DEVELOPMENT, VALIDATION, QUANTIFICATION AND APPLICATIONS OF REFINERY PRIMARY REFERENCE GAS MIXTURES USING VARIOUS ANALYTICAL TECHNIQUES

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DECLARATION

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

Signature of candidate

24th day of May 2023 in Pretoria

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ABSTRACT

The carbon-intensive energy economy of South Africa has increasingly become an environmental issue contributing to climate change, with little study done on the refinery gases contribution to air pollution in the country. Refinery gas is a mixture of complex hydrocarbons and non-combustible gases recovered from refining and conversion processes in the fuel industry, with some intermediate products used as energy sources. The sale of these fuels often follows the guidelines of carbon trading schemes as stipulated by the environmental protection frameworks. Furthermore, refinery gas measurements are challenging because of plausible cross-interferences among target gases during preparation and value assignment. Thus, development of technical capabilities for reliable measurements and reference materials for refinery reference gas mixtures is crucial for measurement solution in the energy industry.

This study focused on the development of complex multicomponent refinery gas mixtures with target gases of carbon dioxide (CO_2), carbon monoxide (CO), oxygen (O_2), nitrogen (N_2), methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and 1,3-butadiene (C_4H_6) in helium (He) at two amount fractions ranges of 1 000 to 4 000 µmol.mol^{-1} (low range) and 1 to 22 %mol.mol^{-1} (high range) to shorten the traceability chain while developing technical skills and measurement equivalence. This was achieved through purity analysis of starting materials in accordance with International Organization for Standardization (ISO) 19229:2019 and gravimetric preparation in accordance with ISO 6142:2015. Verification of gas mixtures was done using gas chromatography with thermal conductivity detection for the quantification of components CO, CO_2, O_2 and N_2 and flame ionisation detection for the quantification of components CH_4, C_2H_6, C_3H_8, and C_4H_6 in accordance with ISO 6143:2001.

Quantification of trace-level impurities during purity analysis was performed on a gas chromatography coupled with a flame ionisation detector, a pulse discharge helium ionisation detector, and a thermal conductivity detector. The final purities of the starting materials were successfully quantified at > 99.99 %mol.mol^{-1} for

C_2H_6, C_4H_6, and C_3H_8 and > 99.999 %mol.mol^{-1} for CH_4, CO, CO_2, O_2, N_2 and He. Two ranges of refinery reference gas mixtures were prepared using static gravimetric method. The high range gas mixtures were prepared using a single-step dilution method, while the low range gas mixtures used a multi-step dilution method that posed challenges related to the pressures, purities, and chemistries of the starting materials.

Single-point calibration method was deployed for the verification of the matrix-matched refinery reference gas mixtures. The final percentage relative expanded uncertainty ranged from 0.313 to 3.281% for hydrocarbons (CH_4, C_2H_6, C_3H_8, and C_4H_6) and 0.150 to 3.045% for CO, CO_2, N_2, and O_2 at 95% confidence level ($k = 2$). The analytical method using gas chromatography coupled with various detectors developed in this study was successful in corroborating the gravimetric amount fractions and the verification amount fractions for the specified components of interest in the developed refinery reference gas mixtures accurately within a 1% difference.

DEDICATION

This dissertation is dedicated to my dearest mother, Nelly Muhanganei Mphaphuli, I am because you are.

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Firstly, I would like to thank God, who has enabled me to complete this work through the provision of strength, wisdom, and understanding that was well beyond anything I could have ever asked for or imagined. Throughout this journey, I found comfort in knowing that He who began a good work in me will see it through to completion.

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MANUSCRIPT AND PRESENTATION IN CONFERENCE

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NOMENCLATURE

AWS	Automatic Weighing System
BIPM	International Bureau of Weights and Measures
CCQM	Consultative Committee for Amount of Substance
CMC	Calibration and Measurement Capabilities
GC	Gas Chromatography
GUM	Guide to the Expression of Uncertainty in Measurement
FID	Flame Ionisation detector
TCD	Thermal Conductivity Detector
PDHID	Pulse Discharge Helium Ionisation Detector
ISO	International Standards Organisation
KRISS	Korea Research Institute of Standards and Science
LoD	Limit of Detection
NAAQS	National Ambient Air Quality Standards
NACA	National Association of Clean Air
NMI	National Metrology Institute
NMISA	National Metrology Institute of South Africa
NPL	National Physical Laboratory
PDHID	Pulsed Discharge Helium Ionisation Detector
PRGMs	Primary Reference Gas Mixtures
PSGM	Primary Standard Gas Mixture
SA	South Africa
SI	International System of units
REU	Relative Expanded Uncertainty
VOC	Volatile Organic Compound
PM	Particulate Matter
RGA	Refinery Gas Analysis
KCRV	Key Comparison Reference Value

NMS	National Measurement Standard
VSL	Van Swinden Laboratorium
VNIIM	D.I. Mendeleyev Institute for Metrology

CHAPTER ONE: INTRODUCTION

This chapter gives an overview of refinery gases and their relevance to air quality monitoring in South Africa.

1.1. Air pollution monitoring

Poor air quality with increased levels of airborne pollutants such as CO and PM, poses a threat to human and environmental health. Therefore, because of the deterioration of air quality in the region and new air quality management prioritisation objectives, South Africa has shifted from its past environmental legislation, replacing the Atmospheric Pollution Prevention Act (APPA) of 1965 due to its ineffectiveness in the preservation of air quality. The South African Constitution's Bill of Rights (108 of 1996), Section 24a, prescribes the right *"(a) to an environment that is not harmful to their health or wellbeing, and (b) to have the environment protected, for the benefit of present and future generations, through reasonable legislative and other measures that (i) prevent pollution and ecological degradation)."* However, the APPA did not prescribe the responsibility of emission management to the government and inadvertently endorsed air pollution priority areas such as the Highveld and the Vaal Triangle, which are characterised by intense mining, power stations, and chemical plants (Wright et al., 2011).

The country then shifted to an appropriate air quality management strategy that implements national initiatives to mitigate air pollution while maintaining and regulating ambient air quality through the development of national ambient air quality standards and the declaration of priority air pollutants using the Air Quality Act (AQA) No. 39 of 2004 (Naiker et al., 2012). This new approach also included the implementation of an air quality monitoring programme (AQA, 2004), and these new management tools seek to lessen illnesses and diseases linked to air pollution to provide a clean environment as prescribed by the constitution (Garland et al., 2017). Furthermore, the AQA provides the requirements for air quality management plans, includes minimum emission guidelines with regard to air polluting substances, and specifies licencing application procedures.

Monitoring air emissions entails the continuous tracking of the quantities of gases recognised as pollutants that have the potential to harm human health and cause a variety of environmental dangers. The accurate quantification of these pollutants in the atmosphere is done by comparing the signal level of the equipment being used to monitor air emissions with calibration gases with known concentrations. Considering this, the Department of Trade, Industry and Competition designated the National Metrology Institute of South Africa as the custodian for measurement traceability (Measurement Units and Measurement Standards Act 18 of 2006) from the International System of Units (SI unit) to the air monitoring and energy sectors, as well as other stakeholders, through the provision of gravimetrically prepared primary reference gas mixtures. These reference gas mixtures can be used as calibration standards and are meant to provide traceability of gas measurements to the SI.

1.2. Energy refineries and associated environmental effects

1.2.1. Refinery industries in the African continent

Refineries in Africa date back to 1954. Prior to that, refined products were shipped into Africa from European and American refineries through the West Africa Regional Governance Program in West Africa. However, since then, Africa has managed to build fifty-eight (58) refineries of its own by 2016. The first refineries were Mobil in Durban and Total in Algiers. These opened doors to the building of many more refineries stretching into Luanda refinery, Kenya (Shell/BP), Ghana (ENI/Agip), and Senegal (Consortium) in 1963. And more refineries were assembled in Gabon, Cote d’Ivoire, Nigeria, Tanzania, and Cape Town in the 1960s. Because of the success of these refineries in manufacturing fuels in and around Africa, this discovery led to the nationalisation of the oil industry in countries like Nigeria, Algeria, Congo, and Cameroon, which had state-controlled refineries (Mbendi, 2020).

1.2.2. South African refinery industry

South Africa has a highly industrialised and energy-intensive economy with various refineries and synthetic fuel plants that form part of the largest refineries on the African continent. A large part of the locally produced petroleum in the country is attributed to these refineries and synthetic fuel plants (Graham, 2019). These refineries produce a wide array of fuels, including diesel, paraffin, petrol, coal, and natural gas, using separation techniques such as distillation, hydrotreating, cracking, and fractionation (Kraus, 1998).

However, these separation processes result in the emission of pollutants into the atmosphere through stack emissions, water through oil spills during the distillation processes, and land through substantial amounts of untreated hazardous waste. The growth levels of these refineries are evident in the increasing trend of petroleum consumption, resulting in pollution of gases such as carbon dioxide, carbon monoxide, and methane as by-products that have been reported by the South African Petroleum Industry Association to be detrimental to air pollution (Mohale, 2014).

In South Africa, the oil industry is classified into two categories; upstream and downstream activities where the upstream activities refer to crude oil’s examination and production. The downstream activities refer to processes that take place before achieving end products including the refining, transporting, and marketing of the products. These processes result in the large releases of refinery gases into the atmosphere, which pollutes the air. These refinery gases are acquired from the refining and conversion of crude oil into lubricating oils, fuel products and chemical feedstock (Adebiyi, 2022). The intermediate products of the refining process that are rich in saturated hydrocarbons and hydrogen are used as energy sources by the environmental industry. With South Africa currently having service stations of over 4 500 since the first licensing of the petroleum industry in 2005, new regulations need to be adopted to minimise the threats that the oil refinery sector have on South Africa's environment.

The major companies in the oil industry of South Africa include Engen Petroleum, Sasol Oil, BP Southern Africa, Total South Africa, and Shell South Africa. These companies distribute their products throughout the country using storage terminals. Petrol, jet fuel, fuel oils, paraffin, diesel, and liquefied petroleum gases are examples of primary petroleum products that are retailed in South Africa. The South African government further regulates petrol pricing based on the import parity price formula, which is influenced by international market supply and demand (South African Petroleum Industry Association, 2020).

1.2.3. Impacts of air pollution from oil refineries on human health and the environment

Crude oil is a raw natural petroleum product found in underground reservoirs made of organic material and hydrocarbon deposits that form as sediments every 50 metres every million years (Jukić, 2013). In its original state, crude oil is not suitable for direct use because of its makeup of a multitude of hydrocarbons and thus undergoes industrial processing to produce usable fuels. The refining process helps remove the phospholipids, high sulphur and nickel ash, odours and fatty acids from the crude oil and make cleaner-burning fuels (Allison, 2018). In a refinery, emissions may arise from a variety of sources, such as equipment leaks, combustion processes, the heating of steam and process fluids, and the transfer of products. Over time, harmful air pollutants are released into the environment through regular emissions, fugitive releases, or plant system failures.

Therefore, these oil refineries are considered a major source of air and land pollution. Associated impacts include but are not limited to 1) damage caused by lead (Pb) to the nervous system that may result in neurological disorders at airborne levels (Rudolph et al., 2003); and 2) tiny dust particles, Particulate Matter of Size 10 micrometres (PM10), that can cause weakened oxygen transportation to the placenta in pregnant women, inflammation, and endocrine disruption (Erickson, 2014).

The refining of fossil fuels produces greenhouse gases and other various air pollutants such as carbon dioxide, carbon monoxide, butane, methane, 1,3-butadiene, sulphur dioxide, nitrous oxides, and chlorine, amongst other as by-products that are poisonous to the environment (Wei et al., 2016). Butane and 1,3-butadiene are known to be cancer-causing agents responsible for developmental and reproductive complications in humans. Volatile organic compounds, released during oil refining, are known to contribute to the formation of ground-level ozone, known as smog. They ascend to the troposphere, where they interact and combine with oxygen and other substances to form acid rain, also known as acid pollution (Adebiyi, 2022). Other negative environmental impacts include loss of biodiversity, degradation of the ecosystem, poorer water quality, and groundwater contamination, among others.

CHAPTER TWO - LITERATURE REVIEW

This chapter provides a detailed background on refinery gas and the development of refinery reference gas mixtures and technical methods. Metrological traceability and the validation of analytical techniques are also discussed in detail.

2.1. An overview on refinery gases

The federal Clean Air Act of 1990 established programmes through the Environmental Protection Agency (EPA) for the regulation of toxic pollutants. These pollutants were classified into two (2) classes: criteria pollutants and hazardous air pollutants (HAPs) (Currie and Walker, 2019). Criteria pollutants are air pollutants for which acceptable quantifiable exposure levels have been established as part of an ambient air quality standard. Examples of these gases are carbon monoxide, nitrogen oxides, lead, ground-level ozone, particulate matter, and sulphur oxides. HAPs are toxic air pollutants that have negative impacts on the environment and the ecosystem, including the possibility of causing cancer and other major health effects in humans. Over 70% of HAPs fall into the category of volatile organic compounds (VOCs) (Suh et al., 2000). Refinery gas is a complex gas made up of greenhouse gases, criteria pollutants, and HAPs.

Criteria pollutants pose a threat to both the environment and human health. The most pervasive health risks from the common criteria pollutants are ground-level ozone and particulate matter. These pollutants are referred to as "criteria" air pollutants by the EPA because it regulates them by establishing criteria (science-based rules) for setting permitted levels that are based on the environment and/or human health. The primary standards are the restrictions based on human health, and the secondary standards are the restrictions meant to protect the environment (Saxena and Sonwani, 2019).

Initial regulations for 189 hazardous air pollutants were established by the Clean Air Act amendments of 1990. Due to rulemaking, two (2) pollutants were removed from the original list after 1990: caprolactam in 1996 and methyl ethyl ketone in 2005. Subsequently, 1-bromopropane was added at the beginning of 2022. Currently, 188 HAPs are subject to federal regulation. (North Carolina Department of Environmental Quality, 2022). HAPs are known to be persistent in various environments depending on the elements of the environment they are found in. Their lifetime depends on their reactions with atmospheric constituents such as hydroxyl radicals, ozone, and photolysis. Over time, measurements of these components have been used to study atmospheric trends and the influence of increasing VOC concentrations on climate change.

Refinery gases are recovered from the fuel industry's refining and conversion processes. These processes are used to transform crude oil into a variety of petroleum products that may be traded or sold, while harmful gases are released to the atmosphere as by-products (Sojinu and Ejeromedoghene, 2019). Refinery gas’s composition varies depending on the origin of the crude oil and the treatments it has gone through. Refinery gas is classified as a flammable and compressed gas. The presence of carbon monoxide in the refinery gas classifies it as a reproductive toxicant in category 1A and a specific target organ systemic toxicant. This classification is in accordance with the Globally Harmonized System of Classification and Labelling of Chemicals (GHS) (OSHA, 2013).

Greenhouse gases are known to be responsible for the greenhouse effect by absorbing infrared light. Carbon dioxide, methane, nitrous oxide, hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and ozone in the lower atmosphere have been identified by the World Metrology Organization (WMO) as the key greenhouse gases whose concentrations are on the rise. The Global Atmosphere Watch (GAW) is responsible for the monitoring, analysis, and publication of greenhouse gas data for carbon dioxide, methane, nitrous oxide, halocarbons, sulphur hexafluoride, and molecular hydrogen collected by fifty different nations throughout the world, from the High Arctic to the South Pole (Prinn et al., 2018).

This research focused on the following components of refinery gas: 1,3-butadiene, carbon dioxide, carbon monoxide, ethane, methane, nitrogen, oxygen, and propane, with helium as the balance gas. These gases have been covered in detail below in **sections 2.1.1 to 2.1.9**. **Table 2.1** lists the category of pollutant each gas falls under. Although oxygen and nitrogen are not direct pollutants, their study was significant as they react at heightened temperatures to form nitrous oxide, which is a greenhouse gas.

Table 2.1 Gas pollutant category for the components of interest in the study's refinery primary reference gas mixtures.

Component	Category
Methane (CH_4)	Greenhouse gas
Ethane (C_2H_6)	Volatile Organic Compounds
Propane (C_3H_8)	Volatile Organic Compounds
1,3-Butadiene (C_4H_6)	Volatile Organic Compounds
Carbon monoxide (CO)	Criteria pollutant/ greenhouse gas
Carbon dioxide (CO_2)	Greenhouse gas
Oxygen (O_2)	Oxidiser*
Nitrogen (N_2)	Inert gas*
Helium (He)	Inert gas

* *Oxygen and nitrogen react in high temperatures to form nitrous oxides (greenhouse gas)*

2.1.1. 1,3-Butadiene

1,3-Butadiene is a colourless, non-corrosive, volatile compressed gas with a mild gasoline-like odour (Himmelstein et al., 1997). It is mainly produced from anthropogenic processes such as steam cracking during ethylene production and emissions from petroleum and refinery processes. It serves a significant role in the production of synthetic rubbers such as polybutadiene, styrene-butadiene, and other synthetic rubbers. Because butadiene is extremely volatile, inhalation and absorption via the respiratory system account for the vast majority of butadiene consumption. Exposure can come through industrial processes used in production, transportation, and end-use as well as from cigarette smoke, fossil fuel burning, and vehicular gasoline. 1,3-butadiene has been classified by the United States Environmental Protection Agency (USEPA) as a human carcinogen with retrospective studies of styrene-butadiene rubber workers offering the first internally consistent evidence of a connection between 1,3-butadiene exposure and leukaemia (Yarandi et al., 2019).

1,3-Butadiene has a short lifespan due to its reactive nature. In the presence of air, it oxidises to form explosive peroxides, and in the presence of ultraviolet radiation, reactions are accelerated. It reacts with ozone under atmospheric conditions to form formaldehydes, OH radicals, carbon dioxide, carbon monoxide, and acrolein (Kramp and Paulson, 2000).

2.1.2. Carbon dioxide

Carbon dioxide (CO_2) is a greenhouse gas that is a non-flammable, colourless gas with a muted, piercing odour. It is made of one carbon and two oxygen atoms and is often referred to as dry gas. CO_2 is considered one of the essential greenhouse gases associated with global warming, but it is present in low concentrations in the Earth’s atmosphere and is a vital part of the carbon cycle in the environment. Atmospheric carbon dioxide is formed from the combustion of organic matter, the respiration of animals, volcanic outgassing, and man-made sources such as the burning of fossil fuel for power and transportation use. The presence of CO_2 in the atmosphere keeps some of the radiant energy received by Earth from being returned to space, thus producing the so-called greenhouse effect (Lacis et al., 2010).

Industrially, carbon dioxide is recovered for numerous diverse applications from flue gases as a by-product of the preparation of hydrogen for the synthesis of ammonia, from limekilns, and from other sources (Ibrahim, 2018). The natural greenhouse effect is accelerated by the increased emissions of carbon dioxide and other greenhouse gases into the atmosphere, causing a rise in the earth's temperature, that is, global warming. The National Oceanic and Atmospheric Administration (NOAA) Global Monitoring Lab found that in 2021, carbon dioxide, averaging 414.72 parts per million (ppm), would account for nearly two-thirds of the total heating influence of all greenhouse gases created by humans. This set the new record for the biggest jump of 2.58 ppm from the previous year, despite the COVID-19 pandemic that caused multiple industrial shutdowns. **Figure 2.1** shows the rising trend of carbon dioxide in blue and the human emissions in grey in the timeline from 1975 to 2021 (Lindsey and Dlugokenckey, 2022).

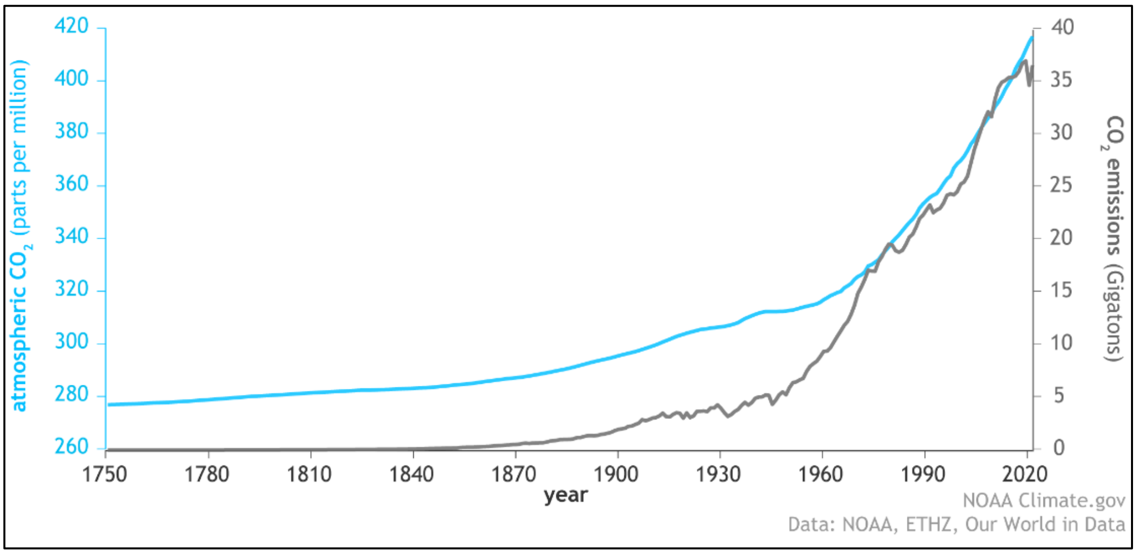

Figure 2.1 Atmospheric carbon dioxide amounts and annual emissions between 1750 and 2021 (Lindsey and Dlugokenckey, 2022).

2.1.3. Carbon monoxide

Carbon monoxide is a highly poisonous flammable gas formed by incomplete fuel combustion and partial oxidation of carbon-containing compounds and is a vital component in many industrial processes (Bierhals, 2000). Carbon monoxide is prone to accumulating indoors, where people are unable to detect it until they become ill because it has no taste, smell, or colour. When exposed to CO gas, it poisons the body by replacing oxygen. Additionally, because the symptoms resemble those of the flu, people may overlook the early signs of carbon monoxide poisoning (McDonald et al., 2013).

Despite not being considered a greenhouse gas, carbon monoxide reacts with oxygen to form carbon dioxide and surface carbonate (CO_3) and reacts in the atmosphere with OH radicals to produce tropospheric ozone and methane (Isaksen et al., 2014). Carbon monoxide breakdown produces some of the highest priority greenhouse gases that the Kyoto Protocol agreement intends to control in efforts to reduce climate change.

2.1.4. Ethane

Ethane is a naturally occurring gaseous hydrocarbon. It has a lifespan of a few months in the atmosphere and is composed of 2 carbons and 6 hydrogens. Additionally, it is less effective in absorbing sunlight compared to other natural gases and significantly contributes to global warming due to its atmospheric conversion to methane (Hodnebrog, Dalsøren and Myhre, 2018). Ethane poses a greater risk for air pollution than global warming because of its saturated structural composition.

2.1.5. Helium

Helium is the second most prevalent element in the known universe, making up 23% of its baryonic mass while also being rare on Earth (Emsley, 2011). According to Weiss (2007), between one and three minutes after the Big Bang, nucleosynthesis produced most of the helium that exists today. Because of this, cosmological theories are influenced by measurements of its abundance. Helium is only present in the Earth's atmosphere at a volumetric concentration of 5.2 parts per million (ppm). Most of the helium in the Earth's atmosphere escapes into space through several processes; thus, the concentration is low and relatively constant despite the ongoing synthesis of new helium (National Weather Service, 2007).

Helium is a noble gas that only exists as an elemental atom that has no covalent bonds. It is also referred to as an inert gas. This characteristic of helium is frequently used in analytical chemistry as a carrier gas because of its very low chemical reactivity with the columns’ stationary phases in gas chromatography. It is also often employed as a diluent gas during the manufacturing of gases, though it is not the most preferred option due to its high cost.

2.1.6. Methane

Methane, a key component of natural gas that ranges in percentage from 50 to 90 depending on the source, is a colourless, highly combustible gas (Hensher et al., 2003). The gas easily reacts with air to produce carbon dioxide and water vapor. Termites, volcanoes, and the anaerobic bacterial degradation of plant matter under water are all natural producers of methane in nature. Additionally, the manufacturing and burning of coal and natural gas, animal agriculture, and burning biomass are all anthropogenic sources of methane that substantially contribute to air pollution (Augustyn, 2022).

The increased methane concentrations in the atmosphere as a product of air pollution contribute to the greenhouse effect, where the absorption of infrared radiation by the gas is redirected back onto the earth’s surface, trapping heat and substantially changing the climate (Wertz and Bédué, 2013). Because methane is abundant in the environment, humans can be exposed to high concentrations when breathing the air and to lower concentrations indoors when using gas products and appliances, which have not been expected to cause adverse health issues yet (Public Health England, 2019).

Since 1983, the Global Monitoring Division of NOAA's Earth System Research Laboratory has been measuring methane at a network of air sample locations all around the world. The data for each site is first smoothed as a function of time, and the smoothed values for each site are then plotted as a function of latitude for 48 equal time steps every year to create the global average. **Figure 2.2** displays the increasing monthly global averaged methane readings with red lines and circles, as well as the long-term trend in the black line and squares between 1983 and 2023 (Lan, Thoning and Dlugokencky, 2023).

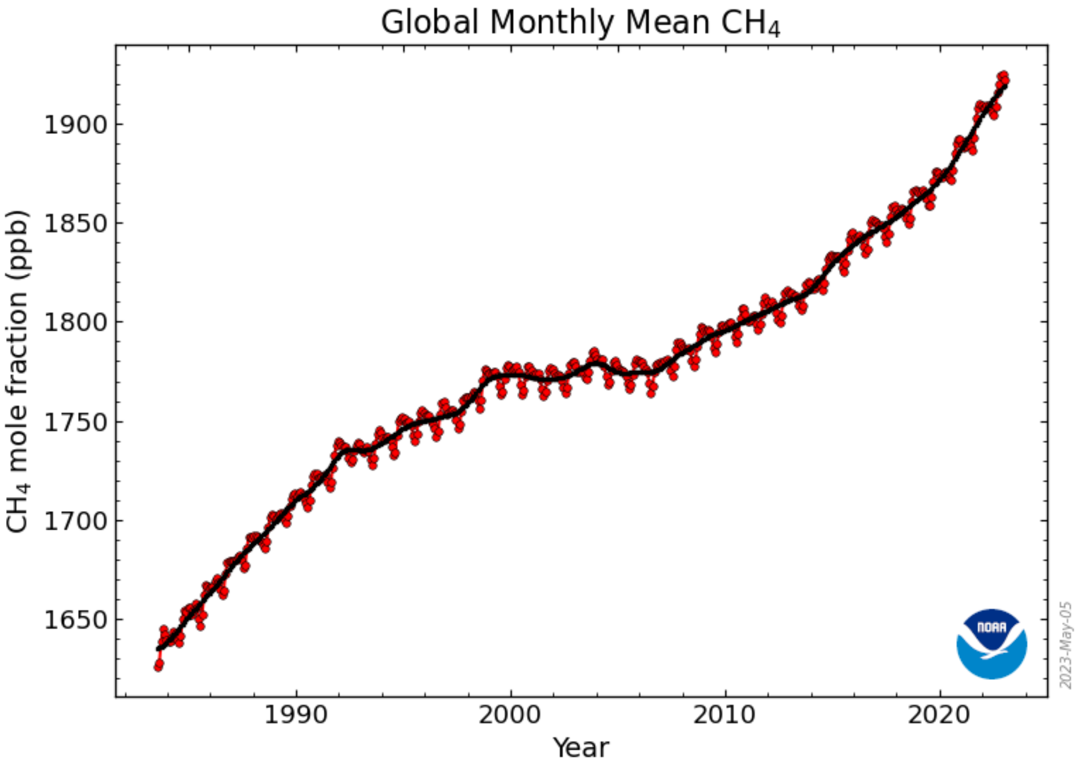

Figure 2.2 Global averaged, monthly mean atmospheric methane abundance determined from marine surface sites (Lan, Thoning and Dlugokencky, 2023).

2.1.7. Nitrogen

Nitrogen (N_2) is a non-metallic element and a member of the pnictogen group (group 15) on the periodic table of elements. The atmosphere is the largest repository of nitrogen, accounting for seventy-eight percent (78%) of its volume (Chivers, 2005). Nitrogen is of interest to environmentalists because of its ability to change into other chemically reactive forms such as ammonia, nitrous oxides (NOx), nitric acid, organic nitrates, and cyanides. Some are necessary for life itself, while others contribute to costly and harmful nitrogen pollution. The production of a variety of reactive nitrogen is due to anthropogenic activities such as various industrial processes that endanger the health of humans, the climate, and the ecosystem, making nitrogen one of the most significant environmental challenges confronting humanity. Although the scope of the issue is largely recognised, the extent of the issue is not yet known (Kolodziejczyk et al., 2019).

The five main targets of nitrogen pollution identified by the European Nitrogen Assessment, were biodiversity, ecosystem health, greenhouse gas balance, water, and air quality (Sutton et al., 2011). The rise in demand in the agriculture, transportation, industrial, and energy sectors has resulted in elevated nitrogen pollution levels and associated greenhouse gas emissions. For example, nitrous oxide is over 300 times more effective than carbon dioxide at trapping heat in the atmosphere, making it a highly potent greenhouse gas. Particulate matter and acid rain are caused by other nitrogen pollutants such as ammonia, nitrogen oxide, and nitrous oxide. Most of these gases are carcinogenic and cause respiratory problems in humans. In the environment, nitrogenous gases are a significant contributor to the global warming trend. (Reis et al., 2009).

2.1.8. Oxygen

Oxygen (O_2) is a colourless, odourless, and tasteless gas essential to living organisms. It is taken up by animals and converted to carbon dioxide; plants, in turn, use carbon dioxide as a source of carbon and return the oxygen to the atmosphere. At 46 percent of the mass, oxygen is the most plentiful element in Earth’s crust (Atkins, Jones and Laverman, 2016). The proportion of oxygen by volume in the atmosphere is 21 %, and by weight in seawater it is 89 %.

The O_2 is extracted from the air for industrial use using two main techniques. The first technique uses fractional distillation of liquefied air, where the O_2 is left as a liquid form and the N_2 is distilled as a vapor. This technique is the most common. The second technique involves a stream of dry, clean air passing through a bed of identical molecular sieves, which produces a stream of gas that is 90 to 93% oxygen and absorbs the residual nitrogen (John, 2001). Oxygen can also be produced through the electrolysis of water into oxygen and hydrogen.

Reference materials of oxygen are used as span gas calibration mixtures in engine emission testing in the automotive industry. Oxygen gas mixtures are also used in environmental, industrial hygiene and safety, and laboratory applications. It is generally used synonymously in the diving industry as pressurised diving gas mixtures containing various oxygen concentrations greater than standard air.

2.1.9. Propane

Propane (C_3H_8), also referred to as liquefied petroleum gas (LPG), is a three-carbon alkane gas that is compressed into a liquid and stored under pressure inside a tank as a tasteless, colourless, and odourless liquid. The liquefied propane vaporises and converts into gas as the pressure is released. The production of propane is a result of crude oil refining and natural gas processing. Its primary applications include home and water heating, food preparation and storage, clothes drying, and the powering of industrial and farm machinery.

The chemical industry also uses propane as a raw material in the manufacture of automotive fuel. This is due to its higher-octane rating of 104-112 compared to that of gasoline at 87-92. Octane rating measures the fuel stability. Consequently, a higher-octane rating indicates better fuel stabilisation and balance against spontaneous combustion (Amaral et al., 2021). The high-octane rating makes propane a better suited fuel for internal combustion engines (Han and Yao, 2015). Propane is a sought-after alternative transportation fuel due to its domestic availability, high energy density, clean-burning characteristics, and relatively low cost. It is believed to be the third most popular transportation fuel in the world, following gasoline and diesel, and is classified as an alternative fuel under the Energy Policy Act of 1992.

According to its photochemical ozone generation potential, propane is one of the volatile organic compounds (VOCs) that most significantly contributes to ozone formation in the troposphere (Yan et al., 2017). Atmospheric emission of these VOCs has been measured over several years by monitoring stations that adhered to tight quality control and assurance measures. The data collected was used to monitor atmospheric changes and the contribution of rising VOC concentrations to climate change (Schultz et al., 2015).

2.2. Adaptation of reference materials in analytical chemistry

The research and production of reference materials were driven by the resolution adopted by the International Congress of Chemists in Chicago in 1888 that stated that analytical chemistry’s reference materials should be equated to the metre in length and the kilogram in mass measurements with the aim of creating measurements that are independent of space and time. The principles of metrology necessary to develop suitable quality assurance systems for chemical measurements, are all covered in this literature review, include ensuring measurement traceability, developing reference materials, estimating measurement uncertainty, validating analytical procedures, and participating in interlaboratory comparisons (Słomińska, Konieczka and Namieśnik, 2014).

The International Organization for Standardization (ISO) Guide 34 of 2009, "*General requirements for the competence of reference material producers’ defines a reference material as "a substance that has been demonstrated to be suitable for its intended use because it is sufficiently homogeneous and stable with regard to one or more specified properties*" (ISO Guide 34, 2009). In the context of this study, these materials are also known as primary reference gas mixtures (PRGMs). Additionally, PRGMs are produced using a method that is technically sound and is validated by a traceable certificate given by a competent certifying institution, such as the National Metrology Institute (NMI), for one or more analytes that have been quantified.

2.3. Metrological traceability of reference gas mixtures

The capacity to verify the accuracy of measurements is a human necessity as it allows for accurate conclusions about the behaviour of substances, and modern metrology provides this capability. A standard, uniform method of measurement was developed because of this necessity. The International Bureau of Weights and Measures (BIPM) was founded in Paris in 1875 as a result of the ongoing advancement of science and technology as well as the requirement that measurements be independent of space and time (Słomińska, Konieczka and Namieśnik, 2014).

One of the fundamental requirements for gas analysis that ought to be acknowledged and integrated into measurement procedures is metrological traceability. Without traceability to the SI, instrument calibration would not be accurate. The ability to ensure metrological traceability in instrument calibration is aided by an understanding of traceability principles and requirements based on ISO/IEC 17025, "*General requirements for the competence of testing and calibration laboratories*" (Belezia and de Almeida, 2021). These requirements for quality assurance enable the attainment and maintenance of reliable and accurate measured values. That is, a standard weight of 1 kg remains the same no matter where you are. This section seeks to provide a thorough understanding of the metrological traceability chain.

2.3.1. Introduction to metrological traceability chain

Metrological traceability is the fundamental notion of metrology, defined in the International Vocabulary of Metrology as "*the property of a measurement result whereby the result can be related to a reference through a documented, unbroken chain of calibrations, each contributing to the measurement uncertainty*" (VIM, 2008). As a result, traceability may be explained much more simply as a series of comparisons between an instrument's measured value and uncertainty and the value of a more accurate standard (De Bièvre, 2011), is linked to an even more accurate standard until it reaches an International System of Units (SI) of either metre (m), second (s), mole (mole), kilogram (kg), ampere (A), kelvin (K), or candela (cd). It is crucial to emphasise that traceability does not refer to the instrument but rather to the measurement result. Measurement traceability is vital for the provision of quality-assured results with reference standards traceable to the SI. The reduction of method variability so that results are independent of location and time, the promotion of inter-organisational collaboration to ensure the same or acceptable specifications for comparable and guaranteed product safety of produced goods and services, and the elimination of barriers to trade.

The metrological traceability chain, also referred to as the unbroken chain of measurements, is defined as "*the sequence of measurement standards and calibrations that are used to relate a measurement result to a reference*" (VIM, 2008). The traceability chain shown in **Figure 2.3** demonstrates an unbroken traceability chain that links the reference standards in a hierarchy pyramid from higher to lower accuracy. Traceability is provided by dissemination from the top to the bottom of the pyramid and is disconnected when the chain is broken by overdue calibration or expired reference standards since the measurements can no longer be traced all the way to the SI.

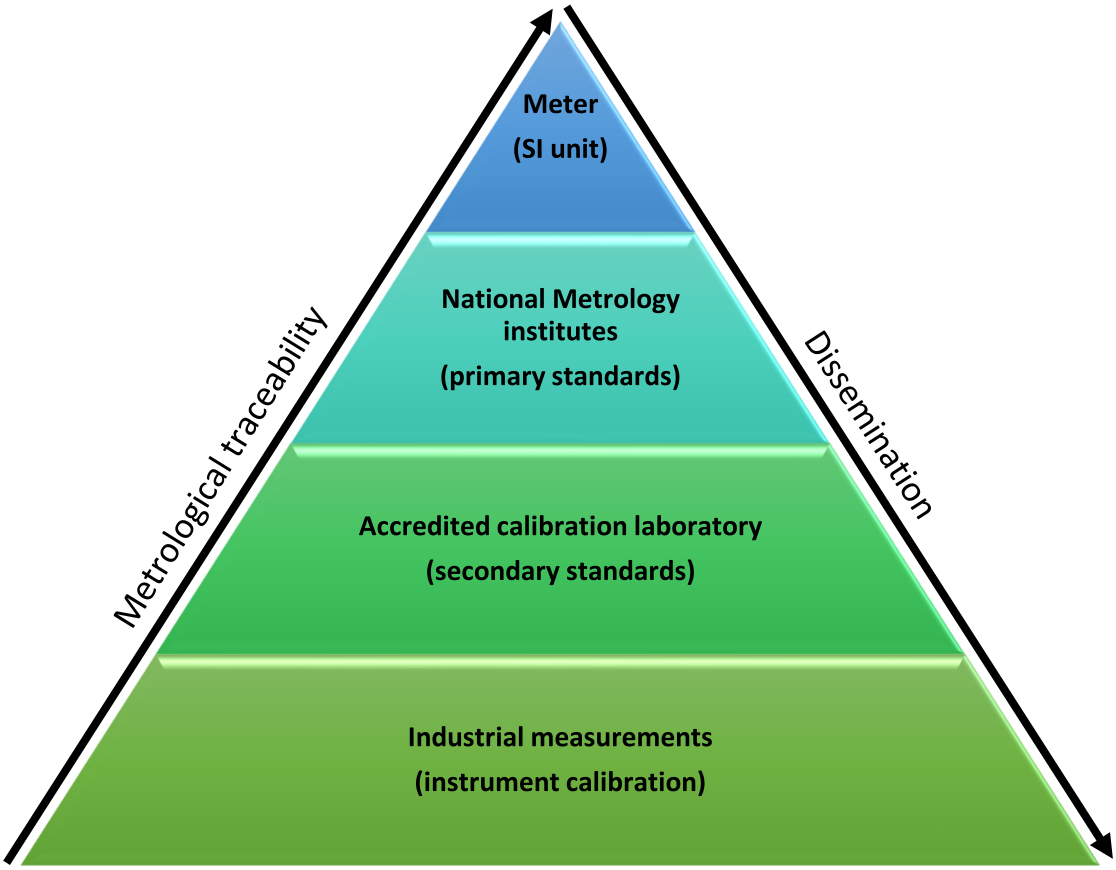

Figure 2.3 Metrological traceability pyramid chain

In addition to establishing measurement traceability, it needs to be maintained. According to ISO 17025, laboratories are required to establish and maintain the metrological traceability of their measurement results using a recorded, uninterrupted chain of calibrations, each of which adds to the measurement uncertainty and links the results to the suitable reference (ISO/IEC 17025, 2017). Establishing metrology traceability necessitates a clear, unbroken chain of traceability for calibration or reference material, as well as documentation of the environmental conditions, calibration techniques used, staff competency, assigned uncertainty values, and identification of reference standards (Matsakis, Levine and Lombardi, 2018). Additionally, maintaining metrological traceability includes routine internal audits, method validation, and ongoing verification of the reliability of results through participation in proficiency testing schemes and/or laboratory comparisons.

