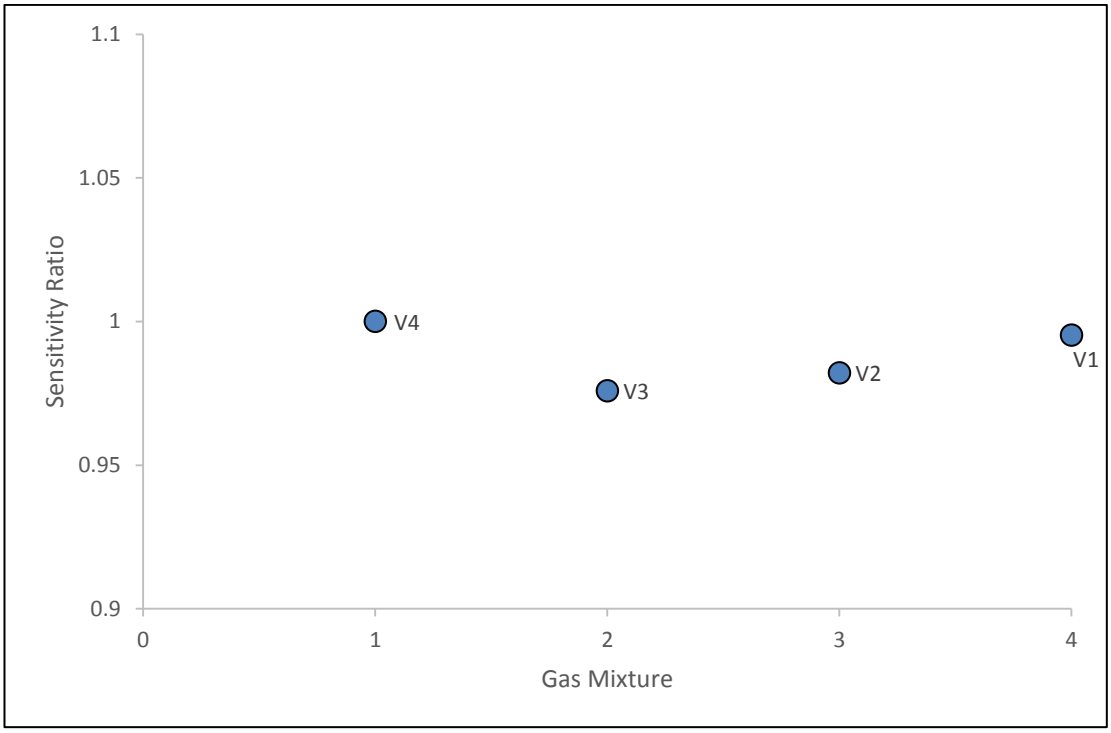



Figure 4. 12: PSM-V4 as reference

## 4. 8 Development of binary primary reference gas mixture of tetrachloroethylene

### 4.8.1 Gravimetric Results

Three primary standard gas mixtures were prepared, PSM-TT1-9.996µmol, PSM-TT2-9.999 µmol/mol and PSM-TT3-10.07 µmol/mol shown in **Table 4.42**. In all mixtures argon and nitrogen have the highest gravimetric uncertainty due to their high mole fraction. Good analytical conditions were obtained when PSM-TT1 was used as a reference gas mixture in **Table 4.43** with instrumental drift of less than 0.060. This was accompanied by good repeatability of measurement falling within 0.05 %. Accuracy of determining gravimetric mole fraction, for PSM-TT2 difference was 2.9 % and for PSM-TT3 percentage difference was 0.5 %.

When PSM-TT3 was used as reference gas mixture in **Table 4.45**, good instrumental drift of less than 0.09 was obtained, with repeatability of measurements within 0.38, accuracy of measurements for PSM-TT2 is 0.50 % and for PSM-TT1 is 0.90 %.

The development of tetrachloroethylene is achieved within relative expanded uncertainty within 2 % at K=2 at 95 % confidence level indicated in **Table 4.47** and **4.48**. The developed method of analysis showed good instrumental drift to be within 0.6 % and overall accuracy was determined within 3 %. Hence the primary standard gas mixtures are deemed to be representable references.

Table 4. 42: Gravimetric Results of Tetrachloroethylene

| | Standard Gas Mixtures | | | | | |
|---|---|---|---|---|---|---|
| Component | PSM-TT1 | | PSM-TT2 | | PSM-TT3 | |
| | $X_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $X_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $N_2$ | 999936.05 | 2.7 | 999936.04 | 2.7 | 999989.92 | 2.7 |
| Ar | 53.899 | 2.7 | 53.899 | 2.7 | 53.899 | 2.7 |
| $C_2Cl_4$ | 9.996 | 0.048 | 9.999 | 0.046 | 10.07 | 0.044 |
| $H_2O$ | 0.0104998 | 0.0058 | 0.0104998 | 0.0058 | 0.0104998 | 0.0058 |
| $CO_2$ | 0.0097499 | 0.0012 | 0.0097499 | 0.0012 | 0.0097499 | 0.0012 |
| $H_2$ | 0.0089999 | 0.0052 | 0.0089999 | 0.0052 | 0.0089999 | 0.0052 |
| CO | 0.0068499 | 0.0040 | 0.0068499 | 0.0040 | 0.0068499 | 0.0040 |
| $C_2H_6$ | 0.0062999 | 0.0037 | 0.0062999 | 0.0037 | 0.0062999 | 0.0037 |
| $O_2$ | 0.0049995 | 0.0029 | 0.0049995 | 0.0029 | 0.0049995 | 0.0029 |

| | | | | | | |
|---|---|---|---|---|---|---|
| $CH_4$ | 0.0042899 | 0.0025 | 0.0042899 | 0.0025 | 0.0042899 | 0.0025 |

Table 4. 43: Reference PSM-TT1 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-TT1 | 0.28 | | | |
| PSM-TT2 | 0.50 | 10.30 | 0.060 | |
| PSM-TT1 | 0.06 | | | 0.22 |
| PSM-TT3 | 0.37 | 10.02 | 0.057 | |
| PSM-TT1 | 0.37 | | | 0.51 |

Table 4. 44**:** Comparison of mole-fraction from PSM-TT1

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-TT2 | 9.999 | 10.30 | 2.9 |
| PSM-TT3 | 10.07 | 10.02 | 0.50 |

Table 4. 45: Reference PSM-TT3 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-TT3 | 0.02 | | | |
| PSM-TT2 | 0.13 | 10.05 | 0.045 | |
| PSM-TT3 | 0.18 | | | 0.09 |
| PSM-TT1 | 0.32 | 9.906 | 0.048 | |
| PSM-TT3 | 0.08 | | | 0.07 |

Table 4. 46: Comparison of mole-fraction from PSM-TT3

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-TT2 | 9.999 | 10.05 | 0.50 |
| PSM-TT1 | 9.996 | 9.906 | 0.90 |

Table 4. 47: Uncertainty evaluation for PSM-TT1 reference

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|
| PSM-TT3 | 0.092 | 0.090 | 0.13 | 1.3 |
| PSM-TT1 | 0.096 | 0.096 | 0.14 | 1.3 |

Table 4. 48: Uncertainty evaluation for PSM-TT3 reference

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|
| PSM-TT2 | 0.096 | 0.16 | 0.19 | 1.9 |
| PSM-TT1 | 0.096 | 0.14 | 0.17 | 1.8 |

### 4.8.2 Internal Consistency Studies

Internal consistency of the developed primary gas mixtures is good. When PSM-TT3 was chosen as reference, the internal consistency of the mixtures was within sensitivity ratio of 0.03, and when PSM-TT1 was chosen as reference sensitivity ratio was within 0.01 and for PSM-TT2 it was within 0.06, Results are shown in **Figure 4.25-4.27**.

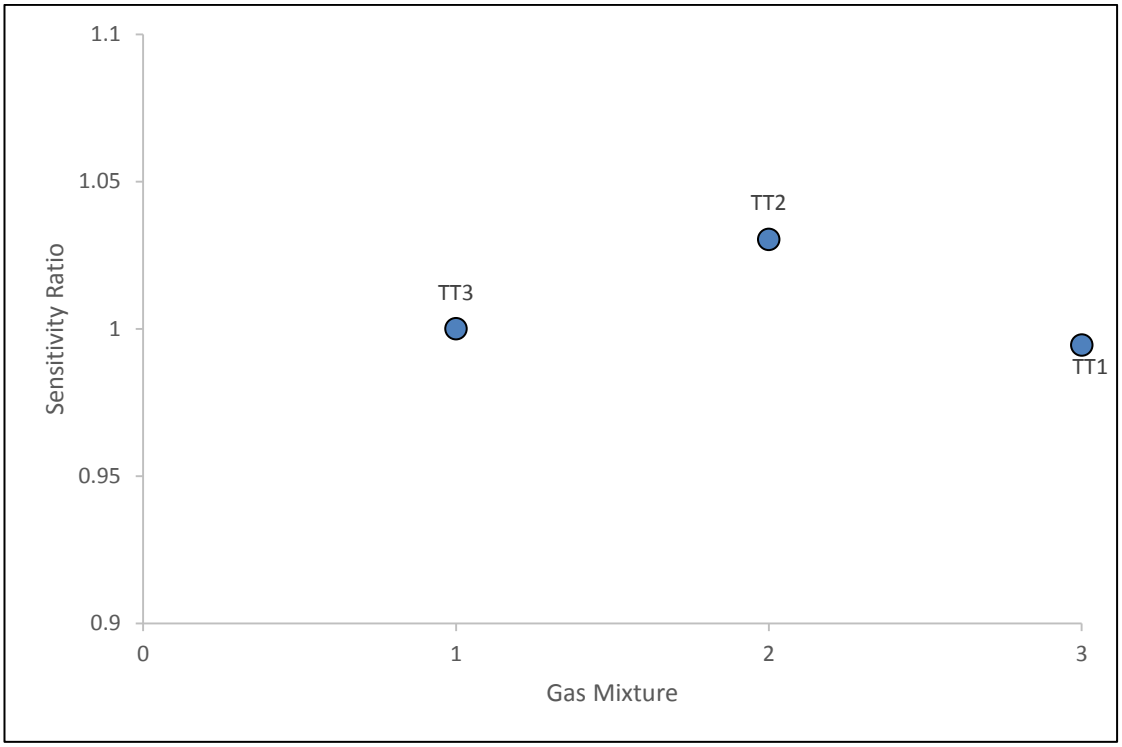



Figure 4. 13: Internal Consistency graph of when PSM-TT3 was chosen as reference gas mixture

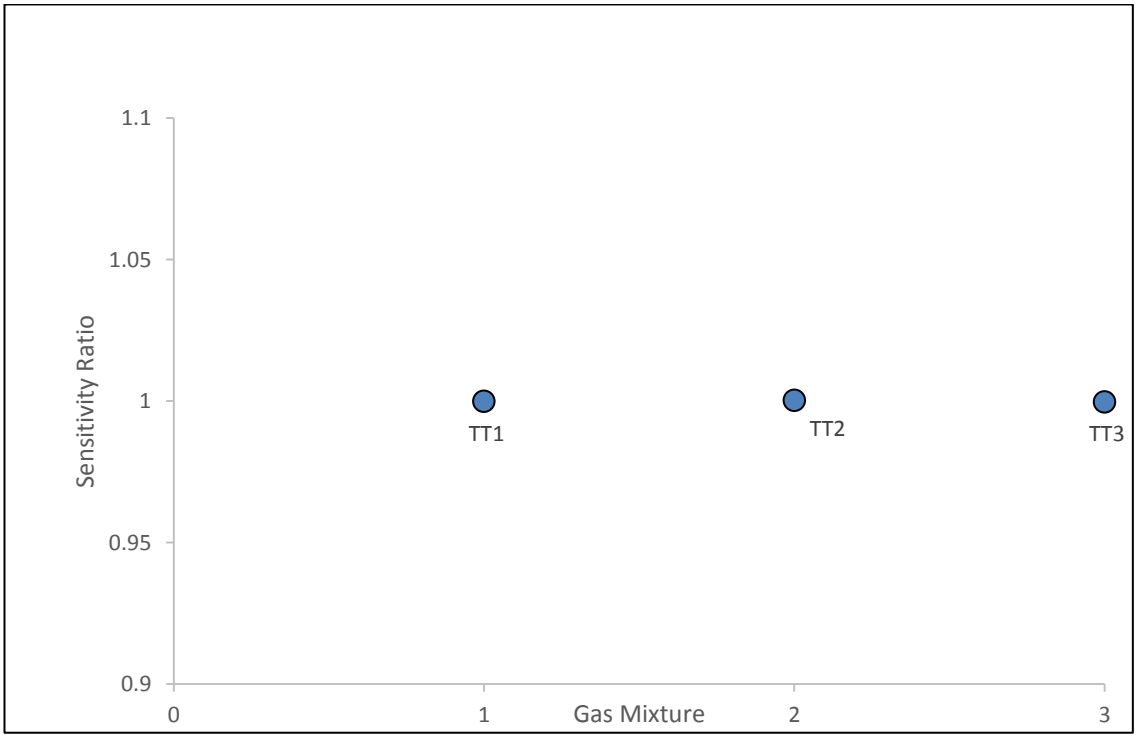



Figure 4. 14: Internal Consistency graph of when PSM-TT1 was chosen as reference gas mixture