2.3.2. Traceability of reference gas mixtures to the SI

Traceability of reference gas mixtures is achieved through the realisation of the SI unit of mole by a national metrology institute (NMI). This is done through the gravimetric preparation of primary gas standards of known amount fractions, which are retained in-house as reference standards for gas measurements in the laboratory. These standards are also known as primary standard gas mixtures (PSGMs) and sit at the highest tier of gas standards with the smallest uncertainties. Primary reference gas mixtures (PRGMs) are the NMI’s certified gas standards that are validated against the PSGMs and provided to accredited laboratories as a form of traceability dissemination. The accredited laboratories prepare their own secondary gas mixtures (SGMs) and compare the gas amount fractions with those of a PRGM from an NMI. PRGMs and SGMs are used in industry to calibrate analytical instruments to support accurate measurements. **Figure 2.4** shows the traceability flow of gas mixtures with examples of varying tolerable errors (uncertainties) as you go down the traceability chain.

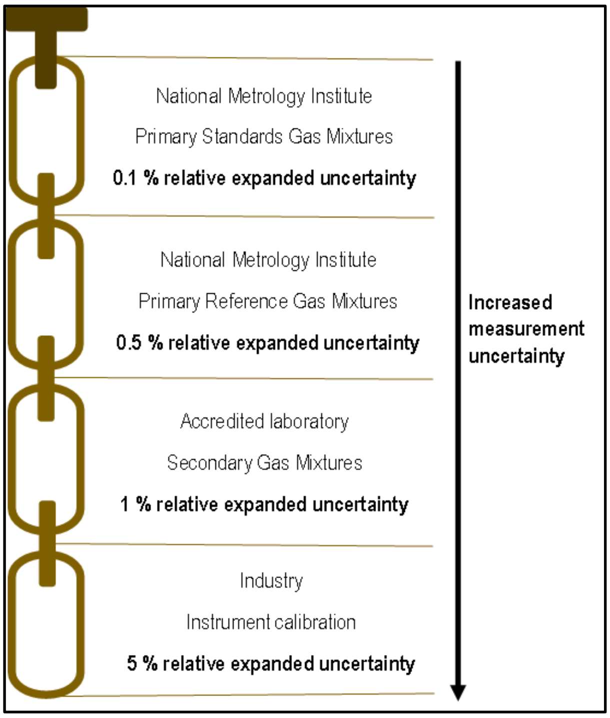

Figure 2.4 Chain of unbroken metrological traceability for reference gas mixtures with examples of uncertainty for each link.

2.3.3. Traceability challenges of reference gas mixtures

Due to the complexity of the measurements in chemistry, metrological traceability can be challenging. This is because, in contrast to physical measurements, which focus on the magnitude of a single quantity, multicomponent matrix combinations are much more complex. Therefore, the capability of NMIs to satisfy the traceability requirements of all components in a multicomponent gas mixture in the chemical measurement field is challenging. Because there are more sources of uncertainty, the complex multicomponent gas mixtures have larger uncertainties than those that have a single component. For example, the developed reference gas mixtures used in this study are made up of nine different components, all of which add to the overall uncertainty of the prepared mixture.

In chemistry, traceability is distributed either through reference material or reference measurements with shorter traceability chains that significantly reduce uncertainties. Whereas in physical measurement, traceability is disseminated through the calibration of equipment or calibrated physical artefacts (Brown et al., 2017). Other traceability challenges include adsorption that makes value assignment difficult, limited stability data, and isotopic composition issues.

2.4. Purity analysis of starting material

There is a sizeable market for pure gas products related to a variety of applications, including pharmaceutical, analytical, metrological, and petrochemical. Although the gases are considered to be pure, it is inevitable that impurities are introduced either before, during, or after their purification processes. This then makes it imperative to quantify the impurities in the pure gases because the above-mentioned applications require unique pure gases with specific purity requirements, and the quality of the gas products is purity dependent (Mulyana et al., 2019). Therefore, purity analysis is one of the essential steps in the quantification of the composition of gas mixtures. According to the International Organization for Standardization's ISO 19229:2019, the identification of the trace-levels of various components in the matrix of a gas mixture is done to establish metrological traceability of the certified gas composition. This can be done through literature, manufacturer-provided information, prior experience with the material, or knowledge of the production process of the material.

The impurities present in a gas mixture can be classified as critical or significant, depending on their nature. Critical impurities are those that are present in both the parent gas and diluted gas mixtures at low concentrations, as they have the potential to influence the analytical results of the mixture composition or are reactive with other components in the mixture. Significant impurities are those that contribute over 10% to the target uncertainty of the content of any of the components in the gas mixture. The purity of the pure gas is determined using the subtraction method, where the calculation of the component with the most abundant amount fraction in the pure gas is done using **equation 2.1** which suggests that the most abundant amount fraction (x_{jy}) is equal to the subtraction of the sum of the amount fraction of all the impurities x_{iy} from 1 (ISO 19229, 2019).

$$x_{jy} = 1 - \sum_{i=1;\, i\neq j}^{n} x_{iy} \qquad \textbf{2.1}$$

And the standard uncertainty ($u(x_{jy})$) associated with the amount fraction of the abundant component is determined by **equation 2.2**.

$$u^2(x_{jy}) = \sum_{i=1;\, i\neq j}^{n} u^2(x_{iy}) \qquad \textbf{2.2}$$

One of the commonly investigated parameters before the preparation of standard gas mixtures is the purity of the starting materials. An example of this is the case study done on permanent gas impurities in pure nitrogen by the Metrology in Chemistry Research Group at the Research Centre for Metrology-Indonesian Institute of Sciences. The study was carried out using a validated gas chromatograph coupled with a pulsed discharge helium ionisation detector (GC-PDHID) fitted with a PoraPLOT Q (50m x 530μm x 20μm) for separation of heavy gas components such as carbon dioxide impurities and a MolSieve 5A that was used for separation of light gas components such as argon, oxygen, hydrogen, carbon monoxide, and methane. The sample flow on the pure nitrogen was set at 40 mL.min^{-1} while the flow for the carrier gas was programmed at 10 mL.min^{-1} for the first 11.5 minutes. It was then ramped down to 5 mL.min^{-1} for 3.4 min, and finally ramped up to 10 mL.min^{-1} for the rest of the run. The experiment was done with the detector temperature set at 220 ℃ and the oven temperature programmed initially at 40 ℃ for the first 6.5 minutes. Then ramped down to 30 ℃ and held for 8.4 minutes, ramped up to 75 ℃ with increments of 6 ℃ per minute and finally ramped up again to 160 ℃ for the rest of the run. This method yielded good separation of the impurities with no significant issues encountered (Mulyana et al., 2019).

2.5. Literature for the gravimetric preparation method of reference gas mixtures

There are two kinds of preparation methods: static methods and dynamic methods. The static method involves the transfer of a known mass of a gas or liquid into a vessel of a defined volume. This method has been recognised as cost-effective with maximum accuracy; however, it is time-consuming and susceptible to adsorption and stability issues when preparing liquified gases. The dynamic method, which involves the continuous flow of gas into a system at a known rate, is also highly accurate and provides stable gas mixtures. However, its technology is costly, and controlling the flow rate of gases can be difficult (Słomińska, Konieczka and Namieśnik, 2014). This study followed the static method and studied the adsorption and stability of the prepared reference gas mixtures.

The availability of gravimetrically prepared reference gas mixtures with SI-traceable values and uncertainties serves as the foundation for measurements applicable in the monitoring of indoor and atmospheric air quality, the determination of the physical characteristics of fuel gases, waste gas technological installation, and the regulation of emissions into the atmosphere (Macé et al., 2022).

2.5.1. Gravimetric preparation of reference gas mixtures

Reference gas mixtures have specific known compositions of the analyte and diluent gas that are prepared by a gravimetric method. They are produced by successively adding the starting material(s) or pre-mixture and diluent gas to a cylinder, normally made of aluminium material. This technique, known as the gravimetric preparation method, is a quantitative method where the determination of the composition of the analyte(s) added to the gas cylinder is measured by the weighing difference between the sample and reference cylinder. The results are directly traceable to the International System unit of mass (kg) and the amount of substance (mol). This method is thought to be the most accurate because it relies on the mass comparison of a sample cylinder to a reference cylinder with the same physical properties to account for differences in environmental conditions and draws critical examination of factors such as cylinder volume, pressures, and mass comparators, essentially minimising the buoyancy effect (Milton, Vargha and Brown, 2011). These weighing cycles use the substitution method (van Andel, van der Veen and Zalewska, 2012). The amount fractions of the reference gas mixtures can be traced back to the SI unit of amount of substance from the preparation process by determining the correct masses of the gases added, converting the added masses to amount fractions using the chemicals' purity and molecular masses, and comparing the final prepared gas mixture to other independent reference gas mixtures.

ISO 6142-1:2015 "*Gas Analysis Preparation of Calibration Gas Mixtures, Part 1: Gravimetric method for class I mixtures*" is universally used as a common method for the preparation of reference gas mixtures. An equation derived from the ideal gas law equation (**equation 2.3**) is used to calculate the target mass of the parent gas needed to be added to the sample cylinder for a specified amount fraction of the component of interest.

$$m_i = \frac{x_i \times P_{cyl} \times V_{cyl} \times M_i}{RTZ_f} \qquad \textbf{2.3}$$

Where m_i is the target mass of component i, x_i is the desired amount fraction of component i, P_{cyl} is the pressure of the final mixture expressed in pascal (Pa), V_{cyl} is the volume of the cylinder used in cubic meter (m^3), M_i is the molar mass of component i, R is the gas constant (8.314 J.mol^{-1}.K^{-1}), T is the temperature expressed in Kelvin (℃ +273.15 K) and Z_f is the compressibility factor (Z=1)

2.5.2. Gas dilution methods

The use of reference gas mixtures in high-pressure cylinders is common practise in traditional laboratories. However, in order to acquire increasingly lower amount fractions of different analytes in the calibration gas mixtures, appropriate dilution procedures must be established (Słomińska, Konieczka and Namieśnik, 2014). Two of these dilution methods, single-step and multi-step, have been employed in the gravimetric preparation of reference gas mixtures. The choice of either of the above methods is determined by the target mass required for the mixture cylinder to prepare the amount fraction of interest.

2.5.2.1. Single-step preparation dilution method

This preparation dilution method is preferred when the mass of each component added into the sample mixture is large enough to be measured accurately with appropriate gravimetric uncertainties (ISO 6142, 2015). To obtain accurate measurements, the mass of the parent gas required should be more than 10 g. Further to this, a dilution factor can be used to calculate permissible dilution levels in the preparation of gas mixtures. The dilution factor is expressed as an equation based on the mass fractions of the small and large parts, which are given in **equation 2.4**.

$$D_i = \frac{m_x}{m_x + m_y} \qquad \textbf{2.4}$$

where D_i is the dilution factor of gas x and gas y for a single-step dilution, m_x is the mass required for minor component and m_y is the mass required for the major component (Milton, Vargha and Brown, 2011). And D_i's relative uncertainty can be determined using internationally acknowledged methods using **equation 2.5**.

$$\frac{u(D_i)^2}{D_i^2} = \frac{m_y^2}{(m_x + m_y)^2}\left(\frac{u(m_x)^2}{m_x^2} + \frac{u(m_y)^2}{m_y^2}\right) \qquad \textbf{2.5}$$

Where $\frac{u(D_i)^2}{D_i^2}$ is the standard uncertainty associated with D_i, $\frac{u(m_x)^2}{m_x^2}$ is the standard uncertainty associated with the mass required for the minor component m_x and $\frac{u(m_y)^2}{m_y^2}$ is the standard uncertainty associated with the mass required for the major component m_y(Milton et al., 2011).

Figure 2.5 illustrates a single-step dilution method with a preparation plan of 10 %mol.mol^{-1} of CO in N_2 from high purity CO.

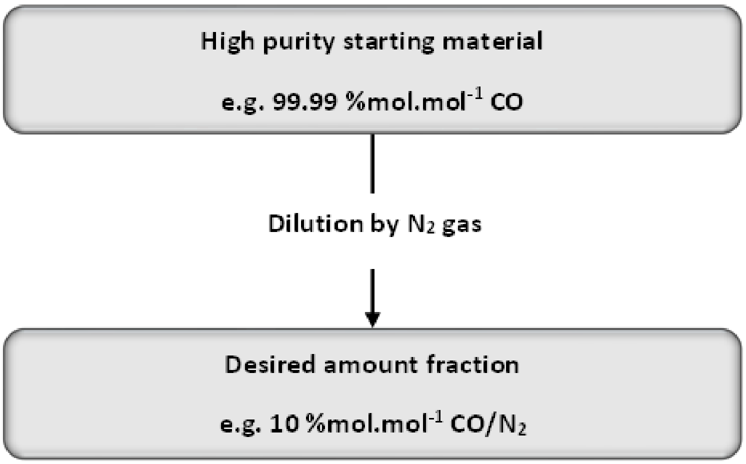

Figure 2.5 Schematic representation of the single-step dilution method.

2.5.2.2. Multi-step preparation dilution method

This dilution method is preferred for the preparation of mixtures of low amount fractions with acceptable uncertainty to allow for significant mass addition of the components of interest (ISO 6142, 2015). This is due to the inherent limitations of preparing gas mixtures with small gravimetric uncertainties using one-step dilution (Kim et al., 2022). Milton et al. (2011) proposed a mathematical relationship for establishing effective multi-step dilution methods to minimise the uncertainty associated with weighing the smallest quantity possible. In other words, more dilution steps used in the preparation of low-amount fraction gas mixtures can be optimised to achieve the lowest total dilution uncertainty when compared to one-step dilution. This method uses “pre-mixtures” that are prepared gravimetrically as parent gases in one or more of the dilution steps to reduce uncertainties. **Figure 2.6** shows an example of this dilution method with the dilution of carbon monoxide from 99.99 %mol.mol^{-1} CO to 1000 µmol.mol^{-1} CO using N_2 as the diluent gas in three steps. The deployed dilution is a 10-times dilution.

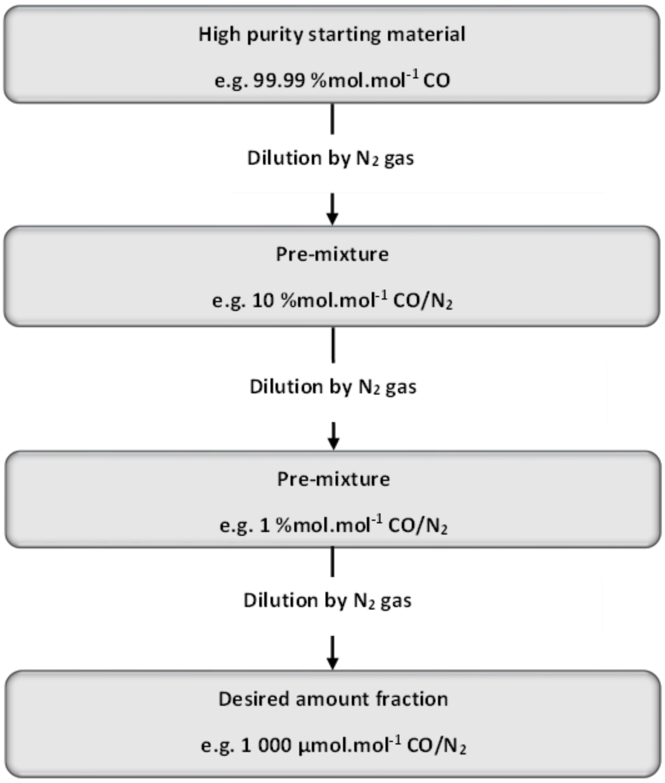

Figure 2.6 Schematic representation of the multi-step dilution method.

2.5.3. Challenges associated with gravimetric preparation methods

The preparation of gases is often more complex than that of solids and liquids. This is due to the gas's chemical and physical properties, which are influenced by temperature and pressure changes. It is difficult to weigh gases accurately because the volume of the vessel of the gas is suspectable to fluctuations during the mixture handling during preparation (Lekoto, 2018). Furthermore, gas preparation includes the mixing of several gases into one vessel which presents challenges related to reactivity of the mixed components and the compressibility of the gases. Therefore, before the preparation of the reference gas mixture, considerations of any potential chemical reactions between the mixture components, materials of a high-pressure cylinder, cylinder valve, and the transfer system must be made. Some of the methods used to study the behaviour of the gases in the cylinders to produce lucrative literature include studies on adsorption and matrix effect to monitor a few of the issues mentioned.

2.6. Verification techniques for refinery reference gas mixtures measurements

2.6.1. Gas Chromatography introduction and principles

The idea of chromatography was first introduced by a Russian scientist named Tswett in 1903 while he was studying chlorophyll and other plant pigments. This method was called liquid-adsorption column chromatography. Thereafter, the idea of chromatography was occasionally employed until Martin and Synge published a well-known paper that described their invention of liquid-liquid partition in column and planar (paper) chromatography forms. This invention fast-tracked the use of chromatography. With major progressive steps in gas-liquid chromatography work done by James and Martin that fundamentally impacted analytical chemistry in unprecedentedly ways. Other milestones that followed included:

i. Steric exclusion chromatography work done by Porath and Flodin in 1949 which discussed the technique for easy separation of macromolecules.
ii. Marcel Golay invented open tubular gas chromatography in 1956, which increased efficiency and separation.
iii. Extensive treatment of chromatography theory in Giddings' Dynamics of Chromatography, published in 1961, that sheds light on the various aspects of chromatography, such as nonequilibrium, diffusion, pressure variations, and temperature-programmed gas chromatography.
iv. Introduction of high-performance liquid chromatography that allowed efficient separation of an extended range of components in the early 1970s (Littlewood, 2013).

Gas chromatography is now well defined as a measurement method based on the separation of target gases or two immiscible phases of liquids. A mobile gaseous phase in the form of a high purity chemically inert carrier gas for sample transportation and a solid stationary phase in the form of a column. The column is the main central apparatus for gas chromatography, with its long tube packed with an adsorbent that allows for component separation. Columns are readily available as packed and capillary columns, where the main difference between them is that the packed column’s stationary phase is made up of fine particles, and the capillary column’s stationary phase is coated on the inner surface and is predominantly used for the separation of polar samples (van Lieshout, 1999). In most applications, peak separations are performed to identify and quantify each component in a sample of a mixture. A sample is introduced into a heated inlet system where it is vaporised, in the case of a liquid sample, and transported to the GC column through a gaseous carrier. The carrier gas used depends on the sample being analysed and the detector being used (McNair, Miller and Snow, 2019). The sample analytes are then adsorbed on the stationary phase in the column and eluted according to their affinity for the stationary phase (Taha, 2018).

2.6.2. Gas chromatography application in the verification of refinery reference gas mixtures

The capacity of gas chromatography to simultaneously separate multiple components in a mixture makes it the method of choice for the analysis of complex multi-component gas mixtures. For the analysis of refinery gases, specialised energy and chemical analyzers have been developed. For refinery gas analysis (RGA), gas chromatography is a frequently used test method for identifying gases produced during crude oil refining (Ferracci, 2015). The RGA is advantageous in its rapid and simultaneous determination of the chemical composition of gaseous mixtures containing components such as hydrocarbons (C_1 – C_{6+}), carbon dioxide, carbon monoxide, helium, hydrogen, oxygen, and nitrogen. However, challenges with the separation of compounds with comparable chemical properties still exist and are addressed in this study.

In gas chromatography, several detectors are used based on their selectivity and sensitivity to the components of interest. The thermal conductivity detector (TCD) and the flame ionisation detector (FID) are the most widely used detectors for analysing permanent gases and hydrocarbons, respectively. This is due to their association with high sensitivity to numerous components across a wide composition range (Ghosal and Avasthi, 2018). These detectors are crucial for the refinery gas analysis study. The pulsed discharge ionisation detector (PDID), whose sensitivity exceeds that of the TCD and FID, is also frequently employed for the quantification of trace quantities of permanent gases for purity analysis. The following sections detail the detectors that are used in literature for purity analysis and multi-gas analyses of refinery gas mixtures that were also used in this study.

2.6.2.1. Flame Ionisation Detector

The flame ionisation detector is based on the detection of organic compound ions, such as hydrocarbons, in a hydrogen flame. The ions generated are proportional to the composition of the component of interest. Although CO and CO_2 are not hydrocarbons, an FID equipped with a methanizer (typically a nickel-based catalyst) can detect them. The Nickel catalyst converts CO and CO_2 to methane, which is detectable by the detector as shown in **equations 2.6 and 2.7** (Mok, Jwa and Lee, 2013). However, the matrix of the mixture of CO and CO_2 is crucial since the methanizer is prone to being damaged by some substances included in GC effluents, such as compounds containing sulphur (Badger, 2019).

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad \textbf{2.6}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad \textbf{2.7}$$

2.6.2.2. Thermal Conductivity Detector

The thermal conductivity detector attributes its universal functionality to its ability to detect various gases such as hydrogen, nitrogen, inorganic gases, and many others. Its operating principle is based on the differences in thermal conductivities between the constituents of column effluent flow and those of the carrier gas, producing a proportional voltage signal. The resulting signal is proportional to the composition of the component of interest (Hinshaw, 2006).

2.6.2.3. Pulsed-Discharge Helium Ionisation Detector

A pulsed discharge helium ionisation detector is designed to use a low-powered, direct-current pulse discharge that is stable in helium as an ionisation source (Poole, 2015). It is a sensitive and universal detector that can be used for the analysis of trace volatile organic compounds and oxidised analytes in a single analysis. The PDHID sensitivity is 50 times better than that of the FID and can detect trace compositions of gases such as oxygen, nitrogen, argon, and methane that cannot be detected on the FID and has greater sensitivity than the TCD (Roberge et al., 2004).

2.7. Adsorption and desorption

Adsorption is the accumulation of a substance due to atoms of a molecule attaching to the surface of the adsorbent (Osouleddini and Rastegar, 2019). Instabilities of gas composition in high-pressure cylinders have been documented in past studies as either pressure-dependent composition variations in the cylinder lifetime or temporal drifts. These drifts have been linked to either changes in the surface interactions or variations of diffusional fractionation mechanisms, including effusion, thermal, and ordinary diffusion (Langenfelds et al., 2005; Keeling et al., 2007). Gases tend to instantly adsorb on metallic surfaces. The changes in the surface interactions, namely adsorption and desorption, have been examined in greater detail and are crucial for the stability of gas composition in mixtures, more so for species of trace gases. Although the use of passivated aluminium cylinders has been adopted for the preparation of reference gas mixtures to minimise adsorption, further adsorption studies are necessary because measurement accuracy is compromised by the interactions of the gas molecules with the cylinder surfaces (Leuenberger, Schibig and Nyfeler, 2015).

Studies have investigated adsorption and desorption using various methods. The Center for Gas Analysis at the Korean Research Institute of Standards and Science (KRISS) has studied the physical adsorption loss of different standard gas mixtures using cylinder-to-cylinder division. The test included a three-step division hierarchy shown in **Figure 2.7**, where x_i' is the actual amount fraction of the gas component i that is the same as the gravimetric amount fraction (x_0) and r_o is the analytical response to x_0 and r_i' is the analytical response to x_i'. The adsorption was estimated using the original (mother) standard gas mixture's gravimetric amount fractions and the analytical responses (Lee et al., 2017).

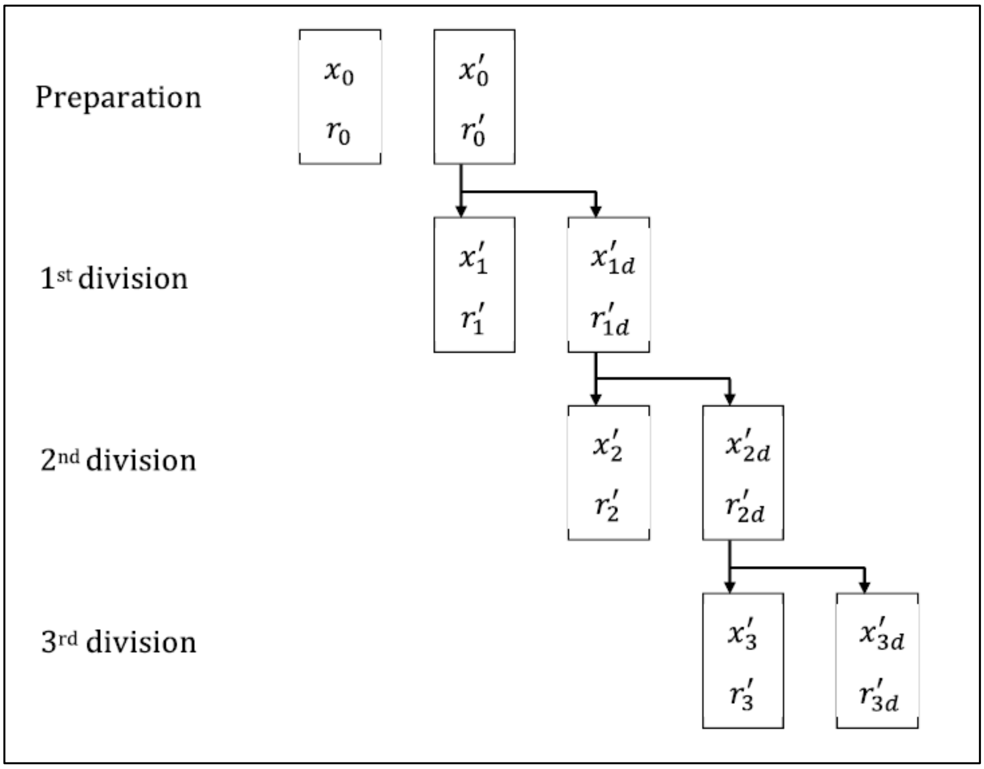

Figure 2.7 Hierarchy of three-step divisions for the same type of cylinders (Lee et al., 2017).

The National Physical Laboratory (NPL) and the Van Swinden Laboratorium (VSL) studied the adsorption of oxygenated volatile organic compounds using gas chromatography responses and the known composition of a stable internal standard to determine the effective carbon number (ECN) for the compounds under investigation. This method assumes that there is no significant adsorption of the internal standard and is thus used together with the gas chromatography response to estimate the adsorption of the components that are likely to adsorb on the cylinder walls (Worton et al., 2022).

2.8. International efforts for the development of measurement capabilities for primary reference gas mixtures of refinery gases

The International System of Units is important in defining and assigning reference measurements for international member states of the International Committee of Weights and Measures (CIPM). These quantities are then given meaning by assigning unique corresponding units that allow for the most reproducible and precise measurements that can be made (BIPM, 2006). This subsequently permits value assignment along with the associated uncertainties of an equivalent unit of measurement. When this is done, the measurement is then distributed across different countries and compared to determine the comparability of the same measurements in the different countries. These measurement standards are known as the national measurement standards (NMS) (Czichos, Saito and Smith, 2011).

National Metrology Institutes (NMIs) participate in international comparisons through the Consultative Committee for Amount of Substance Gas Analysis Working Group (CCQM-GAWG) to establish measurement capabilities. The CCQM-GAWG is an international body aimed at establishing comparability of gas analysis measurements to the SI, contributing to the implementation of the International Committee of Weights and Measures Mutual Recognition Arrangement (CIPM MRA) in gas measurements, and providing developing NMIs with access to core comparisons to fast-track development.

An example of such a comparison is CCQM-K77. In 2009, the Consultative Committee for Amount of Substance Gas Analysis Working Group agreed to a protocol and participants for the comparison of refinery gas to assist its members with establishing measurement capabilities for refinery gas, provide a benchmark platform, and validate new and existing Calibration and Measurement Capabilities (CMC) claims in the BIPM database. The metrology institute of the Netherlands, Van Swinden Laboratory (VSL) was the coordinating laboratory for the key comparison. For the preparative comparison, the eight participants had to gravimetrically prepare a gas mixture containing the components of interest and respective amount fractions listed in **Table 2.2**.

Table 2.2 The nominal composition of the CCQM K77 comparison gas mixtures (Nieuwenkamp et al., 2012).

Component	x (10^{-2} mol mol^{-1})
Methane	10 – 15
Ethene	10 – 15
Ethane	1 – 5
Propene	1 – 5
Propane	0.4 – 1
1,3-Butadiene	0.5 – 3
1-Butene	0.3 – 0.7
Iso-butene	0.3 – 0.7
Hydrogen	7 – 10
Nitrogen	3 – 5
Helium	Balance

Gas chromatography with flame ionisation detectors and thermal conductivity detectors were the overwhelming measurement techniques of choice used by all participants, with calibration methods varying between single-point and bracketing methods. All participants used the FID for the analysis of hydrocarbons and the TCD for hydrogen and nitrogen.

The results of the degrees of equivalence for each component relative to the key comparison reference value (KCRV) are used to benchmark the laboratory's performance. These results can be seen in **Appendix A**. The results of the comparison show some challenges with the overall analysis of refinery-type gas mixtures worldwide. The laboratories that had satisfactory results for all the studied components in the comparison were VSL, the National Institute of Metrology (NIM) of China, the National Physical Laboratory (NPL) of the United Kingdom, and the D.I. Mendeleyev Institute for Metrology (VNIIM) of Russia. This benchmarking measurement report has confirmed that the use of similar measurement techniques, i.e., gas chromatography coupled with flame ionisation and thermal conductivity detection, is indicative of the accuracy of the analytical methods employed (Nieuwenkamp et al., 2012). One of the highlighted challenges encountered by most participants included hydrocarbon separation, baring testament to the very limited literature on the preparation, analysis, stability, adsorption, and desorption behaviour of these complex multi-component gas mixtures. This study adopted the preparative and analytical techniques used in CCQM-K77 for the development of refinery reference gas mixtures and analytical methods with the aim of providing solutions to the energy industry in South Africa and contributing to the literature on the stability, adsorption, uncertainty, and matrix effect associated with the preparation and analysis of primary reference gas mixtures of refinery gases.

2.9. Method validation and data evaluation

The Eurachem Guide for the Fitness for Purpose of Analytical Methods defines method validation as the development of measurement criteria that the instrument can meet to achieve its best performance (Magnusson, 2014). For any given analytical method, the results need to be fit for the purpose that it is intended to fulfil. Therefore, method validation is an essential requirement of a developed analytical method.

The performance parameters of a method that must be characterised during method development depend on what the validation seeks to achieve. Frequently investigated parameters in analytical chemistry include accuracy, precision, selectivity, stability, limit of detection and quantification, measurement uncertainty, linearity, and ruggedness.

2.9.1. Accuracy

The accuracy of an analytical method expresses the degree of agreement of the test results produced by the method with the true value. In most analytical cases, accuracy is studied using two techniques: method and reference comparison. The method comparison technique compares the same sample results obtained from the newly developed analytical method and an existing validated analytical method. The reference comparison technique compares a sample to a known composition reference material or compares the analytical results to the gravimetric compositions of the sample (Magnusson, 2014).

2.9.2. Precision

The degree of agreement between results is known as measurement precision. The standard deviation (or relative standard deviation), which is calculated from results obtained by repeating measurements on a sample under predetermined conditions, is a commonly used statistical factor to represent the statistical factors that define the spread of results. Two extreme measures of precision are measurement repeatability and reproducibility (Magnusson, 2014; Gupta, 2015).

2.9.2.1. Repeatability

Repeatability is defined as the proximity in conformity of successive measurement results of the measurand performed under identical conditions (Peris-Vicente, Esteve-Romero and Carda-Broch, 2015). Repeatability is a measure of a method's most optimistically anticipated precision. When performed by the same analyst on the same analytical equipment over a short period of time, it yields predictable inconsistencies of a method.

2.9.2.2. Reproducibility

Reproducibility is a more conservative measure of precision encountered in a measurement method expected to give large variations in results. It can be measured using the standard deviations acquired when the measurement is done under variable conditions of measurement (VIM, 2008). The variable conditions include different days, different analysts, or different analytical methods.

2.9.3. Selectivity

To accurately detect an analyte of interest in the presence of other components that may be anticipated to be present in the sample matrix, such as contaminants, degradation products, and matrix components, an analytical method must be selective. Selectivity can be verified by evaluating chromatographic blanks from a sample that is known not to contain any analytes of interest throughout the anticipated time window of the analyte peak (Stauffer, 2018). When evaluating selectivity using the peak area identification test, the method should be able to demonstrate good resolution between compounds with closely related structural relationships that are likely to be present in the mixture (Gupta, 2015).

2.9.4. Stability

According to ISO 6142 of 2015, gas mixtures undergo a stability evaluation immediately after preparation and then at regular intervals to determine their shelf life. Traditionally, stability evaluation is conducted on non-reacting components. Multicomponent gas mixtures, however, are difficult to monitor because of the stability that is impacted by the gases' adsorption to the cylinder walls, their reactivity at high pressures, and the overall pressure of the mixture. A short stability period results in a small level of stability uncertainty, whereas a long stability period results in a greater level of stability uncertainty.

2.10. Measurement Uncertainty

Measurement uncertainty is a property of the result of a measurement that shows how far apart the values given to the measurand are. Although the word "uncertainty" relates to doubt, measurement uncertainty does not mean doubt about a measurement result’s validity; however, uncertainty knowledge relates to the confidence in the validity of the measurement results (Ellison and Williams, 2012). Uncertainty is made up of a number of factors, many of which are evaluated based on the statistical distribution of the results of a series of measurements and can be characterised by experimental standard deviations, as well as assessments of presumptive probability distributions based on prior knowledge or available data.The Guide of Uncertainty of Measurement categorises these different cases as Type A and Type B measurement uncertainty estimations. Type A is based on statistical calculations such as the mean and estimated standard deviations, and Type B is based on experience and data collection that is not related to the experiment performed, such as calibration certificates, proficiency testing reports, and datasheets (ISO/IEC Guide 98-3, 2008).

The calculation of measurement uncertainty is based on a model that identifies all sources of measurement uncertainty for the measurand. In analytical chemistry, common sources of uncertainty include sampling, purity of the reagents, storage conditions, instrument effects, measurement conditions, and random errors. In the uncertainty evaluation of prepared gas mixtures, for example, uncertainty contributions resulting from the purity of the starting material, preparation, and analysis processes are considered. All minor and major uncertainty contributors are identified and quantified. The Guide to the Expression of Uncertainty in Measurement (GUM) lists the following six steps as integral parts of the evaluation of measurement uncertainty:

i. Specification and modelling of the measurement.
ii. identification of the components that contribute to the measurand's uncertainty.
iii. calculations of the standard uncertainty of each identified contributor based on their category.
iv. determination of the combined standard uncertainties
v. determination of the expanded uncertainty using the appropriate coverage factor for the desired confidence level.
vi. Report on the uncertainty (Linsky, 2017).

2.10.1. Evaluation of measurement uncertainty

Measurement uncertainty calculations are quite complex, with each uncertainty contributor calculated based on its type and probable distribution. Three factors—the measured amount fraction, coverage interval, and coverage probability—form the basis of the measurement uncertainty equation. The measured amount fraction is the true value of the measurement, expressed with its associated expanded uncertainty. Traceable measurement results are always reported with their expanded uncertainties (**equation 2.8**). The expanded uncertainty provides a range where the measured value is thought to lie at a specific confidence level and is obtained by multiplying the combined standard uncertainty by the coverage factor.

$$X = x \pm U \qquad \textbf{2.8}$$

Where X is the measurement result, x is the measured amount fraction and U is the expanded uncertainty associated with the measurement result.

2.10.2. Probability distribution functions

Probability distribution is a statistical function that gives information on the spread of a data set; how the data spreads determines the interpretation thereof. In analytical chemistry, the probability distribution is used to determine measurement uncertainty by determining the interval the measured value falls within. The interval is constrained by the minimum and maximum possible values, but the location of the possible value on the probability distribution relies on various variables. These variables include the mean and standard deviation of the distribution. Depending on the distribution, the interval values can be converted to equivalent standard deviations by dividing the range with an appropriate divisor (**Table 2.3**). This standard deviation equivalent can be used to estimate the standard uncertainty.

Table 2.3 Probability distribution functions and corresponding divisors.

Distribution	**Divisor**
Normal	$K(Coverage\ factor)$
Rectangular	$\sqrt{3}$
Triangular	$\sqrt{6}$

2.10.2.1. Normal distribution

The Gaussian distribution, also known as the normal or bell-shaped distribution, is one of the most common distributions for measurement results because it characterises naturally occurring processes. That is, a probability distribution is used to evaluate the uncertainty of measurement results accumulated data falls near the average of the measurements taken (Magnusson, 2014). **Figure 2.8** represent the normal distribution curve with a coverage probability of 68.27 % in interval A.

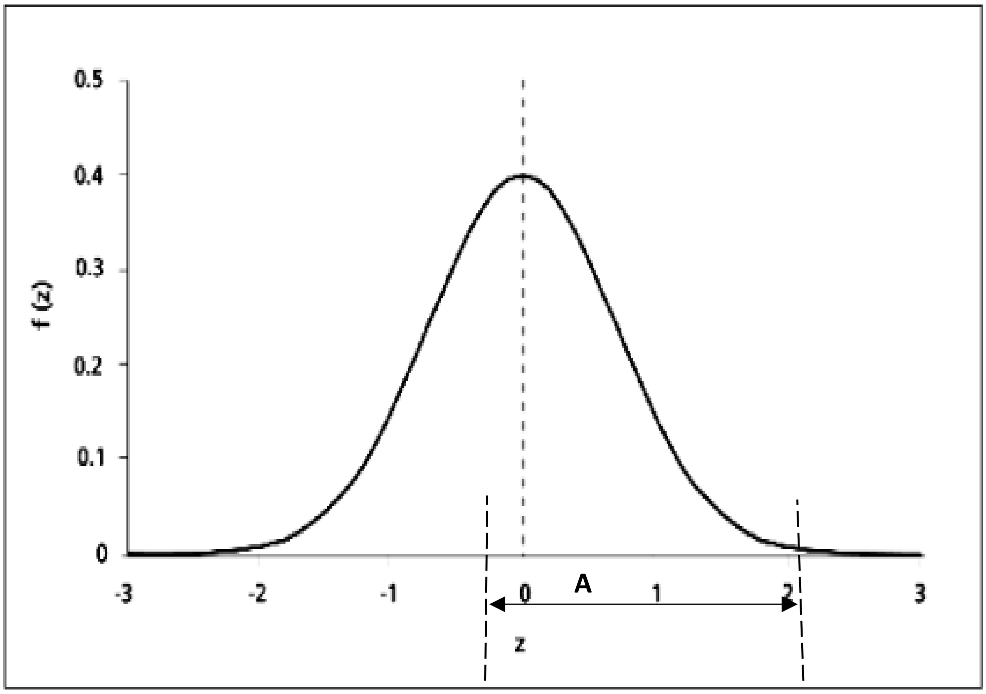

Figure 2.8 Normal distribution curve.

2.10.2.2. Rectangular distribution

Rectangular or uniform distribution is used when there is no specific information about the measured value. The distribution is evenly distributed between the lowest (a-) and highest (a+) values, with a zero probability of falling outside the specified interval. This distribution function is assumed when calculating the impurities of the starting material based on the manufacturer's specification and the limit of detection (Linsky, 2017). **Figure 2.9** illustrates the rectangular distribution curve.

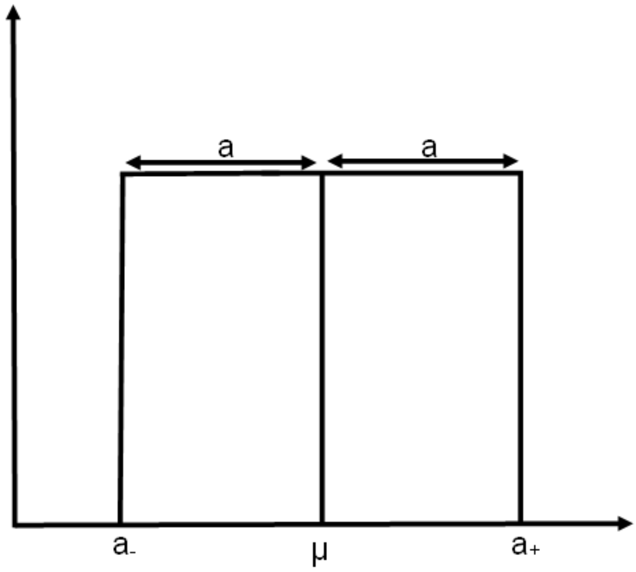

Figure 2.9 Rectangular distribution curve.

2.10.2.3. Triangular distribution

A triangular distribution is a continuous probability function that takes the shape of a triangle with a lower limit, an upper limit, and means a, b, and c, respectively where a < b and a ≤ c ≤ b. This distribution assumes that the measured value falls closer to the midpoint or mean than to the limits, as illustrated in **Figure 2.10**.

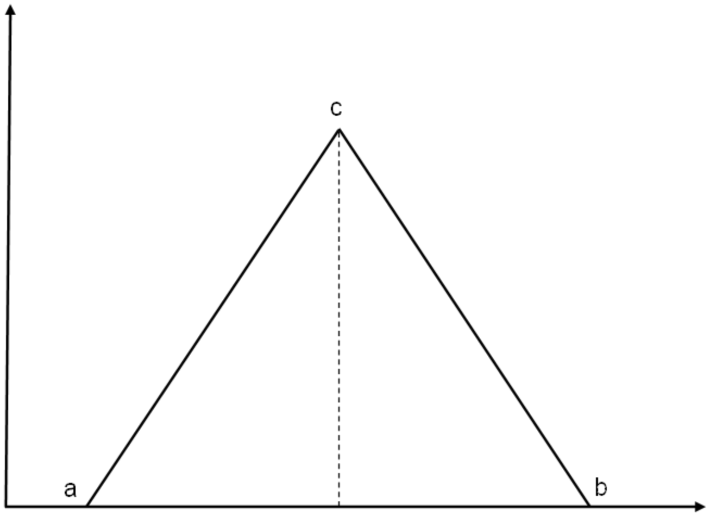

Figure 2.10 Triangular distribution curve.

CHAPTER THREE – RESEARCH RATIONALE AND OBJECTIVES

This chapter introduces the study’s motivation and rationale, problem statement, research aim and objectives, research questions, and hypothesis for the development of refinery reference gas mixtures and further document structure.

3.1. Motivation and rationale of research

The AQA was implemented to embed air quality regulations in South Africa (Republic of South Africa, 2018) promulgated for effective air pollution control, promotion of conservation, sustainable development, and the responsible use of natural resources while encouraging social and economic development. The Act provides the compliance framework for air quality governance in South Africa (Naiker et al., 2012). For compliance monitoring and reporting to government structures, air quality monitoring requires accurate, reliable, and traceable data. Therefore, the use of traceable reference gas mixtures for environmental monitoring is central to the validity of measurement activities.

The best measurement capabilities for reference gas mixtures are achieved through the development and continuous improvement of reference material production and value assignment methods. This continuous improvement in measurement capabilities contributes to scientific literature, the development of technical knowledge, and measurement solutions for the air monitoring framework and, thus, the mitigation of air pollution by providing appropriate standard gas mixtures for instrument calibration, proficiency testing services to benchmark the performance of local laboratories and disseminating traceability.

The purpose of this project is to develop refinery reference gas mixtures consisting of CO_2, CO, O_2, N_2, CH_4, C_2H_6, C_3H_8, and C_4H_6 in He by gravimetry in accordance with the ISO 6142:2015 and verification of these gases using a variety of analytical techniques.

This research also aims to provide a local measurement solution to the energy industry in South Africa and develop technical measurement capabilities for these gases. This project is furthermore beneficial in developing the technical skills and abilities at the National Metrology Institute of South Africa to participate in international comparisons to establish and maintain measurement comparability of refinery reference gas mixtures with the SI. The measurement comparability allows South Africa to benchmark its measurement capabilities to the rest of the world through international comparisons.

3.2. Problem statement

The intensive energy economy of South Africa is an environmental issue that contributes to reduced air quality in affected communities. Although the adoption of the AQA has assisted in providing practical safeguards to prevent pollution, there are no local suppliers because no traceable reference materials for energy gases have been developed in South Africa.

The study will assist in shortening the refinery gas standards' traceability chain and eliminating South Africa's dependency on international institutes for traceability while developing technical skills, encouraging measurement equivalence, and adding value to literature. Some of the global challenges in the energy gas industry are the lack of studies regarding stability, measurement uncertainty, and matrix effect issues associated with the production and measurement of refinery reference gas mixtures. This study will address these challenges by studying the behaviour of the mixture of these gases and the stability thereof.

3.3. Research aim and objectives

3.3.1. Aim

The focus of this research study is to develop multi-component refinery reference gas mixtures that comprise of carbon dioxide, carbon monoxide, 1,3-butadiene, methane, ethane, propane, nitrogen and oxygen in helium with amount fractions ranging between 1 000 $\mu mol.mol^{-1}$ and 22 $\%mol.mol^{-1}$.

3.3.2. Objectives

The following research objectives enabled the achievement of the project's aim:

a. Purity analysis of the starting materials

Quantification of methane, ethane, carbon dioxide, carbon monoxide, argon, nitrogen, oxygen, hydrogen and helium impurities associated with the starting materials by Gas Chromatography - Thermal Conductivity Detection (GC-TCD), Gas Chromatography - Flame Ionisation Detection (GC-FID), Gas Chromatography - Pulse Discharge Ionisation Detection (GC-PDHID), Gas Chromatography - Electron Capture Detection (GC-ECD).

b. Gravimetric preparation of refinery reference gas mixtures according to ISO 6142

   Preparation of refinery reference gas mixtures comprising of carbon dioxide, carbon monoxide, 1,3-butadiene, methane, ethane, propane, nitrogen and oxygen in helium in one cylinder by gravimetric preparation according to the International Organization for Standardization (ISO 6142-1:2015).

c. Method development and validation

   Develop, optimise and validate the analytical method which determines carbon dioxide, carbon monoxide, 1,3-butadiene, methane, ethane, propane, nitrogen and oxygen by investigating the repeatability, reproducibility, accuracy, selectivity and measurement uncertainty of the results.

d. Analysis of refinery reference gas mixtures

   Identification and quantification of the prepared refinery reference gas mixtures using gas chromatography coupled with various detection methods; FID, TCD, and PDHID.

e. Stability and internal consistency studies

   Make use of equal division to investigate the stability of the gas mixtures by analysing the adsorption of the prepared refinery reference gas mixtures.

   Evaluation of the internal consistency for all the prepared refinery reference gas mixtures.

f. Measurement comparability test

   Comparability of measurements between NMISA-developed refinery reference gas mixtures and other NMI-purchased refinery gas mixtures of similar matrix.

g. Matrix effect

   Study the effects of combining carbon dioxide, carbon monoxide, 1,3-butadiene, methane, ethane, propane, nitrogen, and oxygen gases in one gas cylinder on measurement results.

3.4. Research question and hypothesis

3.4.1. Research question

The research questions for this study were:

a. Is the gravimetric preparation of refinery gas mixture according to ISO 6142-1:2015 feasible?
b. How effective are the analytical methods for verification of the components of interest?
c. What properties of the major component affect the quantification of the smaller amount fraction components in the gas cylinder?
d. Are these mixtures stable?
e. Is there any matrix effect in the refinery reference gas mixtures if the matrix of the gas is changed?
f. What are the effects of the gas mixtures in relation to analytical methods and measurements uncertainties?

3.4.2. Hypothesis

Accurate gravimetric preparation of gas mixtures in accordance with ISO 6142-1:2015, the deployment of effective analytical methods, and correct quantification of gas components result in accurate and reliable multi-component refinery gas mixture production.

3.5. Dissertation structure

The purpose of this dissertation is to outline the development of refinery reference gas mixtures in a systematic manner presented as follows:

CHAPTER ONE: INTRODUCTION

This chapter gives an overview of refinery gases and how they relate to air quality monitoring in South Africa.

CHAPTER TWO: LITERATURE REVIEW

This chapter focuses on the theoretical framework that guides the development of refinery reference gas mixtures and detailed background on the components of interest in the study.

CHAPTER THREE: RESEARCH RATIONALE AND OBJECTIVES

This chapter underpins the study's motivation and rationale, the problem statement highlighting refinery gas exploration, the project's aims and objectives, as well as the research questions and hypothesis.

CHAPTER FOUR: RESEARCH DESIGN AND METHODOLOGY

This chapter provides the framework of the study by detailing the apparatus, preparation, and analytical methods used to produce refinery reference gas mixtures.

CHAPTER FIVE: RESULTS AND DISCUSSION

This chapter details and interprets the results of the purity assessment of the starting materials, gravimetric preparation, and analysis of the multicomponent refinery standard gas mixtures. It further details the numerous analytical tests performed on the developed refinery reference gas mixtures to demonstrate the suitability of the deployed analytical method for the verification of the mixtures.

CHAPTER SIX: CONCLUSIONS AND RECOMMENDATIONS

This chapter provides a summary and conclusions on the development of refinery reference gas mixtures study, including its impact, limitations, and recommendations for further research.

CHAPTER FOUR – RESEARCH DESIGN AND METHODOLOGY

This chapter provides the framework of the study by detailing the apparatus, the step-by-step preparation process followed, and analytical methods used to produce refinery reference gas mixtures.

4.1. Research design

The framework for the study was established by first quantifying impurities in high purity starting materials, followed by gravimetric preparation of refinery reference gas mixtures. The mixtures then underwent various analytical examinations on parameters such as verification of amount fractions, repeatability, reproducibility, stability of gases in the cylinders, internal consistency, adsorption/desorption, and matrix effects.

This research focused on the development of multi-component refinery reference gas mixtures with interest in the amount fraction ranges of the components of interest stated in **Table 4.1**.

Table 4.1 Amount fraction ranges for the components of interest in the development of refinery reference gas mixtures.

Component of interest	Amount fraction (μmol.mol^{-1})
Methane (CH_4)	4 000 to 60 000
Ethane (C_2H_6)	4 000 to 40 000
Propane (C_3H_8)	4 000 to 50 000
1,3-Butadiene (C_4H_6)	2 000 to 15 000
Carbon monoxide (CO)	1 000 to 100 000
Carbon dioxide (CO_2)	2 000 to 80 000
Oxygen (O_2)	1 000 to 30 000
Nitrogen (N_2)	4 000 to 220 000
Helium (He)	Balance gas

4.2. Materials

4.2.1. Starting material

High purity gases were used as starting materials for the preparation of the multi-component refinery reference gas mixtures. The high purity gases used were C_4H_6 (99.5%), CO (4.7), C_2H_6 (3.5), and C_3H_8 (3.5) sourced from Air Liquide (Pty) Ltd, a local distributor that supplies industrial and specialty gases. He and N_2 with a Built-in-Purifiers (BIP^{TM}), CO_2 (4.5), CH_4 (4.5), and O_2 (5.0) were purchased from Air Products South Africa (Pty) Ltd.

The high purity gases were stored in well-ventilated gas cages equipped with low-slope roofing and gas cylinder retaining chains outside the laboratory to protect them from the extremely varying weather conditions. The gases were further separated according to their hazard identification characteristics.

4.2.2. Instrumentation

a) *Aluminium cylinders*

Cylinders of 5 and 10 dm^3 volumes fitted with diaphragm valves of BS 341 No. 2 and 3 used for the preparation of the multi-gas refinery reference gas mixtures were purchased from Luxfer Gas Cylinders Ltd United Kingdom. After the cylinders were delivered, they underwent pre-treatment for fluorination and helium leak test to passivate the inner surfaces. Pelchem (Pty) Ltd performed the fluorination process to permanently prevent any distortions of the inner walls of the cylinders, Air Products South Africa (Pty) Ltd valved the cylinders and performed the helium leak test after the valving of the cylinders to ensure no leaks were present after the fitting of the valves.

b) *Evacuation system*

Air and Vacuum Technologies (Pty) Ltd evacuation station equipped with a turbo molecular pump (model HiCube 400) with the capability of reaching pressures as low as 8.4×10^{-8} mbar and a residual gas venting line. The vent lone is connected to an extraction system was used for the removal of residual gas from the cylinders before the commencement of the preparation of the gas mixtures.

c) *Mass comparators*

Automated Weighing System (AWS) mass comparator with a Mettler Toledo calibrated balance (model XPE26003LC) manufactured and commissioned by the Korean Research Institute of Standards and Science (KRISS) with a resolution of 0.001 g was used for the weighing of the gas cylinders to ensure traceability of the gas mixtures to the SI through the kg. The balance has a capacity of 26 kg and can weigh three sample cylinders against a reference cylinder simultaneously. The RADWAG mass comparator calibrated balance (model APP 30.4Y.KO) was used for targeting the mass of the desired amount fraction of the parent gas mixtures required during the filling of the cylinders.

d) *Calibrated mass pieces*

The 10 and 20 kg calibrated mass pieces were used to perform internal and external adjustments on the mass comparator balances.

e) *Filling station systems*

Air and Vacuum Technologies designed filling stations equipped with a turbo molecular pump (model TC110) fitted with gas transfer lines and vacuum pumps were used for the gas transfer from the parent cylinder to the sample cylinder.

f) *Gas blending system*

Roller bench designed by AmadwalaSA was used to mix the gases in the cylinder to enable homogeneity of the gases.

g) *Analysis equipment*

Agilent CP-3800 gas chromatographs coupled with various detectors such as TCD, FID and PDHID were used for the purity analysis of the high purity gases and quantification of the components of interest in the gravimetrically prepared reference gas mixtures.

h) *Software*

The AWS mass weighings were recorded using LabVIEW software, which was supplemented by GravCalc Version 2.03.001 software, which was used to calculate the final amount fractions of the prepared gas mixtures using the mass data from the LabVIEW software and generate a report known as a purity table. Openlab software was used to control and store the analysis data on the Agilent CP-3800 gas chromatography instruments.

4.3. Purity analysis of starting material

Purity analysis forms part of the essential initial step in the development of multi-component refinery gas mixtures. Identification of the trace levels of critical and significant impurities in the matrix of high purity gas starting materials is done to establish metrological traceability by verifying the gas composition. The International Organization for Standardization's ISO 19229:2015 (Gas analysis — Purity analysis and the treatment of purity data) was used as a guide for the trace analysis of all high purity gas starting materials. The starting materials used were of the highest purity the manufacturer could provide, which minimised the impurities in the gases.

In this study, the quantification of impurities in the starting materials was done using traceable primary standard gas mixtures that were gravimetrically prepared to closely match the estimation of the impurities in the high purity starting materials. And where quantification was not possible due to a lack of analytical techniques, the manufacturer's specification (MS) was divided by 2 to calculate the amount fraction of the impurities in the high purity gases, assuming a rectangular distribution as shown in **equation 4.1**.

$$x_i = \frac{ms_i}{2} \qquad \textbf{4.1}$$

Where x_i is the amount fraction of the impurities and ms_i is the manufacturer's specification.

Impurities that were below the limit of detection (LOD) of the analytical method used were calculated using **equation 4.2**.

$$LOD = 3\frac{\sigma}{S} \qquad \textbf{4.2}$$

Where σ is the standard deviation of the analytical response and S is the slope of the calibration curve (Shrivastava, A. and Gupta, V.B., 2011).

The standard uncertainties (u) associated with x_i and LOD were evaluated assuming a rectangular distribution using **equation 4.3**.

$$u = \frac{LOD/x_i}{\sqrt{3}} \tag{4.3}$$

Purity analysis was done using Agilent gas chromatographs coupled with a pulse discharge ionisation detector for permanent gas analysis and gas chromatographs coupled with a flame ionisation detector fitted with a methanizer (nickel-based catalyst) for carbon dioxide, carbon monoxide, and hydrocarbon analysis. The GC is made up of a carrier gas, sampling, separation, detection, and data recording systems, as shown in **Figure 4.1**. This process separates the different gas components in the mixture by injecting the sample into the inlet, letting the gas pass through a column coated with a suitable adsorbent material inside the oven with the help of the carrier gas to the detector, and monitoring the eluent from the column through the computer.

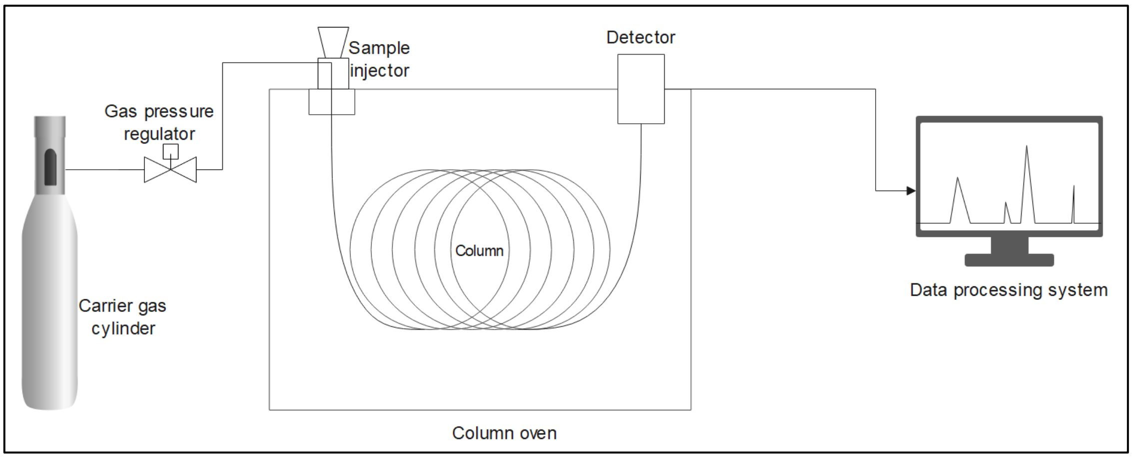

Figure 4.1 Schematic diagram of the gas chromatography system.

4.3.1. Purity assessment of high purity gases using flame ionisation detector

Purity assessment of CO, CO_2, CH_4, and C_2H_6 in all high purity gas starting materials was done by making use of the Agilent gas chromatograph coupled with three different detectors: the electron capture detector, the pulsed discharge ionisation detector, and the flame ionisation detector. Moreover, the flame ionisation detector was used for the quantification of trace of CO, CO_2, CH_4, and C_2H_6. The FID was used as it is a technique that is selective for C-H bonds and, paired with a methanizer, converts CO and CO_2 to methane that is detectable by the detector. **Table 4.2** details the optimised experiment conditions on the GC for the analysis of CO, CO_2, CH_4, and C_2H_6. Two multicomponent gas standards of 1 µmol.mol^{-1} CO/ CO_2/ CH_4/ C_2H_6 in N_2 and 6 µmol.mol^{-1} CO/ CO_2/ CH_4/ C_2H_6 in N_2 were used to verify the amount fractions of the impurities in the high purity gases. At a sample flow rate of 35 mL.min^{-1}, the standards and high-purity gases were randomly connected to the VICI multi-position micro-electric valve actuator. The LOD was calculated using **equation 4.2**, where quantification was not possible.

Table 4.2 GC FID channel's analytical conditions on the Agilent GC GC-FID/PDHID/ECD for analysis of trace CO, CO_2, CH_4, and C_2H_6 in the high purity starting materials.

Parameters	**Experimental conditions**
Detector	Flame ionisation detector (FID)
Column	ShinCarbon ST 80/100 2m 2mmID 1/8''OD Silico
Oven temperature	35℃ and ramped to 170℃ @ 1.6 minutes
Carrier gas	Nitrogen
Sample loop	500 µL
Sample flow	35 mL/min^{-1}
Total run time	7.45 minutes

The analysis of CO, CO_2, CH_4, and C_2H_6 was performed using a ShinCarbon ST 80/100 packed column because of its capacity to separate hydrocarbons and permanent gases. As shown in **Figure 4.2**, the FID channel was configured on two valves, one 6-port and one 10-port diaphragm valve. The sample was introduced to the GC by a VICI multi-position micro-electric valve actuator, facilitated by Varian Serial Stream Selection Valve (SSV) 5.31 control software, and the valve switch is supported by the Galaxie Chromatography program.

Valve 1 was used to introduce the sample into the GC. The sample entered the GC through port 3 and was then loaded into the 500 µL sample loop by moving the valve to the "loading position". The sample was then moved to the ShinCarbon ST 80/100 packed column through port 5 by switching Valve 1 to the "injecting" position. The sample then flowed through the methanizer, where the CO_2 and CO were converted to CH_4. The FID separated and detected carbon dioxide, carbon monoxide, methane, and ethane.

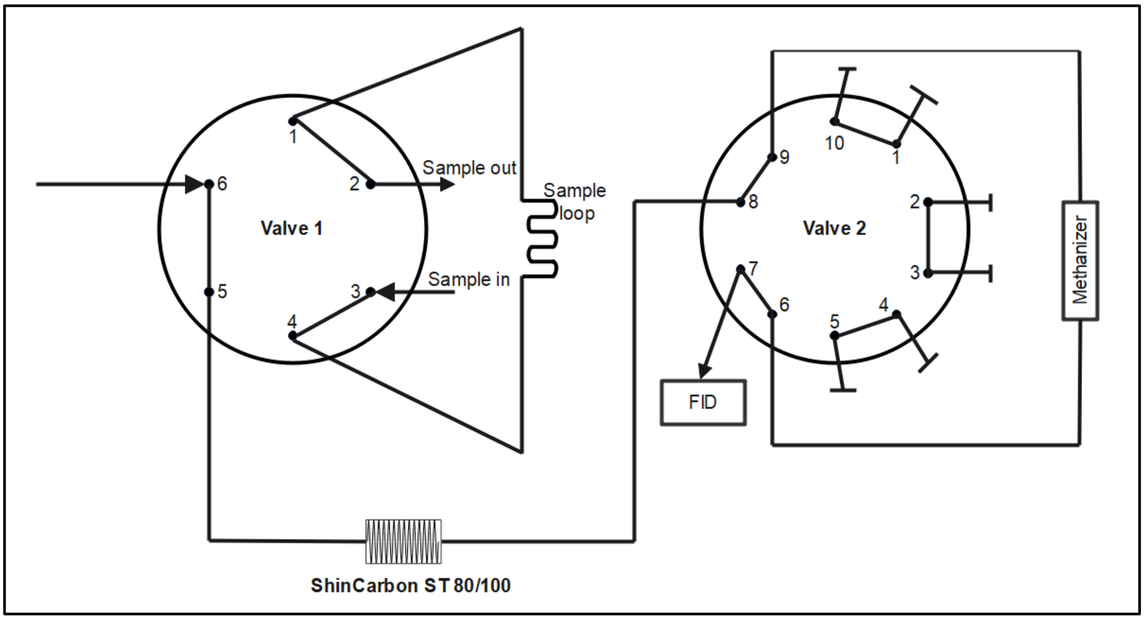

Figure 4.2 GC FID configuration on the Agilent GC-ECD/FID/PDHID used for purity assessment of CO, CO_2, CH_4 and C_2H_6.

4.3.2. Purity assessment of high purity gases using pulsed discharge helium ionisation detector

The analysis of trace H_2, N_2, Ar, and O_2 was performed using an Agilent gas chromatograph equipped with a pulsed discharge helium ionisation detector, a thermal conductivity detector, a flame ionisation detector, and a nitrogen chemiluminescence detector (NCD). The PDHID channel was fitted with a 50 m long, 0.53 mm internal diameter and 50 µm film thickness capillary Molecular Sieve 5Å column, 250 µL sample loop and helium carrier gas. The sample was introduced into the system through a 250 µL sample loop and a 6-port diaphragm valve in the 40℃ column oven and ran for 9 minutes. **Figure 4.3** shows a schematic representation of the GC-PDHID system with a 6-port valve in the "load" position (shown as the solid lines) and the "inject" position (shown in the dotted orange lines).

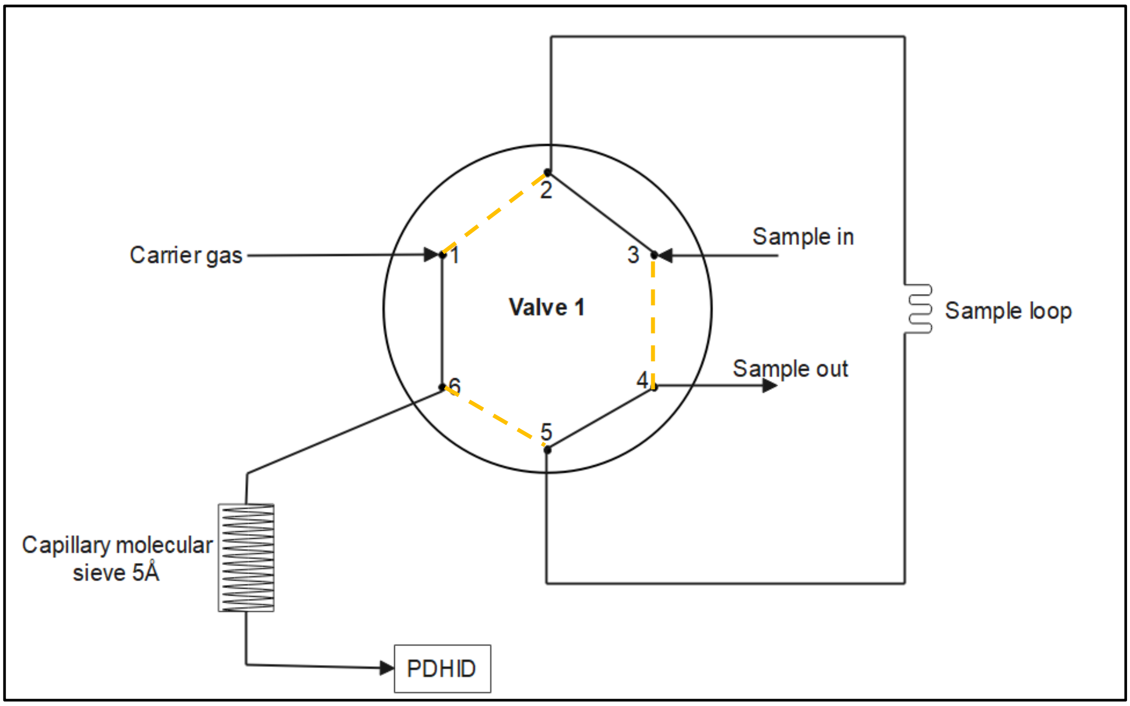

Figure 4.3 Schematic representation of a 6-port valve on the GC-PDHID system with the "load" position (shown as the solid lines) and "inject" position (shown in the dotted orange lines.

4.4. Gravimetric preparation of reference gas mixtures

The refinery reference gas mixtures were prepared gravimetrically in accordance with the ISO 6142-1:2015 Gas analysis — *Preparation of calibration gas mixtures — Part 1: Gravimetric method for Class I mixtures* detailing the preparation of calibration gas mixtures that are traceable to the amount fraction of at least one component in the gas mixture making use of a gravimetric method. The gravimetric preparation of the gas mixtures used a quantitative method where the determination of the amount fraction of the components of interest added into the gas cylinder were measured by the weighing difference between the sample and reference cylinder.

The gravimetric preparation process included the pre-treatment of the cylinder, cleaning of the cylinder exterior of dust particles, and evacuation of the cylinders using a Pfeiffer turbo molecular pump vacuum to achieve a vacuum. The evacuated cylinders were then weighed against a reference cylinder with a similar valve type on the AWS, then connected to a filling system to add the components of interest. This process was done until all the gases of interest were transferred into the sample gas cylinder. The cylinders were then homogenised by rolling on the roller bench for a minimum of 2 hours. The process for the gravimetric preparation of the refinery reference gas mixtures is illustrated by the flow diagram in **Figure 4.4**.

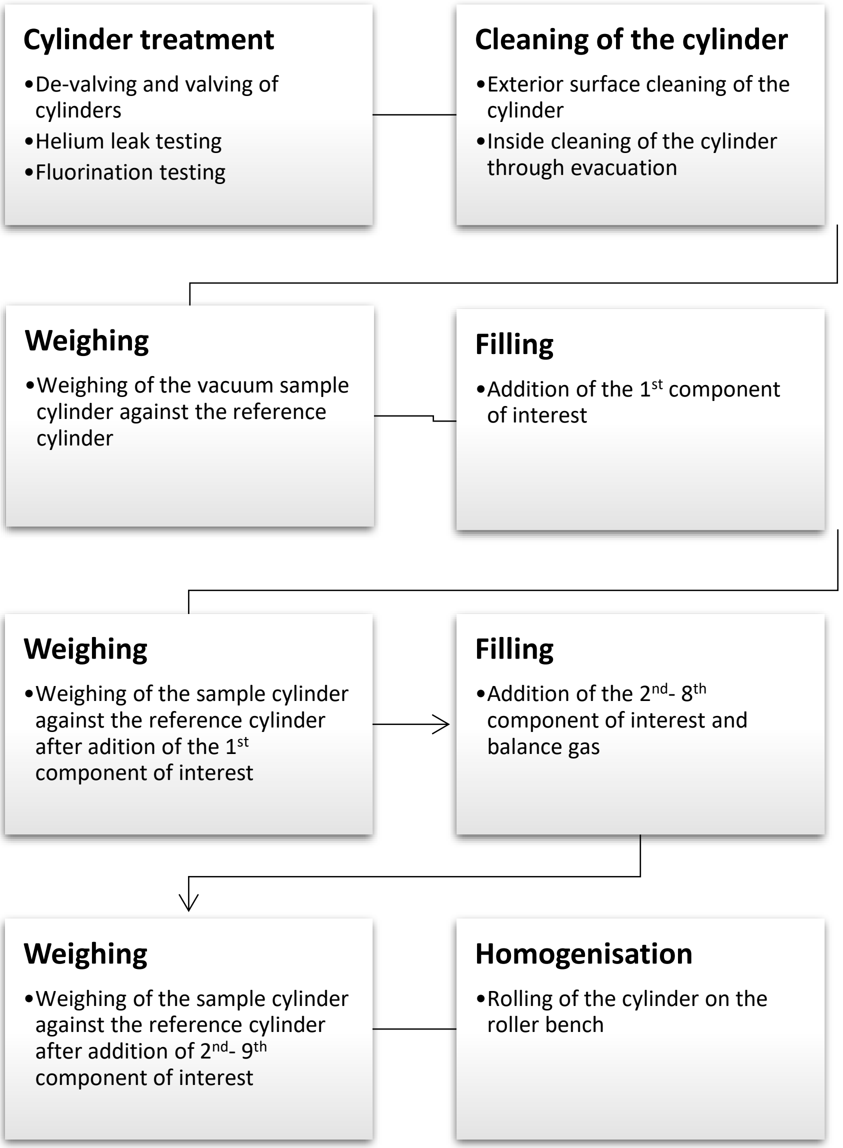

Figure 4.4 The process of gravimetric preparation of refinery reference gas mixtures.

4.4.1. Environmental controls maintained during preparation of the gas mixtures.

Throughout the study, the laboratory's environmental conditions were kept at an ambient temperature of 20 ± 2 ºC and relative humidity of 45 ± 20 %RH. Calibrated Rotronic HygroLog HL-1D electronic data loggers were used for the monitoring of temperature and relative humidity.

4.4.2. Cleaning and evacuation of the gas cylinders

The exterior walls of the cylinders were cleaned inside a fume cupboard with thinners and paper towels to remove any marks and dust particles that had accumulated on the cylinder walls to achieve a similar finish to the reference cylinder. This reduced uncertainty during the weighing process. The cleaning was done while wearing nitrile gloves for protection from the harmful properties of the thinners used.

The cylinders were then connected to an evacuation system equipped with a turbo molecular pump and a residual gas venting line. The turbo molecular pump extracts residual gas and maintains a high vacuum in the cylinders, while the venting lines are connected to an extraction system and the atmosphere to allow for the removal of residual gas and moisture particles from the inside walls of the cylinders to the atmosphere, as shown in **Figure 4.5**. The cylinders were left to be evacuated overnight to a desired vacuum pressure of less than 2.5 x 10^{-6} mbar.

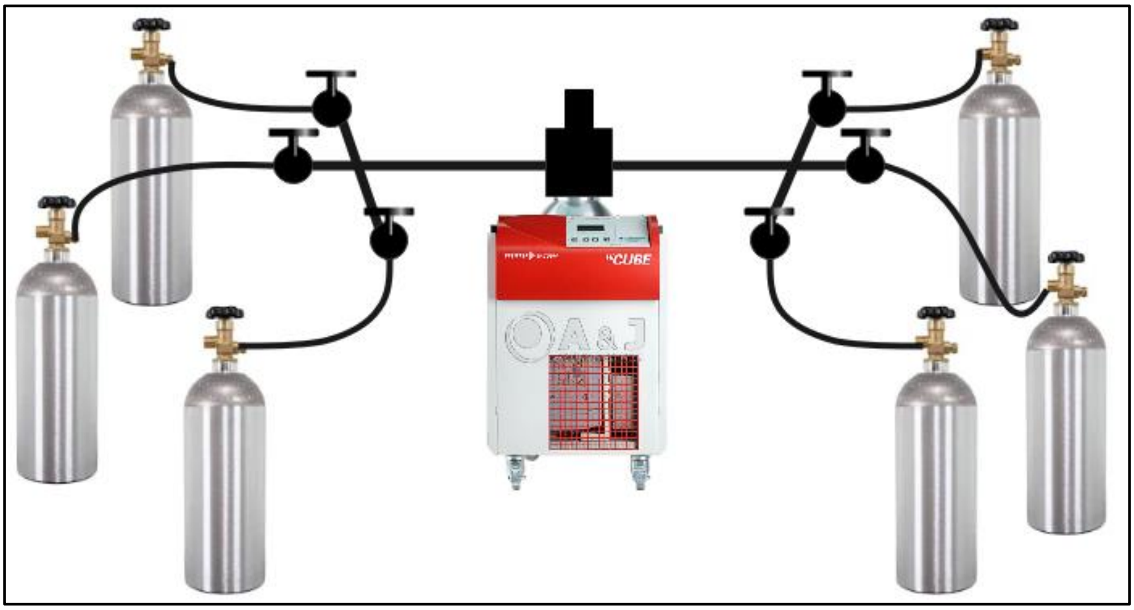

Figure 4.5 Gas cylinder evacuation system.

4.4.3. Weighing of the gas cylinders

Each evacuated cylinder was weighed on the AWS mass comparator against a reference cylinder of similar valve type and mass to allow for correction of the buoyancy effect and account for balance drift and changing atmospheric conditions during weighing (Aoki et al., 2019). With each addition of the components of interest, the sample cylinder is weighed against the reference cylinder. The difference between the masses of the sample and the reference cylinder represents the mass of the component of interest added into the sample cylinder; this is known as the substitution method. This method is based on mass difference weighing and is thus directly traceable to the SI unit of mass (kg). The phrase "weighing by difference" is used interchangeably with the substitution method because of the nature of the method. **Figure 4.6** shows the automatic weighing system used for the preparation of the gas mixtures.

The weighing sequence followed was $R \rightarrow S$ method, where R is the reference gas cylinder and S is the sample cylinder. The LabVIEW software was used to collect the data for the weighing from the AWS mass comparator. With each measurement, the software takes an average of 90 readings in 20 seconds. The cycle was continued until the standard deviation of the latest three measurement differences was less than 2 mg.