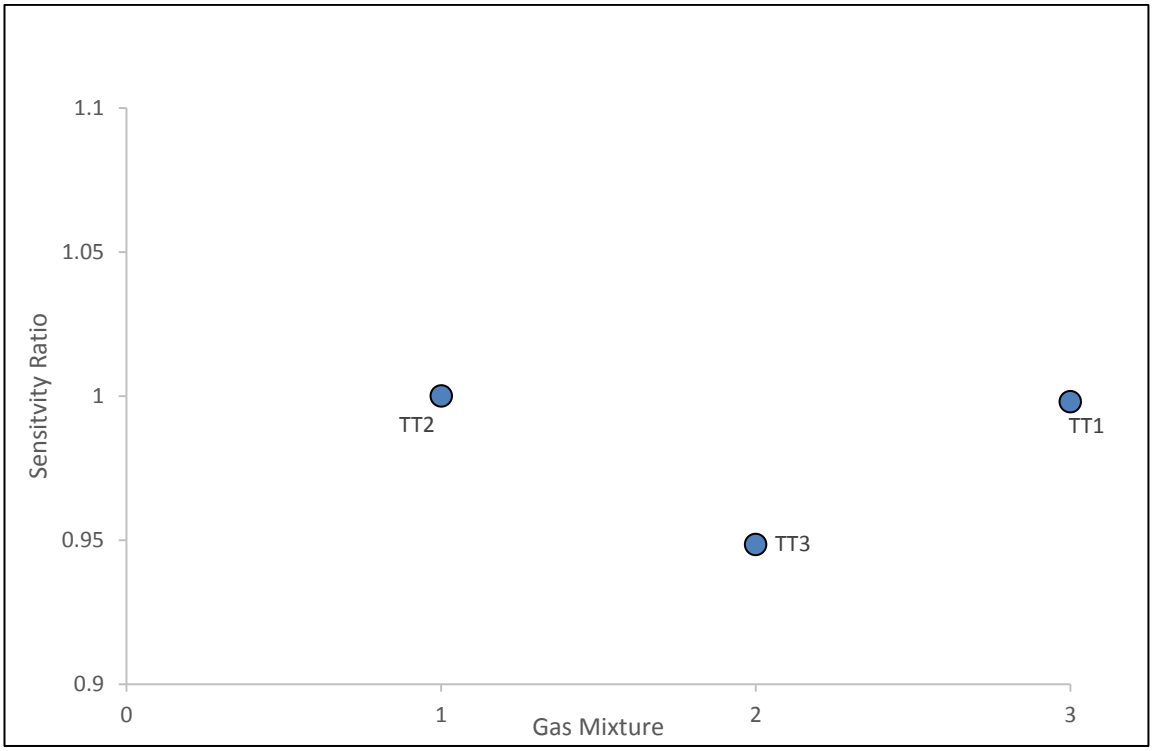



Figure 4. 15: Internal Consistency graph of when PSM-TT2 was chosen as reference gas mixture

## 4.9 Development of binary primary reference gas mixture of 1,2-dichloroethane

### 4.9.1 Gravimetric Results

Four gas mixtures of 1,2-dichloroethane were prepared from high pure liquid sample. All four mixtures were chosen as references to verify the most accurately prepared and only two gas mixtures showed good results. **Table 4.49** show the gravimetric mole fraction and uncertainty of the developed standards. **Table 4.50** show the results of when PSM-DD1 was chosen as reference. Repeatability of the analysis method was achieved at ≤ 0.82 % and the instrumental drift was ≤ 0.55. Accuracy of determining sample gas mixtures was achieved ≤ 0.23.

when PSM-DD2 was chosen as reference in **Table 4.52** repeatability of measurements was achieved within 0.43 % and instrumental drift within 0.55, good accuracy was obtained within 1.28 %. PSM-DD3 and PSM-DD4 results showed variations in percentage difference for the gases taken as samples, hence both gases were verified by PSM-DD1 and PSM-DD2.

The standards chosen to be references in 1,2-dichloeomethane were developed with 2.5 % relative expanded uncertainty at coverage factor of K=2 and confidence level of 95 %. Showed in **Table 4.54 and 4.55.**

Table 4. 49: Gravimetric Results of 1,2-dichloroethane

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-DD1 | | PSM-DD2 | | PSM-DD3 | | PSM-DD4 | |
| | $Y_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $Y_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $N_2$ | 999935.95 | 2.7 | 999935.95 | 2.7 | 999935.95 | 2.7 | 999935.957 | 2.7 |
| Ar | 53.899 | 2.7 | 53.899 | 2.7 | 53.899 | 2.7 | 53.899 | 2.7 |
| $C_2H_4Cl_2$ | 9.880 | 0.076 | 9.740 | 0.070 | 10.15 | 0.081 | 9.956 | 0.080 |
| $H_2O$ | 0.100 | 0.0057 | 0.100 | 0.0057 | 0.100 | 0.0057 | 0.100 | 0.0057 |
| $CO_2$ | 0.0097499 | 0.0011 | 0.0097499 | 0.0011 | 0.0097499 | 0.0011 | 0.0097499 | 0.0011 |
| $H_2$ | 0.008999 | 0.0052 | 0.008999 | 0.0052 | 0.008999 | 0.0052 | 0.008999 | 0.0052 |
| CO | 0.0068 | 0.0039 | 0.0068 | 0.0039 | 0.0068 | 0.0039 | 0.0068 | 0.0039 |
| $C_2H_6$ | 0.0063 | 0.0037 | 0.0063 | 0.0037 | 0.0063 | 0.0037 | 0.0063 | 0.0037 |

| | Standard Gas Mixtures | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Component | PSM-DD1 | | PSM-DD2 | | PSM-DD3 | | PSM-DD4 | |
| | $Y_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mo) | $Y_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mo) | $u_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mol) | $u_{grav}$ (µmol/mol) |
| $O_2$ | 0.004999 | 0.0029 | 0.004999 | 0.0029 | 0.004999 | 0.0029 | 0.004999 | 0.0029 |
| $CH_4$ | 0.004289 | 0.0025 | 0.004289 | 0.0025 | 0.004289 | 0.0025 | 0.004289 | 0.0025 |

Table 4. 50: Reference PSM-DD1 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-DD1 | 0.22 | | | |
| PSM-DD2 | 0.23 | 9.762 | 0.078 | |
| PSM-DD1 | 0.47 | | | 0.55 |
| PSM-DD3 | 0.82 | 10.16 | 0.077 | |
| PSM-DD1 | 0.41 | | | 0.31 |
| PSM-DD4 | 0.36 | 9.966 | 0.084 | |
| PSM-DD1 | 0.17 | | | 0.05 |

Table 4. 51: Comparison results gravimetric and analytical mole-fraction in PSDM-DD1

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-DD2 | 9.740 | 9.762 | 0.08 |
| PSM-DD3 | 10.15 | 10.16 | 0.06 |
| PSM-DD4 | 9.956 | 9.966 | 0.23 |

Table 4. 52: Reference DD2 analytical results

| Sample Name | Relative Standard Deviation (%) | $X_{analy}$ (µmol/mol) | $u_{analy}$ (µmol/mol) | Instrumental Drift |
|---|---|---|---|---|
| PSM-DD2 | 0.36 | | | |
| PSM-DD4 | 0.17 | 9.844 | 0.082 | |
| PSM-DD2 | 0.28 | | | 0.32 |
| PSM-DD1 | 0.38 | 10.16 | 0.083 | |
| PSM-DD2 | 0.41 | | | 0.05 |
| PSM-DD3 | 0.33 | 9.616 | 0.084 | |
| PSM-DD2 | 0.14 | | | 0.11 |

Table 4. 53: Comparison results gravimetric and analytical mole-fraction in PSDM-DD2

| Sample Name | $X_{grav}$ (µmol/mol) | $X_{analy}$ (µmol/mol) | % Difference |
|---|---|---|---|
| PSM-DD4 | 9.880 | 9.844 | 0.36 |
| PSM-DD1 | 10.15 | 10.16 | 0.098 |
| PSM-DD3 | 9.740 | 9.616 | 1.28 |

Table 4. 54: Uncertainty evaluation for PSM-DD1 reference

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|
| PSM-DD2 | 0.14 | 0.16 | 0.21 | 2.2 |
| PSM-DD3 | 0.17 | 0.16 | 0.23 | 2.3 |
| PSM-DD4 | 0.16 | 0.17 | 0.23 | 2.3 |

Table 4. 55: Uncertainty evaluation for PSM-DD2 reference

| Gas Mixture | $U_{grav}$ | $U_{analy}$ | $\sqrt{U_{grav}^2 + U_{analy}^2}$ | RU (%) |
|---|---|---|---|---|
| PSM-DD4 | 0.16 | 0.16 | 0.23 | 2.5 |
| PSM-DD1 | 0.16 | 0.17 | 0.23 | 2.3 |
| PSM-DD3 | 0.17 | 0.17 | 0.24 | 2.4 |

### 4.9.2 Internal Consistency Studies

**Figure 4.28** and **4.29** show internal consistency of 1,2-dichloroethane gas mixtures. Good internal consistency is observed in all mixtures, the mixtures for PSM-DD1 fall within 0.003 and 0.01 in PSM-DD2. This indicates good similar behaviour within various cylinders.