Figure 4.6 A mass comparator with an automated weighing system and a Mettler Toledo balance for weighing gas cylinders.

4.4.4. Filling of gas cylinders

The weighed vacuum sample cylinder was connected to a filling station, where the parent gas mixtures were transferred into it. The filling station, depicted in **Figure 4.7**, is a closed system that comprises of stainless-steel gas transfer lines on both sides of the station to transfer gas from one cylinder to another, a vacuum pump that evacuates the gas transfer lines to a vacuum of at least 2.0 x 10^{-5} mbar, a Pfeiffer D-35614 Asslar digital display and operating unit (Model DCU 110), needle valves to control the flow of the gas, and a gas venting line connected to an extraction system. On the right-hand side of the filling station is a RADWAG mass comparator balance that measures the mass of the gas added into the sample cylinder during transfer.

For the addition of the first target component, the weighed vacuum sample cylinder was placed on the mass comparator to the right of the filling station and connected to the filling station through the stainless-steel gas transfer line. To the left of the filling station, the parent gas mixture was connected. Any potential leaks in the system were checked by using high-pressure BIP N_2 gas cylinder that was purged through the system and Snoop liquid leak detector. The presence of a leak could be identified by a pressure drop on the filling station's digital pressure display and bubbling in the gas line connection when the SNOOP comes into contact with gas leaks. After the leak inspections, the gas transfer lines were purged at least eight times with the parent gas to minimise cross-contamination. With each purge of gas, the gas was vented out of the system and the system was evacuated to a vacuum of less than 2.0×10^{-5} mbar. After purging, the system was pressured with the target pressure of the component of interest. Then the RADWAG mass comparator balance was zeroed prior to adding the component of interest. When the balance reading was at zero, the sample cylinder was opened to start transferring the desired amount of the parent gas. When the targeted mass was added to the sample cylinder, the cylinder was closed, and the rest of the gas left in the system was vented into the atmosphere. This procedure was repeated until all target components were added into the cylinder.

Figure 4.7 Filling station system with a RADWAG mass comparator balance used for gas transfer into the sample cylinder.

4.4.5. Homogenising of the gas mixtures

After the addition and weighing of all components of interest into a sample cylinder, the cylinder was rolled on the roller bench for a minimum of 2 hours to homogenise the gas mixture, as shown in **Figure 4.8**. This step is crucial to facilitate the uniform mixing of the sample's components.

Figure 4.8 Roller bench for the homogenization of gas mixtures.

4.5. Gravimetric preparation of multi-component refinery reference gas mixtures

The multi-component refinery reference gas mixtures in this study were classified into two amount fraction ranges of 1 to 22 %mol.mol^{-1} and 1 000 to 4 000 µmol.mol^{-1}. These gas mixtures were referred to as the high range and low range, respectively, to provide a clear contrast. The compositions of the refinery reference gas mixtures in the study were expressed in molar expressions of %mol.mol^{-1} and µmol.mol^{-1} that can be converted to mass fraction unit of mg.dm^{-3}. For the gravimetric preparation of the refinery gas mixtures, ISO 6142:2015 was followed.

Factors such as cylinder volume, pressure of parent gas mixtures, and target pressures are critical as they affect the target mass for the components of interest and the final pressure of the sample gas mixture. The ideal gas law (**equation 4.4**) was assumed for the mass estimation of the components of interest needed from the parent gas.

$$m_i = \frac{x_i \times P_{cyl} \times V_{cyl} \times M_i}{R \times T \times Z_f} \qquad \textbf{4.4}$$

where m_i is mass (g) of component i, x_i is the intended amount fraction of component i, P_{cyl} is the final fill pressure (Pa) of the mixture, V_{cyl} is the volume (m^3) of cylinder used, M_i is molar mass(g.mol^{-1}) of component i, R is the gas constant (8.31451 J.mol^{-1}.K^{-1}), T is the temperature in Kelvin (0 ℃ + 273.15 K) and Z_f is the compressibility factor (1).

4.5.1. Gravimetric preparation of the high range multi-component refinery reference gas mixtures.

Four refinery reference gas mixtures of amount fractions 1 %mol.mol^{-1} O_2/ 1.5 %mol.mol^{-1} C_4H_6/ 4 %mol.mol^{-1} C_2H_6/ 5 %mol.mol^{-1} C_3H_8/ 6 % mol.mol^{-1} CH_4/ 8 %mol.mol^{-1} CO_2/ 10 %mol.mol^{-1} CO and 22 %mol.mol^{-1} N_2 in He were prepared in 10 dm^3 using a one-step dilution from high purity gases, as shown in **Figure 4.9**. The evacuated sample cylinders were weighed on the AWS mass comparator balance using the substitution method. The sample cylinders were then connected to the filling station, which was used (one at a time) to add the refinery gas components of interest. The sample cylinder and high purity gases were connected on opposite ends of the station, and the filling process was completed as described in **Section 4.4.4**, where the target pressure was calculated using **equation 4.5**.

$$P_{target} = \frac{C_{required}}{C_{hp}} \times P_{required} \qquad \textbf{4.5}$$

Where P_{target} is the target pressure (bar) needed in the sample cylinder, $C_{required}$ is target amount fraction (%mol.mol^{-1}) of the sample mixture, C_{hp} is the amount fraction (%mol.mol^{-1}) of the high purity gas and $P_{required}$ is the pressure (bar) required from the pre-mixture to the sample mixture.

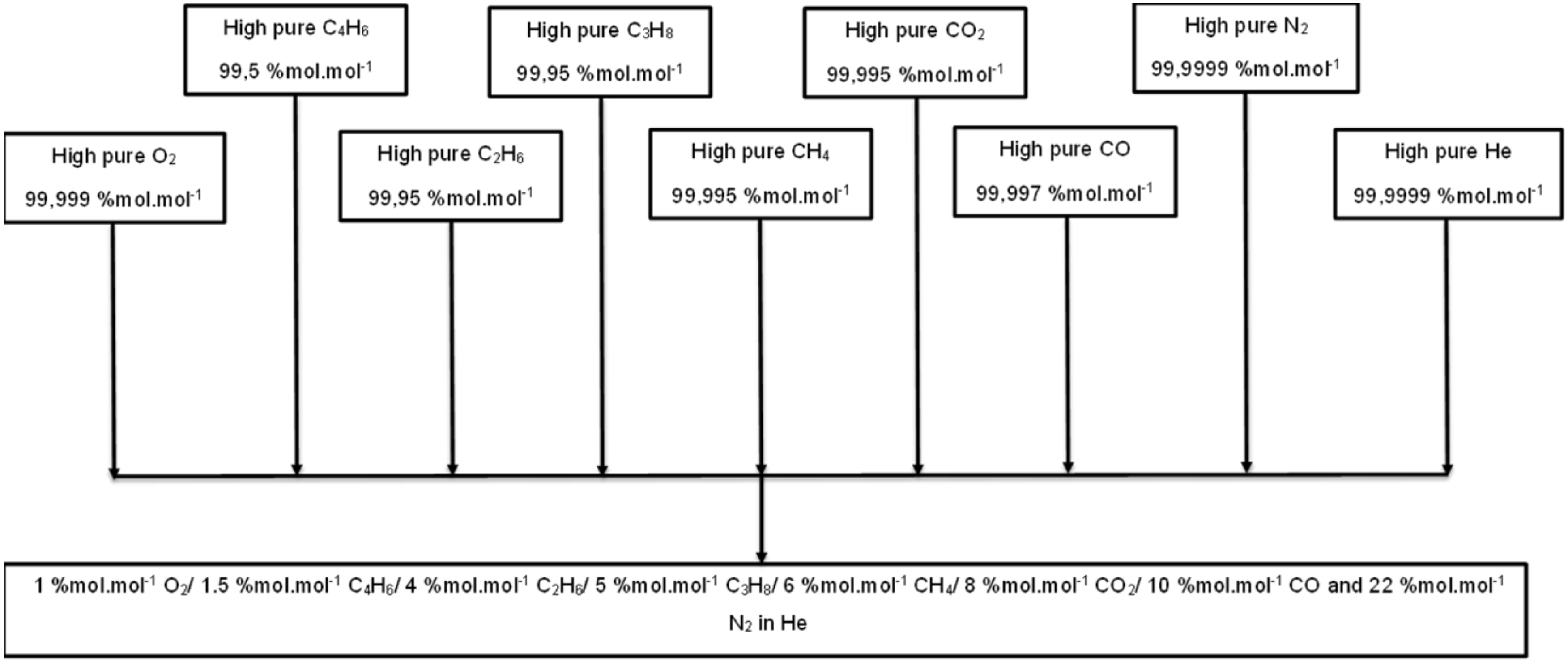

Figure 4.9 A schematic diagram for the production of the high range refinery reference gas mixtures.

The target masses of the starting materials required to produce 1 %mol.mol^{-1} O_2/ 1.5 %mol.mol^{-1} C_4H_6/ 4 %mol.mol^{-1} C_2H_6/ 5 %mol.mol^{-1} C_3H_8/ 6 %mol.mol^{-1} CH_4/ 8 %mol.mol^{-1} CO_2/ 10 %mol.mol^{-1} CO and 22 %mol.mol^{-1} N_2 in He were calculated to determine the target amount fractions of the components of interest in the gas mixtures. **Table 4.3** tabulates the molar masses of all the components of interest, the amount fractions of each component of interest in the high purity gases, mass and pressure estimations, and the final calculated amount fractions. The mass required for the starting material was roughly calculated, and after each component of interest was added, a re-calculation was performed by considering the actual added mass to approximate the mass needed for the next high purity gas starting material. Purity tables displaying the actual composition of the prepared gas mixtures were created using the GravCalc Version 2.03.001 programme after all the components had been added and are presented in **Chapter Five**. For this project, the composition of the gases listed on the purity tables was expressed in molar fractions (µmol.mol^{-1}).

Table 4.3 Estimated masses and pressures for the preparation of 1 %mol.mol^{-1} O_2/ 1.5 %mol.mol^{-1} C_4H_6/ 4 %mol.mol^{-1} C_2H_6/ 5 %mol.mol^{-1} C_3H_8/ 6 %mol.mol^{-1} CH_4/ 8 %mol.mol^{-1} CO_2/ 10 %mol.mol^{-1} CO and 22 %mol.mol^{-1} N_2 in He gas mixtures.

		CO_2	**CO**	**O2**	**N_2**	**CH_4**	**C_2H_6**	**C_3H_8**	**C_4H_6**	**He**
Components of interest	M^1 $(g.mol^{-1})$	x^2 $(mol.mol^{-1})$								
CO_2	44.0099	1.00 x 10^{0}	5.00 x 10^{-7}	1.33 x 10^{-6}	6.00 x 10^{-8}	5.40 x 10^{-8}	5.00 x 10^{-7}	2.50 x 10^{-6}	0.00 x 10^{0}	1.25 x 10^{-8}
CO	28.0106	2.24 x 10^{-8}	1.00 x 10^{0}	2.45 x 10^{-7}	5.00 x 10^{-8}	0.00 x 10^{0}	5.00 x 10^{-7}	0.00 x 10^{0}	0.00 x 10^{0}	1.25 x 10^{-8}
O_2	31.9988	0.00 x 10^{0}	5.90 x 10^{-6}	1.00 x 10^{0}	6.00 x 10^{-9}	1.09 x 10^{-7}	5.00 x 10^{-7}	5.00 x 10^{-6}	0.00 x 10^{0}	5.00 x 10^{-9}
N_2	28.013	3.16 x 10^{-5}	2.50 x 10^{-6}	4.11 x 10^{-4}	1.00 x 10^{0}	3.11 x 10^{-6}	1.50 x 10^{-6}	9.20 x 10^{-4}	6.81 x 10^{-3}	5.00 x 10^{-8}
CH_4	16.043	6.71 x 10^{-6}	1.00 x 10^{-6}	1.44 x 10^{-7}	1.00 x 10^{-8}	1.00 x 10^{0}	0.00 x 10^{0}	2.04 x 10^{-6}	0.00 x 10^{0}	2.50 x 10^{-8}
C_2H6	30.070	6.00 x 10^{-9}	0.00 x 10^{0}	6.00 x 10^{-8}	5.00 x 10^{-9}	6.50 x 10^{-8}	1.00 x 10^{0}	8.72 x 10^{-5}	0.00 x 10^{0}	0.00 x 10^{0}
C_3H_8	44.097	0.00 x 10^{0}	1.95 x 10^{-7}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	9.99 x 10^{-1}	0.00 x 10^{0}	0.00 x 10^{0}
C_4H_6	54.092	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	9.99 x 10^{-1}	0.00 x 10^{0}
He	4.003	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	0.00 x 10^{0}	1.00 x 10^{0}
Estimated mass (g)		125.51	99.49	12.84	218.20	32.91	43.92	78.47	28.70	61.00
Pressure (bar)		6.93	8.63	0.98	18.93	4.99	3.55	4.33	1.29	37.05
Calculated amount fractions (%$mol.mol^{-1}$)		8	10	1	22	6	4	5	1.5	42.5

^1M is the molar mass of the components of interest in $g.mol^{-1}$

^2x is the the amount fraction of the components of interest in the high purity gases.

4.5.2. Gravimetric preparation of the low range multi-component refinery reference gas mixtures.

Figure 4.10 shows the production diagram for the development of four refinery reference gas mixtures, highlighting the multi-step dilutions deployed to achieve the desired amount fractions of 4 000 µmol.mol^{-1} N_2 / 4 000 µmol.mol^{-1} CH_4 / 4 000 µmol.mol^{-1} C_2H_6 / 2 000 µmol.mol^{-1} C_4H_6/ 4 000 µmol.mol^{-1} C_3H_8 / 1 000 µmol.mol^{-1} O_2 / 1 000 µmol.mol^{-1} CO/ 2 000 µmol.mol^{-1} CO_2 in He. The multi-step dilution was necessary due to the one-step dilution's mass, pressure, and acceptable uncertainty limitations (Milton et al., 2011). Milton et al. (2011) described a mathematical relationship for "developing optimal serial dilution strategies" to minimise uncertainties associated with the smallest mass of 15 g that can be weighed.

The first-dilution step consisted of three sets of different multi-component pre-mixtures utilised for the preparation of the final multi-component reference gas mixtures containing all components of interest mentioned in **Table 4.1**. All the multi-component pre-mixtures were gravimetrically prepared from the high purity gas starting materials. In each set, four identical pre-mixtures were prepared and verified before further dilutions. **Set 1** had four reference gas mixtures of 10 %mol.mol^{-1} N_2 /10 %mol.mol^{-1} CH_4 and 10 %mol.mol^{-1} C_2H_6 in He prepared in 5 dm^3 gas cylinders with maximum pressures of 11.0 Megapascals (MPa). **Set 2** had four gas mixtures of 2 %mol.mol^{-1} C_4H_6 and 4 %mol.mol^{-1} C_3H_8 in He prepared in 5 dm^3 gas cylinders with maximum pressures of 8.7 MPa. And **Set 3** included four gas mixtures of 4 %mol.mol^{-1} O_2/ 4 %mol.mol^{-1} CO and 8 %mol.mol^{-1} CO_2 in He prepared in 5 dm^3 gas cylinders with maximum pressures of 13.0 MPa.

The final dilution step included four reference gas mixtures of 4 000 µmol.mol^{-1} N_2 / 4 000 µmol.mol^{-1} CH_4 / 4 000 µmol.mol^{-1} C_2H_6 / 2 000 µmol.mol^{-1} C_4H_6/ 4 000 µmol.mol^{-1} C_3H_8 / 1 000 µmol.mol^{-1} O_2 / 1 000 µmol.mol^{-1} CO/ 2 000 µmol.mol^{-1} CO_2 in He amount fractions. The mixtures were prepared in 10 dm^3 gas cylinders at 11.0 MPa. These mixtures were prepared in 10 dm^3 instead of 5 dm^3 to ensure pre-mixture mass additions of at least 10 g to ensure that the final prepared gas mixture's weighing uncertainty is minimised.

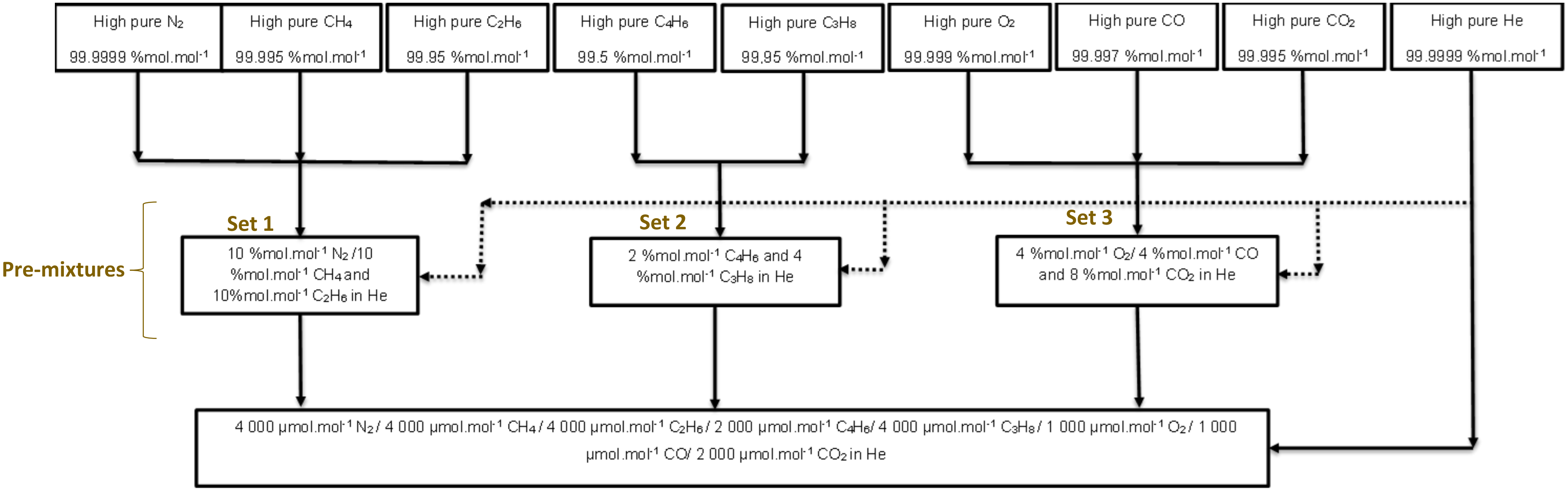

Figure 4.10 A schematic diagram for the production of the low range refinery reference gas mixtures.

4.6. Calibration model

The verification of the amount fractions of the different components of interest in the gas mixtures was done using the single-point calibration method. In this method, the sample mixture is compared to a reference mixture with the assumption that the calibration curve intercept is zero and that the change in response of the reference mixture is directly proportional to that of the sample mixture (Cuadros-Rodríguez et al., 2001). The verification sequence followed was *reference-sample-reference*, and the sample amount fraction was calculated using **equation 4.6**. This is also known as the A-B-A method where A is the reference gas mixture and B is the sample gas mixture in the analysis sequence. This method allowed for repeatability and drift analysis studies.

$$x_{Sample} = \frac{y_{Sample}}{y_{Reference}} \times x_{Reference} \qquad \textbf{4.6}$$

Where x_{sample} and y_{sample} are the amount fraction and GC response of the sample gas mixture, and $x_{ref}$and y are the amount fraction and GC response of the reference gas mixture respectively.

4.7. Verification of refinery reference gas mixtures

The gas mixtures were analysed using the single-point calibration method on the Agilent 7890B gas chromatographs in accordance with ISO 6143:2001 ‘*Gas analysis — Comparison methods for determining and checking the composition of calibration gas mixtures*’ (ISO 6143:2001). This was done to provide evidence of the consistency of the analytical values and the gravimetric values. The TCD and FID channels were used for the analysis of all the gas mixtures prepared in this study. These channels use a measurement method based on the separation of target gases between two immiscible phases: a mobile gaseous phase, in the form of a carrier gas, for sample transportation, and a solid stationary phase, in the form of a column. The sample is introduced into a heated inlet system where it is vaporised and transported to the GC column through a gaseous carrier. The sample analytes are then adsorbed on the stationary phase in the column and eluted according to their affinity for the stationary phase (Taha, 2018).

ISO 6143's criterion in **equation 4.7** to determine reliability and verification of each component of interest in the mixture was adopted.

$$\left|x_{grav} - x_{ver}\right| \leq 2\sqrt{u(x_{grav})^2 + u(x_{ver})^2} \qquad \textbf{4.7}$$

where x_{grav} and x_{ver} is the gravimetric and verification amount fractions; and $u(x_{grav})$ and $u(x_{ver})$ is the gravimetric and verification standard uncertainty, respectively.

4.7.1. Verification of CH_4, C_2H_6 and N_2 in He multi-component pre-mixtures

After preparation, a multi-detector GC with dual TCD (auxiliary and front) and FID channels was used for the verification of the 10 %mol.mol^{-1} CH_4, 10 %mol.mol^{-1} C_2H_6 and 10 %mol.mol^{-1} N_2 in He pre-mixtures. The front TCD channel was used for the quantification of the nitrogen component in the mixture, and the FID channel was used for the verification of the methane and ethane components in the gas mixture. Hydrogen and nitrogen gases were used as carrier gases for TCD and FID channels. The sample was loaded into the injection port and further reduced by a split ratio of 2:1 using the split injection system, where a controlled fraction of the injected sample ends up entering the column. The sample then travelled to the column where component separation happens. The Molecular Sieve 13X column was used on the TCD, and the PLOT Al_2O_3 KCl 50m x 0.320 mmID column was used on the FID, with the oven temperature held isothermally at 40℃ for 4 minutes. The pre-mixture gases were connected to the detector through a series of connections: a gas pressure regulator that was flushed several times into an extraction arm to prevent possible gas line contamination, sampler box to measure the inlet pressurised sample gas, quick connector, and 1/16” stainless steel tubing. The sample mixtures were pressurised to 35 ml/min. **Figures 4.11 and 4.12** show schematic representations of the front TCD and FID channels, respectively. The optimised analytical conditions are listed in **Table 4.4**.

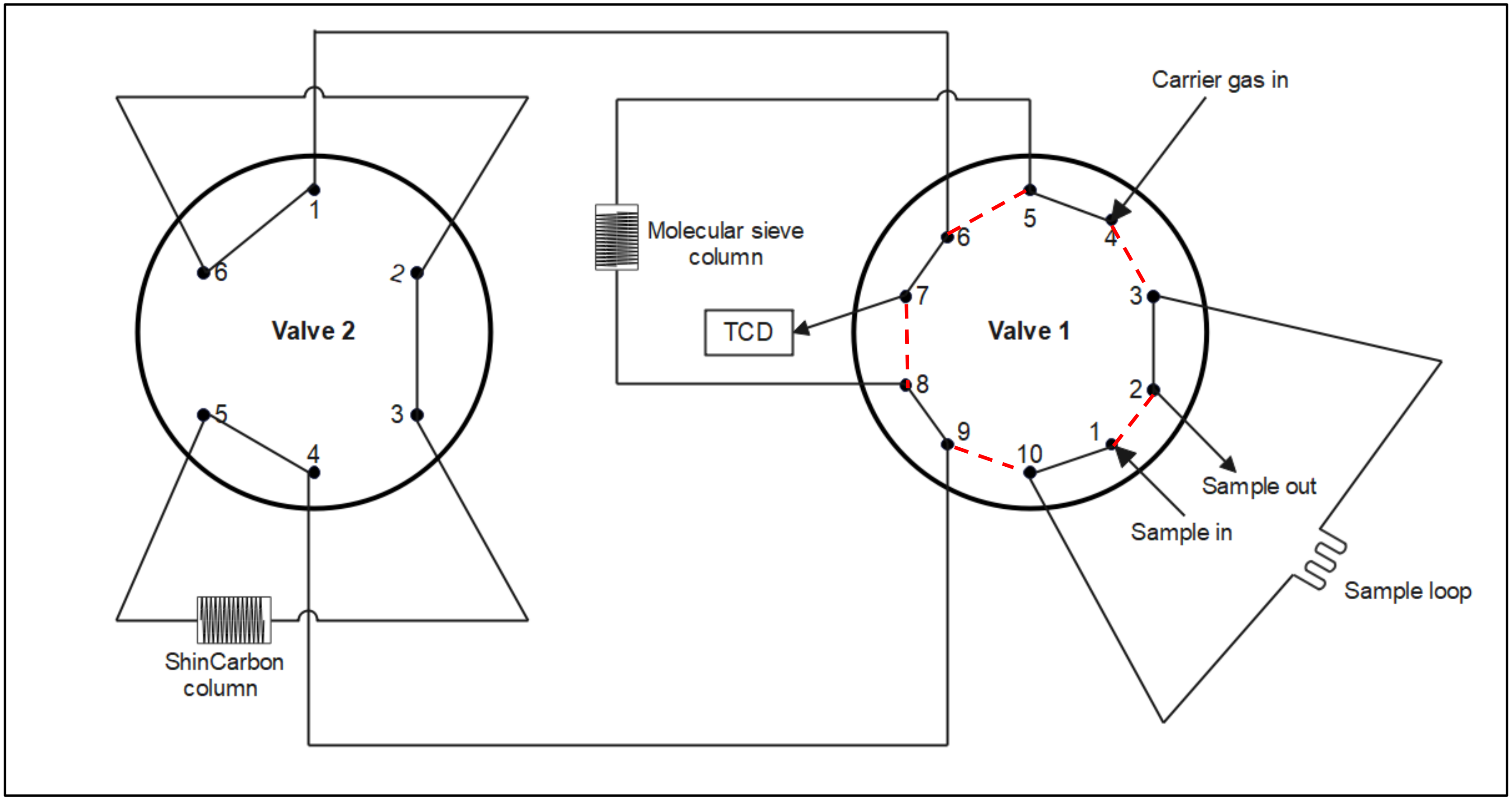

Figure 4.11 Schematic representation GC-dual TCD/FID's front TCD channel with the "load" position (shown as the solid lines) and "inject" position (shown in the dotted red lines.

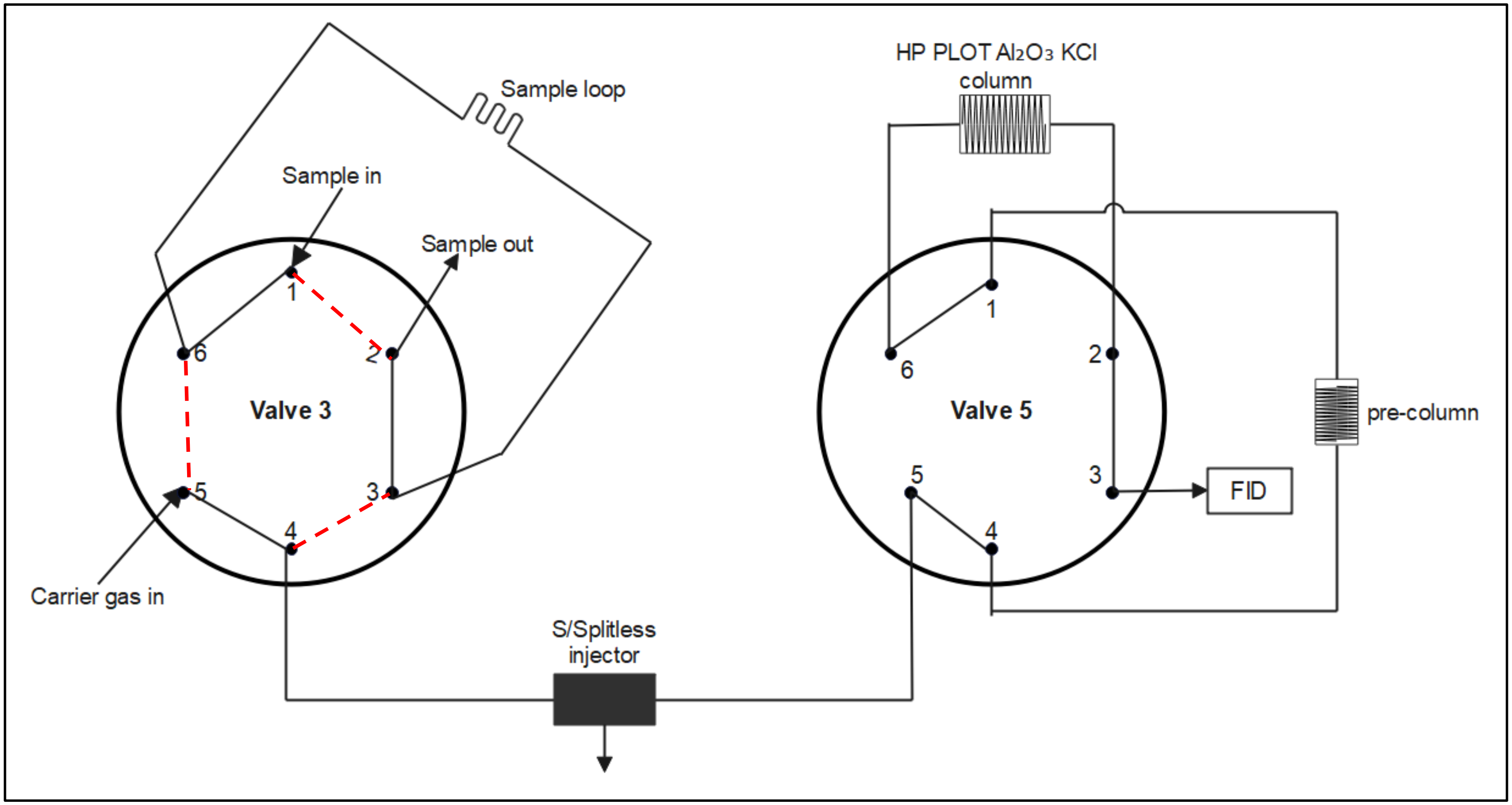

Figure 4.12 Schematic representation GC-dual TCD/FID's FID channel with the "load" position (shown as the solid lines) and "inject" position (shown in the dotted red lines.

Table 4.4 Analytical conditions used for the analysis of the CH_4, C_2H_6 and N_2 in He multi-component gas mixtures.

Parameters	**Analytical conditions**
Detectors	Thermal conductivity detector and flame ionisation detector
Oven temperature	40℃
Carrier gases	TCD - Hydrogen
	FID - Nitrogen
Sample loops	FID - 500 µL Front TCD - 500 µL
Columns	FID - HP PLOT Al_2O_3 KCl 50m x 0.320 mmID
	TCD - Molecular Sieve 13X 80/100 2m x 2mmID
Sample flow	35 ml/min
Run time	4 minutes
Split ratio	2:1
Split flow	2 mL/min

4.7.2. Verification of C_3H_8 and C_4H_6 in He multi-component pre-mixtures

The four 4 %mol.mol^{-1} C_3H_8 and 2 %mol.mol^{-1} C_4H_6 in He multi-component pre-mixtures were verified using the Agilent 7890B gas chromatography coupled with a dual FID using single point calibration. The measurement's optimised method parameters are tabulated in **Table 4.5**. The FID was used because paired with the CP-Sil 5 CB column, that allowed for simultaneous analysis of propane and 1,3-butadiene. Hydrogen was used as a carrier gas to carry the sample gas through the column. Synthetic air and make-up gas nitrogen were set at flow rates of 350 mL.min^{-1} and 5 mL.min^{-1}, respectively. A 500 µL sample loop was used to store a predetermined amount of sample that was later injected onto the CP-Sil 5 CB column. The CP-Sil 5 CB column was used as its separation technique is nearly entirely dependent on boiling points, making this column fit for a wide temperature range. The split/splitless injector was set at a temperature of 250℃, pressure of 161.69 kPa, total flow of 213.79 mL.min^{-1}, septum flow of 1 mL.min^{-1}, split flow of 201.6 mL.min^{-1} and split ratio of 40:1.

Table 4.5 Analytical conditions used for the analysis of the C_3H_8 and C_4H_6 in He pre-mixtures on the GC dual FID.

Parameters	Analytical conditions
Detector	Flame ionisation detector (FID)
Oven temperature	120℃
Carrier gas	Hydrogen
Sample loop	500 µL
Column	CP-Sil 5 CB
Sample flow	35 ml/min
Run time	1.8 minutes
Split ratio	40:1
Split flow	207.6 mL/min

4.7.3. Verification of CO_2, CO and O_2 in He multi-component pre-mixtures

The verification of CO_2, CO, and O_2 in the four gravimetrically prepared pre-mixtures of 8 %mol.mol^{-1} CO_2, 4 %mol.mol^{-1} CO and 4 %mol.mol^{-1} O_2 in helium gas mixtures used gas chromatography with dual TCD and FID channels. The cylinders were connected to regulators that were purged several times before they were connected to the sampler box connected to the inlet injector. The TCD channel illustrated in **Figure 4.11** was used for the analysis using valves 1 and 2. The columns used were Molecular Sieve 13X in valve 1 and ShinCarbon ST in valve 2. The temperature programming was configured so that the oven maintains a temperature of 35°C for 3 min for O_2 to elute, and then increases to 160°C through an increase rate of 80 °C/min and holds for a further 2 min for the elution of CO and CO_2 which are retained longer in the column to total the run time to 6.7 min. The split ratio of 5:1 was applied at a flow rate of 2.1 mL/min. **Table 4.6** tabulates the optimised conditions for the analysis of CO_2, CO and O_2.

Table 4.6 Analytical conditions used for the analysis of the CO_2, CO and O_2 in He pre-mixtures on the GC dual TCD/FID.

Parameters	**Analytical conditions**
Detector	Thermal conductivity detector (TCD)
Oven temperature	35℃ and ramped to 160℃ @ 3 minutes
Carrier gas	Hydrogen
Sample loop	500 µL
Column	Molecular Sieve 13X and ShinCarbon ST
Sample flow	35 ml/min
Total run time	6.7 minutes
Split ratio	5:1
Split flow	2.1 mL/min

4.7.4. Verification of the nine multi-component refinery reference gas mixtures

The dual TCD/FID was used to analyse the two amount fraction ranges of the gravimetrically prepared refinery reference gas mixtures, 1 to 22 %mol.mol^{-1} and 1 000 to 4 000 µmol.mol^{-1}. The mixtures were prepared in 10 dm^3 cylinders. For the analysis of CO_2, CO, N_2, and O_2, the front TCD was utilised, while the FID was employed for the analysis of the hydrocarbons, namely, CH_4, C_2H_6, C_3H_8, and C_4H_6. Prior to analysis, the gas mixtures were connected to regulators with the appropriate bullnose for the cylinders' valve type. The next step was purging the regulators, which involved opening and closing the cylinder valves while releasing gas into the extraction system to get rid of any residual gas inside the regulator. The cylinders were randomly connected to the VICI multi-position micro-electric valve actuator, and the flow was set at 35 mL.min^{-1} which is facilitated by Varian Serial Stream Selection Valve (SSV) 5.31 control software.

The front TCD channel used valves 1 and 2 equipped with Molecular Sieve 13X 80/100, 1 m long, and 1 mm ID and ShinCarbon ST 100/120 columns, respectively, as shown in **Figure 4.11**, while the FID used the same configuration of valves 3 and

5 as shown in **Figure 4.12**. However, instead of the PLOT Al_2O_3 KCl column, it was fitted with a CP-Sil 5 CB column in valve 5. The sample was injected and loaded at 0.1 min with all the valves open at 0.05 min and closed at 3 min, held at 45℃ for 3 min, ramped to 180℃ at 100 °C.min^{-1} and held for a further 8 min. The total run time of a sample injection was 12.35 min.

The front TCD was set to a hydrogen makeup flow of 5 mL.min^{-1} with no negative polarity, a reference flow of 30 mL.min^{-1}, and a heating temperature of 275 °C. The FID was programmed to operate at 222 °C for heating, 40 mL/min for hydrogen flow, 300 mL/min for synthetic air flow, and 10 mL/min for nitrogen makeup flow. At a flow rate of 2.1053 mL/min, the split/splitless ratio was set at 5:1. The heater was set to 150 °C at a pressure of 29.107 kPa, with the septum purge flow set at 3 mL/min. At two minutes after each injection, the gas-saving mode was activated. Table 3.7 tabulates the optimised analytical conditions of the GC during the analysis of the multi-component refinery reference gas mixtures.

Table 4.7 Analytical conditions used for the analysis of the multi-component refinery reference gas mixtures.

Parameters	**CO_2, CO, N_2 and O_2**	**CH_4, C_2H_6, C_3H_8 and C_4H_6**
Detector	Thermal conductivity detector (TCD)	Flame ionisation detector (FID)
Detector temperature	275 °C	222 °C
Oven temperature	45℃ and ramped to 180℃ @ 3 mins	45℃ and ramped to 180℃ @ 3 mins
Carrier gas	Hydrogen	Nitrogen
Sample loop	500 µL	500 µL
Column	Molecular Sieve 13X and ShinCarbon ST	CP-Sil 5 CB
Sample flow	35 ml/min	35 ml/min
Run time	12.35 minutes	12.35 minutes
Split ratio	5:1	5:1

4.8. Stability study

Certified reference material producers are required to declare the validity period for all reference material produced (ISO 17034:2016). Stability is defined as the unchanging state of a system (Hansson and Helgesson, 2003), and so the stability period can be defined as the period where a mixture is constant before noticeable degradation. As a result, the stability of gas mixtures is critical for the development of reference materials, and it is heavily influenced by the reactivity of the gas components. This is one of the known challenges with the development of refinery reference gas mixtures due to the reactive nature of gases such as carbon monoxide and oxygen.

The stability period of the refinery reference gas mixtures was evaluated to evaluate the behaviour of the components of interest. This was done by using Agilent 7890B gas chromatographs coupled with TCD and FID to monitor the precision and accuracy of the mixtures for short-term stability by taking a minimum of three measurements after preparation and then taking measurements at different intervals throughout the study.

4.9. Adsorption and desorption study

The study of adsorption and desorption is crucial in monitoring the stability of the prepared gas mixtures, as their interactions with the cylinder walls affect the accuracy of the measurements. By making use of aluminium cylinders, desorption and thermal diffusion effects are minimised because temperature fluctuations are greatly lowered (Leuenberger et al., 2015).

The test was performed by connecting a “mother cylinder” of a known amount fraction of 1 %mol.mol^{-1} O_2/ 1.5 %mol.mol^{-1} C_4H_6/ 4 %mol.mol^{-1} C_2H_6/ 5 %mol.mol^{-1} C_3H_8/ 6 %mol.mol^{-1} CH_4/ 8 %mol.mol^{-1} CO_2/ 10 %mol.mol^{-1} CO and 22 %mol.mol^{-1} N_2 to an evacuated “daughter cylinder” through transfer lines connected to a vacuum pump, as illustrated in **Figure 4.13**. The gas lines were flushed with gas from the mother cylinder several times and evacuated to a vacuum of less than 1.0 x 10^{-5} mbar. This was done to clear the lines of any other gas and debris that would have the potential to contaminate the target gas mixtures. After flushing the system, the gas was transferred from the mother cylinder to the daughter cylinder until equal pressure was reached in both cylinders, and then the cylinders were closed. The gas was introduced gradually to prevent the Joules Thompson effect (Ahmad et al., 2012). Then both cylinders were analysed by GC-FID and GC-TCD.

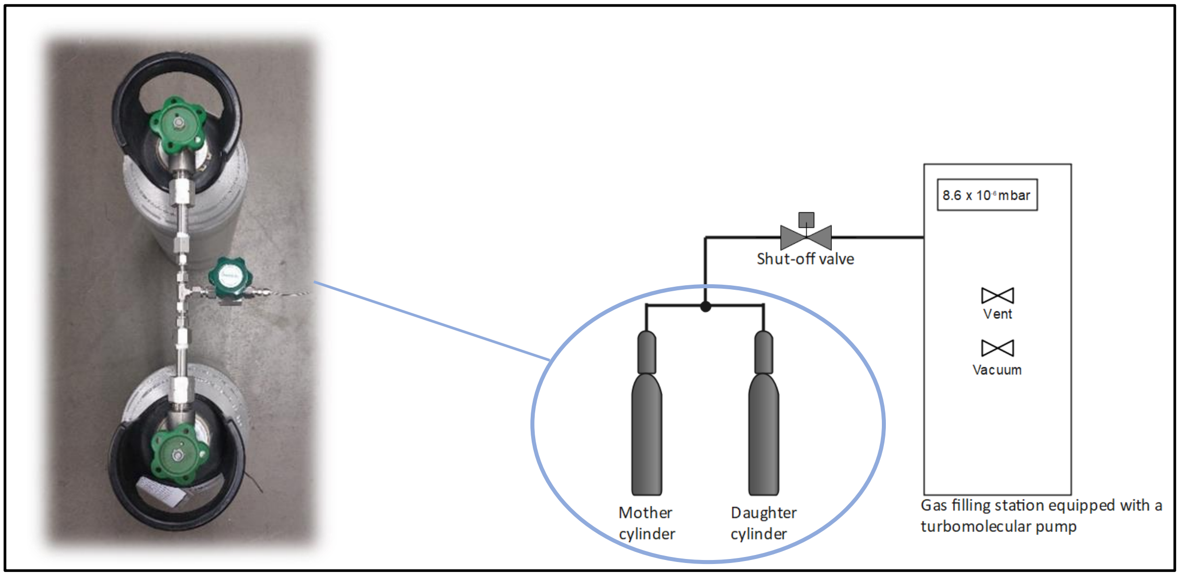

Figure 4.13 Schematic representation cylinder setup of the equal division method for adsorption study.

4.10. Data analysis

The data analysis for the results of the gas mixtures produced when verified on the GC considered the average peak area of the samples, standard deviations, instrument drift, and uncertainties associated with the measurement. The GC peak areas were used to calculate the amount fractions of the components in the gas mixture by extrapolating the peak sides to the baseline. The standard deviation was used to measure the distribution of the data relative to the mean and was calculated using **equation 4.8.**

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n}(-\bar{x})^2}{(n-1)}} \qquad \textbf{4.8}$$

Where σ refers to the standard deviation, x_i is the measurement result of component i, $\bar{x}$ is the arithmetic mean of measurement results and n is the total number of measurements performed.

Standard deviation is also expressed as a percentage relative standard deviation (%RSD) to depict how the measurement results are dispersed around the mean. And in analytical measurement, the estimated standard deviation of the mean (ESDM) calculated using **equation 4.9** is used to express the standard uncertainty where n is the number of measurement results.

$$ESDM = \frac{\sigma}{\sqrt{n}} \qquad \mathbf{4.9}$$

Furthermore, the drift of the instrument is monitored to safeguard any changes in the performance of the instrument that can compromise the validity of the conclusions drawn. Instrument drift is expressed in percentage and calculated using **equation 4.10**.

$$Drift = \frac{A_{ref(b)} - A_{ref(a)}}{A_{ref(a)}} \times 100 \qquad \mathbf{4.10}$$

Where $Drift$ is the measure of the change during analysis, $A_{ref(b)}$ is the average peak area of the reference gas mixture analysed after the sample gas mixture and $A_{ref(a)}$ is the average peak area of the reference mixture analysed before the sample gas mixture.

4.11. Internal consistency

Internal consistency is a metric that considers the correlations between different test items (Ponterotto and Ruckdeschel, 2007). This is done to evaluate the sample mixture's behaviour relative to the reference mixtures by use of the sensitivity ratios illustrated in **equation 4.11**.

$$sensistivity\ ratio = \frac{sensitivity_{sample}}{sensitivity_{reference}} \qquad \mathbf{4.11}$$

And $sensitivity = \frac{\bar{x}}{grav_{conc}}$ **4.12**

Where $\bar{x}$ refers to the average of the measurement results and $grav_{conc}$ is the gravimetric amount fraction.

4.12. Method validation and data evaluation

For the development of refinery reference gas mixtures, the analytical method needs to be fit for purpose and meet the measurement criteria set. The validation was conducted through the investigation of the following parameters: accuracy, precision (repeatability and reproducibility), and measurement uncertainty.

4.12.1. Accuracy

The accuracy of a measurement is important in the development of refinery reference gas mixtures as it relates to how close the measurement results are to the true value. In this study, the measure of bias was used to assess accuracy. This was done by comparing the gravimetric amount fraction against that of the verification amount fraction using **equation 4.13**.

$\% \, difference = \frac{|x_{grav} - x_{veri}|}{x_{grav}} \times 100$ **4.13**

Where x_{grav} is the gravimetric amount fraction of the component of interest and x_{veri} is the calculated amount fraction obtained from the analysis.

4.12.2. Precision

Precision is defined as the degree to which independent test results obtained under specified conditions agree. In this study, precision was expressed as %RSD and calculated using **equation 4.14**.

$$\%RSD = \frac{\sigma}{\bar{x}}\ x\ 100 \qquad \mathbf{4.14}$$

where σ refers to the standard deviation of a measurement results and $\bar{x}$ refers to the average of the measurement results.

4.12.2.1. Repeatability

To examine the repeatability of the method, an average and standard deviation of a set of measurements for each amount fraction level performed on the same day under the same conditions were determined.

4.12.2.2. Reproducibility

Reproducibility was studied using the relative standard deviations of the measurement results taken over different days.

4.12.3. Selectivity

The selectivity of the chromatographic analysis methods used in this study was determined by studying the resolution and the retention time of the components-of-interest. This was done by running the multicomponent, then running a binary mixture for the identification of the component under study.

4.12.4. Ruggedness/ extreme conditions test

The extreme conditions test is typically used as a method validation parameter. This test improves a method’s usefulness for evaluating constraints that might require a set system to behave outside historical regions of behaviour. This test progressively builds confidence in a method's capacity to function reasonably under a broad range of circumstances that are outside its normal operational range (Senge and Forrester, 1980). In this study, a gas mixture was subjected to extremely varying temperatures to evaluate the stability of the gases inside. The gas mixture was first analysed at a standard laboratory-controlled temperature of 21.5 °C, after which it was exposed to the sun for four hours at 36 °C, allowed to reach room temperature, and analysed yet again. It was then again placed in a walking refrigerator for four hours at 2 °C, after which it was allowed to cool to room temperature and then analysed for the last time. This enabled the stability of the gases in the mixtures to be verified by subjecting the gas mixture to extreme temperature conditions. An extreme condition test is therefore a qualitative validation method.

4.12.3. Measurement Uncertainty

All measurement uncertainty contributors, minor and significant, were considered and quantified to produce refinery primary reference gas mixtures of the highest metrological value by means of gravimetry preparation. Uncertainty contributors considered in this study include those associated with the purity of starting material, molar mass of the components of interest, gravimetric preparation process and verification of the primary reference gas mixtures. Uncertainties associated with weighing include the sensitivity, repeatability, and resolution of the balance and the precision of the weighing data. And the uncertainties associated with the verification results include the stability of the gas mixture, the precision of the data, and the instrument drift.

A detailed uncertainty budget model was established for the evaluation of all uncertainty contributors for the development of the refinery reference gas mixtures, as shown in **Figure 4.14**. The gravimetric uncertainty contributors considered are the repeatability of the weighing and the starting material and/or pre-mixtures used, which are calculated using the Gravcal software. The verification uncertainties stem from the instrumentation's peak area repeatability during analysis. This model combines all the standard uncertainties associated with the gravimetric preparation (ISO 6142-1:2015) and verification measurements (ISO 6143:2001) using **equation 4.15**.

$$u_c(y) = \sqrt{\sum_{i=1}^{n} [c_i u(x_i)]^2} \qquad \mathbf{4.15}$$

Where $u_c(y)$ is the combined standard uncertainty, c_i is the sensitivity coefficient for input i and $u(x_i)$ is the standard uncertainty for input x_i.

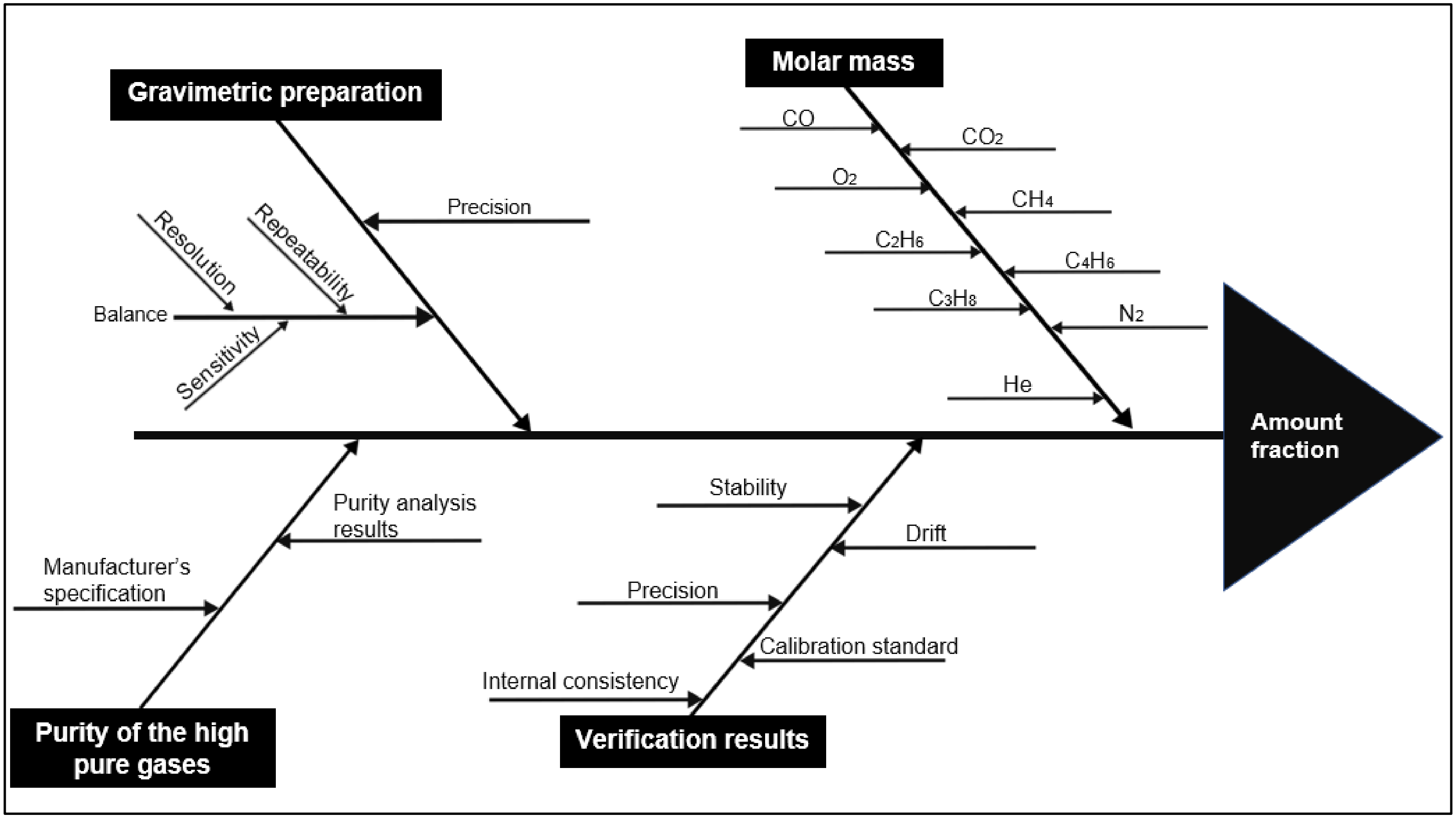

Figure 4.14 Fishbone diagram of uncertainty contributors associated with the development of refinery reference gas mixture.

4.13. Matrix effect study of refinery reference gas mixtures

Matrix effect is defined as the impact caused by other coeluting components except the component of interest that is being evaluated in an analytical analysis (Van Eeckhaut et al., 2009). In this study, matrix effects were investigated by comparing the amount fractions between the prepared multicomponent reference gas mixtures and binary gas mixtures of matched component of interest amount fractions. That is, a gas mixture of 1 %mol.mol^{-1} O_2/ 1.5 %mol.mol^{-1} C_4H_6/ 4 %mol.mol^{-1} C_2H_6/ 5 %mol.mol^{-1} C_3H_8/ 6 %mol.mol^{-1} CH_4/ 8 %mol.mol^{-1} CO_2/ 10 %mol.mol^{-1} CO and 22 %mol.mol^{-1} N_2 in He was analysed against 1 %mol.mol^{-1} O_2 in N_2 for comparison of oxygen peak area to highlight any observed matrix effect. This was done for all the components studied in this work and evaluated using **equation 4.16**.

$$ME = \left(\frac{c_{standard} - c_i}{c_{standard}}\right) \times 100 \qquad \textbf{4.16}$$

Where ME is the matrix effect, c_i is the calculated sensitivity of component i in the multicomponent gas mixture, $c_{standard}$ is the calculated correlated sensitivity of the binary gas standard.

Sensitivity is calculated using **equation 4.17**.

$$c_i = \frac{y_i}{x_i} \qquad \textbf{4.17}$$

Where y_i is the GC analysis response and x_i is the gravimetric amount fraction of component i.

In the study of matrix effect, ME of ~ 0% represents no matrix effect. A ME of > 0% shows an ion-suppression in which the ionisation efficiency of a component of interest is decreased by the presence of other components in the mixture. ME of < 0% represents an ion-enhancement in which the ionisation efficiency of a component of interest is increased by the presence of other components in the mixture (Zhou, Yang and Wang, 2017).

CHAPTER FIVE – RESULTS AND DISCUSSION

This chapter presents the results of the purity assessment of the starting materials, gravimetric preparation and analysis of both pre-mixtures and multicomponent refinery reference gas mixtures. It also discusses the numerous analytical tests performed on the developed refinery reference gas mixtures to demonstrate the suitability of the deployed analytical method for the verification of the mixtures.

5.1. Purity analysis of pressurised high purity gas starting materials using gas chromatography

Purity analysis was done to establish the gas composition of the high purity gas starting materials by accurately measuring the impurities present in the high purity starting materials that were supplied by various manufacturers. Although the manufacturers of these high purity gases provide a certificate of analysis (CoA) as a manufacturer's specification with quantified impurities, they often report very conservatively and provide a limited set of impurities. For example, in the manufacturer's specifications for high purity N_2, CO_2, CO, He, C_3H_8, and CH_4, all hydrocarbons were quantified as a single defined amount fraction of CH_4, and traces of CO_2 and CO in high purity He and N_2 were not separated. The separation and quantification of these impurities was necessary for this study as these impurities in the starting materials were also present as major components of interest in the refinery reference gas mixtures. Additionally, according to ISO-19229:2015 *'Purity analysis and the treatment of purity data,'* that was used as a guide for the conduct of purity analysis, the provided specification can only be used for noncritical impurities if it is based on nontraceable measurements.

According to the manufacturer's specifications, the purity estimations of the high purity starting materials were reported to be ≥ 99.95% for methane, ethane, propane, and 1,3-butadiene; 99.9999% for both helium and nitrogen, each with a built-in purifier; and 99.995%, 99.997% and 99.999% for carbon dioxide, carbon monoxide and oxygen respectively. Helium with a Built-in Purifier (BIP^{TM}) was used as the diluent gas in the preparation of all the refinery reference gas mixtures. **Tables 5.1** to **5.9** show the purity analysis results for high purity starting materials of 1,3-butadiene, carbon dioxide, carbon monoxide, ethane, helium, methane, nitrogen, oxygen, and propane, respectively. Purity analysis was performed using GC-FID for quantification of CO, CO_2, CH_4, and C_2H_6, GC-PDHID for quantification of argon, hydrogen, nitrogen, and oxygen, and GC-TCD for quantification of helium, as described in **Chapter 4 Section 4.4**.

Impurities of CH_4, C_2H_6, CO, CO_2, O_2, and N_2 were expected in all the high purity gases as per the manufacturer's specifications. Components of air such as Ar, H_2, and moisture (H_2O) were also expected to be impurities as they are prevalent in the atmosphere. Unfortunately, H_2O could not be quantified by the techniques employed in this study; as a result, the manufacturer's specifications were adopted, assuming type B rectangular distribution.

5.1.1. Purity analysis results for 1,3-butadiene

The purity analysis results for 1,3-butadiene are shown in **Table 5.1**. The most significant impurity was N_2, with a calculated amount fraction of 5 747 µmol.mol^{-1}. However, the manufacturer's specification for trace N_2 was estimated to be less than 800 µmol.mol^{-1}, which is substantially lower than the results of the analysis. Trace O_2 was quantified to 20 µmol.mol^{-1}. H_2 was not included as an impurity in the manufacturer's specification and was presumptively excluded as an impurity, yet, analysis showed a trace of H_2 of 51 µmol.mol^{-1}. The estimations of N_2, O_2, and H_2 uncertainties used a normal distribution. Discrepancies between the measured amount fractions and the manufacturer specifications during purity analysis have the potential to cause issues in medical, metrological, and electronic applications that require high purity criteria (Matsumoto et al., 2013, Mulyana et al., 2019). The observed high levels of N_2, O_2, and H_2 impurities could be attributed to the steam cracking in olefin plants for the production of high purity 1,3-butadiene, which is highly dependent on the feedstock used by crackers (Tripathi et al., 2019).

Traces of carbon dioxide, carbon monoxide, ethane, and methane were not detected on FID; therefore, the limit of detection was used to quantify them. The limit of detection in this study was 0.056, 0.077, 0.023, and 0.013 µmol.mol^{-1} for CO, CO_2,

CH_4, and C_2H_6, respectively. With all impurities quantified, the final quantified amount fraction for 1,3-butadiene > 99.42 %mol.mol^{-1}.

Table 5.1 Purity analysis results for high purity 1,3-butadiene starting material.

Component	**Manufacturer specification (µmol.mol^{-1})**	**Distribution**	**Amount fractions (µmol.mol^{-1})**	**Standard uncertainties (µmol.mol^{-1})**	**Analysis technique**
CO	Not specified	Rectangular	0.0557	0.0322	GC-FID
CO_2	Not specified	Rectangular	0.0771	0.0445	GC-FID
CH_4	Not specified	Rectangular	0.0232	0.013	GC-FID
C_2H_6	Not specified	Rectangular	0.0126	0.0073	GC-FID
Ar	Not specified	Rectangular	0.0769	0.0444	GC-PDHID
O_2	< 200	Normal	20.4368	0.7824	GC-PDHID
H_2	Not specified	Normal	51.5057	2.1577	GC-PDHID
N_2	< 800	Normal	5 747.9460	180.8912	GC-PDHID
H_2O	< 4	Rectangular	2.000	1.1547	MS
C_4H_6	**≥ 995 000**		**994 177.8660**	**180.9095**	

5.1.2. Purity analysis results for carbon dioxide

The main impurities in high purity CO_2 gas were determined to be ethane, methane, hydrogen, oxygen, moisture, nitrogen, and helium, as shown in **Table 5.2**. These impurities can be attributed to the combustion processes that result in the generation of high purity CO_2 (Kumar and Kumar, 2018). Helium and nitrogen had the highest amount fractions at 22 and 13 µmol.mol^{-1}, respectively. Inaccurate reporting of the final composition of high purity CO_2 and subsequently inaccurate amount fractions for the final refinery reference gas mixtures may have resulted from neglecting to quantify trace helium and nitrogen after the MS. The overall purity of CO_2 was calculated to be > 99.996%.

Table 5.2 Purity analysis results for high purity carbon dioxide starting material.

Component	Manufacturer specification (µmol.mol^{-1})	Distribution	Amount fractions (µmol.mol^{-1})	Standard uncertainties (µmol.mol^{-1})	Analysis technique
CH_4	< 0.5	Normal	0.4623	1.3704	GC-FID
C_2H_6	< 0.5	Normal	0.0344	0.0744	GC-FID
Ar	Not specified	Rectangular	0.0738	0.0426	GC-PDHID
O_2	< 5	Normal	1.2508	0.0400	GC-PDHID
H_2	Not specified	Normal	0.3086	0.0387	GC-PDHID
N_2	Not specified	Normal	13.1595	0.3906	GC-PDHID
H_2O	< 4	Rectangular	2.0000	1.1547	MS
He	Not specified	Normal	21.8000	0.1800	GC-TCD
CO_2	**≥ 999 950**		**999 960.9106**	**1.8457**	

5.1.3. Purity analysis results for carbon monoxide

The manufacturer's specification reported the purity of high purity CO as ≥ 99.997 %. Further to this, impurities of CO_2, CH_4+C_2H_6, Ar, O_2, N_2, H_2, and moisture were reported and can be seen in **Table 5.3**. The calculated impurities found in high purity CO were H_2, He, CO_2, N_2, and Ar at amount fractions of 1.2, 0.6, 0.7, 0.2 and 0.02 µmol.mol^{-1}, respectively. These calculated amount fractions of the impurities were far more than those reported by the manufacturer, resulting in the estimated purity of CO to be 99.993%.

Table 5.3 Purity analysis results for high purity carbon monoxide starting material.

Component	Manufacturer specification (µmol.mol^{-1})	Distribution	Amount fractions (µmol.mol^{-1})	Standard uncertainties (µmol.mol^{-1})	Analysis technique
CO_2	≤ 1	Normal	0.6976	4.8535	GC-FID
CH_4	≤ 2	Rectangular	0.0191	0.0110	GC-FID
C_2H_6	≤ 2	Rectangular	0.1953	0.1127	GC-FID
Ar	≤ 15	Normal	0.0106	0.0003	GC-PDHID
O_2	≤ 5	Rectangular	2.5000	1.4434	MS
H_2	≤ 2	Normal	1.1763	0.0927	GC-PDHID
N_2	≤ 5	Normal	0.1977	0.0089	GC-PDHID
H_2O	≤ 3	Rectangular	1.5000	0.8660	MS
He	Not specified	Normal	0.5529	0.3192	GC-TCD
CO	**≥ 999 970**		**999 993.1697**	**5.1491**	

5.1.4. Purity analysis results for ethane

Ethylene was the most significant impurity in high purity ethane at an amount fraction of 175 µmol.mol^{-1}. Despite being listed as an impurity in the manufacturer's specification for high purity ethane, ethylene could not be quantified due to a lack of gas standards; ethylene results were reported as an input from the manufacturer's specification as shown in **Table 5.4**. Other impurities that were not quantified and relied on the manufacturer's specification included oxygen, nitrogen, and moisture. In accordance with ISO 19229 (2015), which covers purity analysis calculations based on the manufacturer's specification, a rectangular distribution was assumed, and the amount fractions of the expected impurities were estimated by using **equation 4.1**, where the reported manufacturer specification is divided by divisor (2) and the associated standard uncertainty is estimated by using **equation 4.3**. The final calculated purity of ethane was > 99.974%.

Table 5.4 Purity analysis results for high purity ethane starting material.

Component	Manufacturer specification (µmol.mol^{-1})	Distribution	Amount fractions (µmol.mol^{-1})	Standard uncertainties (µmol.mol^{-1})	Analysis technique
CO	Not specified	Normal	0.0959	0.0553	GC-FID
CO_2	< 5	Normal	11.2692	1.4571	GC-FID
CH_4	< 25	Normal	0.0382	0.0221	GC-FID
C_2H_4	< 350	Normal	175.0000	101.0363	MS
Ar	Not specified	Normal	0.0160	0.0005	GC-PDHID
O_2	< 10	Rectangular	5.0000	2.8868	MS
H_2	< 40	Normal	23.0430	0.2525	GC-PDHID
N_2	< 40	Rectangular	20.0000	11.5470	MS
H_2O	< 5	Rectangular	2.5000	1.4434	MS
He	Not specified	Normal	14.3100	0.6600	GC-TCD
C_2H_6	**≥ 999 500**		**999 748.7277**	**101.7581**	

5.1.5. Purity analysis results for helium

BIP^{TM} He purchased from Air Products was used as the diluent gas in all the prepared refinery gas mixtures and pre-mixtures. **Table 5.5** shows purity analysis results of the amount fractions of the impurities in high purity He. Impurities of CO, CO_2, CH_4 and C_2H_6 were assessed using GC-FID with a diaphragm valve design shown in **Figure 4.2**. The amount fractions reported were calculated using the limit of detection **equation 4.2** with a rectangular distribution assumed.

Hydrogen, quantified using GC-PDHID at 1 µmol.mol^{-1}, was the primary impurity present in high purity helium. The quantifiable impurity was ten times more than what was specified on the MS. This highlights even more how crucial it is to thoroughly quantify all possible impurities, even though they were already reported by the manufacturer. This is because manufacturers frequently perform batch analysis, which is not recommended for reference material production.

Table 5.5 Purity analysis results for high purity helium starting material.

Component	Manufacturer specification (µmol.mol^{-1})	Distribution	Amount fractions (µmol.mol^{-1})	Standard uncertainties (µmol.mol^{-1})	Analysis technique
CO	< 0.05	Rectangular	0.0557	0.0322	GC-FID
CO_2	< 0.05	Rectangular	0.0771	0.0445	GC-FID
CH_4	< 0.05	Rectangular	0.0232	0.0134	GC-FID
C_2H_6	< 0.05	Rectangular	0.0126	0.0073	GC-FID
Ar	Not specified	Normal	0.0028	0.0002	GC-PDHID
O_2	< 0.01	Rectangular	0.0050	0.0029	MS
H_2	< 0.1	Normal	1.0096	0.0451	GC-PDHID
N_2	< 0.1	Normal	0.5065	0.2924	GC-PDHID
H_2O	< 0.02	Rectangular	0.0100	0.0058	MS
He	**> 999 999**		**999 998.2976**	**0.3014**	

5.1.6. Purity analysis results for methane

Table 5.6 shows the purity analysis results for high purity methane performed on the GC-TCD, GC-PDHID, and GC-FID. Hydrogen was the most significant impurity contributor, accounting for 11.7 µmol.mol^{-1}. Other impurities that have contributed to the decrease in purity of the high purity methane include oxygen at 5.4 µmol.mol^{-1}, helium at 3.1 µmol.mol^{-1} and moisture (H_2O) at 2.5 µmol.mol^{-1}. The final calculated amount fraction of methane was > 99.997%.

Table 5.6 Purity analysis results for high purity methane starting material.

Component	Manufacturer specification (µmol.mol^{-1})	Distribution	Amount fractions (µmol.mol^{-1})	Standard uncertainties (µmol.mol^{-1})	Analysis technique
CO_2	< 1	Rectangular	0.0540	0.0310	GC-FID
C_2H_6	< 15	Normal	0.0650	0.0370	GC-FID
Ar	Not specified	Rectangular	0.0769	0.0444	GC-PDHID
O_2	< 5	Normal	5.3558	0.08019	GC-PDHID
H_2	< 1	Normal	11.7206	0.1566	GC-PDHID
N_2	< 15	Normal	0.4478	0.0467	GC-PDHID
H_2O	< 5	Rectangular	2.5000	1.4434	MS
He	Not specified	Normal	3.0500	0.0930	GC-TCD
CH_4	**> 999 950**		**999 976.7299**	**1.4592**	

5.1.7. Purity analysis results for nitrogen

Impurities in BIP^{TM} N_2 were evaluated using GC-FID and GC-PDHID. According to the manufacturer's specification, total hydrocarbons were reported as CH_4 at 0.01 µmol.mol^{-1} and combined CO and CO_2 impurities at 0.5 µmol.mol^{-1}. The final calculated purity of high purity N_2 and all quantified impurities are tabulated in **Table 5.7**. The most substantial impurity, at just over 17 µmol.mol^{-1}, was argon. Another noticeable impurity was H_2 at 1.95 µmol.mol^{-1}. These impurities of argon and hydrogen have a considerable negative impact on the final amount fraction of nitrogen. These impurities are found in high purity nitrogen and can be attributed to the air used to produce the nitrogen or to contamination during storage or handling. Thus, it is imperative that the levels of these impurities be quantified (Prabhu and Murty, 2017).

Table 5.7 Purity analysis results for high purity nitrogen starting material.

Component	Manufacturer specification ($\mu mol.mol^{-1}$)	Distribution	Amount fractions ($\mu mol.mol^{-1}$)	Standard uncertainties ($\mu mol.mol^{-1}$)	Analysis technique
CO	< 0.5	Rectangular	0.0557	0.0322	GC-FID
CO_2	< 0.5	Rectangular	0.0771	0.0445	GC-FID
CH_4	< 0.1	Rectangular	0.0232	0.0134	GC-FID
C_2H_6	Not specified	Normal	0.2864	0.0038	GC-FID
Ar	Not specified	Normal	17.0415	0.7870	GC-PDHID
O_2	< 0.01	Rectangular	0.0050	0.0029	MS
H_2	< 1	Normal	1.9499	0.2089	GC-PDHID
H_2O	< 0.02	Rectangular	0.0100	0.0058	MS
He	Not specified	Rectangular	0.5529	0.3192	**GC-TCD**
N_2	**> 999 999**		**999 979.9984**	**0.8765**	

5.1.8. Purity analysis results for oxygen

The results of the purity analysis performed on GC-PDHID and GC-FID for high purity oxygen are tabulated in **Table 5.8**. There were significant amounts of H_2, N_2, and moisture impurities at 5.6 $\mu mol.mol^{-1}$, 2 $\mu mol.mol^{-1}$, and 1 $\mu mol.mol^{-1}$ respectively. These impurities can be attributed to the production and purification processes of O_2. In the purity analysis for high purity oxygen, the separation of the oxygen, and nitrogen peaks proved challenging even though an analytical technique had been established with adequate separation of H_2, Ar, O_2, and N_2 peaks on the PDHID. The oxygen peak co-eluted with the nitrogen peak as a result of the high percentage of oxygen that was injected into the column, which greatly increased the peak height, retention time, and retention volume. Therefore, for the purpose of quantifying nitrogen, manufacturer specifications were used.

Table 5.8 Purity analysis results for high purity oxygen starting material.

Component	**Manufacturer specification (μmol.mol^{-1})**	**Distribution**	**Amount fractions (μmol.mol^{-1})**	**Standard uncertainties (μmol.mol^{-1})**	**Analysis technique**
CO	< 0.2	Rectangular	0.0738	0.0426	GC-FID
CO_2	< 0.2	Rectangular	0.0975	0.0563	GC-FID
CH_4	< 0.1	Rectangular	0.0221	0.0127	GC-FID
C_2H_6	Not specified	Rectangular	0.0118	0.0068	GC-FID
Ar	< 5	Normal	0.0769	0.0444	GC-PDHID
N_2	< 4	Rectangular	2.0000	1.1547	MS
H_2	Not specified	Normal	5.5819	0.1462	GC-PDHID
H_2O	< 2	Rectangular	1.0000	0.5774	MS
O_2	**> 999 990**		**999 991.1361**	**1.3020**	

5.1.9. Purity analysis results for propane

In the manufacturer's specification, high purity propane was predicted to have impurities of argon, oxygen, nitrogen, and carbon dioxide, which are constituents of air. This is because of the nature of the natural gas processes that are responsible for the production of propane, where petrochemical mixtures are isolated by either separation from the natural gas phase of petroleum or by refinement of crude oil carry other natural occurring gases into the gas traps (Devold, 2013). Ar, O_2, H_2, and N_2 were quantified using GC-PDHID, and GC-FID was used for the quantification of CO, CO_2, CH_4, and C_2H_6 impurities. A GC-PDHID chromatogram of hydrogen, argon, oxygen, and nitrogen impurities in a high purity propane injection is shown in **Figure 5.1**. Even though the argon and oxygen peaks eluted quite close to one another, they were still properly integrated without any substantial difficulties.

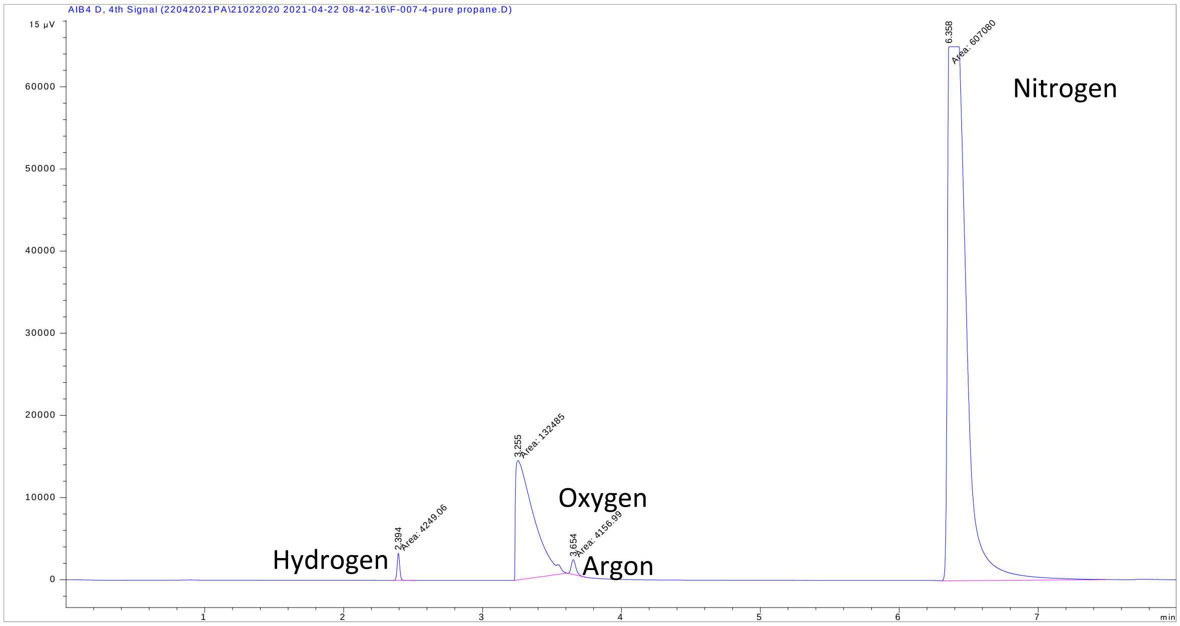

Figure 5.1 H_2, O_2, Ar and N_2 impurities in high purity propane.

Table 5.9 lists the quantified amount fractions for the impurities as well as the final calculated amount fraction of high purity propane. Nitrogen is the most significant impurity quantified at 3 387 µmol.mol^{-1} followed by oxygen and hydrogen at amount fractions of 46 and 40 µmol.mol^{-1}. The nitrogen impurity in the high purity propane caused a considerable reduction in the purity of propane. Furthermore, CO, CO_2, CH_4 and C_2H_6 may have been present in high purity propane, but their amount fractions were below the detection limit of the FID. The final purity for high purity propane was > 99.652% after the quantification of all the impurities.

Table 5.9 Purity table with the amount fraction of high purity propane starting material.

Component	Manufacturer specification ($\mu mol.mol^{-1}$)	Distribution	Amount fractions ($\mu mol.mol^{-1}$)	Standard uncertainties ($\mu mol.mol^{-1}$)	Analysis technique
CO	Not specified	Rectangular	0.0738	0.0426	GC-FID
CO_2	< 5	Rectangular	0.0975	0.0563	GC-FID
CH_4	Not specified	Rectangular	0.0221	0.0127	GC-FID
C_2H_6	Not specified	Rectangular	0.0118	0.0068	GC-FID
Ar	Not specified	Normal	0.3251	0.0027	GC-PDHID
O_2	< 10	Normal	45.5970	1.5236	GC-PDHID
H_2	< 40	Normal	38.9825	0.5926	GC-PDHID
N_2	< 40	Normal	3387.6525	22.0171	GC-PDHID
H_2O	< 5	Rectangular	2.5000	1.4434	MS
C_3H_8	**≥ 999 500**		**996 524.7378**	**22.1249**	

5.2. Development of high range refinery reference gas mixtures

5.2.1. Gravimetric preparation of high range refinery reference gas mixtures results

DM1, DM2, DM3, and DM4 refinery reference gas mixtures with nominal amount fractions of 8 % $mol.mol^{-1}$ CO_2, 10 % $mol.mol^{-1}$ CO, 1 % $mol.mol^{-1}$ O_2, 6 % $mol.mol^{-1}$ CH_4, 4 % $mol.mol^{-1}$ C_2H_6, 22% $mol.mol^{-1}$ N_2, 5 % $mol.mol^{-1}$ C_3H_8 and 1.5 % $mol.mol^{-1}$ 1,3-C_4H_6 in the balance of He were prepared directly from the high purity starting materials in accordance with ISO 6142:2015. The mixtures were prepared in 10 L aluminium cylinders at 8.5 MPa. These mixtures are traceable to the SI unit of mass (kg) through the use of a calibrated mass comparator balance used to weigh the gases added into the sample mixtures and the amount of substance (mol) through mass conversion to amount fraction. The GravCalc Version 2.03.001 software was connected to the AWS balance, and LabView software was used to generate the purity tables.