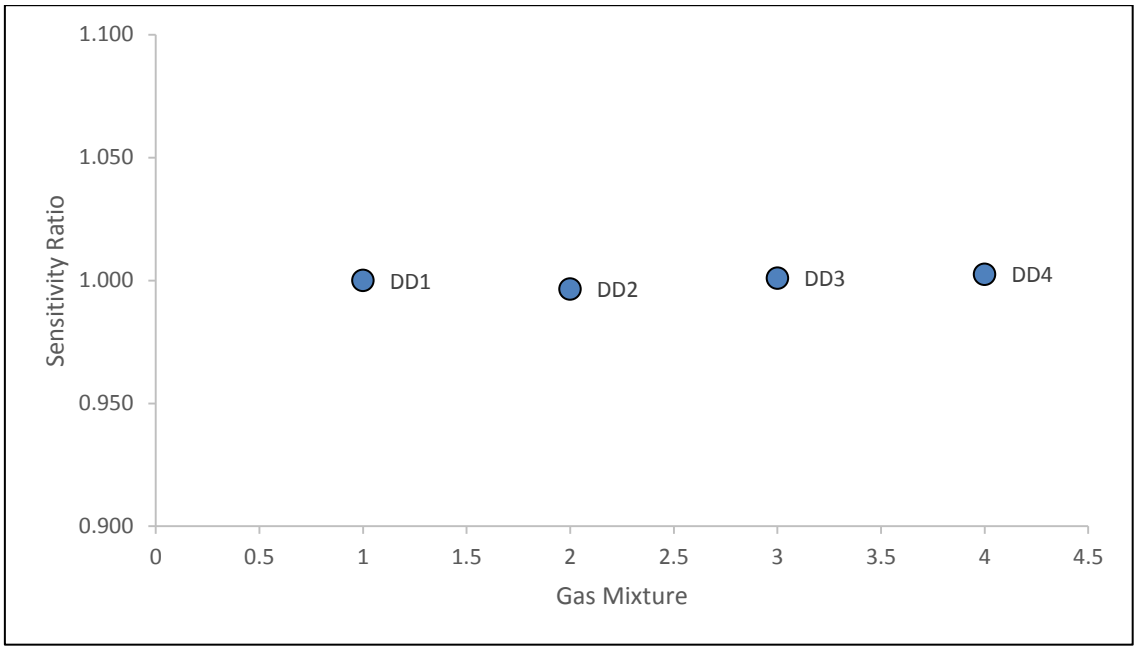



Figure 4. 16: PSM-DD1 as reference

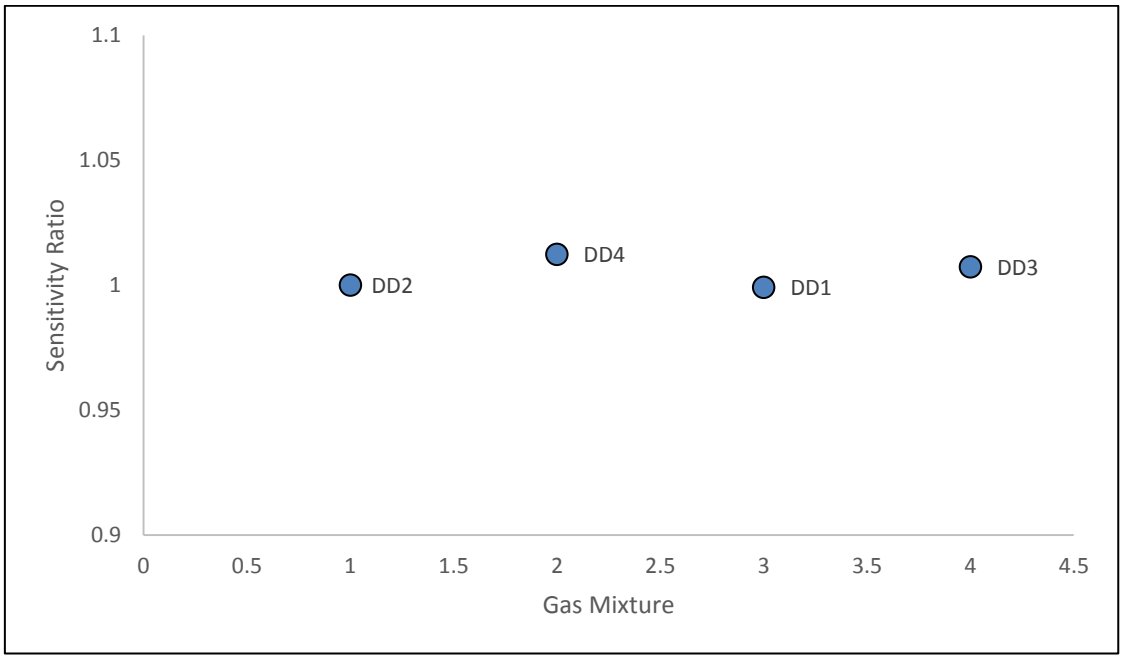



Figure 4. 17: PSM-DD2 as reference

## 4.10 Development of binary primary reference gas mixture of Dichloromethane

### 4.10.1 Gravimetric Results

Gravimetric amount-of-substance of dichloromethane primary gas standard mixtures prepared are PSM-D1-9.888 µmol/mol, PSM-D2-11.15 µmol/mol and PSM-D3-9.958 µmol/mol, indicated in **Table 4.56**. Each standard was taken as reference and the other two were taken as sample. **Figure 4.30** indicate measurement set trend, of each standard taken as sample. For verification of gravimetric mole fraction on GC-FID, when PSM-D1 was taken as reference in analytical conditions were good as the instrumental drift was within 0.61 %, repeatability of measurement results is 1.6 accuracy of determining gravimetric mole fraction was good because the highest percentage difference is 0.34 %.

When PSM-D2 was chosen as reference, instrumental drift was within 0.71 %, repeatability of measurement is ≤ 1.6 and accuracy of results was determined at

2.1 %. For PSM-D3 as reference in good analytical conditions were obtained, instrumental drift is within 0.84 %, repeatability of measurements is within 0.84 %. Accuracy of measurements was determined within 0.27 %.

Table 5.55 to .57 indicates the overall results of development of dichloromethane standard gas mixture. The method of analyses from the discussed results was achieved at instrumental drift of less than one, repeatability measurements within three percent and accuracy to determine the amount-of-substance prepared is within three percent. The uncertainty related to the values shown is within 3.1 % at coverage factor of K=2 and confidence level of 95 %.

Table 4. 56: Gravimetric Results of Dichloromethane

| | Standard Gas Mixtures | | | | | |
|---|---|---|---|---|---|---|
| Component | PSM-D1 | | PSM-D2 | | PSM-D3 | |
| | $Y_{grav}$ (µmol/mo) | $U_{grav}$ (µmol/mo) | $Y_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) |
| $N_2$ | 999936.05 | 2.7 | 999936.04 | 2.7 | 999989.92 | 2.7 |
| Ar | 53.899 | 2.7 | 53.899 | 2.7 | 53.899 | 2.7 |
| $CH_2Cl_2$ | 9.959 | 0.079 | 11.13 | 0.0900 | 9.889 | 0.086 |
| $H_2O$ | 0.0100 | 0.0058 | 0.0100 | 0.0058 | 0.0100 | 0.0058 |
| $CO_2$ | 0.0097499 | 0.0012 | 0.0097499 | 0.0012 | 0.0097499 | 0.0012 |
| $H_2$ | 0.0089999 | 0.0052 | 0.0089999 | 0.0052 | 0.0089999 | 0.0052 |
| CO | 0.0068499 | 0.0040 | 0.0068499 | 0.0040 | 0.0068499 | 0.0040 |

| | Standard Gas Mixtures | | | | | |
|---|---|---|---|---|---|---|
| Component | PSM-D1 | | PSM-D2 | | PSM-D3 | |
| | $Y_{grav}$ (µmol/mo) | $U_{grav}$ (µmol/mo) | $Y_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) | $Y_{grav}$ (µmol/mol) | $U_{grav}$ (µmol/mol) |
| $O_2$ | 0.0049995 | 0.0029 | 0.0049995 | 0.0029 | 0.0049995 | 0.0029 |
| $CH_4$ | 0.0042899 | 0.0025 | 0.0042899 | 0.0025 | 0.0042899 | 0.0025 |
| $C_2H_6$ | 0.0062999 | 0.0037 | 0.0062999 | 0.0037 | 0.0062999 | 0.0037 |

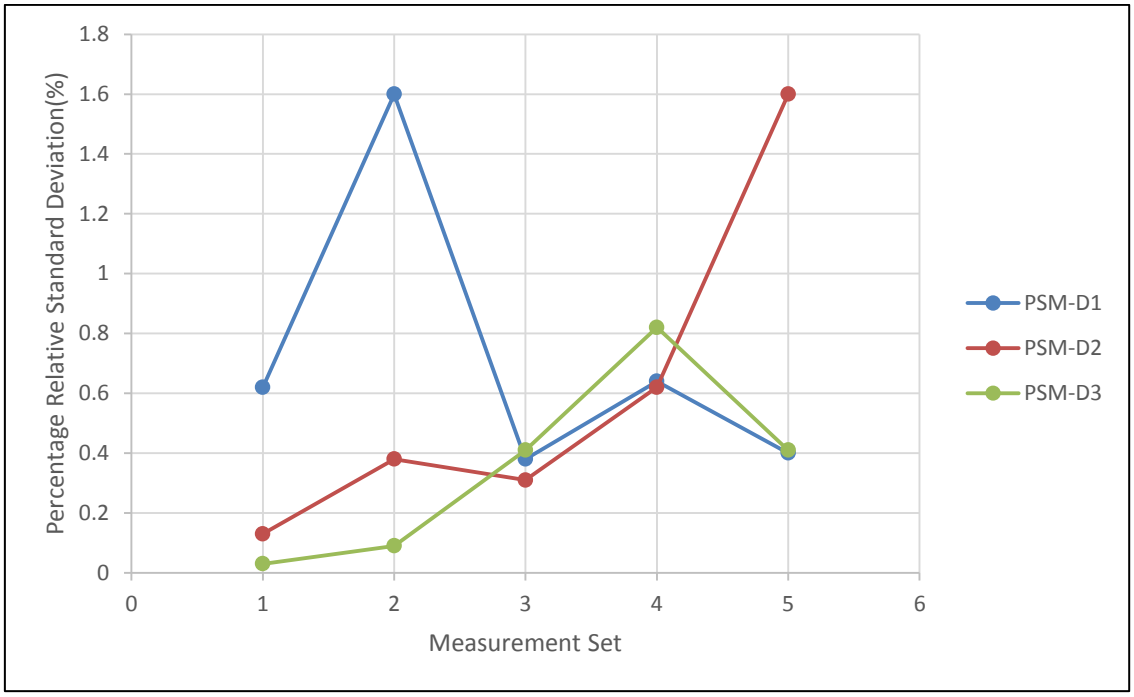



Figure 4. 18: Repeatability Trend of Dichloromethane

Table 4. 57: When B1 was taken as reference

| Gas Mixture | $X_{grav}$ (µmol/mol) | $U_{grav}$ | $X_{analy}$ (µmol/mol) | $U_{analy}$ | U | RU(%) |
|---|---|---|---|---|---|---|
| PSM-D2 | 11.15 | 0.18 | 11.13 | 0.28 | 0.34 | 3.1 |
| PSM-D3 | 9.889 | 0.18 | 9.855 | 0.18 | 0.26 | 2.7 |

Table 4. 58: When PSM-D2 was taken as reference

| Gas Mixture | $X_{grav}$ (µmol/mol) | $U_{grav}$ | $X_{analy}$ (µmol/mol) | $U_{analy}$ | U | RU(%) |
|---|---|---|---|---|---|---|
| PSM-D3 | 9.889 | 0.18 | 9.868 | 0.20 | 0.27 | 2.8 |
| PSM-D1 | 9.958 | 0.16 | 9.943 | 0.17 | 0.24 | 2.5 |

Table 4. 59: When PSM-D3 was taken as reference

| Gas Mixture | $X_{grav}$ (µmol/mol) | $U_{grav}$ | $X_{analy}$ (µmol/mol) | $U_{analy}$ | U | RU(%) |
|---|---|---|---|---|---|---|

| Gas Mixture | $X_{grav}$ (µmol/mol) | $U_{grav}$ | $X_{analy}$ (µmol/mol) | $U_{analy}$ | U | RU(%) |
|---|---|---|---|---|---|---|
| PSM-D2 | 11.13 | 0.18 | 11.12 | 0.20 | 0.27 | 2.5 |
| PSM-D1 | 9.958 | 0.17 | 9.932 | 0.18 | 0.25 | 2.6 |

### 4.10.2 Internal Consistency Studies

The developed standard gas mixtures show similar results in internal consistency shown in **Figure 4.31-4.33**. For each case, when the standards were taken as reference the mixtures which were taken as samples fall within sensitivity ratio of 0.04. This indicates that the mixtures are of the same component and that mole fraction prepared are not far from each other.

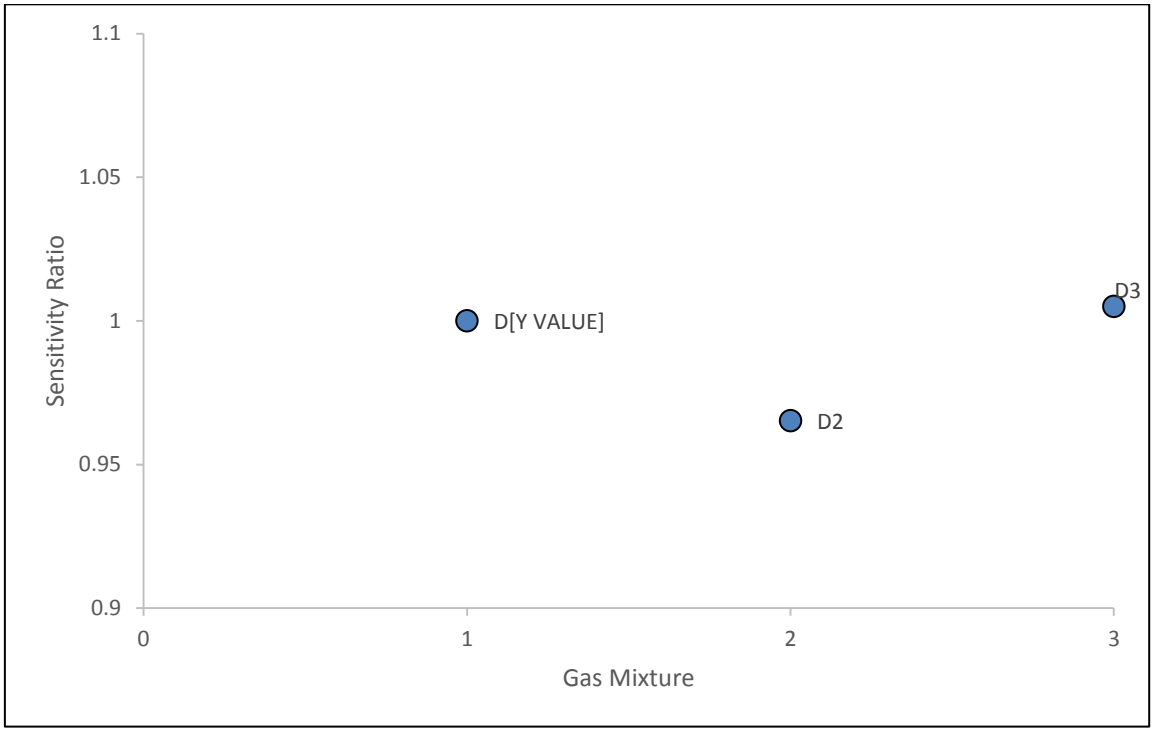



Figure 4. 19: PSM-D1 as reference

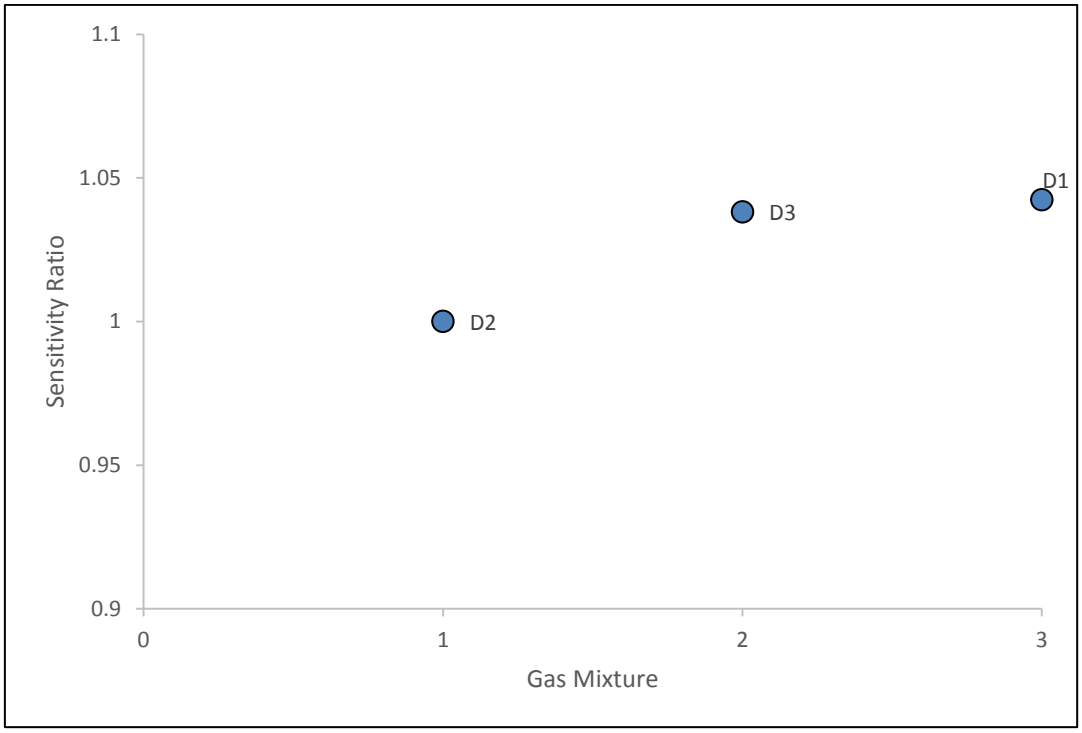



Figure 4. 20: PSM-D2 as reference

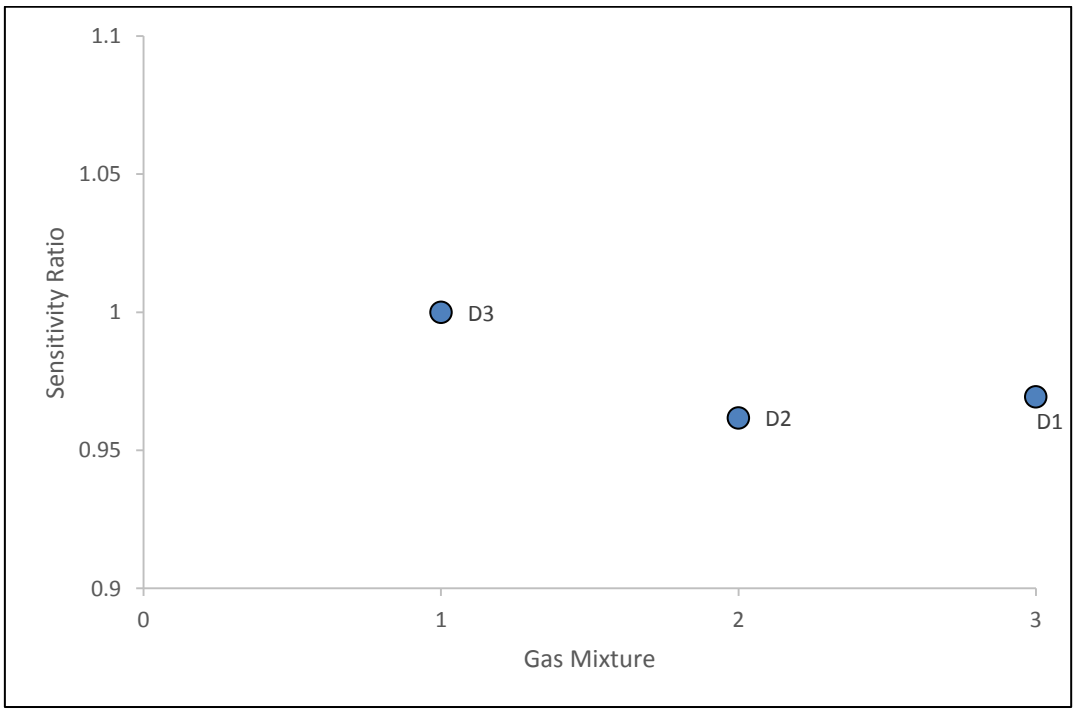



Figure 4. 21: PSM-D3 as reference

The internal consistency results correlate well with verification of gravimetric mole fraction. The analysis method was achieved at lower instrumental drift, ≤ 1.0, good repeatability was achieved and accuracy of determining the gravimetric mole fraction was also satisfactory. It can be concluded that the development of dichloromethane was successful.

### 4.10 Comparison of Results with Previous Data

There has been limited research in binary gas mixtures of hazardous air pollutants, hence comparison in terms of accuracy of gravimetric preparation will be through multicomponent with same matrix of nitrogen. Rhoderick (1988) in development of VOCs multimucomponent containing similar components in the study found expanded uncertainity of 3-10 %. For precision of analytical method for analysis Rhoderick et al (1990) obtained percentage relative standard devision of 0.4-1.2 %. In this study expanded uncertainity of all components ranged from 0.15-3.2 % and analytical precision of 0.02-1.7 %. Hence it can be concluded that the use of syringe method for development of primary standard gas mixtures , using one-point calibration following ABA sequence produce comparable results with previous research

### 4.11 Uncertainty Evaluation of Binary Standards

Uncertainty of nitrogen and argon in all standards are between 2.7-2.8 µmol/mol and 2.6-2.8 µmol/mol that is because the high pure nitrogen used is the same for all components. The uncertainties of these components are higher than other components in the mole fraction. That is due to their higher mole-fraction, hence resulting in greater uncertainties. Ar has higher mole-fraction in all gas standards, this is particularly from high pure nitrogen used as a diluent. Ar is a stable, inert gas hence its availability does not contaminate the standard gas mixtures.

It has also been observed that analytical uncertainty is greater than gravimetric uncertainty. This is due to introduction of many sources of uncertainty during analysis. From **Equation 4.1** response are from FID is taken into consideration. This is factor is from the instrument GC which was not in the initial calculation of gravimetric uncertainty. The calculation also considers gravimetric mole-fraction of both the reference and sample (Di Meane, 2009).

# CHAPTER FIVE – Development of Hazardous Air Pollutants Multicomponent Standard Gas Mixture

This chapter is composed of development of multi-component of HAPs in one aluminium cylinder. It was difficult to obtain good resolution during analysis, hence it explains in detail how the method was optimized. Behaviour of each component in a cylinder is thoroughly investigated and discussed. The developed primary standard gas mixture is used to identify and quantify HAPs in air sample.

## 5.1 Optimising Separation of Six-Multicomponent Mixture Using Various Column

The first level of multicomponent mixtures prepared was a dilution of 10µmol/mol benzene,1,2-dichloroethane, dichloromethane, chloroform, tetrachloroethylene and trichloroethylene in nitrogen from high pure materials. These components were chosen due to their liquid physical state, excluding nitrogen as a diluent gas. Vinyl chloride and 1,3-butadiene are liquified gases, hence can only be diluted separately.

The multicomponent gas mixtures were analysed on different columns under various analytical conditions to obtain good resolution. The mixtures were initially analysed on Agilent HP-Innowax column and only four peaks were identified. To identify the peaks, 10 µmol/mol binary primary standards were used. This led to the discovery of co-elution of benzene at 4.05 min and dichloromethane at 4.04 min; tetrachloroethylene at 5.36 min and trichloroethylene at 45.25 min. Retention time was used as measure or tool for identification of components due to basic principles of GC. To achieve proper separation of peaks various analytical parameters such as temperature and flow were changed however co-elution of peaks was not resolved. Another factor which plays a major role in retention time is how soluble the analyte is relative to the stationary phase. This is the intermolecular interaction of the analyte with the stationary phase.

Components which co-elute have similar interactions with the stationary phase (Cordero et al., 2012). To optimize on resolution again, the column was changed to Agilent DB-624, this was to change the interaction between the stationary phase and analyte. Only five peaks were observed, there was co-elution of benzene at 5.2 min and 1,2-dichloroethane at 5.3 min. This indicates similar interaction of the components with the stationary phase of DB-624 column.

Finally, the gas mixtures were analysed on Agilent CP-Sil 5CB. Six separated peaks were observed with good resolution. The elution order on the column is dichloromethane, chloroform, benzene, 1,2-dichloroethane, trichloroethylene and tetrachloroethylene. Another advantage of this column was also shorter length which impacted on the run analysis time. Longer columns lead to longer analysis time while shorter columns result in analysis time. HP-Innowax column is 60 m and took 8 minutes to elute four peaks. DB-624 column is 60 m hence it took 10 minutes for all the five peaks to be eluted, CP-Sil 5CB eluted all 6 peaks in 7 minutes with column length of 30 m.