The final gravimetric amount fractions, expanded uncertainties, and relative expanded uncertainties of the components of interest in each gas mixture are tabulated in **Table 5.10**. The amount fractions were obtained by considering the composition of components obtained during purity analysis and the mass of starting materials added during gravimetric preparation, including their uncertainties. The gas mixtures were prepared with comparable amount fractions for each component of interest in order to use the single point calibration method for analysis. The full, detailed purity tables with all the impurities can be found in **Appendix B**.

Table 5.10 Gravimetric amount fractions and associated uncertainties of the eight components of interest in the high range refinery reference gas mixtures.

Cylinder ID	**Component**	$\boldsymbol{x_{grav}}$ **(%mol.mol^{-1})**[1]	$\boldsymbol{U_{grav}}$ **(%mol.mol^{-1})**[2]	**%REU**[3]
DM1	N_2	21.7538	0.0006	0.003
	CO	9.9992	0.0004	0.004
	CO_2	8.0376	0.0003	0.004
	CH_4	5.8224	0.0005	0.009
	C_3H_8	4.9371	0.0003	0.006
	C_2H_6	4.0981	0.0005	0.012
	C_4H_6	1.4850	0.0002	0.013
	O_2	1.0694	0.0002	0.019
DM2	N_2	21.8281	0.0006	0.003
	CO	9.8884	0.0004	0.004
	CO_2	8.0894	0.0003	0.004
	CH_4	5.9783	0.0005	0.008
	C_3H_8	4.9573	0.0003	0.006
	C_2H_6	4.1736	0.0005	0.012
	C_4H_6	1.4905	0.0002	0.013
	O_2	0.9764	0.0002	0.020
DM3	N_2	21.8464	0.0006	0.003
	CO	9.9506	0.0004	0.004
	CO_2	7.9899	0.0003	0.004
	CH_4	5.7472	0.0005	0.009
	C_3H_8	4.9745	0.0003	0.006
	C_2H_6	4.0910	0.0005	0.012
	C_4H_6	1.4819	0.0002	0.013
	O_2	1.1243	0.0002	0.018
DM4	N_2	22.1284	0.0006	0.003
	CO	10.0850	0.0004	0.004
	CO_2	8.0446	0.0003	0.004
	CH_4	5.9359	0.0005	0.008
	C_3H_8	4.9569	0.0003	0.006
	C_2H_6	4.0191	0.0005	0.012
	C_4H_6	1.4703	0.0002	0.014
	O_2	0.9537	0.0002	0.021

[1] $\boldsymbol{x_{grav}}$ is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142

[2] $\boldsymbol{U_{grav}}$ is the expanded uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*)

[3] **%REU** is the percentage relative expanded uncertainty associated with the gravimetric amount fraction.

5.2.2. Challenges in the preparation of refinery gas mixtures in a balance of he

The gravimetric preparation of high-pressure refinery reference gas mixtures at the desired target amount fractions for all the components of interest directly from high purity gases presented multiple challenges. Some of these challenges included but were not limited to the pressures, purities, and chemistry of the starting materials.

5.2.2.1. Starting material cylinder pressures

Since the pressure of the high purity gases supplied is directly proportional to the amount of substance in the final gas mixtures according to the ideal gas law (Milton and Mills, 2009), the varying pressures of the starting materials posed a challenge in the preparation. High purity propane and 1,3-butadiene, for example, were manufactured and packaged as liquefied gases with low vapour pressures, resulting in pressures lower than 0.7 MPa, whereas other high purity gases, such as helium and nitrogen, were packaged at 20 MPa. This pressure difference made it challenging for the addition of each component as the pressure of the sample mixtures increased with each addition while the pressures of the starting material remained constant. This was accounted for by considering the pressure needed from each starting material to make up the final desired target amount fraction for each component of interest before preparation.

5.2.2.2. Gas purity

In addition, because some components of interest can be found as impurities in other starting materials, affecting the final amount fractions of each component, the purity of each component had a significant impact on the final amount fractions of the sample gas mixtures. This can be seen from the purity analysis results. For example, adding high purity propane caused a change in the sample mixture's oxygen content since high purity propane contained a considerable amount of oxygen as an impurity.

5.2.2.3. Chemical interactions

The chemistry of the starting materials played a role in the preparation of the refinery reference gas mixtures, especially at high concentrations. Because oxygen is known to be reactive and that its reactivity increases the risk of ignition significantly, the amount fractions of oxygen, for example, were carefully monitored and considered to avoid producing oxygen-enriched mixtures that would pose as highly flammable gases. Gas mixtures become easier to ignite because their flammable ranges expand and their autoignition temperatures drop in the presence of oxygen (Pekalski et al., 2002). The liquid condensation of high purity carbon dioxide also posed another challenge during preparation. When the CO_2 was added into the sample gas mixtures through the filling station too quickly at high pressures, it condensed into a liquid and was evident as frozen liquid on the stainless-steel transfer tubing. This was controlled by gradually adding CO_2 to prevent condensation.

5.2.3. Verification of the gas mixtures using GC-FID/TCD

The four gravimetrically prepared high range reference gas mixtures were quantified using GC-FID for quantification of CH_4, C_2H_6, C_3H_8 and C_4H_6 and GC-TCD for quantification of O_2, N_2, CO and CO_2. Single point calibration method was used for the analysis of the four matrix-matched gas mixtures. The averaged analysis response of 4 injections, standard deviations, gravimetric amount fraction (x_{grav}) for each component from the gravimetric preparation in accordance with ISO 6142, calculated verification amount fraction for component $i\,(x_{veri})$, calculated percentage difference between the gravimetric and verification amount fraction, sensitivity ratio and instrument drift during analysis are all tabulated in **Table 5.11**. The statistical data allows for the following interpretation of the result:

- The % difference results allow for the examination of measurement accuracy.
- The %RSD results provide for the evaluation of repeatability and reproducibility of the measurements.

- The sensitivity ratio results relate to the internal consistency of the gas mixture in the cylinder.
- Drift relates to the stability of the instrument during analysis.

Table 5.11 Data analysis of all components of interest in the high range refinery gas mixtures using DM2 as a reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)[1]**	**Standard deviation[2]**	**%RSD[3]**	**x_{grav} (%mol.mol^{-1})[4]**	**x_{veri} (%mol.mol^{-1})[5]**	**Sensitivity ratio[6]**	**Drift[7]**
DM1	CH_4	3524.867	3.659	0.104	5.822	5.795	0.991	-0.439
	C_2H_6	4499.733	8.442	0.188	4.098	4.082	0.992	-0.526
	C_3H_8	7969.350	18.143	0.228	4.937	4.919	0.993	-0.479
	C_4H_6	2827.483	3.227	0.114	1.485	1.480	0.994	-0.435
	O_2	2403.169	0.315	0.013	1.069	1.071	1.003	0.008
	N_2	3501.878	0.729	0.021	21.754	21.755	1.001	0.189
	CO	9666.650	1.366	0.014	9.999	10.053	0.993	0.252
	CO_2	2020.078	1.401	0.069	8.038	8.101	0.996	-0.746
DM3	CH_4	3036.678	8.909	0.293	5.747	5.742	0.998	-0.378
	C_2H_6	4396.289	30.195	0.687	4.091	4.105	0.994	0.094
	C_3H_8	7896.989	54.299	0.688	4.975	4.993	0.993	0.131
	C_4H_6	2788.667	7.158	0.257	1.482	1.489	0.994	-0.098
	O_2	2041.308	3.679	0.180	1.124	1.119	1.003	0.071
	N_2	3516.400	2.610	0.074	21.846	21.840	1.000	-0.379
	CO	10299.633	32.260	0.313	9.951	10.003	1.007	-0.068
	CO_2	2007.311	1.305	0.065	7.990	8.023	0.996	-0.049
DM4	CH_4	3521.333	1.787	0.051	5.936	5.917	0.998	0.164
	C_2H_6	4497.800	4.346	0.097	4.019	4.007	0.994	0.001
	C_3H_8	7968.033	6.811	0.085	4.957	4.942	0.993	-0.004
	C_4H_6	2822.400	0.782	0.028	1.470	1.461	0.989	0.187
	O_2	2394.925	1.036	0.043	0.954	0.958	1.008	0.134
	N_2	3470.633	15.968	0.460	22.128	22.113	1.000	-0.401
	CO	9964.328	6.223	0.062	10.085	10.003	1.007	-0.068
	CO_2	2001.367	1.976	0.099	8.045	8.023	0.993	-0.407

[1]Average peak area of four (4) analytical response of component i, [2]Standard deviation of the four peak areas calculated using, [3]% RSD is the relative standard deviation given by **equation 4.14,** [4]x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142**,** [5]x_{veri} is the average verification amount fraction of 5 runs for component i, [6]%Difference between the gravimetric and verification amount fraction calculated using **equation 4.13,** [7]Sensitivity ratio is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11,** [8]Drift is the measure of the changes in the instrument during analysis calculated using **equation 4.10**

The results in **Table 5.11** show that DM2 was set as the reference gas mixture, while DM1, DM3, and DM4 were set as the sample gas mixtures. This test was done to verify the gravimetric amount fractions of all the components of interest in the sample mixtures. The tabulated averaged analysis response was 4 injections per gas mixture following the substitution method (A-B-A sequence). In other words, the sequence was as follows: 4 injections of reference gas mixture DM2, 4 injections of sample gas mixture DM1, and then 4 injections of DM2. The repeatability results of the analysis ranged from 0.013 to 1.841 %RSD. Three repetitions of this sequence were performed to analyse each sample mixture. The monitored instrumental drifts ranged between 0.008 and 0.746% during analysis of DM1, 0.0499 to 0.379% during analysis of DM3, and 0.002 and 0.401% during analysis of DM4. The measured drift of less than 1% suggests no significant changes in the instrument responses. High instrumental drifts can compromise the validity of the conclusions drawn from measurements made with an instrument (Hayward et al., 2002). Thus, it is imperative to monitor drift.

Furthermore, the accuracy of the high range reference gas mixtures between the gravimetric amount fractions and the verification amount fractions was calculated using percent difference. The results for these are shown in **Table 5.12** for CH_4, C_2H_6, C_3H_8, and C_4H_6 and **Table 5.13** for O_2, N_2, CO, and CO_2. The uncertainties associated with the verification of each component of interest in the study were calculated from the repeatability measurements. The percentage differences of the components of interest in the prepared gas mixtures were less than 0.6018%. This then leads to the conclusion that the verification amount fractions were confirmed to be less than 1% of the gravimetric amount fractions. Each component of interest in the gas mixtures was also determined to be reliable and validated given that the absolute difference between the gravimetric and analytical amount fractions is less than the calculated combined standard uncertainty following ISO 6143:2001's acceptable criteria stated in **equation 4.7** except for O_2, CO, and CO_2 for gas mixture DM3. This is because of the exceptionally low verification uncertainties that could be attributed to the fact that gas mixture DM3 was the last sample mixture to be analysed, giving the instrument time to stabilise.

Table 5.12 Verification results for the measurement of CH_4, C_2H_6, C_3H_8 and C_4H_6 in high range refinery reference gas mixtures.

Component	**Cylinder ID**	x_{grav} **(%mol.mol^{-1})**[1]	u_{grav} **(%mol.mol^{-1})**[2]	x_{veri} **(%mol.mol^{-1})**[3]	u_{veri} **(%mol.mol^{-1})**[4]	**Difference**[5]	**%Difference**[6]	$U_{combined}$ **(%mol.mol^{-1})**[7]	**%REU**[8]
CH_4	DM1	5.8224	0.0005	5.7947	0.0174	0.0277	0.4771	0.0348	0.5978
	DM2	5.9783	0.0005	5.9561	0.0386	0.0222	0.3723	0.0772	1.2921
	DM3	5.7472	0.0005	5.7420	0.0234	0.0052	0.0906	0.0467	0.8127
	DM4	5.9359	0.0005	5.9170	0.0392	0.0189	0.3190	0.0784	1.3203
C_2H_6	DM1	4.0981	0.0005	4.0818	0.0125	0.0163	0.3971	0.0250	0.6091
	DM2	4.1736	0.0005	4.1804	0.0302	0.0068	0.1617	0.0604	1.4471
	DM3	4.0910	0.0005	4.1049	0.0234	0.0139	0.3407	0.0468	1.1445
	DM4	4.0191	0.0005	4.0072	0.0242	0.0119	0.2961	0.0485	1.2066
C_3H_8	DM1	4.9371	0.0003	4.9193	0.0148	0.0178	0.3613	0.0297	0.6015
	DM2	4.9573	0.0003	4.9752	0.0383	0.0179	0.3598	0.0766	1.5461
	DM3	4.9745	0.0003	4.9927	0.0289	0.0182	0.3660	0.0578	1.1613
	DM4	4.9569	0.0003	4.9420	0.0369	0.0149	0.3006	0.0737	1.4876
C_4H_6	DM1	1.4850	0.0002	1.4799	0.0046	0.0051	0.3414	0.0091	0.6150
	DM2	1.4905	0.0002	1.4880	0.0152	0.0025	0.1683	0.0304	2.0388
	DM3	1.4819	0.0002	1.4888	0.0062	0.0069	0.4625	0.0124	0.8356
	DM4	1.4703	0.0002	1.4615	0.0066	0.0088	0.6018	0.0131	0.8923

[1] $\boldsymbol{x_{grav}}$ is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142, [2] $\boldsymbol{u_{grav}}$ is the standard uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*), [3] $\boldsymbol{x_{veri}}$ is the average verification amount fraction of 5 runs for component i, [4] $\boldsymbol{u_{veri}}$ is the standard uncertainty associated with the verification amount fraction for component i, [5] **Difference** between the gravimetric and verification amount fraction $|x_{grav} - x_{ver}|$, [6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13,** [7] $\boldsymbol{U_{combined}}$ is the combined expanded uncertainty, [8] Percentage relative expanded uncertainty associated with the gravimetric amount fraction

Table 5.13 Verification results for the measurement of O_2, N_2, CO and CO_2 in high range refinery reference gas mixtures.

Component	Cylinder ID	x_{grav} (%mol.mol^{-1})[1]	u_{grav} (%mol.mol^{-1})[2]	x_{veri} (%mol.mol^{-1})[3]	u_{veri} (%mol.mol^{-1})[4]	Difference[5]	%Difference[6]	$U_{combined}$ (%mol.mol^{-1})[7]	%REU[8]
O_2	DM1	1.0694	0.0002	1.0707	0.0008	0.0013	0.1154	0.0016	0.1508
	DM2	0.9764	0.0002	0.9782	0.0010	0.0018	0.1851	0.0021	0.2121
	DM3	1.1243	0.0002	1.1193	0.0012	0.0050	0.4481	0.0023	0.2090
	DM4	0.9537	0.0002	0.9575	0.0016	0.0038	0.3980	0.0323	0.3314
N_2	DM1	21.7538	0.0006	21.7548	0.0342	0.0010	0.0048	0.0684	0.3142
	DM2	21.8281	0.0006	21.8203	0.0853	0.0078	0.0355	0.1706	0.7816
	DM3	21.8464	0.0006	21.8395	0.0727	0.0069	0.0316	0.1453	0.6652
	DM4	22.1284	0.0006	22.1132	0.0647	0.0152	0.0685	0.1294	0.5848
CO	DM1	9.9992	0.0004	10.0531	0.0448	0.0539	0.5391	0.0896	0.8961
	DM2	9.8884	0.0004	9.8828	0.0575	0.0056	0.0567	0.1150	1.1631
	DM3	9.9506	0.0004	10.0035	0.0173	0.0575	0.5315	0.0346	0.3480
	DM4	10.0850	0.0004	10.0713	0.0379	0.0137	0.1362	0.0757	0.7508
CO_2	DM1	7.9899	0.0003	8.0225	0.0587	0.0326	0.4086	0.1174	1.4699
	DM2	8.0894	0.0003	8.1078	0.0740	0.0184	0.2278	0.1481	1.8304
	DM3	7.9899	0.0003	8.0228	0.0084	0.0329	0.4126	0.0168	0.2106
	DM4	8.0446	0.0003	8.0225	0.0192	0.0221	0.2739	0.0384	0.2138

[1]x_{grav} is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142, [2]u_{grav} is the standard uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*), [3]x_{veri} is the average verification amount fraction of 5 runs for component i, [4]u_{veri} is the standard uncertainty associated with the verification amount fraction for component i, [5]**Difference** between the gravimetric and verification amount fraction $|x_{grav} - x_{ver}|$, [6]**%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13,** [7]$U_{combined}$ is the combined expanded uncertainty, [8] Percentage relative expanded uncertainty associated with the gravimetric amount fraction

Gravimetric amount fractions of CH_4, C_2H_6, C_3H_8, C_4H_6, O_2, N_2, CO, and CO_2 are plotted against verification amount fractions in **Figures 5.2** and **5.3** for the gas mixes DM1 to DM4, respectively. Each of the four gas mixtures is denoted by a separate symbol: a red diamond for DM1, a blue circle for DM2, a black triangle for DM3, and a green square for DM4. Each graph illustrates the linear relationship between the results by drawing a line through the origin with a 1:1 slope. Linear graphs are used to show the relationship between two quantities, in this case, gravimetric versus verification amount fractions. Because the single-point calibration method is used for linear functions and matrix-matched gas mixtures with similar amount fractions relative to the components in the mixture (Cuadros-Rodrguez et al., 2007), this type of analysis was possible. A good linear relationship between the gravimetric and verification quantity fractions is evident with the data points near and on the linearity line.

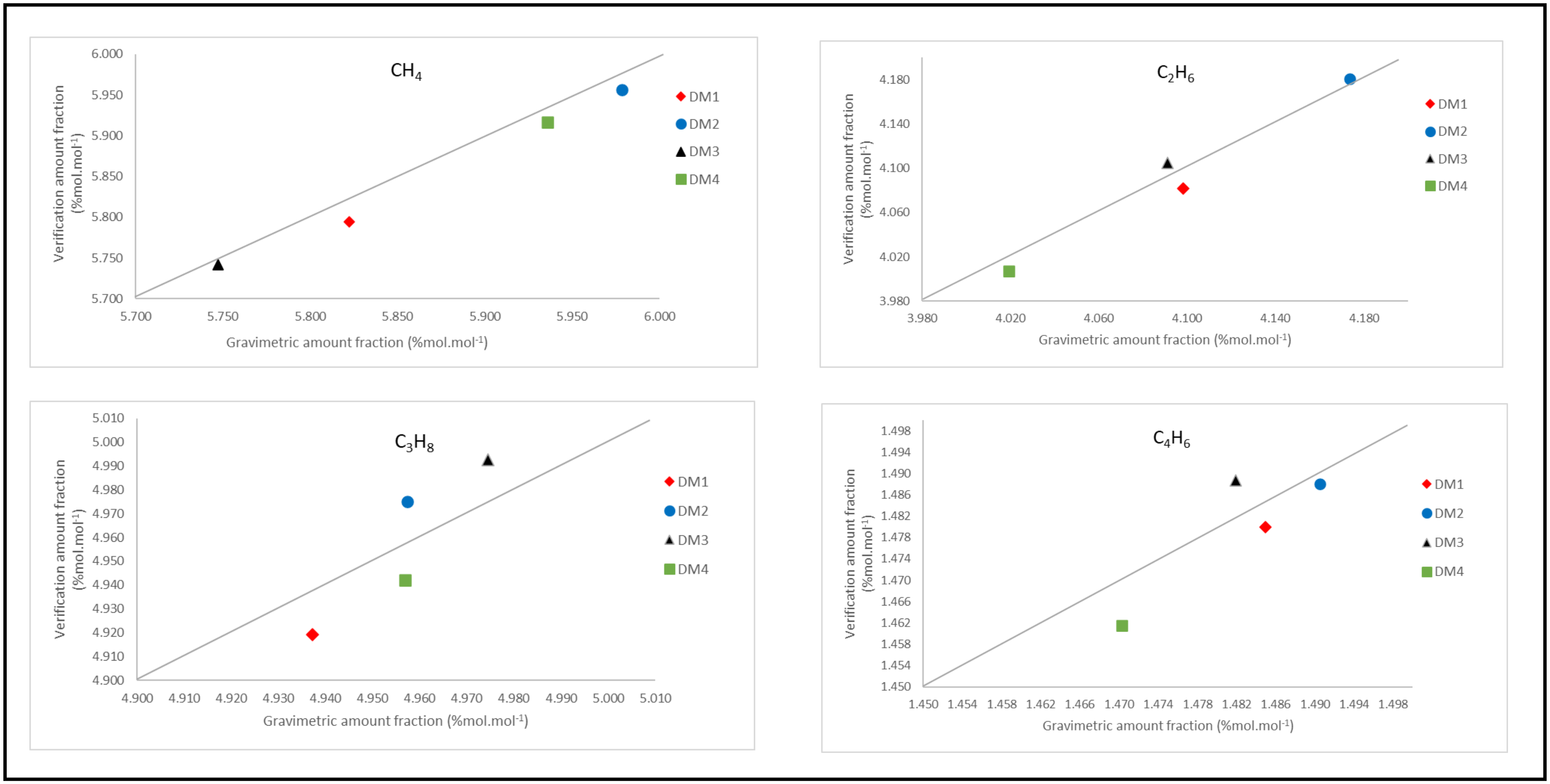

Figure 5.2 Scatterplot graphs of the gravimetric amount fractions against verification amount fractions of CH_4, C_2H_6, C_3H_8 and C_4H_6 in the high range refinery reference gas mixtures.

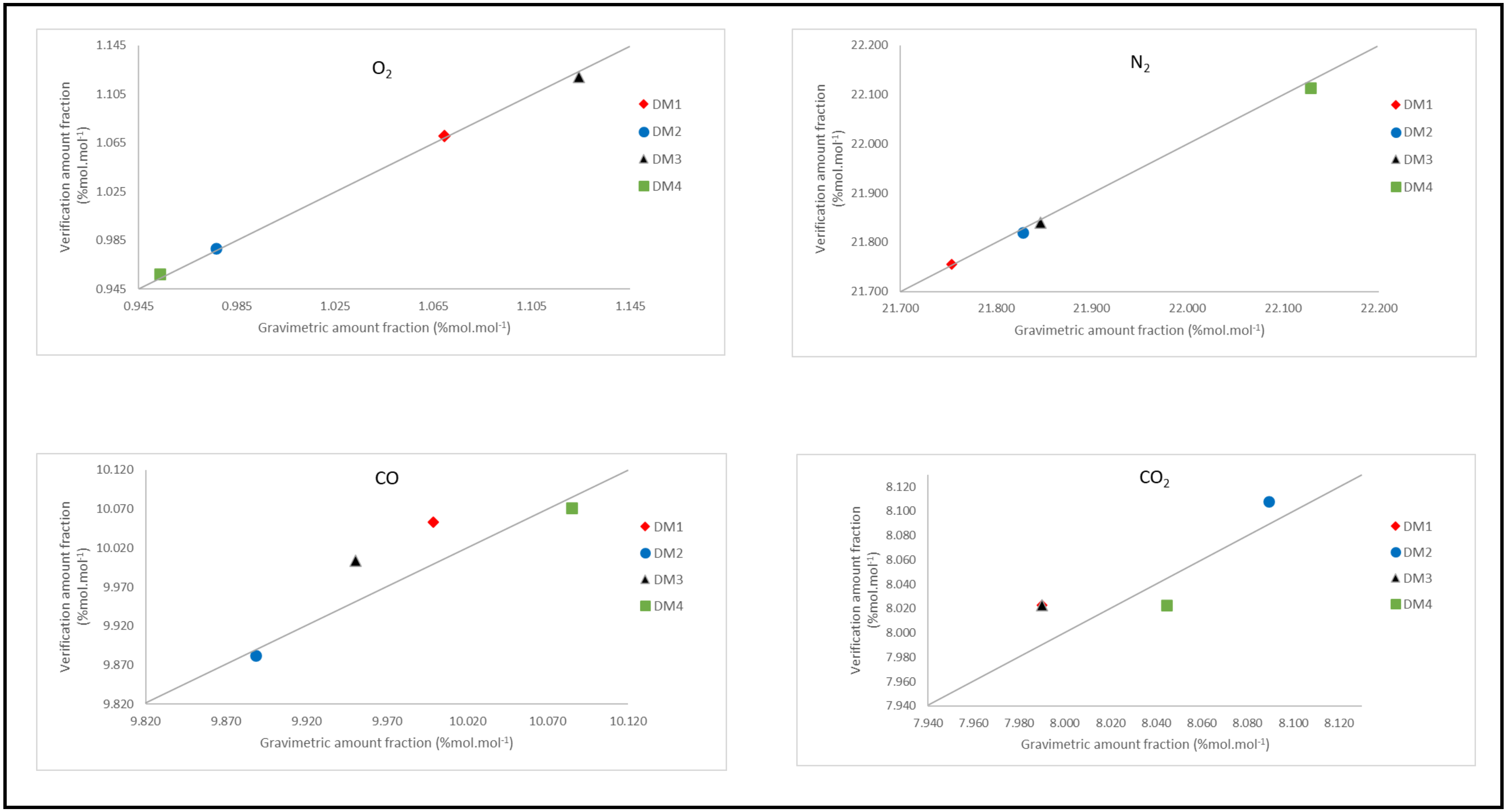

Figure 5.3 Scatterplot graphs of the gravimetric amount fractions against verification amount fractions of O_2, N_2, CO and CO_2 in the high range refinery reference gas mixtures.

5.2.4. Internal consistency results for high range refinery reference gas mixtures

Internal consistency evaluation of the high range refinery reference gas mixtures was done using sensitivity ratios. This was done to examine the comparability of the gas mixtures with one another. Graphical representations of the results can be seen in **Figures 5.4 to 5.6** with gas mixtures DM1, DM3, and DM4 used as samples and gas mixture DM2 as a reference. A sensitivity ratio close to one demonstrates ideal internal consistency between the sample and reference gas mixtures. Depending on how much each sample deviates from the reference, the sensitivity ratios will vary from the value of one. As a result, samples with sensitivity ratios that are closer to one demonstrate acceptable internal consistency.

The sensitivity ratios for all components of interest in the study ranged from 0.991 to 1.003 for gas mixture DM1, 0.993 to 1.007 for gas mixture DM3 and 0.989 to 1.007 for gas mixture DM4, all relative to gas mixture DM2. The calculated sensitivity ratios demonstrated uniformity of gas mixtures DM1, DM2, and DM3 to the reference gas mixture DM2 for all the components of interest.

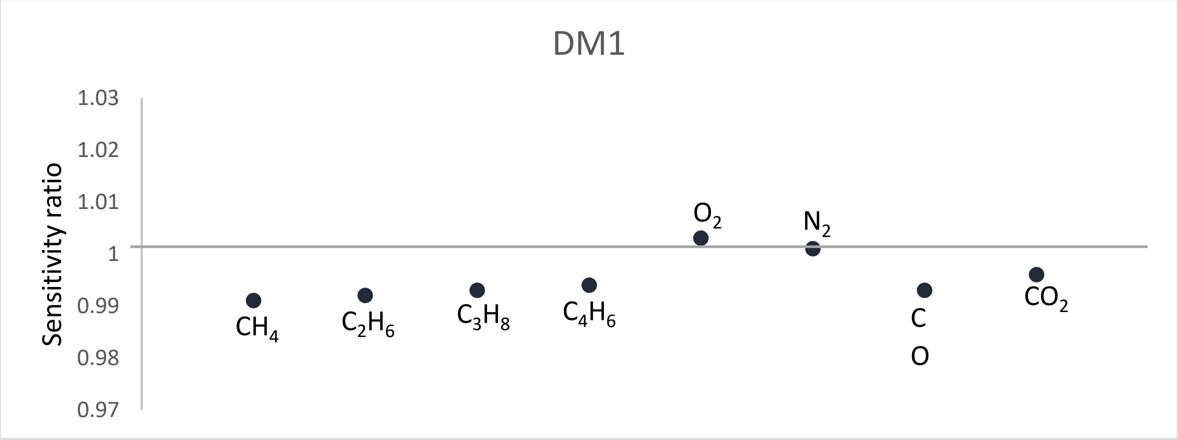

Figure 5.4 Internal consistency results for all eight components of interest in gas mixture DM1 with DM2 as a reference.

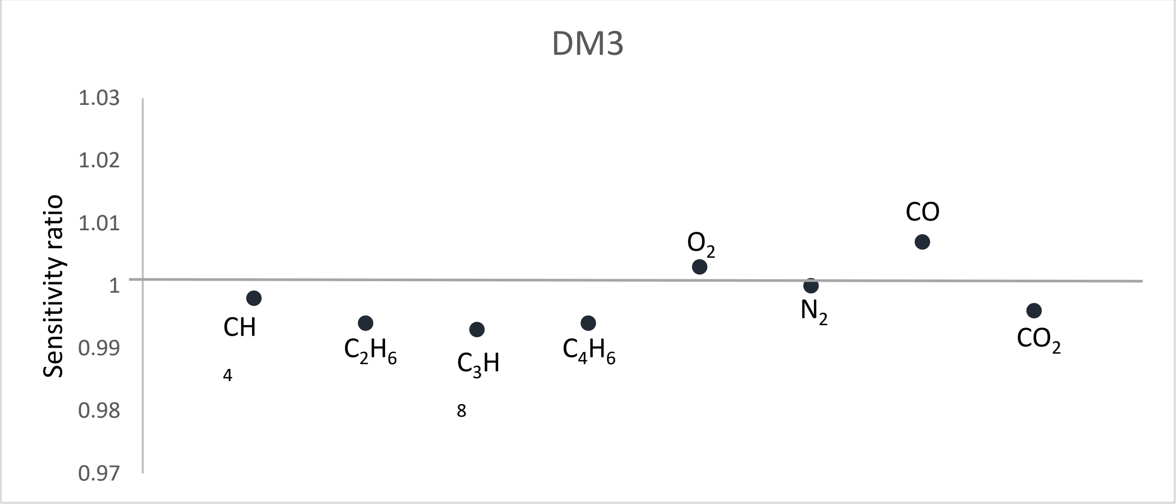

Figure 5.5 Internal consistency results for all eight components of interest in gas mixture DM3 with DM2 as a reference.

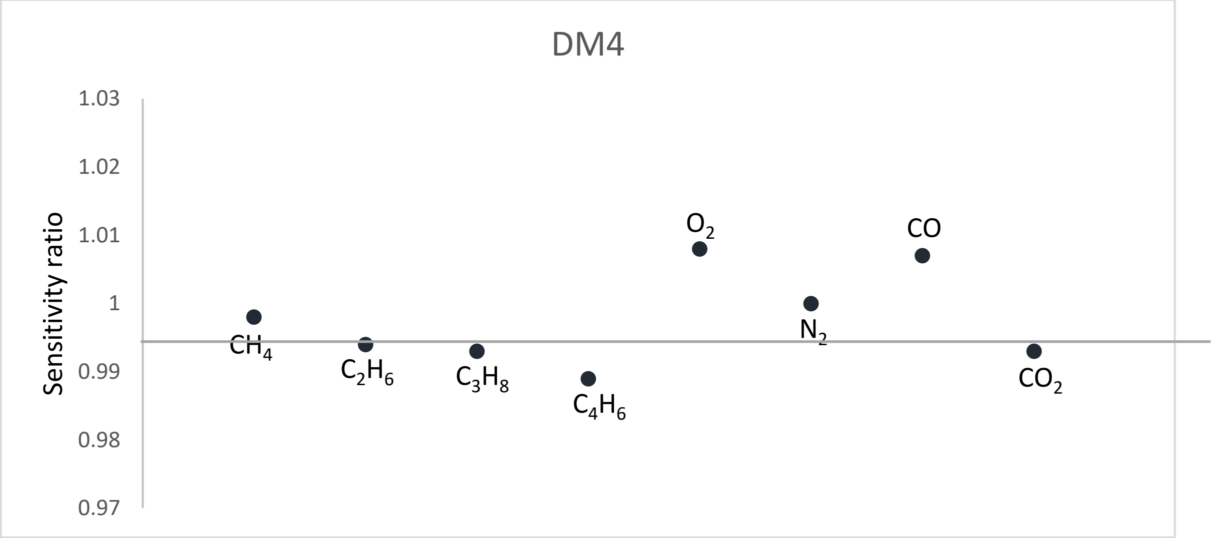

Figure 5.6 Internal consistency results for all eight components of interest in gas mixture DM4 with DM2 as a reference.

5.2.5. Measurement comparability test results

Measurement comparability tests were conducted in order to quantitatively assess the capabilities and competence required for purity analysis, gravimetric preparation, and value assignment of the NMISA-produced refinery gas mixes against those of another National Metrology Institute, in this case, NPL. This was achieved by comparing the developed refinery reference gas mixture DM3 to NPL-purchased certified reference material of refinery reference gas standard (NPL-1) that were at similar amount fractions on the GC FID/TCD as explained in **Chapter 4 section 4.13**. Gas mixture NPL-1 was used as a standard, while gas mixture DM3 was treated as the unknown and the verification amount fractions were determined using single point calibration.

The comparison results between the developed refinery reference gas mixture and the NPL gas standard for the percentage difference between the gravimetric preparation value and the verification amount fractions for DM3 are shown in **Table 5.14** and **Figure 5.7**. The overall absolute percentage difference between the gravimetric and verification amount fractions of all components of interest ranged from 0.051 to 1.1945%, according to the results. Oxygen had the most noticeable % difference of 1.1945% which can be attributed to its reactive nature due to the biradical electron configuration (Krumova and Cosa, 2016). The percentage difference was calculated using **equation 4.13**, where it is equal to the absolute difference between the gravimetric and average verification amount fractions divided by the gravimetric amount fraction multiplied by 100. These results demonstrate measurement equivalence between the developed refinery reference gas mixture DM3 and the NPL refinery gas standard by illustrating a negligible difference between the gravimetric and verification amount fractions, with percentage difference measurement results lower than 1.2% for all components of interest.

Table 5.14 Measurement results for comparison between cylinder DM3 against NPL-1 using gas chromatography.

Cylinder number	**Component**	$\boldsymbol{x_{grav}}$ **(%mol.mol^{-1})**[1]	$\boldsymbol{u_{grav}}$ **(%mol.mol^{-1})**[2]	$\boldsymbol{x_{veri}}$ **(%mol.mol^{-1})**[3]	$\boldsymbol{u_{veri}}$ **(%mol.mol^{-1})**[4]	**% Difference**[5]	**Combined expanded uncertainty ($\boldsymbol{k=2}$)**[6]
D62 6432	N_2	21.8464	0.0006	21.8574	0.0405	0.0501	0.0419
	CO	9.9506	0.0004	9.9645	0.0283	0.1392	0.0298
	CO_2	7.9899	0.0003	8.0067	0.0269	0.2101	0.0275
	CH_4	5.7472	0.0005	5.7602	0.0202	0.2255	0.0229
	C_3H_8	4.9745	0.0003	4.9940	0.0184	0.3896	0.0207
	C_2H_6	4.0910	0.0005	4.0987	0.0145	0.1884	0.0164
	C_4H_6	1.4819	0.0002	1.4890	0.0064	0.4775	0.0070
	O_2	1.1243	0.0002	1.1379	0.0042	1.1945	0.0042

[1] $\boldsymbol{x_{grav}}$ is the gravimetric amount fraction for component i from the gravimetric preparation in accordance with ISO 6142

[2] $\boldsymbol{u_{grav}}$ is the standard uncertainty associated with the gravimetric amount fraction for component i

[3] $\boldsymbol{x_{veri}}$ is the average verification amount fraction of 5 runs for component i

[4] $\boldsymbol{u_{veri}}$ is the verification standard uncertainty associated with the verification repeatability measurement

[5] **%difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[6] **Combied expanded uncertainty** of the gravimetric and verification uncertainties ($U = 2\sqrt{(u_{grav})^2 + (u_{veri})^2}$)

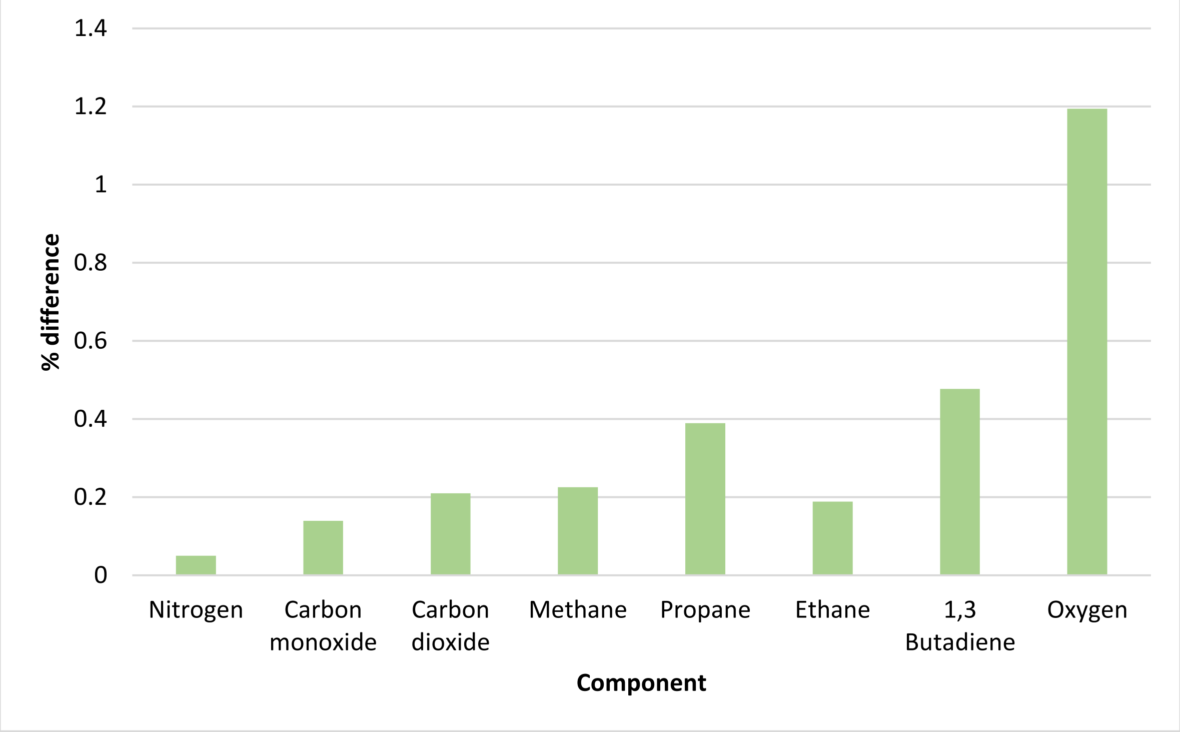

Figure 5.7 Calculated percentage difference of the eight components of interest in the developed high range refinery gas mixtures.