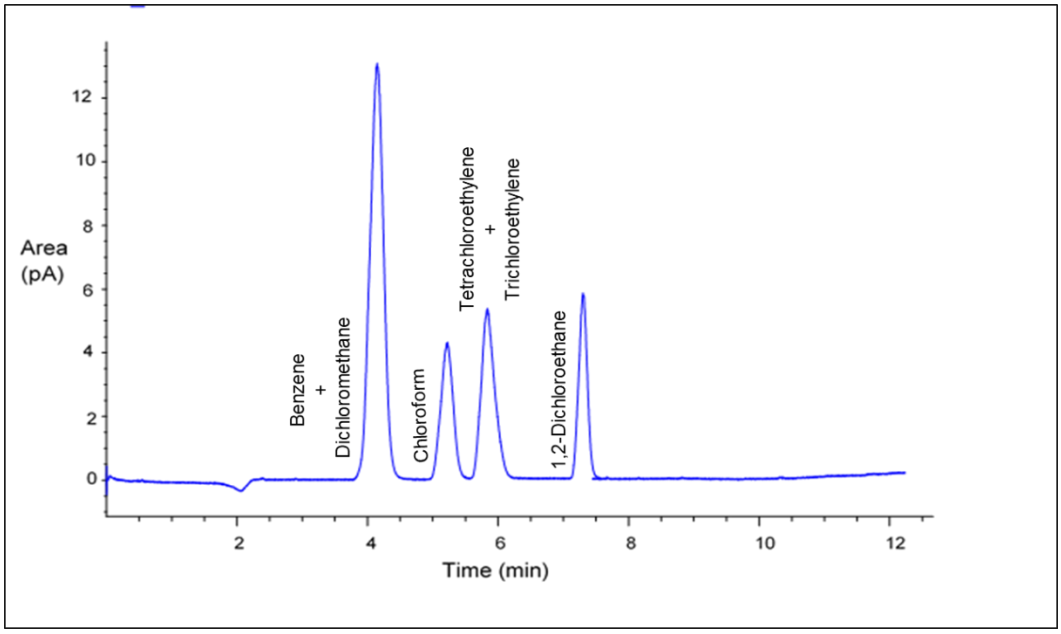



Figure 5. 1: HP-Innowax column peak separation

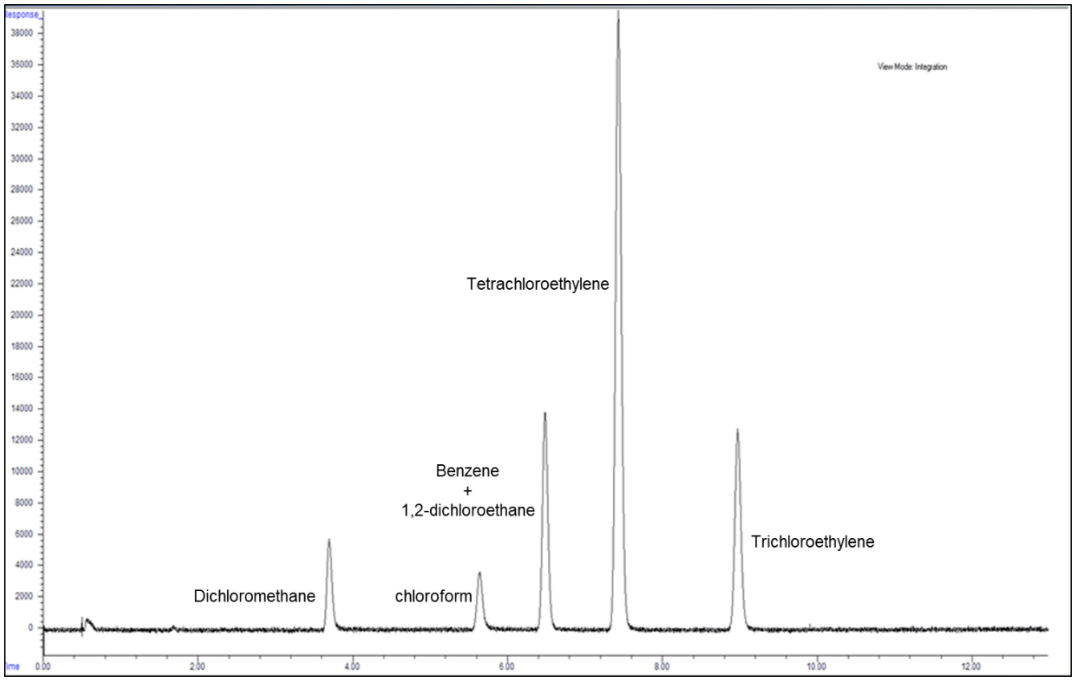



Figure 5. 2:DB-624 column peak separation

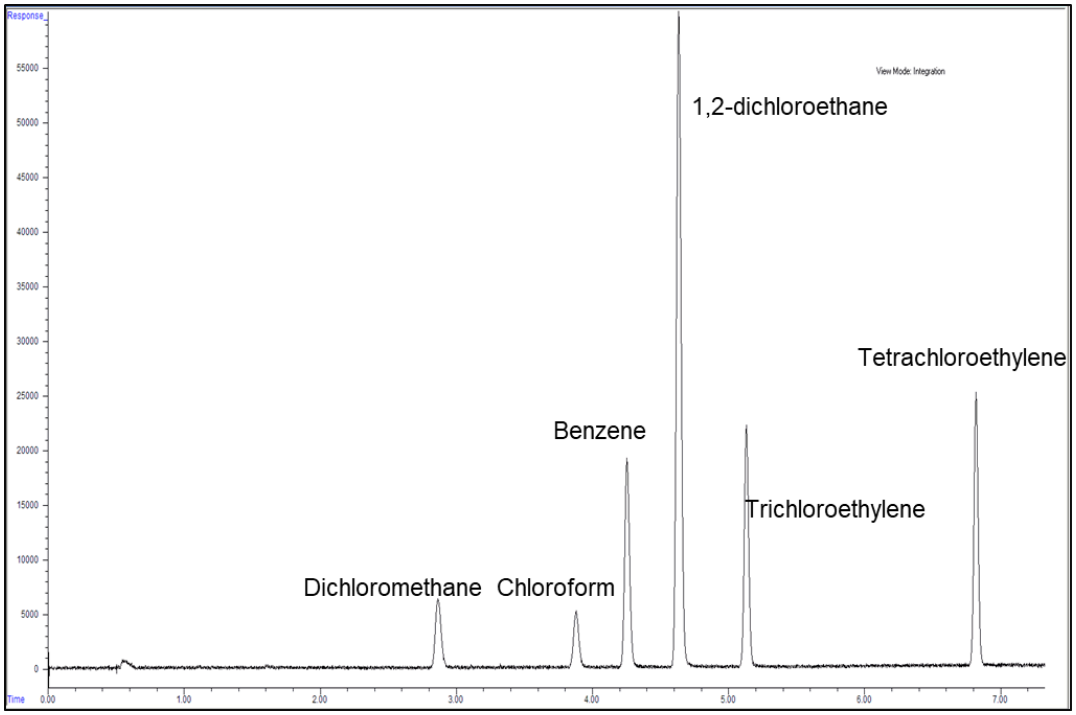



Figure 5. 3: CP-Sil 5CB column peak separation

In gas chromatography, area is proportional to concentration. However, **Figure 5.3** show that GC-FID responded differently to individual

components of same concentration. There is difference in sensitivity towards flame-ionisation detector in different components due to number of C-H bonds available. Sensitivity increases with the number of increasing C-H bonds (Tsujino et al., 1993). The order of increasing sensitivity in the HAPs multicomponent is chloroform followed by dichloromethane, benzene, trichloroethylene, tetrachloroethylene and 1,2-dichloroethane. Chloroform is the least sensitivity because of containing only one C-H bond and three chlorines. The chlorine atoms shield the component from being detected by FID. Dichloromethane has two C-H bonds. Tetrachloroethylene is more sensitive due to increased carbon atoms and trichloroethylene. 1,2-dichloroethane is the most sensitive due to containing more C-H bonds amongst all the components.

## 5.2 Gravimetric Results of 6-multicomponent HAPs primary standard gas mixtures

In chapter 5, binary gas mixtures were developed and the results were satisfactory. Development of multi-component is however different due to matrix being different. There is interference of components within the same cylinder. It is necessary to observe if it affects determination of gravimetric concentration prepared or not. Each component was individually analysed within the cylinder and its mole-fraction was determined using single-point calibration.

**Table 5.1-5.7** show repeatability of the four standard gas mixtures which were developed. From the results good analytical method was developed, with good repeatability. **Table 5.8-5.12** show the gravimetric results of development of multicomponent mixture. The tables indicate gravimetric concentration, analytical concentration, percentage difference and relative expanded uncertainty which is obtained from Equation 6.1 at cover factor of K=2 at 95 % confidence level.

Benzene shows good accuracy with percentage difference of ≤1.4 % and the highest relative expanded uncertainty of 5.6 %. Trichloroethylene

results show percentage difference of ≤ 0.62 % and of % RU 5.0 %. Tetrachloroethylene results in **Table 5.10** show good accuracy of 0.84 % and highest % RU 4.7 %. Chloroform show % difference of 1.39 % and highest relative expanded uncertainty of 9.8 %. Dichloromethane showed accuracy of 2.03 % and 9.8 % gravimetric uncertainty. 1,2-dichloroethane showed accuracy of ≤0.76 % and % RU 4.6 %.

Chloroform and dichloromethane showed highest percentage difference and relative standard percentage difference. The overall multicomponent mixture has been developed at uncertainty ranging from 3.8 to 9.8 %. Higher percentages are attributed to chloroform and dichloromethane. The contribution of uncertainty is traced back to obtaining higher analytical uncertainties in components. Sample D626608 showed the lowest possible uncertainty achieved for the development of multicomponent mixtures at 10µmol/mol ranging from 4.4 to 7.0 % at 95 % confidence level. The overall mixtures correlates well with Rhoderick studies on relative expandanded uncertainity falling between 3-10 % (Rhoderrick, 1988).

Another objective was to check for interferences during analyses between the multicomponent and the binary mixtures. The determination of accuracy in these mixtures is comparable, hence it can be concluded that there is no chemical interference in the multicomponent mixture during analyses. This indicates that in HAPs, matrix effect does not have an impact in determining the amount-of-substance of each components

Table 5. 1 :Repeatability of Benzene in HAPS multicomponent

| Gas Mixture | % RSD | % RSD | % RSD | % RSD |
|---|---|---|---|---|
| D626608 | Reference | 0.24 | 0.41 | 0.09 |
| D626473 | 0.32 | Reference | 0.15 | 0.25 |
| D626594 | 0.35 | 0.42 | Reference | 0.09 |
| D626415 | 0.74 | 0.57 | 0.56 | Reference |

For all references of benzene in HAPs multicomponent gas mixture, readability of analyses method is ≤ 0.74 %. Good repeatability was attained. In binary gas mixture repeatability of ≤ 0.54 % was attained for method of analyses.

Table 5. 2: Repeatability of Trichloroethylene in HAPS multicomponent

| Gas Mixture | % RSD | % RSD | % RSD | % RSD |
|---|---|---|---|---|
| D626608 | Reference | 0.73 | 0.39 | 0.33 |
| D626473 | 0.45 | Reference | 0.21 | 0.31 |
| D626594 | 0.46 | 0.26 | Reference | 0.33 |
| D626415 | 0.65 | 0.33 | 0.15 | Reference |

Good repeatability in method of analyses of Trichloroethylene was achieved at ≤ 0.73 %. in binary gas mixture, repeatability was ≤ 1.7 %. There was an improvement in repeatability in the multicomponent analysis.

Table 5. 3: Repeatability of Tetrachloroethylene in HAPS multicomponent

| Gas Mixture | % RSD | % RSD | % RSD | % RSD |
|---|---|---|---|---|
| D626608 | Reference | 0.66 | 0.54 | 0.27 |
| D626473 | 0.29 | Reference | 0.15 | 0.20 |
| D626594 | 0.35 | 0.12 | Reference | 0.27 |
| D626415 | 0.26 | 0.57 | 0.20 | Reference |

Tetrachloroethylene multicomponent show good repeatability in analysis method of ≤ 0.66 %. in binary gas mixture development, repeatability of ≤ 0.50 % was achieved.

Table 5. 4: Repeatability of 1,2-Dichloroethane in HAPS multicomponent

| Gas Mixture | % RSD | % RSD | % RSD | % RSD |
|---|---|---|---|---|
| D626608 | Reference | 0.18 | 0.33 | 0.19 |
| D626473 | 0.03 | Reference | 0.16 | 0.21 |
| D626594 | 0.17 | 0.14 | Reference | 0.19 |
| D626415 | 0.33 | 0.15 | 0.15 | Reference |

1,2-dichloroethane multicomponent show improved repeatability of ≤ 0.33 %. In binary gas mixture development method of analysis showed repeatability of 0.82 % in both measurements repeatability is good.

Table 5. 5: Repeatability of Chloroform in HAPS multicomponent

| Gas Mixture | % RSD | % RSD | % RSD | % RSD |
|---|---|---|---|---|
| D626608 | Reference | 0.58 | 1.72 | 2.13 |
| D626473 | 0.25 | Reference | 0.99 | 0.25 |
| D626594 | 2.90 | 1.15 | Reference | 2.13 |
| D626415 | 1.10 | 2.27 | 1.94 | Reference |

Good repeatability of ≤ 2.90 % was achieved in chloroform in multicomponent, however its greater than binary gas mixture which was ≤ 0.31 %.

Table 5. 6: Repeatability of Dichloromethane in HAPS multicomponent

| Gas Mixture | % RSD | % RSD | % RSD | % RSD |
|---|---|---|---|---|
| D626608 | Reference | 0.64 | 2.15 | 0.99 |
| D626473 | 0.46 | Reference | 1.04 | 0.99 |
| D626594 | 2.20 | 0.44 | Reference | 0.09 |
| D626415 | 0.64 | 0.09 | 0.63 | Reference |

Good repeatability of ≤ 2.20 % was achieved in dichloromethane in multicomponent, however its greater than binary gas mixture which was ≤ 1.6 %

Table 5. 7: Gravimetric Verification Results for benzene in HAPs Multicomponent

| Gas Mixture | Gravimetric Value (µmol/mol) | Analytical Value (µmol/mol) | % Difference | Relative Expanded Uncertainty (µmol/mol) |
|---|---|---|---|---|
| D626608 | 10.27 | 10.22 | 0.41 | 5.4 |
| D626473 | 10.33 | 10.25 | 0.78 | 5.1 |
| D626594 | 10.27 | 10.13 | 1.34 | 5.6 |
| D626415 | 10.21 | 10.21 | 0.08 | 5.6 |

Table 5. 8: Gravimetric Verification Results for trichloroethylene in HAPs Multicomponent

| Gas Mixture | Gravimetric Value (µmol/mol) | Analytical Value (µmol/mol) | % Difference | Relative Expanded Uncertainty (µmol/mol) |
|---|---|---|---|---|
| D626608 | 10.08 | 10.04 | 0.38 | 5.0 |
| D626473 | 10.14 | 10.08 | 0.54 | 4.3 |
| D626594 | 10.08 | 10.02 | 0.62 | 4.6 |
| D626415 | 10.03 | 10.03 | 0.05 | 4.2 |

Table 5. 9: Gravimetric Verification Results for tetrachloroethylene in HAPs Multicomponent

| Gas Mixture | Gravimetric Value (µmol/mol) | Analytical Value (µmol/mol) | % Difference | Relative Expanded Uncertainty (µmol/mol) |
|---|---|---|---|---|
| D626608 | 10.08 | 10.04 | 0.38 | 5.0 |
| D626473 | 10.14 | 10.08 | 0.54 | 4.3 |
| D626594 | 10.08 | 10.02 | 0.62 | 4.6 |
| D626415 | 10.03 | 10.03 | 0.05 | 4.2 |

Table 5. 10: Gravimetric Verification Results for 1,2-dichloroethane in HAPs Multicomponent

| Gas Mixture | Gravimetric Value (µmol/mol) | Analytical Value (µmol/mol) | Percentage Difference | Relative Expanded Uncertainty (µmol/mol) |
|---|---|---|---|---|
| D626608 | 10.20 | 10.13 | 0.76 | 4.4 |
| D626473 | 10.26 | 10.22 | 0.40 | 4.4 |
| D626594 | 10.20 | 10.13 | 0.70 | 4.4 |
| D626415 | 10.15 | 10.16 | 0.07 | 4.6 |

Table 5. 11: Gravimetric Verification Results for chloroform in HAPs Multicomponent

| Gas Mixture | Gravimetric Value (µmol/mol) | Analytical Value (µmol/mol) | % Difference | Relative Expanded Uncertainty (µmol/mol) |
|---|---|---|---|---|
| D626608 | 10.15 | 10.29 | 1.39 | 7.0 |
| D626473 | 10.21 | 10.12 | 0.87 | 5.8 |
| D626594 | 10.15 | 10.17 | 0.18 | 9.8 |
| D626415 | 10.10 | 9.97 | 1.27 | 6.8 |

Table 5. 12: Gravimetric Verification Results for dichloromethane in HAPs Multicomponent

| Gas Mixture | Gravimetric Value (µmol/mol) | Analytical Value (µmol/mol) | % Difference | Relative Expanded Uncertainty (µmol/mol) |
|---|---|---|---|---|
| D626608 | 10.36 | 10.22 | 1.39 | 5.6 |
| D626473 | 10.42 | 10.34 | 0.78 | 6.6 |
| D626594 | 10.36 | 10.45 | 0.85 | 8.6 |
| D626415 | 10.31 | 10.10 | 2.03 | 9.0 |

### 5.2.1 Behaviour of Components in Cylinder

Figure 5.5-5.6 indicates internal consistency obtained from when each cylinder was taken as reference. The x-axis indicates the component in the gas mixture, represented as numbers. 1-dichloromethane, 2-chloroform, 3-benzene,4-1,2-dichloroetane,5-trichloroethylene and 6-tetrachloroethylene. Ideally all components are supposed to be close to 1.0. (Marebane, 2017).

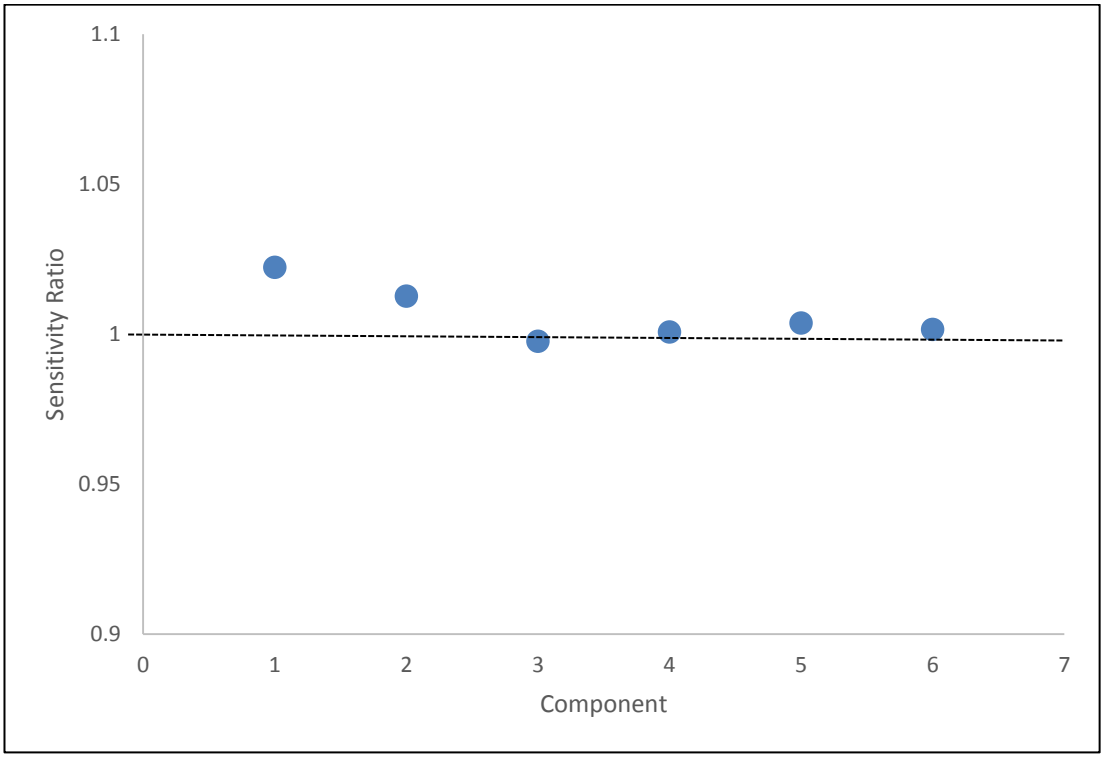



Figure 5. 4: D626608 Consistency

All components are close to 1.0, dichloromethane is the components which is far when compared to other components at ratio of 1.02. Hence all the components fall within ratio of 0.02 which shows good internal consistency.

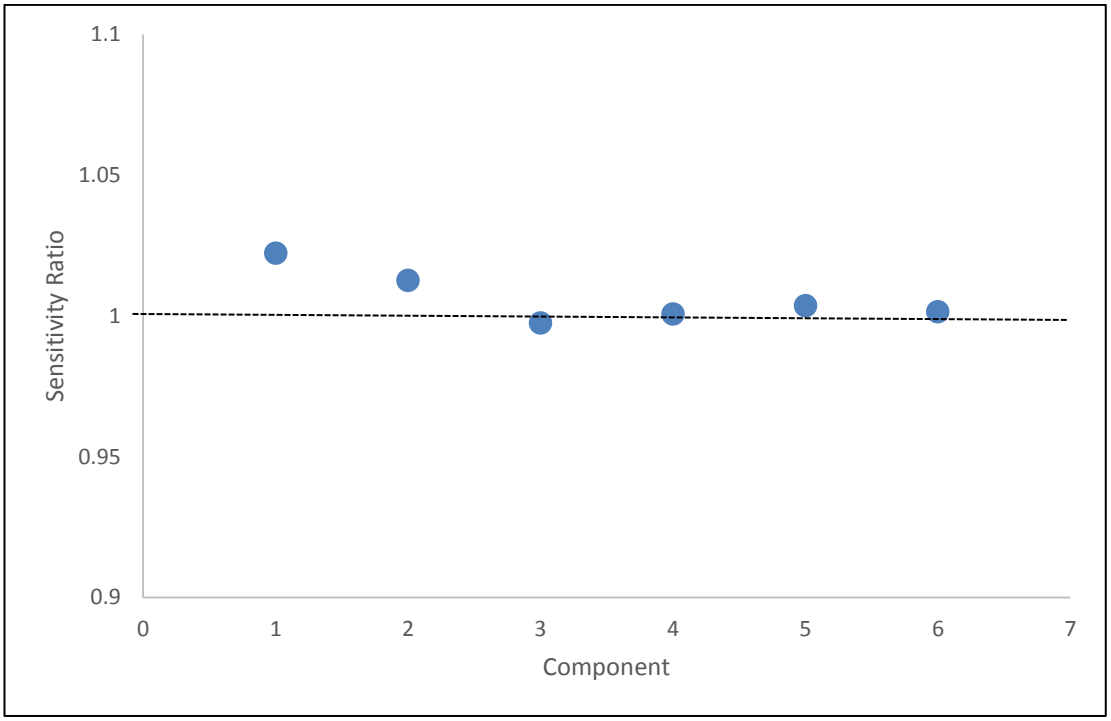



Figure 5. 5: D626594 Consistency

Similar to **Figure 5.4** results, dichloromethane has sensitivity ratio of 1.02. All the components fall within ratio of 0.02 which shows good internal consistency.

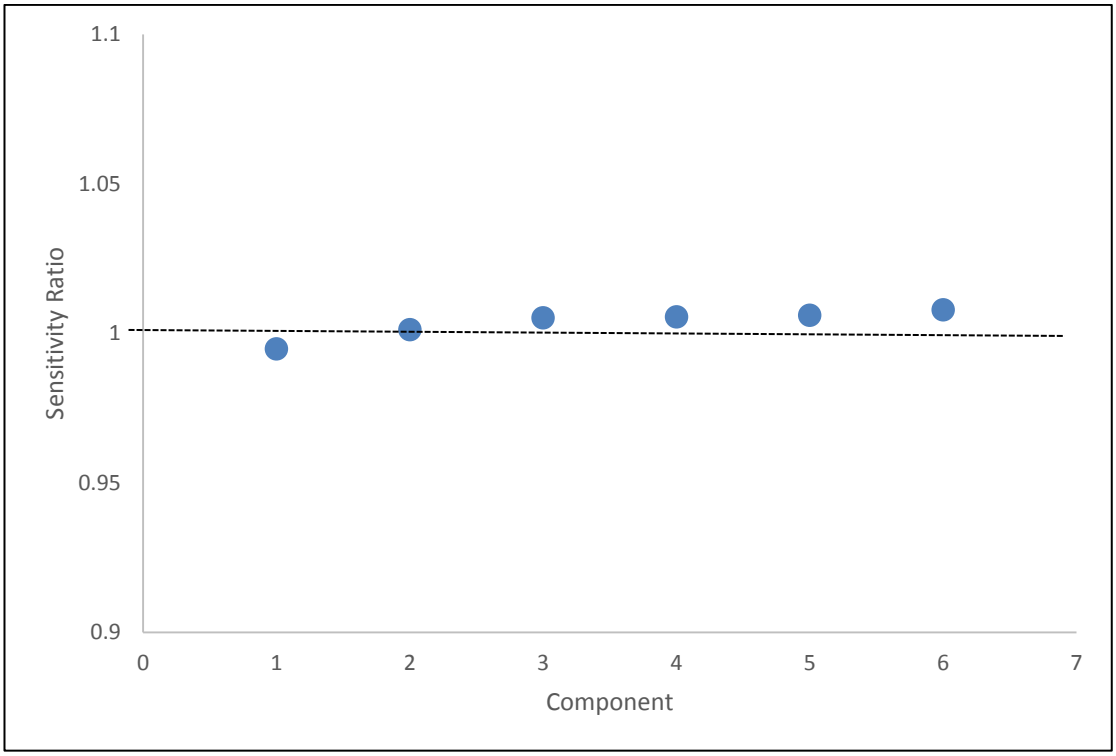



Figure 5. 6: D626473 consistency

This shows the best internal consistency when compared to other components. In this mixture tetrachloroethylene show best sensitivity ratio of 1.007. Indicating that the ratio of the mixture in all components falling within 0.007.

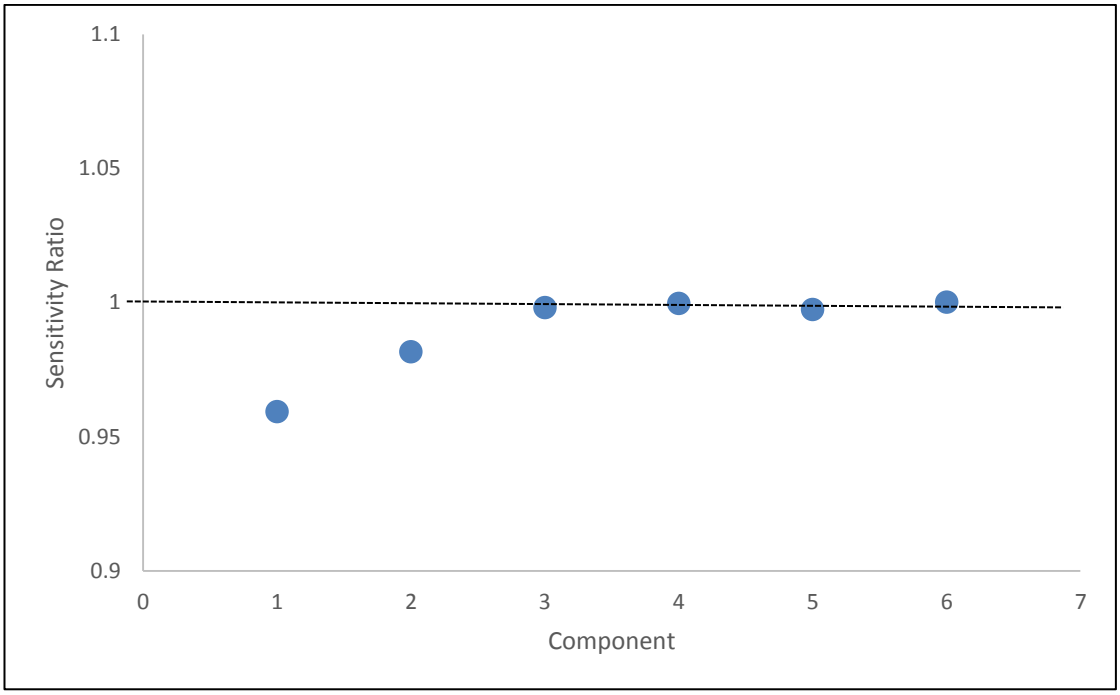



Figure 5. 7:D626415 consistency

Of all the mixtures, this shows the highest sensitivity ratio of dichloromethane at 0.95. Leading to the overall mixture falling within 0.05.