5.2.6. Adsorption study results on the high range refinery reference gas mixtures

The adsorption study was carried out with the mother cylinder DM4 connected to the daughter cylinder $DM4_d$, as detailed in **Section 4.9**. The mother cylinder was gravimetrically prepared according to ISO 6142 in a 10 dm^3 capacity cylinder. Prior to the transfer of gas from one cylinder to another, the mother cylinder was at 7.4 MPa. After transfer into the daughter cylinder, the final pressures in the cylinders were 3.6 MPa for the daughter cylinder and 3.7 MPa for the mother cylinder. **Equation 4.13** was used for the calculation of the percentage difference between the mother and daughter cylinders.

$$\%\ difference = \frac{|A_{MC} - A_{DC}|}{A_{MC}} \times 100 \qquad \textbf{4.13}$$

Where A_{MC} is the average peak area of the mother cylinder for the component of interest and A_{DC} is the average peak area of the daughter cylinder for the component of interest.

From **Table 5.15**, adsorption results ranged from a 0.10 to 0.52% difference between the mother and daughter cylinders for all components of interest. These results indicate that there is little adsorption loss on the internal surfaces of the aluminium cylinders used, based on the analytical response variation between the mother and daughter cylinders.

The sensitivity ratio was also used to study adsorption because it is well defined by the change in the response of the mother cylinder divided by the corresponding change in the response of the daughter cylinder in the gas chromatograph instrument on the FID and TCD channels. The sensitivity ratio is expressed on a scale of 0 to 1, with an ideal ratio of 1 that also translates to 100% accuracy. In **Figure 5.8**, the sensitivity ratio is represented in blue circles, and the error bars represent the verification uncertainty.

All the components demonstrate consistency within the uncertainty, confirming that there is no significant adsorption observed on the cylinder walls, with the sensitivity ratio ranging from 0.995 to 1.004. These results demonstrate very little adsorption, further corroborating the fact that treated aluminium cylinders are highly resilient to adsorption for components of CH_4, C_2H_6, C_3H_8, C_4H_6, CO, CO_2, O_2, and N_2 at amount fractions ranging from 1 – 22 $\%mol.mol^{-1}$.

Table 5.15 Adsorption results for high range refinery reference gas mixtures in 10 L aluminium cylinders.

Component	**Refinery reference gas mixtures**									
	DM4 (Mother cylinder)				**$DM4_d$ (Daughter cylinder)**					
	x_{grav} **(%mol.mol^{-1})**[1]	**average peak area**[2]	**%RSD**[3]	**Sensitivity**[4]	x_{grav} **(%mol.mol^{-1})**	**average peak area**	**%RSD**	**Sensitivity**	**%DIFF**[5]	**Sensitivity ratio**[6]
N_2	22.13	57331.71	0.26	0.26	22.13	57272.24	0.36	0.26	0.10	0.999
CO	10.09	56697.25	2.50	0.56	10.09	56921.46	1.63	0.56	0.40	1.004
CO_2	8.04	32080.10	0.48	0.40	8.04	31928.62	0.19	0.40	0.47	0.995
CH_4	5.94	2540.38	0.69	0.04	5.94	2529.24	0.51	0.04	0.44	0.996
C_3H_8	4.96	6259.58	0.71	0.13	4.96	6226.74	0.56	0.13	0.52	0.995
C_2H_6	4.02	3345.45	0.72	0.08	4.02	3340.81	1.56	0.08	0.14	0.999
C_4H_6	1.47	2432.49	0.74	0.17	1.47	2419.79	0.56	0.16	0.52	0.995
O_2	0.95	2015.99	0.29	0.21	0.95	2010.76	0.32	0.21	0.26	0.997

[1] x_{grav} is the gravimetric amount fraction for component i from the gravimetric preparation in accordance with ISO 6142

[2] **Average peak area** of five (5) peak areas response of component i

[3] **Percentage relative standard deviation** calculated using **equation 4.8**

[4] **Sensitivity** is the average peak area divided by the gravimetric amount fraction component i using **equation 4.12**

[5] **%Difference** between the peak area of the mother cylinder and the daughter cylinder calculated using **equation 4.1**

[6] **Sensitivity ratio** is the sensitivity of the mother cylinder divided the sensitivity of the daughter cylinder using **equation 4.11**

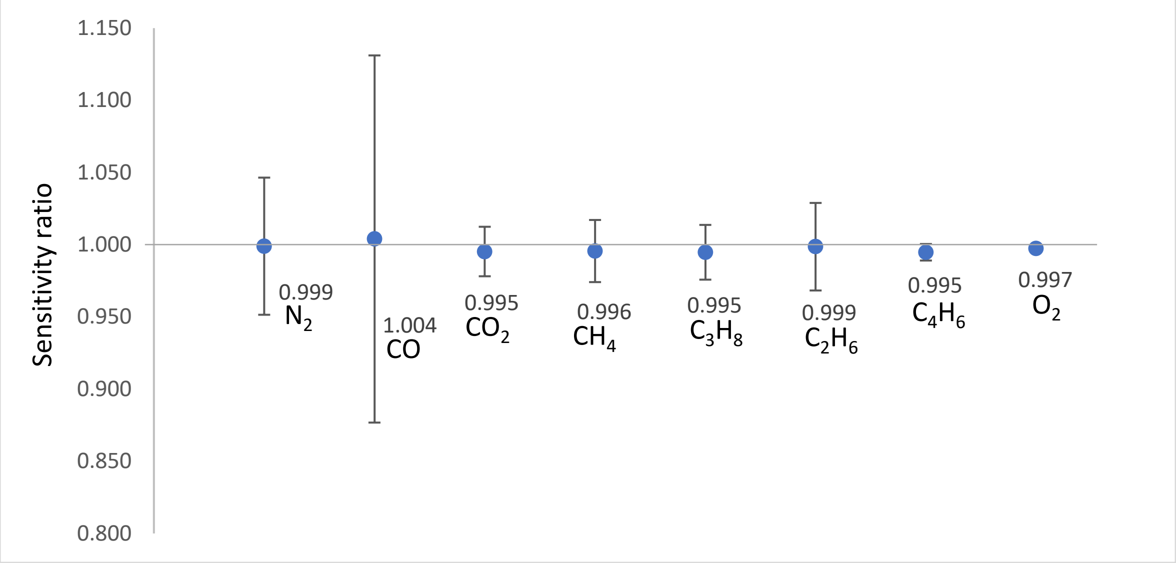

Figure 5.8 Adsorption test for high range refinery reference gas mixtures in an aluminium cylinder.

5.2.7. Stability assessment of high range refinery reference gas mixtures

The results of the long-term stability assessment for the gas mixture DM3 are shown in **Figures 5.9 to 5.16** below. The upper and lower limits of 2% of the gravimetric amount fraction are indicated by the red lines ($k = 2$ at a 95% confidence level). The gravimetric amount fractions are represented by a green line, the verification amount fractions are represented by black diamonds, and the verification uncertainty is represented by the error bars. The stability tests were conducted in four sets of measurements that were taken over a period of nine months: six runs in March 2022, five runs in July 2022, and two runs in December 2022. The stability of all the components of interest in the study, namely methane, ethane, propane, 1,3-butadiene, oxygen, nitrogen, carbon monoxide, and carbon dioxide, shows that the verification amount fractions over the eight months of analysis fall within the 2% of the gravimetric amount fractions. Further to this, the uncertainties of the gas mixture DM3 fall within the calibration measurement capability limits (lower limit and upper limit) of 2%.

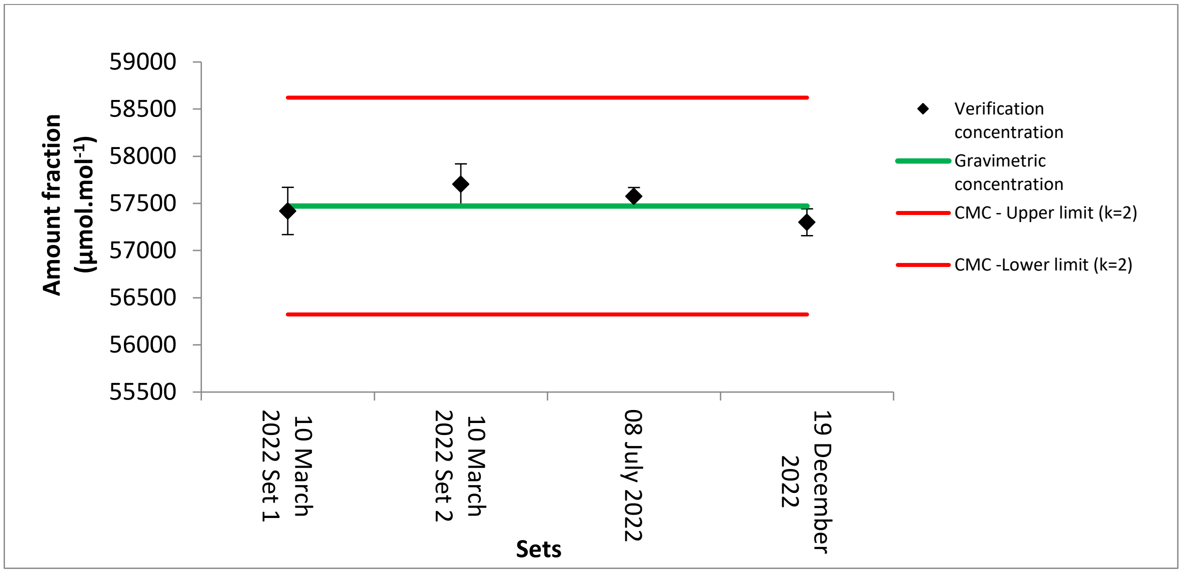

Figure 5.9 Stability results of methane in high range refinery reference gas mixtures.

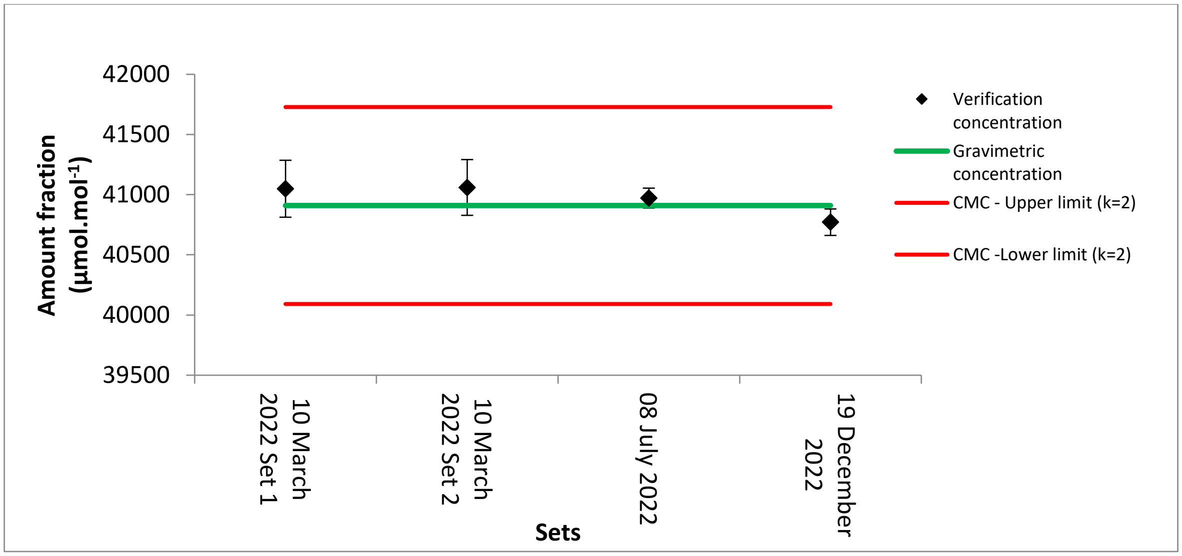

Figure 5.10 Stability results of ethane in high range refinery reference gas mixtures.

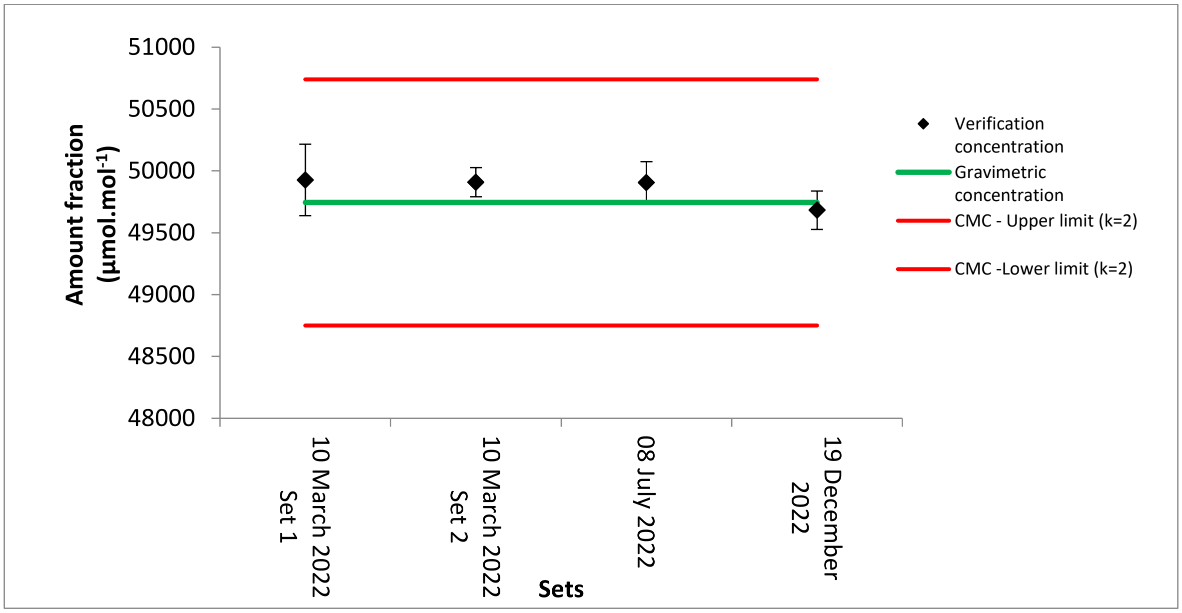

Figure 5.11 Stability results of propane in high range refinery reference gas mixtures.

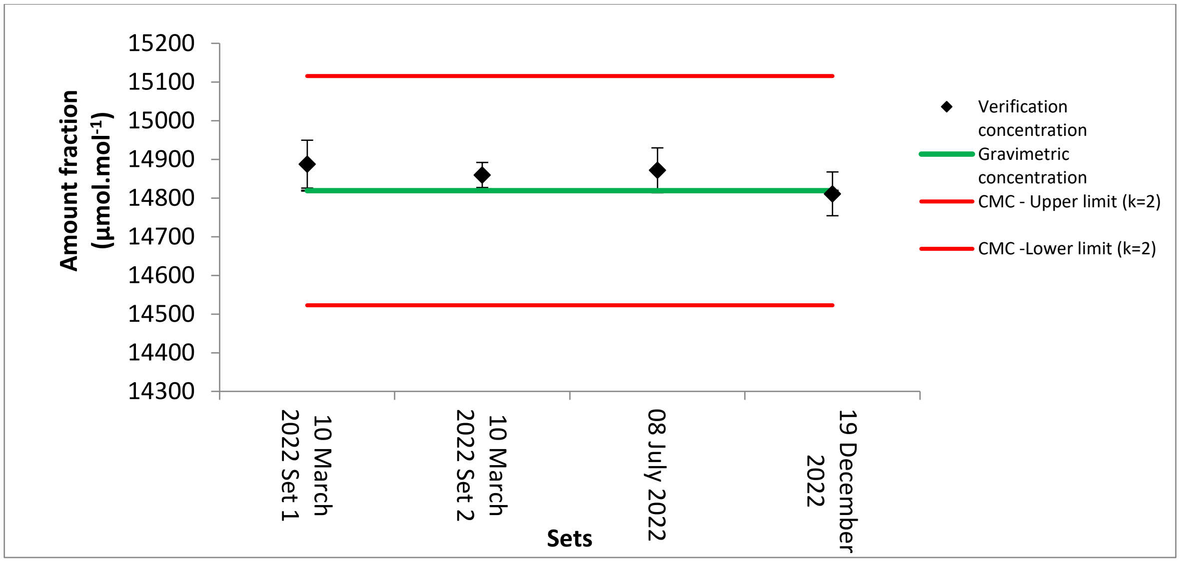

Figure 5.12 Stability results of 1,3-butadiene in high range refinery reference gas mixtures.

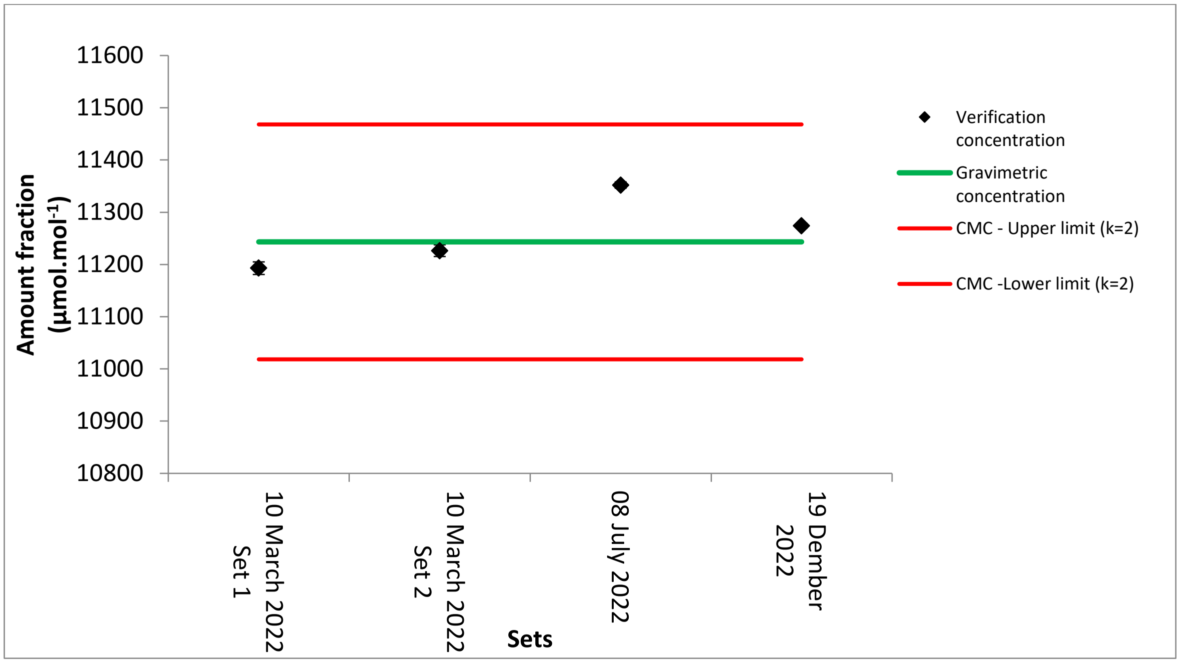

Figure 5.13 Stability results of oxygen in high range refinery reference gas mixtures.

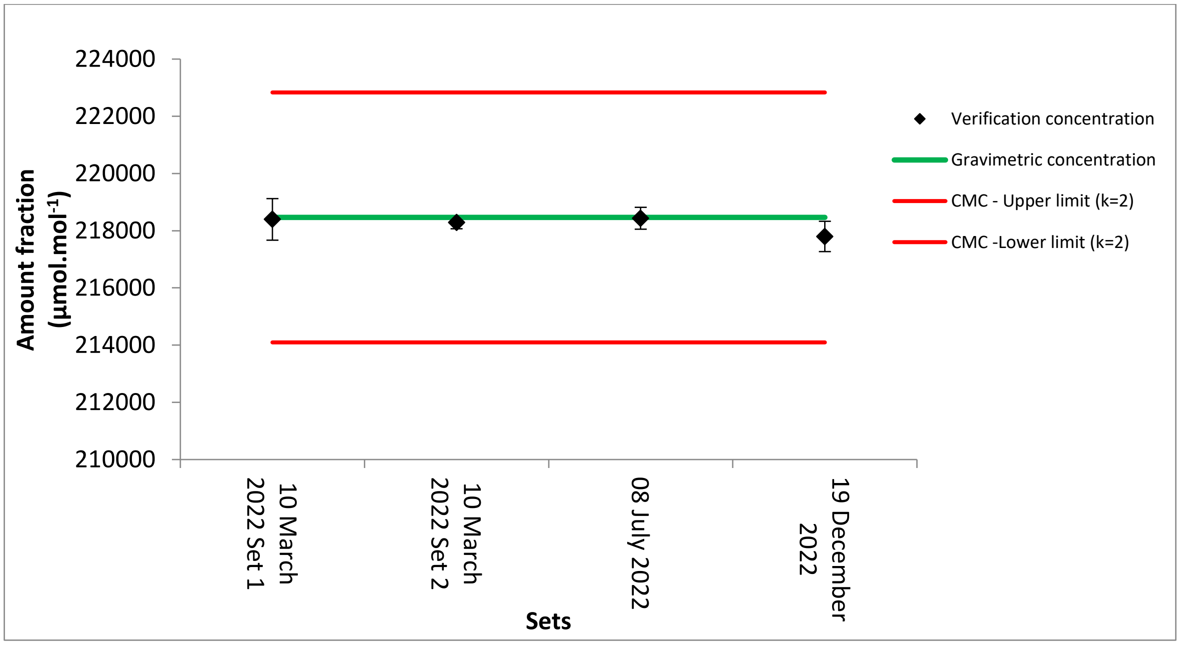

Figure 5.14 Stability results of nitrogen in high range refinery reference gas mixtures.

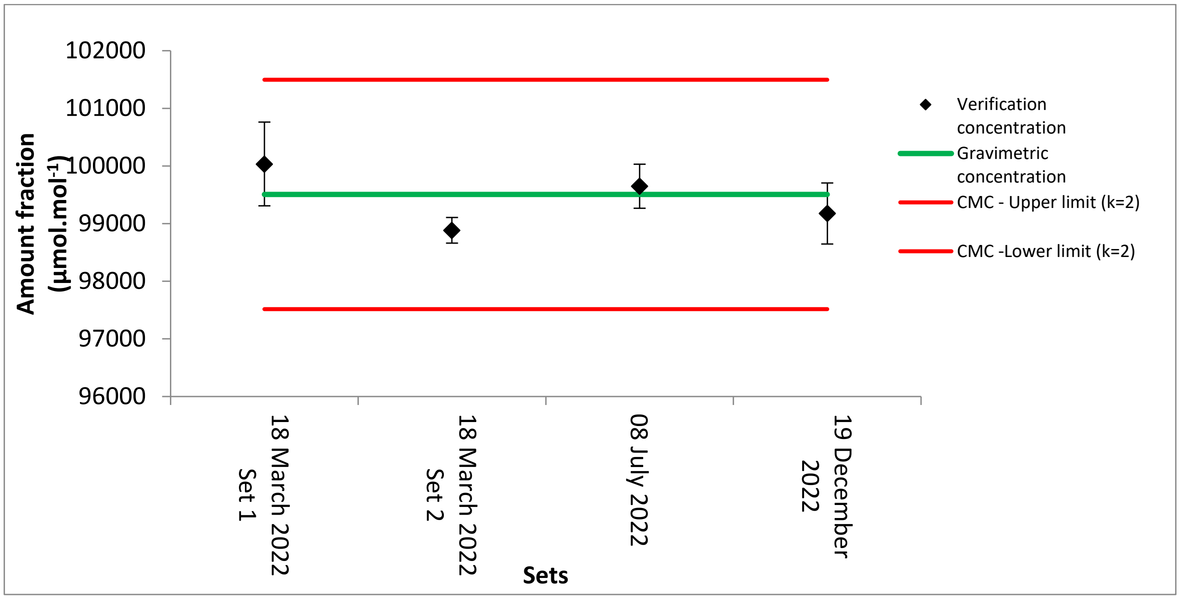

Figure 5.15 Stability results of carbon monoxide in high range refinery reference gas mixtures.

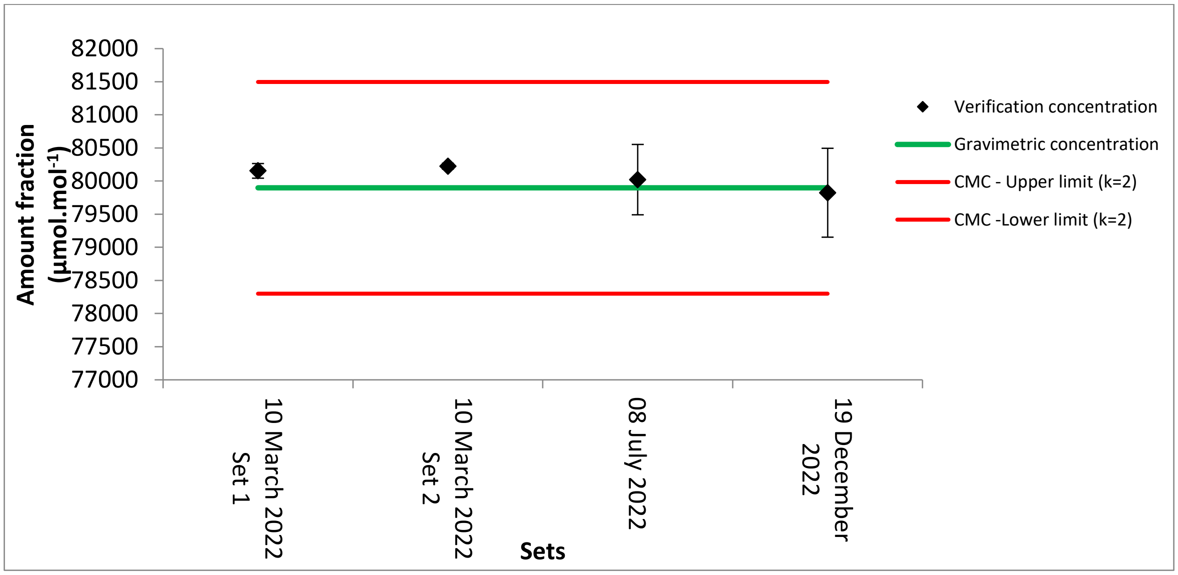

Figure 5.16 Stability results of carbon dioxide in high range refinery reference gas mixtures.

The D statistical test was also performed at a 95 % confidence interval and assuming normal distribution to examine stability of the gas mixtures following ISO 16664:2017 guidelines. The test is given by equation **5.1**.

$$D = \frac{|x_i - x_{i+1}|}{\sqrt{u(x_i)^2 + u(x_{i+1})^2}} \qquad \mathbf{5.1}$$

Where x_i and $u(x_i)$ are the first measurement and its associated uncertainty respectively, and x_{i+1} and $u(x_{i+1})$ are the subsequent measurement and its associated uncertainty respectively.

D < 2 no significant instability

D > 2 significant instability (ISO 16664, 2017).

The results tabulated in **Table 5.16** verify that there were no instabilities detected over the nine-month stability period for all the components of interest in the study, with results ranging from 0.0002 to 1.6328. Despite the fact that all of the components have acceptable stabilities, oxygen is the least stable. This could be attributed to oxygen being the least stable component in the gas mixture.

Table 5.16 Statistical D test for stability assessment for the nine components of interest in the high range refinery reference gas mixtures.

Component	$\boldsymbol{D}$ $\boldsymbol{x_1, x_2}$	$\boldsymbol{D}$ $\boldsymbol{x_2, x_3}$	$\boldsymbol{D}$ $\boldsymbol{x_3, x_4}$
Methane	0.0052	0.0088	0.0082
Ethane	0.0002	0.0092	0.0112
Propane	0.0002	0.0003	0.0077
1,3-butadiene	0.0073	0.0108	0.0177
Oxygen	0.2393	1.6328	0.0313
Nitrogen	0.0002	0.0029	0.0043
Carbon monoxide	0.0382	0.0255	0.0070
Carbon dioxide	0.0007	0.0004	0.0042

$\boldsymbol{D}$ is the test statistic measurement, $\boldsymbol{x_1}$ is the first analysis results, $\boldsymbol{x_2}$ is the second analysis results, $\boldsymbol{x_3}$ is the third analysis results, $\boldsymbol{x_4}$ is the fourth analysis results.

5.2.8. Matrix effect results

Identification and quantification of a specific gas component in a matrix of other gas components, accuracy, precision, and sensitivity of a method are all impacted by matrix effects, which are a key concern in quantitative gas analysis of multi-component gas mixtures. For example, the GC analysis response and accuracy of a component of interest in a multi-component gas mixture may deviate from that found in the binary gas mixture due to matrix effects. As a result, either a false negative result due to ion suppression or a false positive due to ion-enhancement, in which the ionisation efficiency of a compound is increased by the presence of other components in the gas mixture, may occur (Van Eeckhaut et al., 2009).

To evaluate the matrix effect, binary mixtures of each component of interest in the study were compared to the multicomponent refinery reference gas mixture DM1. These binary mixtures were prepared with the same balance as gas mixture DM1 and contained similar amount fractions of the component of interest. For example, for matrix effect analysis of 217537.81 µmol.mol^{-1} of nitrogen in DM1, a binary mixture that consisting of 217072.78 µmol.mol^{-1} nitrogen in helium was prepared. From **Table 5.17** and **Figure 5.17**, the calculated matrix effect ranged from 13.38 to 40.31% indicating a decreased ionisation efficiency of a component of interest is the presence of other components in the mixture. With a ME exceptionally larger than 1%, the ion suppression was evident in all the components of interest in the study. In other words, as a result of competition for ionisation efficiency in the ionisation source, the matrix of the multi-component refinery reference gas mixture led all the individual components to have a lower than usual detector response (Mei et al., 2003).

The variations observed between the binary mixtures and the multi-component refinery reference gas mixtures peak areas allow for the conclusion that the usage of matrix-matched standards for the analysis of multi-component refinery gas mixtures is crucial to obtaining accurate analytical results.

Table 5.17 Matrix effect results for refinery reference gas mixture DM1.

Component	Cylinder ID	Gravimetric amount fraction (μmol.mol^{-1})[1]	Analysis response (Peak area)[2]	Sensitivity[3]	ME[4] (%)
CH_4	$\mathrm{B_{CH_4}}$	59559.58	4687.89	0.08	30.10
	DM1	58224.42	3203.44	0.06	
C_2H_6	$\mathrm{B_{C_2H_6}}$	38885.59	5959.37	0.15	29.65
	DM1	40980.53	4418.49	0.11	
C_3H_8	$\mathrm{B_{C_3H_8}}$	50163.29	11286.80	0.23	27.78
	DM1	49371.46	8022.19	0.16	
C_4H_6	$\mathrm{B_{C_4H_6}}$	4573.09	4573.09	0.31	30.12
	DM1	3209.43	3209.43	0.22	
O_2	$\mathrm{B_{O_2}}$	10094.82	3538.24	0.35	40.10
	DM1	10694.20	2245.15	0.21	
N_2	$\mathrm{BS_{N_2}}$	217072.78	72749.73	0.34	21.51
	DM1	217537.81	57224.03	0.26	
CO	$\mathrm{B_{CO}}$	96226.57	59518.32	0.62	13.38
	DM1	99991.64	53574.20	0.54	
CO_2	$\mathrm{B_{CO_2}}$	80586.87	46249.54	0.57	29.41
	DM1	80375.61	32560.68	0.41	

[1] **Gravimetric amount fraction** for component i obtained from the gravimetric preparation in accordance with ISO 6142

[2] **Analysis response** is the averaged peak area obtained for each measurement for component i

[3] **Sensitivity** is calculated by dividing the gravimetric amount fraction by the analysis response

[4] **%ME** is the matrix effect calculated by equation 3.16 $\mathrm{ME} = \left(\frac{c_{\mathrm{standard}} - c_{\mathrm{i}}}{c_{\mathrm{standard}}}\right) \times 100$

In **figure 5.17**, the matrix effect of oxygen is higher compared to the other components. This might be due to its high reactivity and interactions with the matrix, leading to changes in its signal or measurement. In analytical techniques such as gas chromatography, the presence of reactive matrix components can interfere with the measurement of oxygen, leading to the matrix effect. In these cases, it is important to carefully control the sample matrix and use appropriate sample preparation techniques to minimise the impact of the matrix effect on the accuracy of oxygen measurements. However, the matrix effect for carbon monoxide is lower compared to other components because it is highly volatile and has a low boiling point, which makes it easier to evaporate from the sample matrix (Cradock and Hinchcliffe, 1975). This allows carbon monoxide to be more easily separated from the sample matrix and detected in the final analysis. Additionally, CO is highly reactive, which can help reduce the matrix effect by allowing it to react with other species in the sample matrix. Additionally, other components may have more complex chemical interactions with the sample matrix, which can also contribute to higher matrix effects (Gu and Sun, 2013). The matrix effect can vary greatly depending on the sample matrix and the analysis method used, so it is also possible to observe higher matrix effects for CO in some cases.

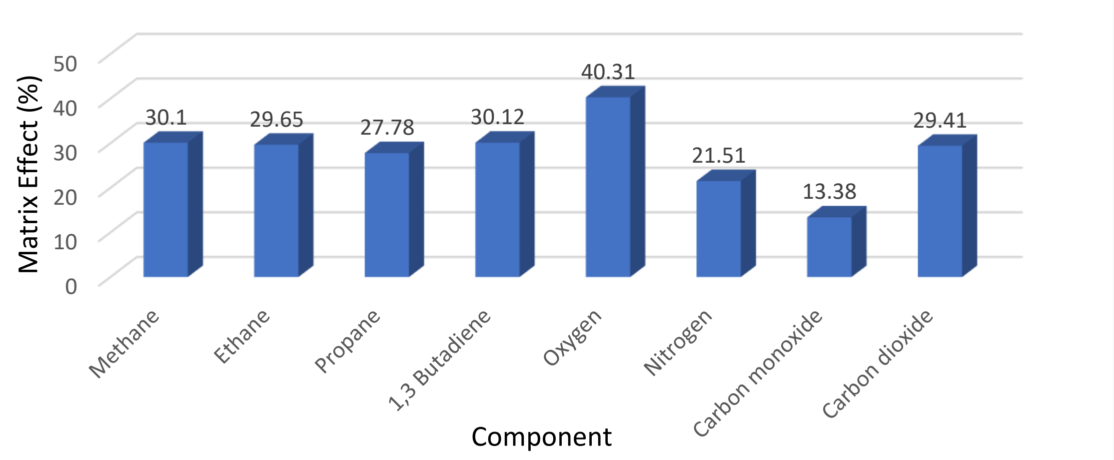

Figure 5.17 Matrix effect results representing signal suppression for refinery reference gas mixture DM1.

5.3. Development of CH_4, C_2H_6 and N_2 in He multi-component pre-mixtures

5.3.1. Gravimetric preparation of CH_4, C_2H_6 and N_2 in He multi-component pre-mixtures results

Five pre-mixtures of CH_4, C_2H_6, and N_2 in He were gravimetrically prepared in accordance with ISO 6142:2015. The gas mixtures were a dilution from high purity CH_4, C_2H_6, and N_2 to 10 %mol.mol^{-1} CH_4, 10 %mol.mol^{-1} C_2H_6, and 10 %mol.mol^{-1} N_2 in the balance of helium. The mixtures were prepared in 5 dm^3 cylinders at 11.0 MPa. Distinctive cylinder identifiers (GE1, GE2, GE3, GE4, and GE5) were used to identify the various gas mixtures. These pre-mixtures were used to prepare the low range refinery reference gas mixtures for this study. The gravimetric results of CH_4, C_2H_6, and N_2 in He multi-component pre-mixtures are shown in **Table 5.18**. The relative expanded uncertainties of the gravimetric reference gas mixtures were found to ≤ 0.0159%, ≤ 0.0219%, and ≤ 0.0090% for CH_4, C_2H_6, and N_2, respectively.

Table 5.18 Gravimetric amount fractions and expanded uncertainties results for CH_4, C_2H_6 and N_2 in He gas mixtures.

Cylinder ID	Component	x_{grav} (%mol.mol^{-1})^1	U_{grav} (%mol.mol^{-1})^2	%REU^3
GE1	CH_4	10.8223	0.0016	0.0151
	C_2H_6	9.7447	0.0021	0.0219
	N_2	9.8294	0.0009	0.0089
GE2	CH_4	9.6879	0.0015	0.0158
	C_2H_6	9.6509	0.0021	0.0219
	N_2	9.7311	0.0009	0.0088
GE3	CH_4	9.9393	0.0016	0.0159
	C_2H_6	9.8815	0.0022	0.0219
	N_2	10.0268	0.0009	0.0090
GE4	CH_4	10.4191	0.0016	0.0156
	C_2H_6	9.9759	0.0022	0.0219
	N_2	10.0524	0.0009	0.0090
GE5	CH_4	11.2811	0.0017	0.0150
	C_2H_6	10.0181	0.0022	0.0219
	N_2	10.0605	0.0009	0.0090

$^1x_{grav}$ is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142,

$^2U_{grav}$ is the expanded uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*) and

^{3}**%REU** is the percentage relative expanded uncertainty associated with the gravimetric amount fraction.