### 5.3 Analysis of Eight Component PSM and Ambient Air Sample

Multiple dilution step method was used for preparation of 100nmol/mol. Figure 6.8 shows the steps taken to achieve the desired amount-of substance of multicomponent mixtures. A pre-concentrator connected to gas chromatography coupled to flame ionisation detector was used to analyse these mixtures. The use of pre-concentrator is to dehydrate the standard, remove excess carbon dioxide and any other components which could interfere with the sample during the analysis.

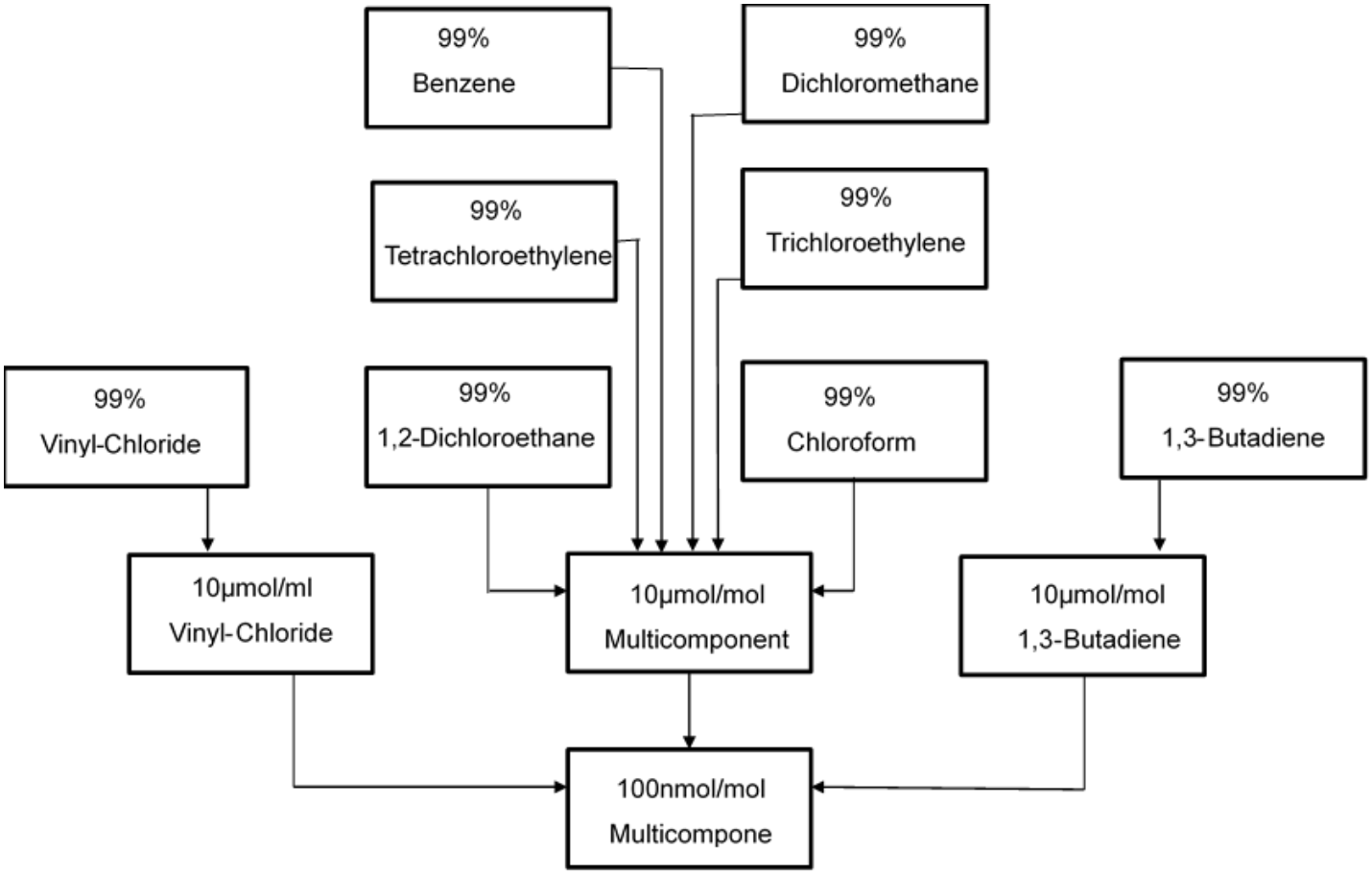



Figure 5. 8: Flow Diagram of Production of 100 nmo/mol Multicomponent

The column used for analysis of the multicomponent and air is CP-Sil 5CB, coated with 100 % dimethyl-polysiloxane as stationary phase which is nonpolar. Separation of components is purely based on boiling point and eluting order is from low to high boiling point. Cordero et al (2012) mentioned that interaction between the analyte and stationery phase is entirely based on dispersion forces, hence eluting order of the prepared mixture is vinyl chloride at -13.4 ℃ followed by 1,3-butadiene at -4.4 ℃, dichloromethane at 39.6 ℃ , chloroform at 61.2 ℃ , benzene at 80.1 ℃, 1,2-dichloroethane at 80.1 ℃ , trichloroethylene at 87.2 ℃ and tetrachloroethylene at 121.1 ℃. **Figure 5.9** chromatogram of the analysed multicomponent PSM. The chromatogram of the standard also show smaller unidentified peaks. This are attributed to unknown impurities, it is due to the sensitivity of the pre-concentrator to lower concentration. This results are similar to analysis of HAPs performed by National Physical Laboratory in CCQMK 22 (2016), were 4 ppb of unidentified impurities were observed in their mixture.

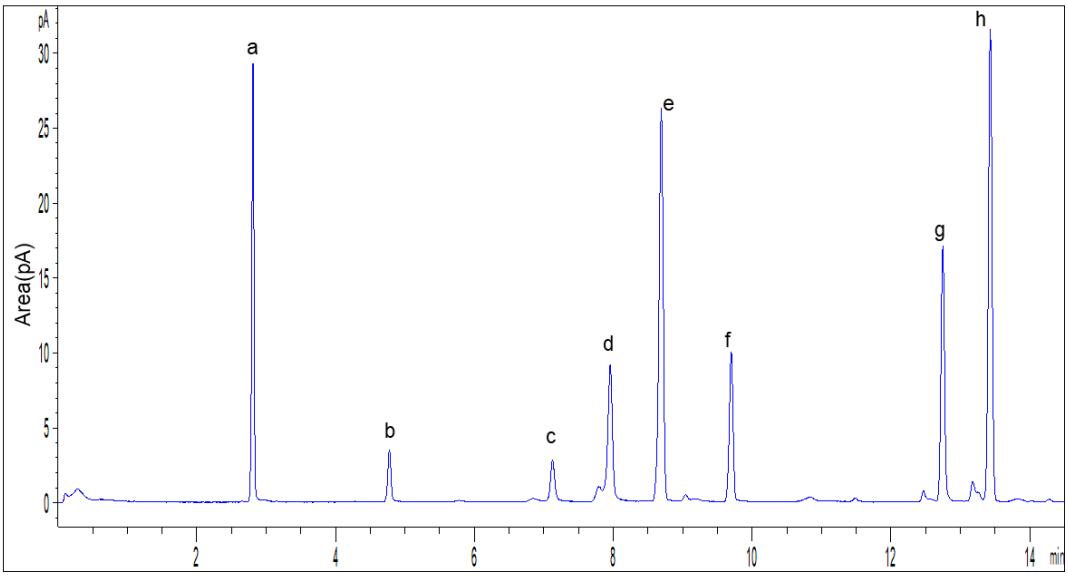



Figure 5. 9: Chromatogram showing peak separation of eight-component PSM. With a-vinyl chloride, b-1,3-butadiene, c-dichloromethane, d-chloroform, e-benzene, f- 1,2-dichloroethane, g-trichloroethylene and h-tetrachloroethylene.

Monitoring stations in South Africa currently focus on BTEX (benzene, toluene, ethylbenzene and xylenes) in the atmosphere ( DEA, 2012). Other developed countries monitor HAPs in the atmosphere because majority of death cases are attributed to cancer which is suspected to come from occupational or enviromental exposure to contaminated air. Japan has been monitoring HAPs in the atmosphere for quite some time and data from 2003 to 2012 shown in **Table 5.13** (Tsai, 2016) . Over the years, data show decreased level of HAPs in the atmosphere.

In this study air sample was collected using grab sampling into an aluminium cylinder. The prepared standards were used to identify the hazardous air pollutants found in the ambient air sample. A pre-concentrator was used to reduce or eliminate $CO_2$ and water components in the sample to properly identify components of interest without interference or suppression. Because previous studies indicate that air contains water and carbon dioxide (Seinfeld, 2016). **Figure 5.10** shows chromatogram of analysed air sample **.**

The developed standards were be used for quantification of HAPs in air, The sample is found in matrix of air. The primary standard gas mixtures are prepared in nitrogen matrix. There are no discrepancies in the sample matrix and nitrogen matrix, because air constitutes 78 % of nitrogen. Min (2014) carried out an experiment to support the statement mentioned above by calculating response factors of nitrogen as matrix and air as matrix under similar analytical conditions to check internal consistency. It was proven that internal consistency of air and nitrogen are similar, indicating how identical the matrices are. There would not be any suppression or differences of using standard in nitrogen to quantify air sample. **Figure 5.19** shows the mole-fraction of HAPs found in air and it is higher than data presented from Japan. Chloroform, 1,3-butadiene and dichloromethane were not found in the air sample.

Table 5. 13: Japan HAPs monitoring data  in nmol/mol (Tsai, 2016)

| HAPs | 2003 | 2004 | 2005 | 2006 | 2007 | 2008 | 2009 | 2010 | 2011 | 2012 |
|---|---|---|---|---|---|---|---|---|---|---|
| Benzene | 1.9 | 1.8 | 1.7 | 1.7 | 1.5 | 1..4 | 1.3 | 1.1 | 1.2 | 1.2 |
| Trichloroethylene | 0.92 | 0.93 | 0.75 | 0.90 | 0.76 | 0.62 | 0.53 | 0.44 | 0.53 | 0.50 |
| Tetrachloroethylene | 0.38 | 0.38 | 0.28 | 0.31 | 0.25 | 0.23 | 2.30.22 | 0.17 | 0.18 | 0.18 |
| Dichloromethane | 2.4 | 2.6 | 2.1 | 2.1 | 2.3 | 2.3 | 1.7 | 1.6 | 1.6 | 1.6 |
| Chloroform | - | 0.26 | 0.33 | 0.23 | 0.21 | 0.22 | 0.21 | 0.19 | 0.21 | 0.20 |
| 1,2-dichloroethane | - | 0.13 | 0.13 | 0.15 | 0.15 | 0.16 | 0.17 | 0.16 | 0.18 | 0.17 |
| 1,3-butadiene | - | 0.26 | 0.22 | 0.23 | 0.16 | 0.18 | 0.16 | 0.14 | 0.15 | 0.14 |

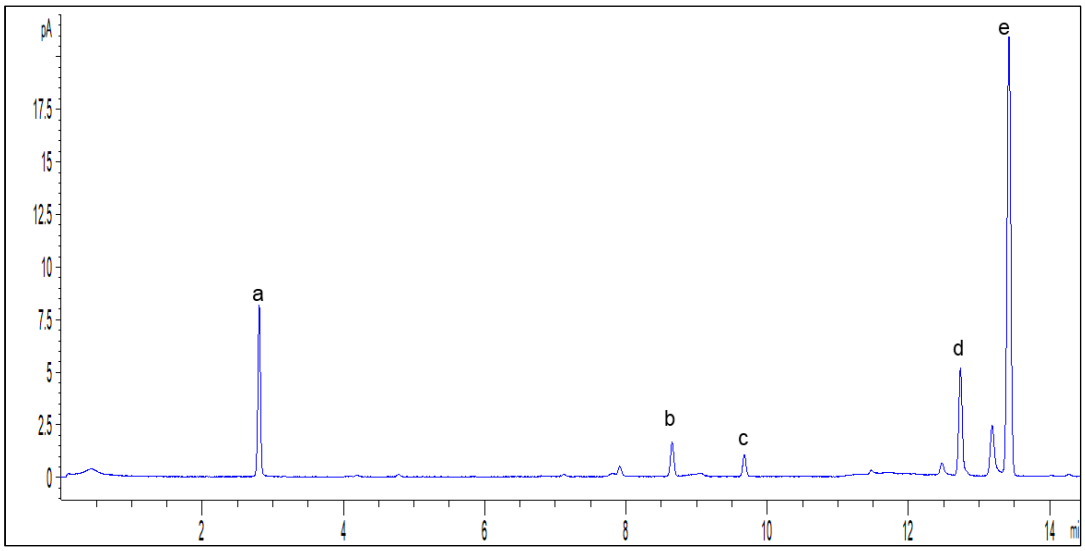



Figure 5. 10: Air sample containing a-vinyl chloride, b-benzene, c- 1,2-dichloroethane, d-trichloroethylene and e-tetrachloroethylene.

Table 5. 14: Quantification of HAPs in Air Sample

| Air Component | Mole-fraction (nmol/mol) |
|---|---|
| Vinyl Choride | 28.77 |
| Benzene | 6.632 |
| 1,2-dichloroethane | 68.99 |
| Trichloroethylene | 12.92 |
| Tetrachloroethylene | 10.98 |

### 5.4. Factors affecting stability

When developing traceable gas mixture, it is essential to have stability over long a period. It is a challenge to obtain stability in gases over a long period of time (Brown et al., 2017). To minimise this effect, certain factors were controlled during preparation.

Internal cracks were investigated within the walls of the cylinders. If identified, it wasn't used to avoid gas mixture components from absorbing.

The choice of container has reactions with the VOCs. In this study aluminium containers were used. To minimise reactions between the internal wall of the aluminium gas cylinder and components, passivation and treatment was performed by Air products Company (Rhoderick, 1991).

Most prominent contaminants which affect long term life of a mixture is availability of oxygen and moisture. The cylinders were evacuated prior to use, to eliminate the contaminants which could change the composition of the mixture.

The process of filling is crucial is taken with precaution because moisture or other contaminant, can be introduced in the system. To reduce this effect, stainless steel tubing was used to transfer gases and a leak system free was ensured by using soapy water (snoop) to check any leak on before filling.

A study carried by Sistern (2001), encompassed stability factors similar to those mentioned in this study. The nmol/mol mole-fraction of VOCs standard gas mixtures showed stability for two years, however 1,3-butadiens showed instability. These results are comparable to study carried out in 2008 for the developments of standard reference material of VOCs at 100 nmol/mol. Stability of the mixtures was found to be three years and 1,3-butadiene showed exceptions (Rhoderick, 2008). This proves that regulating certain factors improves stability of a gas mixture.

### 5.5 Challenges encountered during preparation of gaseous gas mixtures

To obtain a gaseous mixture, from a liquid sample maximum vapour pressure of the sample has to be calculated first. This is used to calculate the minimum liquid to be transferred in the cylinder. Should at any chance when weighing or transferring the liquid mass be lost and only have lower than the required minimum mass the experiment must be repeated. Because it is not enough to transfer to the gaseous phase and there will be condensed liquid in the prepared mixture.

Sample liquid could also be lost during the transferring of liquid from the syringe to the cylinder through nitrogen. If the pressure of nitrogen is high, liquid sample escapes through the injection system. The loss of liquid is only noticed during analytical verification when the primary standard reads lower than the gravimetric mole-fraction. To minimise loss pressure of nitrogen has to be kept lower than 3000 kPa. The syringe is capped with a septa at the needle tip to avoid loss of sample through evaporation and also locked with a twist valve attached to the body of the syringe.

Loss of gas can occur during transferring to the sample cylinder, on the stainless-steel connections. There could be a leak, this was minimized by using soapy water to check for leaks before preparation.

Preparing gaseous primary standard gas mixtures require precise addition of mass. One other challenge of preparing a multicomponent gas mixture is that a slight increase or decrease, lead to imprecision of the target mole-fraction. When preparing lower mole-fractions adding approximately 2.00 g lower or greater than the required mass has great changes in the final mole-fraction and pressure of the mixture.

The environmental conditions of the weighing room is monitored during the experiment due to variation of mass caused by temperature. The reference cylinder is left in the weighing room, during transferring of components in the sample cylinder. When transferring the final component (nitrogen) in the cylinder, the temperature of the cylinder rises due to Joule-Thomson effect. The rise in temperature is because nitrogen cylinder is at high pressure and the sample cylinder which is at lower pressure (Marie, 2005). This could lead to inaccuracy in mass of cylinder if not taken into consideration because when the cylinder is hot, its mass because higher than the actual mass. To resolve inaccurate mass, the sample cylinder is allowed to equilibrate to room temperature after addition of nitrogen.

# CHAPTER SIX – CONCLUSION AND FUTURE WORK

## 6.1 Conclusion

For quality air monitoring purposes, this study was done to provide accurate measurements in South Africa by developing primary standard gas mixture containing benzene, dichloromethane, vinyl-chloride, 1,3-butadiene, tetrachloroethylene, chloroform, 1,2-dichloroethane and trichloroethylene in nitrogen traceable to SI unit. The importance of using traceable primary standards, is that they provide uncertainty leading to more accurate results and they are internationally comparable.

The development of standards was achieved using gravimetric preparation method. Firstly, purity analysis of high pure components was carried out to quantify impurities which will contribute to the final mole-fraction of the gas mixtures. All liquid samples (benzene, chloroform, trichloroethylene, tetrachloroethylene, dichloromethane and 1,2-dichloroethane) were analysed on GC/MS the content results were above 99 % . Moisture concentration was assumed from rectangular distribution guided by ISO 6142. The results were in good agreement with the manufacture's specifications. 1,3-butadiene and vinyl-chloride had no manufacture's specification of impurities, the analyses on GC-TCD revealed presence of nitrogen at concentrations of 681 µmol/mol and 254 µmol/mol. Purity analysis of high pure nitrogen was achieved by analysis using various instrumental technique and rectangular distribution assumption.

The development of liquids preparation involved a direct step and the pressurised liquids, 1,3-butadiene and vinyl chloride involved multiple-step due to large mass to be transferred to get desired concentration.

Syringe system guided by ISO 6142 was employed for preparation of liquids using direct-step to minimise loss of sample, and it was successful. The accuracy determined between gravimetric value and analytical value

was achieved within 3 % with relative expanded uncertainty of all binary gas mixtures within 3.1 % at coverage factor of K=2 at 95 % confidence level.

For analysis of six-components gas mixture, CP-Sil 5CB column was used to achieve good peak resolution. Instrumental drift was obtained at less than 1.0 and good repeatability of measurements attained. The determination of gravimetric concentration was independent of the matrix, indicated by low accuracy within 2.03 %. Relative expanded uncertainty ranged between 4.2 to 9.8 % at coverage factor of k=2 at 95 % confidence level.

Multicomponent of eight mixtures was diluted from the six-component gas mixture, vinyl chloride and 1,3-butadiene in nitrogen. The pre-concentrator was used for analysis and quantification of components in the air sample collected from GAW. Successful identification of components was achieved.

From the study, it was observed that preparation of gases must performed with precautious to avoid loss of components. The overall development of gases was successful.

## 6.2 Future Work

Previous studies have shown that VOCs are very stable in the aluminium cylinder for approximately two years or more. The aluminium cylinders used for the development of cylinders in this study went through treatment of minimise adsorption however the monitoring at which the treatment is affecting the inertness character should be monitored.

Participation in key comparison of NMI's in the world with take place this yea. Participation will require short-term stability studies of the 100nmol/mol multi-components VOCs

To declare a primary standard gas mixture, long term stability studies should also be available to know how long a mixture is accurate for. Hence this will also be monitored yearly for the developed mixtures.

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# APPENDIX A

Table A. 1:

| | Manufactures Specification (%) | Results (%) | NIST-Comparability Percentage |
|---|---|---|---|
| Trichloroethylene | 99.96 | 99.99 | 98.29 |
| Tetrachloroethylene | 99.98 | 99.97 | 99.45 |
| 1,2-dichloroethane | 99.98 | 99.99 | 96.20 |
| Dichloromethane | 99.97 | 99.99 | 90.85 |
| Chloroform | 99.99 | 99.99 | 97.44 |

Table A. 2: Composition of Nitrogen in Argon

| Component | $N_2$ | Ar | $H_2O$ | $CO_2$ | $H_2$ | CO | $C_2H_6$ | $O_2$ | $CH_4$ |
|---|---|---|---|---|---|---|---|---|---|
| Mole-fraction | 997960.84 | 53.79 | 0.0099 | 0.0097 | 0.0089 | 0.0068 | 0.0062 | 0.0049 | 0.0042 |
| Uncertainty | 2.5 | 2.5 | 0.0053 | 0.0010 | 0.0047 | 0.0036 | 0.0033 | 0.0027 | 0022 |

Table A. 3: Purity Table of Benzene

| Component | Manufacture specification | Distribution | Mole-fraction (µmol/mol) | Standard Uncertainty (µmol/mol) | Standard Uncertainty (µmol/mol) |
|---|---|---|---|---|---|
| $H_2O$ | ≤ 0.001 | Type B Rectangular | $5x10^{-4}$ | $2.9x10^{-4}$ | $5.8x10^{-4}$ |
| | | Total Impurities | $5x10^{-4}$ | | |
| Benzene | | % mol/mol | 99.95 | 0.029 | 0.058 |

Table A. 4: Purity Table of Dichloromethane

| Component | Manufacture | Distribution | Mole-fraction | Standard | Standard |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| | specification | | (µmol/mol) | Uncertainty (µmol/mol) | Uncertainty (µmol/mol) |
| $H_2O$ | ≤ 0.001 | Type B Rectangular | $5x10^{-4}$ | $2.9x10^{-4}$ | $5.8x10^{-4}$ |
| | | Total Impurities | $5x10^{-4}$ | | |
| Benzene | | % mol/mol | 99.95 | 0.029 | 0.058 |

Table A. 5: Purity Table of Trichloroethylene

| Component | Manufacture specification | Distribution | Mole-fraction (µmol/mol) | Standard Uncertainty | Standard Uncertainty |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| | | | | (µmol/mol) | (µmol/mol) |
| $H_2O$ | ≤ 0.001 | Type B Rectangular | $5x10^{-4}$ | $2.9x10^{-4}$ | $5.8x10^{-4}$ |
| | | Total Impurities | $5x10^{-4}$ | | |
| Benzene | | % mol/mol | 99.95 | 0.029 | 0.058 |

Table A. 6: Purity Table of Tetrachloroethylene

| Component | Manufacture | Distribution | Mole-fraction | Standard | Standard |
|---|---|---|---|---|---|

| | specification | | (µmol/mol) | Uncertainty (µmol/mol) | Uncertainty (µmol/mol) |
|---|---|---|---|---|---|
| $H_2O$ | ≤ 0.001 | Type B Rectangular | $5x10^{-4}$ | $2.9x10^{-4}$ | $5.8x10^{-4}$ |
| | | Total Impurities | $5x10^{-4}$ | | |
| Benzene | | % mol/mol | 99.95 | 0.029 | 0.058 |

Table A. 7: Purity Table of Chloroform

| Component | Manufacture specification | Distribution | Mole-fraction (µmol/mol) | Standard Uncertainty (µmol/mol) | Standard Uncertainty (µmol/mol) |
|---|---|---|---|---|---|
| $H_2O$ | ≤ 0.001 | Type B Rectangular | $5x10^{-4}$ | $2.9x10^{-4}$ | $5.8x10^{-4}$ |
| | | Total Impurities | $5x10^{-4}$ | | |
| Benzene | | % mol/mol | 99.95 | 0.029 | 0.058 |

Table A. 8: Purity Table of 1,2-dichloroethane

| Component | Manufacture specification | Distribution | Mole-fraction (µmol/mol) | Standard Uncertainty (µmol/mol) | Standard Uncertainty (µmol/mol) |
|---|---|---|---|---|---|
| $H_2O$ | ≤ 0.001 | Type B Rectangular | $5x10^{-4}$ | $2.9x10^{-4}$ | $5.8x10^{-4}$ |
| | | Total Impurities | $5x10^{-4}$ | | |
| Benzene | | % mol/mol | 99.95 | 0.029 | 0.058 |

Table A. 9: Analysis of 2000 µmol/mol of 1,3-Butadiene in Nitrogen

| Injection | D958408 | D194882 | D958408 | M555675 | D958408 |
|---|---|---|---|---|---|
| 1 | 464.83575 | 466.17758 | 463.35141 | 462.43512 | 461.91794 |
| 2 | 462.63107 | 465.91217 | 462.35257 | 462.98032 | 461.09171 |
| 3 | 462.16638 | 464.60321 | 463.50616 | 462.21881 | 461.65353 |
| 4 | 463.1048 | 465.59518 | 462.99661 | 462.67957 | 462.15198 |
| 5 | 462.83804 | 466.34402 | 463.19659 | 463.96356 | 462.35751 |
| 6 | 462.88742 | 465.88666 | 463.1713 | 462.72739 | 461.74939 |
| Average | 462.75 | 462.94 | 463.22 | 462.90 | 461.98 |
| Std Dev | 0.14 | 0.38 | 0.11 | 0.73 | 0.31 |
| % RSD | 0.03 | 0.08 | 0.02 | 0.16 | 0.07 |
| ESDM | 0.08 | 0.22 | 0.06 | 0.42 | 0.18 |
| Sensitivity | 0.23 | 0.23 | 0.23 | 0.23 | 0.23 |
| Corr. Sensitivity | | 0.233 | | 0.233 | |
| % Diff | | 0.07 | | 2.00 | |
| Grav Conc | 1985.7989 | 1984.296 | 1985.7989 | 2026.7907 | 1985.7989 |
| Calc Conc | | 1984.296 | | 2026.7907 | |
| Drift | | | 0.10 | | 0.27 |
| Ratio | | 1.00 | | 0.98 | |