5.3.2. Verification results of CH_4, C_2H_6 and N_2 in He multi-component pre-mixtures using gas chromatography

Single point calibration method on the GC FID/TCD was used for the verification of five matrix-matched gas mixtures of CH_4, C_2H_6, and N_2 in He prepared in the preceding section. The verification results obtained for the CH_4, C_2H_6, and N_2 in He pre-mixtures are shown in **Tables 5.19 to 5.23**. The prepared pre-mixtures had repeatability results of less than 0.7 %RSD, with results ≤ 0.457% for CH_4 and C_2H_6, and ≤ 0.675% for N_2. The repeatability results were steady and exhibited no bias, which can be attributed to the instrument's good stability. The percentage difference ranged from 0.004 to 0.515% for CH_4, 0.001 to 0.521% for C_2H_6, and 0.028 to 0.872% for N_2 for gas mixtures GE1 to GE4, showing good agreement between the gravimetric and verification amount fractions. However, the percentage difference for mixture GE5 ranged from 0.205 to 9.507%, 0.339 to 11.717%, and 0.587 to 7.867% for CH_4, C_2H_6, and N_2 respectively. The largest differences were observed when gas mixtures GE2 and GE3 were set as reference gas mixtures to analyse GE5 and the other way around. These differences showed marginally large inconsistencies between the gravimetric amount fraction and the verification amount fractions of GE5. Because of this, gas mixture GE5 was therefore not used in the preparation of the final low range refinery reference gas mixtures.

Table 5.19 Verification results for CH_4, C_2H_6 and N_2 using GE1 as reference.

Cylinder ID	Component	Average analyser response (Peak area)[1]	Standard deviation[2]	%RSD[3]	x_{grav} (%mol.mol^{-1})[4]	x_{veri} (%mol.mol^{-1})[5]	%Difference[6]	Sensitivity ratio[7]	Drift[8]
GE2	CH_4	61962.485	44.547	0.072	9.688	9.660	0.288	1.003	0.016
	C_2H_6	128714.275	90.237	0.070	9.651	9.700	-0.510	0.995	0.020
	N_2	3963.447	5.406	0.136	9.731	9.786	-0.568	0.995	-0.024
GE3	CH_4	63451.875	56.361	0.089	9.939	9.885	0.549	1.005	0.515
	C_2H_6	131594.245	106.995	0.081	9.882	9.911	-0.302	0.997	-0.319
	N_2	4065.745	5.425	0.133	10.027	10.030	-0.028	0.999	-0.124
GE4	CH_4	66632.070	73.210	0.110	10.419	10.382	0.353	1.003	0.008
	C_2H_6	132723.200	151.674	0.114	9.976	9.996	-0.199	0.998	0.010
	N_2	4064.367	8.026	0.198	10.052	10.036	0.161	1.002	0.008
GE5	CH_4	72196.731	208.840	0.289	11.281	11.258	0.208	0.998	-0.307
	C_2H_6	132643.244	371.432	0.280	10.018	9.984	0.339	0.996	-0.314
	N_2	4066.400	8.743	0.215	10.061	10.001	0.587	0.994	-0.244

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.20 Verification results for CH_4, C_2H_6 and N_2 using GE2 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	**Standard deviation**[2]	**%RSD**[3]	x_{grav} **(%mol.mol^{-1})**[4]	x_{veri} **(%mol.mol^{-1})**[5]	**%Difference**[6]	**Sensitivity ratio**[7]	**Drift**[8]
GE1	CH_4	69411.044	90.433	0.130	10.822	10.852	-0.274	1.003	-0.026
	C_2H_6	129292.444	180.853	0.140	9.745	9.694	0.521	0.995	-0.021
	N_2	3981.083	5.080	0.128	9.829	9.777	0.536	0.995	0.052
GE3	CH_4	63606.225	74.676	0.117	9.939	9.934	0.056	0.999	0.023
	C_2H_6	132017.356	163.027	0.124	9.882	9.881	0.001	1.000	0.023
	N_2	4072.750	6.310	0.155	10.027	9.977	0.497	0.995	0.031
GE4	CH_4	66755.475	30.234	0.045	10.419	10.419	0.004	1.000	0.073
	C_2H_6	133014.100	61.490	0.046	9.976	9.950	0.258	1.002	-0.039
	N_2	4075.565	4.781	0.117	10.052	9.967	0.848	1.009	0.007
GE5	CH_4	65337.575	163.061	0.250	11.281	10.209	9.507	0.905	-0.016
	C_2H_6	119684.298	127.412	0.107	10.018	8.962	10.541	0.895	0.016
	N_2	3788.713	25.587	0.675	10.061	9.269	7.867	0.922	0.008

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.21 Verification results for CH_4, C_2H_6 and N_2 using GE3 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	**Standard deviation**[2]	**%RSD**[3]	x_{grav} **(%mol.mol^{-1})**[4]	x_{veri} **(%mol.mol^{-1})**[5]	**%Difference**[6]	**Sensitivity ratio**[7]	**Drift**[8]
GE1	CH_4	69449.875	46.498	0.067	10.822	10.878	-0.515	1.005	-0.527
	C_2H_6	129346.100	89.975	0.070	9.745	9.712	0.338	0.997	0.328
	N_2	3981.744	4.648	0.117	9.829	9.821	0.084	0.999	0.083
GE2	CH_4	62056.865	93.077	0.150	9.688	9.702	-0.146	0.999	0.045
	C_2H_6	128988.675	193.359	0.150	9.651	9.660	-0.095	1.000	0.047
	N_2	3971.513	18.344	0.462	9.731	9.782	-0.522	0.995	0.041
GE4	CH_4	66663.725	71.263	0.107	10.419	10.436	-0.158	0.998	0.054
	C_2H_6	132821.290	163.432	0.123	9.976	9.962	0.136	1.001	0.057
	N_2	4062.125	8.667	0.213	10.052	10.009	0.431	1.004	0.075
GE5	CH_4	65481.288	105.947	0.162	11.281	10.231	9.309	0.907	-0.028
	C_2H_6	120130.533	137.343	0.114	10.018	8.986	10.305	0.897	-0.049
	N_2	3799.519	20.743	0.546	10.061	9.328	7.282	0.927	-0.004

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.22 Verification results for CH_4, C_2H_6 and N_2 using GE4 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	**Standard deviation**[2]	**%RSD**[3]	x_{grav} **(%mol.mol^{-1})**[4]	x_{veri} **(%mol.mol^{-1})**[5]	**%Difference**[6]	**Sensitivity ratio**[7]	**Drift**[8]
GE1	CH_4	69449.200	103.358	0.149	10.822	10.858	0.328	1.003	0.024
	C_2H_6	129372.150	193.140	0.149	9.745	9.723	0.226	0.998	0.036
	N_2	3981.167	2.561	0.064	9.829	9.848	0.188	1.002	-0.056
GE2	CH_4	62057.813	107.163	0.173	9.688	9.686	0.023	1.000	0.004
	C_2H_6	128981.000	237.193	0.184	9.651	9.673	0.233	1.002	0.010
	N_2	3980.069	4.325	0.109	9.731	9.816	0.872	1.009	-0.029
GE3	CH_4	63465.819	70.614	0.111	9.939	9.919	0.203	0.998	-0.058
	C_2H_6	131679.875	158.917	0.121	9.882	9.890	0.089	1.001	-0.066
	N_2	4068.413	19.471	0.479	10.027	10.072	0.455	1.004	0.036
GE5	CH_4	71726.956	72.983	0.102	11.281	11.314	0.295	1.003	-0.049
	C_2H_6	131781.025	148.261	0.113	10.018	9.982	0.363	0.996	-0.046
	N_2	4041.400	5.964	0.148	10.061	9.996	0.637	0.994	0.042

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.23 Verification results for CH_4, C_2H_6 and N_2 using GE5 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	**Standard deviation**[2]	**%RSD**[3]	x_{grav} **(%mol.mol^{-1})**[4]	x_{veri} **(%mol.mol^{-1})**[5]	**%Difference**[6]	**Sensitivity ratio**[7]	**Drift**[8]
GE1	CH_4	69416.755	310.559	0.447	10.822	10.840	-0.158	0.998	-0.392
	C_2H_6	129483.820	591.383	0.457	9.745	9.773	-0.293	0.996	-0.386
	N_2	3997.340	14.523	0.363	9.829	9.883	-0.543	0.994	-0.368
GE2	CH_4	62001.725	82.842	0.134	9.688	10.699	-10.436	0.905	0.112
	C_2H_6	128871.515	251.314	0.195	9.651	10.782	-11.717	0.895	0.123
	N_2	3976.850	7.404	0.186	9.731	10.558	-8.497	0.922	0.206
GE3	CH_4	63599.825	78.921	0.124	9.939	10.953	-10.194	0.907	-0.187
	C_2H_6	132046.071	271.829	0.206	9.882	11.009	-11.411	0.897	-0.222
	N_2	4084.545	5.709	0.140	10.027	10.819	-7.904	0.927	-0.192
GE4	CH_4	66060.535	93.053	0.141	10.419	10.388	0.295	1.003	-0.003
	C_2H_6	131722.990	193.872	0.147	9.976	10.012	-0.363	0.996	0.006
	N_2	4063.210	7.838	0.193	10.052	10.110	-0.576	0.994	0.009

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

5.3.3. Internal consistency results of CH_4, C_2H_6 and N_2 in He multi-component pre-mixtures using gas chromatography

Internal consistency investigation was conducted using gas mixtures GE1, GE2, GE4, and GE5 when GE3 was used as a reference to evaluate the internal uniformity of the mixtures relative to one another. This was done using the sensitivity ratio calculated using **eq. 4.11.** A sensitivity ratio of 1 shows ideal internal consistency in the sample gas mixture relative to the reference gas mixture. **Table 5.24** shows sensitivity ratio results ranging from 0.994 to 1.009. In other words, the results fell within the sensitivity ratio of 1.000 ± 0.010. These results indicate that gas mixtures GE1, GE2, GE4, and GE5 behave similarly relative to the reference gas mixture GE3.

Table 5.24 Internal consistency results for CH_4, C_2H_6 and N_2 using GE4 as reference.

Cylinder ID	Component	Average analyser response (Peak area)[1]	x_{grav} (%mol.mol^{-1})[2]	Sensitivity ratio[3]	$U_{combined}$ (%mol.mol^{-1})[4]
GE1	CH_4	69449.200	10.822	1.003	0.026
	C_2H_6	129372.150	9.745	0.998	0.025
	N_2	3981.167	9.829	1.002	0.027
GE2	CH_4	62057.813	9.688	1.000	0.030
	C_2H_6	128981.000	9.651	1.002	0.030
	N_2	3980.069	9.731	1.009	0.092
GE3	CH_4	63465.819	9.939	0.998	0.025
	C_2H_6	131679.875	9.882	1.001	0.027
	N_2	4068.413	10.027	1.004	0.096
GE5	CH_4	71726.956	11.281	1.003	0.035
	C_2H_6	131781.025	10.018	0.996	0.033
	N_2	4041.400	10.061	0.994	0.058

[1] **Average analyser response** of four (4) analytical responses of component i

[2] x_{grav} is the gravimetric amount fraction for component i from the gravimetric preparation in accordance with ISO 6142**,**

[3] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 3.11**,

[4] $U_{combined}$ is the gravimetric and verification expanded uncertainty

Figures 5.18 to 5.20 are plots of the sensitivity ratios for CH_4, C_2H_6, and N_2 for the developed pre-mixture gases (GE1, GE2, GE4, and GE5 with GE3 as the reference). The error bars represent the combined expanded uncertainties of the gravimetric and verification uncertainties. The sensitivity ratio of the reference is assumed to be 1. The plots show that all components of interest in the gas mixtures (CH_4, C_2H_6, and N_2) are consistent with those in the reference gas mixture, with sensitivity ratios that are close to 1.

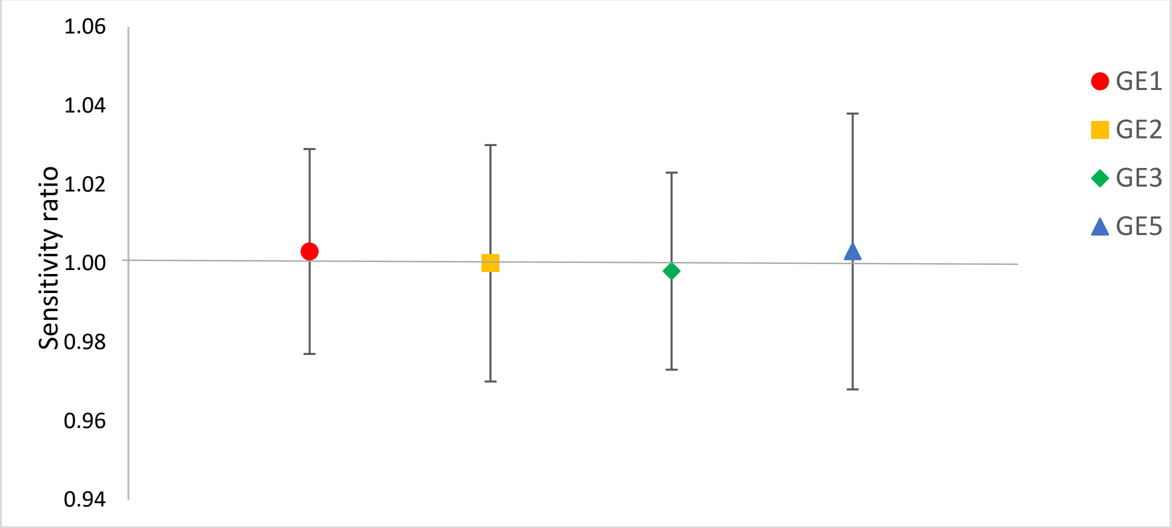

Figure 5.18 Internal consistency of CH_4 in CH_4, C_2H_6 and N_2 in He pre-mixtures with GE4 as a reference.

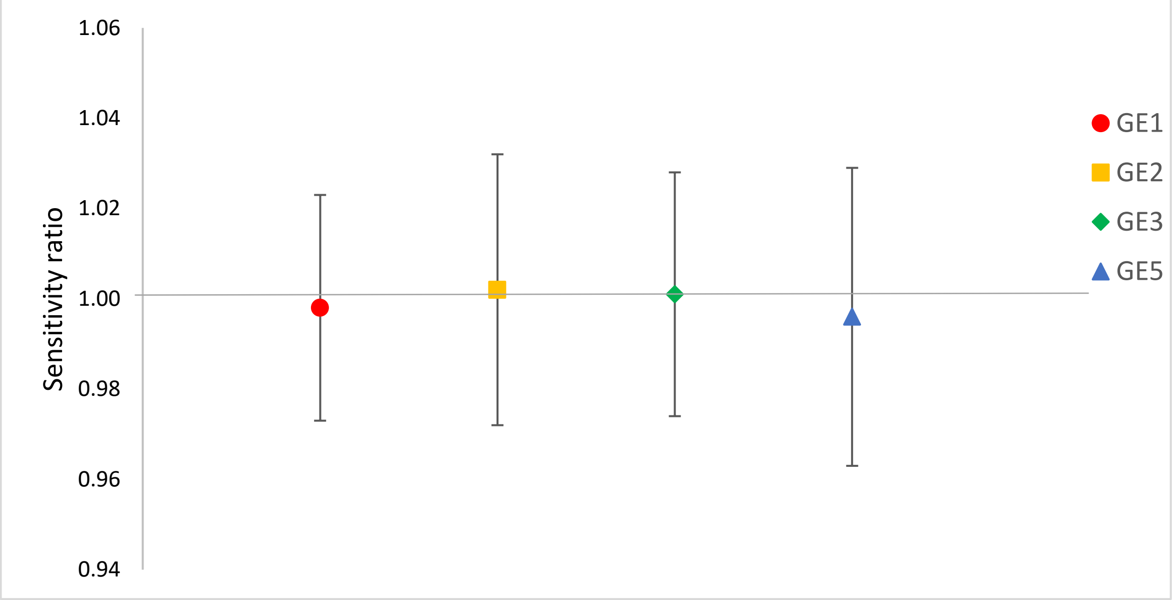

Figure 5.19 Internal consistency of ethane in CH_4, C_2H_6 and N_2 in He pre-mixtures with GE4 as a reference.

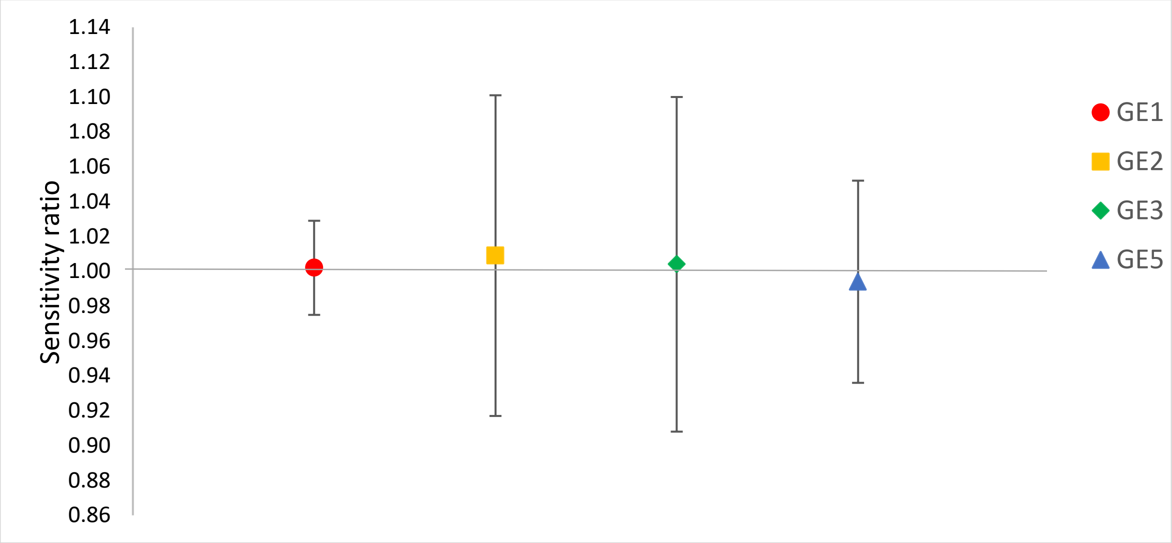

Figure 5.20 Internal consistency of ethane in CH_4, C_2H_6 and N_2 in He pre-mixtures with GE4 as a reference.

The prepared pre-mixtures of CH_4, C_2H_6, and N_2 in He were successfully verified using GC FID/TCD with repeatability results of < 0.7%, %difference results of < 1%, and internal consistencies ranging between 0.994 and 1.009 at monitored instrumental drifts of < 0.6% for gas mixtures GE1, GE2, GE3, and GE4. However, gas mixture GE5 had inconsistencies in the accuracy evaluations and therefore will be excluded in the next dilution steps. It can therefore be concluded that the development of CH_4, C_2H_6, and N_2 in He pre-mixtures was successful.

5.4. Development of CO_2, CO and O_2 in He multi-component pre-mixtures

5.4.1. Gravimetric preparation of CO_2, CO and O_2 in He multi-component pre-mixtures results

Four multi-component gas mixtures of CO, CO_2, O_2 in He were gravimetrically prepared in 5 L aluminium gas cylinders in accordance with ISO 6142. The pre-mixtures were prepared from high purity gas starting materials of methane, ethane, nitrogen and helium to 4 %mol.mo^{-1} CO, 4 %mol.mo^{-1} O_2 and 8 %mol.mo^{-1} CO_2 in He. Cylinder IDs of the gas mixtures, RG1, RG2, RG3, and RG4, allowed for their unique identification. The final amount fractions and expanded uncertainties of CO, CO_2 and O_2 for the prepared gas mixtures are presented in **Table 5.25**. The gravimetric expanded uncertainty for CO, CO_2, and O_2 were all below 0.0006 %mol.mo^{-1} and the percentage relative expanded uncertainty of the prepared reference gas mixtures was found to be ≤ 0.0147% for CO, ≤ 0.0071% for CO_2 and ≤ 0.147% for O_2 for all four mixtures.

Table 5.25 Gravimetric amount fractions and expanded uncertainties results for CO,CO_2,O_2 in He gas mixtures.

Cylinder ID	Component	x_{grav} (%mol.mol^{-1})^1	U_{grav} (%mol.mol^{-1})^2	%REU^3
RG1	CO	4.0450	0.0006	0.0144
	CO_2	8.2710	0.0006	0.0071
	O_2	4.0750	0.0005	0.0119
RG2	CO	4.3489	0.0006	0.0142
	CO_2	8.6132	0.0006	0.0071
	O_2	4.2711	0.0005	0.0119
RG3	CO	3.9694	0.0006	0.0147
	CO_2	8.2412	0.0006	0.0071
	O_2	4.2753	0.0005	0.0115
RG4	CO	4.0184	0.0006	0.0147
	CO_2	8.2284	0.0006	0.0071
	O_2	4.0523	0.0005	0.0122

[1] x_{grav} is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142

[2] U_{grav} is the expanded uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*)

[3] **%REU** is the percentage relative expanded uncertainty associated with the gravimetric amount fraction

5.4.2. Verification results of CO, CO_2 and O_2 in He multi-component pre-mixtures using gas chromatography

The four matrix-matched gas mixtures of CO, CO_2, and O_2 in He were analysed against each other on the GC-TCD to determine their consistency with one another. Single point calibration method was used to analyse the mixtures because the mixtures were of similar amount fractions. All the gas mixtures were analysed using a substitution method (A-B-A method).

Tables 5.26 - 5.29 show the verification results of all the multi-component pre-mixtures as references to verify the gravimetric amount fractions for CO, CO_2, and O_2. That is, when RG1 was a reference, RG2, RG3, and RG4 were samples. This was done until all the samples were reference gas mixtures. This was done to establish the repeatability of the measurements and reduce bias. The calculated percentage difference when RG1 was the reference ranged between 0.02 to 0.79%, 0.32 to 0.90% when RG2 was a reference, 0.01 to 0.78% when RG3 was a reference, and 0.02 to 0.85% when RG4 was a reference for all the components of interest (CO, CO_2, and O_2). For all the components analysed, CO_2 had the highest observed % difference. This could be attributed to the low peak area recovery compared to those of CO and O_2 which could have led to higher variations in the gravimetric and verification amount fractions. The method deployed was repeatable at 0.5%, 0.6 % and 0.2% relative standard deviations for measurements of CO, CO_2, and O_2, respectively, with instrument drift ranging between 0.005 to 0.267% for CO, 0.002 to 0.360% for CO_2 and 0.002 to 0.279% for O_2 modulus during the analysis. These results then lead to conclude that measurements of CO, CO_2 and O_2 using the GC-TCD were accurate, repeatable, and fit for use of dilution to low range refinery reference gas mixtures.

Table 5.26 Verification results for CO, CO_2 and O_2 using RG1 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	**Standard deviation**[2]	**%RSD**[3]	x_{grav} **(%mol.mol^{-1})**[4]	x_{veri} **(%mol.mol^{-1})**[5]	**%Difference**[6]	**Sensitivity ratio**[7]	**Drift**[8]
RG2	CO	4474.338	8.847	0.198	4.349	4.322	0.616	1.006	0.105
	CO_2	4001.900	9.940	0.248	8.613	8.545	0.789	1.004	-0.031
	O_2	16492.550	18.643	0.113	4.271	4.254	0.405	1.008	-0.069
RG3	CO	4152.040	5.267	0.127	3.969	3.965	0.101	0.999	0.067
	CO_2	4050.100	7.071	0.175	8.241	8.237	0.053	0.999	0.002
	O_2	15873.385	8.390	0.053	4.275	4.271	0.100	1.000	-0.019
RG4	CO	4189.356	5.401	0.129	4.018	4.021	0.072	0.999	0.043
	CO_2	3823.781	4.241	0.111	8.228	8.227	0.020	0.999	-0.093
	O_2	15863.056	17.215	0.109	4.052	4.056	0.081	1.000	-0.060

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.27 Verification results for CO, CO_2 and O_2 using RG2 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	**Standard deviation**[2]	**%RSD**[3]	x_{grav} **(%mol.mol^{-1})**[4]	x_{veri} **(%mol.mol^{-1})**[5]	**%Difference**[6]	**Sensitivity ratio**[7]	**Drift**[8]
RG1	CO	4187.165	7.190	0.172	4.045	4.066	0.526	1.006	-0.107
	CO_2	3834.430	3.522	0.092	8.271	8.332	0.741	1.004	-0.270
	O_2	15966.315	19.797	0.124	4.075	4.088	0.319	1.008	-0.279
RG3	CO	4113.660	2.146	0.052	3.969	3.986	0.426	1.004	0.046
	CO_2	4033.580	5.796	0.144	8.241	8.306	0.784	1.008	0.108
	O_2	15879.635	19.917	0.125	4.275	4.307	0.744	1.008	0.041
RG4	CO	4124.985	11.470	0.278	4.018	4.051	0.804	1.008	0.129
	CO_2	3791.050	20.612	0.544	8.228	8.303	0.902	1.002	0.360
	O_2	15961.050	12.349	0.077	4.052	4.066	0.343	1.008	0.015

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.28 Verification results for CO, CO_2 and O_2 using RG3 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	**Standard deviation**[2]	**%RSD**[3]	x_{grav} **(%mol.mol^{-1})**[4]	x_{veri} **(%mol.mol^{-1})**[5]	**%Difference**[6]	**Sensitivity ratio**[7]	**Drift**[8]
RG1	CO	4234.881	1.547	0.037	4.045	4.049	0.090	0.999	0.075
	CO_2	3862.450	1.298	0.034	8.271	8.274	0.032	0.999	0.063
	O_2	15936.581	19.552	0.123	4.075	4.077	0.054	1.000	0.002
RG2	CO	4488.100	4.669	0.104	4.349	4.330	0.426	1.004	0.019
	CO_2	3998.031	8.436	0.211	8.613	8.551	0.729	1.008	0.082
	O_2	16470.650	15.952	0.097	4.271	4.238	0.784	1.008	0.034
RG4	CO	4198.806	1.214	0.029	4.018	4.025	0.170	0.998	0.005
	CO_2	3830.456	7.466	0.195	8.228	8.241	0.150	1.000	0.103
	O_2	15879.281	27.804	0.175	4.052	4.053	0.009	0.999	0.044

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.29 Verification results for CO, CO_2 and O_2 using RG4 as reference.

Cylinder ID	Component	Average analyser response (Peak area)[1]	Standard deviation[2]	%RSD[3]	x_{grav} (%mol.mol^{-1})[4]	x_{veri} (%mol.mol^{-1})[5]	%Difference[6]	Sensitivity ratio[7]	Drift[8]
RG1	CO	4187.165	4.267	0.172	4.045	4.040	0.134	0.999	-0.097
	CO_2	3834.430	6.180	0.092	8.271	8.265	0.067	0.999	-0.105
	O_2	15966.315	20.147	0.124	4.075	4.067	0.187	1.000	-0.183
RG2	CO	4427.625	20.217	0.457	4.349	4.313	0.819	1.008	0.171
	CO_2	3986.713	6.512	0.163	8.613	8.540	0.852	1.002	0.334
	O_2	16567.050	14.767	0.089	4.271	4.259	0.290	1.008	0.035
RG3	CO	4138.775	1.203	0.029	3.969	3.969	0.024	0.998	-0.267
	CO_2	4041.370	8.110	0.201	8.241	8.233	0.105	1.000	0.067
	O_2	15883.105	28.197	0.178	4.275	4.252	0.547	0.999	-0.003

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

5.4.3. Internal consistency results of CO, CO_2 and O_2 in He multi-component pre-mixtures

Internal consistency results for 4 %mol.mol^{-1} CO, 8 %mol.mol^{-1} CO_2, and 4 %mol.mol^{-1} O_2 in He pre-mixtures were studied using gas mixture RG1, RG2, and RG3 with RG4 as a reference. The sensitivity ratio results are tabulated in **Table 5.30** and further graphically represented in **Figures 5.21 to 5.23** for components CO, CO2, and O2 respectively. The further the calculated sensitivity ratio is from 1, the greater the deviation of the sample gas mixture from the reference gas mixture. The calculated sensitivity ratios ranged from 0.998 to 1.008 for CO, 0.999 to 1.002 for CO_2, and 0.999 to 1.008 for O_2, demonstrating acceptable internal consistency of all three components in the gravimetrically prepared pre-mixtures. Therefore, all four prepared mixtures are suitable for use as pre-mixtures for dilution into the final low range refinery reference gas mixtures.

Table 5.30 Internal consistency data for CO, CO_2 and O_2 using RG4 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	x_{grav} **(%mol.mol^{-1})**[2]	**Sensitivity ratio**[3]	$U_{combined}$ **(%mol.mol^{-1})**[4]
RG1	CO	4187.165	4.045	0.999	0.009
	CO_2	3834.430	8.271	0.999	0.015
	O_2	15966.315	4.075	1.000	0.024
RG2	CO	4427.625	4.349	1.008	0.023
	CO_2	3986.713	8.613	1.002	0.019
	O_2	16567.050	4.271	1.008	0.017
RG3	CO	4138.775	3.969	0.998	0.015
	CO_2	4041.370	8.241	1.000	0.015
	O_2	15883.105	4.275	0.999	0.020

[1] **Average analyser response** of four (4) analytical responses of component i

[2] x_{grav} is the gravimetric amount fraction for component i from the gravimetric preparation in accordance with ISO 6142**,**

[3] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 3.11**,

[4] $U_{combined}$ is the gravimetric and verification expanded uncertainty

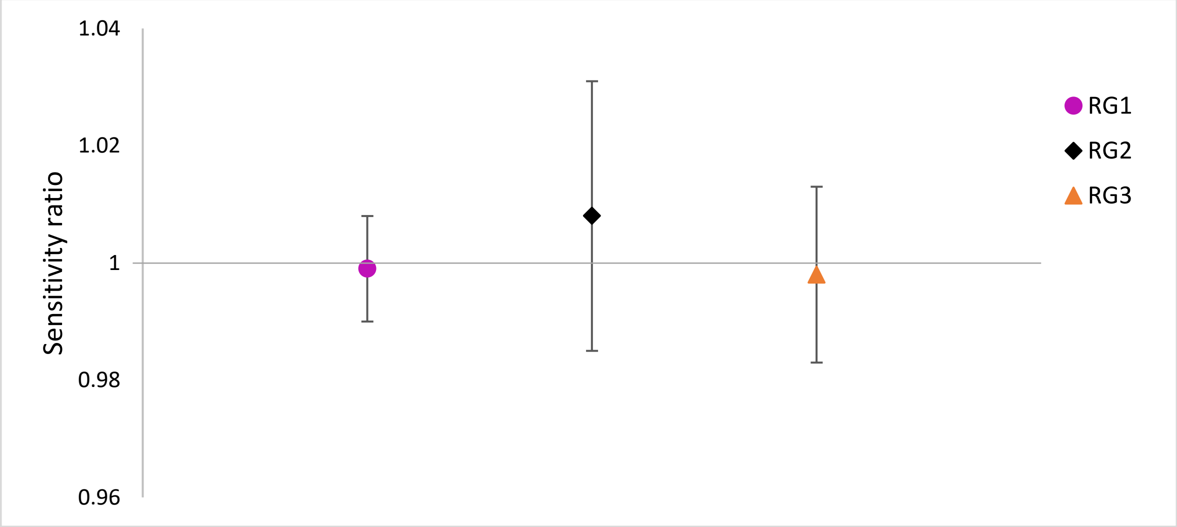

Figure 5.21 Internal consistency of CO in CO, CO_2 and O_2 in helium pre-mixtures with RG4 as a reference.

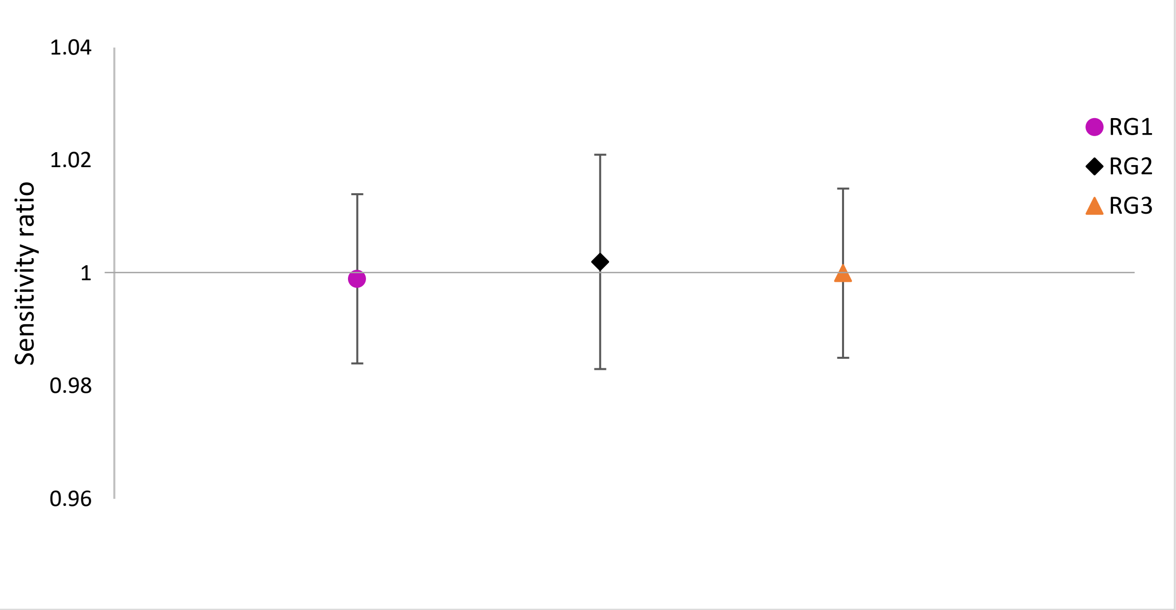

Figure 5.22 Internal consistency of CO in CO, CO_2 and O_2 in helium pre-mixtures with RG4 as a reference.

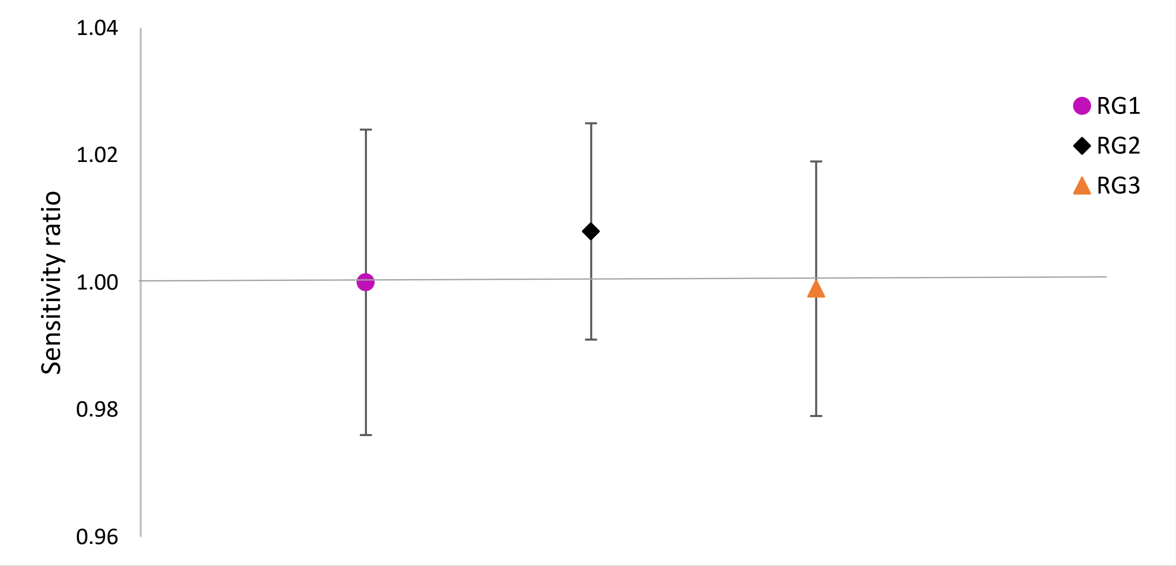

Figure 5.23 Internal consistency of O2 in CO, CO_2 and O_2 in helium pre-mixtures with RG4 as a reference.

5.5. Development of C_3H_8 and C_4H_6 in He multi-component pre-mixtures

5.5.1. Gravimetric preparation of C_3H_8 and C_4H_6 in He multi-component pre-mixtures results

Table 5.31 tabulates the gravimetric amount fractions together with their associated uncertainties for 4 %mol.mol^{-1} C_3H_8, and 2 %mol.mol^{-1} C_4H_6 for the four prepared pre-mixtures. The expanded uncertainties and %REU for all gas mixtures, BP1 to BP4, were found to be ≤ 0.0007% and ≤ 0.0266% for C_3H_8, and C_4H_6 respectively. The actual gravimetric results are within 2% of the target amount fractions for both C_3H_8, and C_4H_6. Milton et al. (2011) suggest that the gravimetric uncertainty of a gas mixture is affected by the smallest mass that may be added and weighed on the mass comparator balance. This dilution of C_3H_8 and C_4H_6 from high purity to 4 %mol.mol^{-1} and 2 %mol.mol^{-1}, respectively, ensured that there was enough high purity starting material added to the gas mixtures for the comparator balance to weigh. A mass of more than 15 grams is ideal to reduce the uncertainty of the mixtures.

Table 5.31 Gravimetric amount fractions and expanded uncertainties results for C_3H_8 and C_4H_6 in He gas mixtures.

Cylinder ID	Component	x_{grav} (%mol.mol^{-1})^1	U_{grav} (%mol.mol^{-1})^2	%REU^3
BP1	C_3H_8	4.0113	0.0007	0.0173
	C_4H_6	1.9849	0.0005	0.0264
BP2	C_3H_8	3.9486	0.0007	0.0176
	C_4H_6	1.9830	0.0005	0.0266
BP3	C_3H_8	4.0229	0.0007	0.0169
	C_4H_6	2.0019	0.0005	0.0256
BP4	C_3H_8	3.9486	0.0007	0.0176
	C_4H_6	1.9732	0.0005	0.0252

$^1x_{grav}$ is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142

$^2U_{grav}$ is the expanded uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*)

^{3}**%REU** is the percentage relative expanded uncertainty associated with the gravimetric amount fraction

5.5.2. Verification results of C_3H_8 and C_4H_6 in He multi-component pre-mixtures on GC-FID

The substitution method (A-B-A) was used to compare four matrix-matched gas mixtures containing nominal amount fractions of 4 %mol.mol^{-1} C_3H_8 and 2 %mol.mol^{-1} C_4H_6 in He were analysed against each other on the GC-FID using the substitution method (A-B-A). The four mixtures were given unique cylinder identities of BP1, BP2, BP3 and BP4. The measurements were achieved at a precision of ≤ 0.333 %RSD and instrumental drift of ≤ 0.486%, as shown in **Tables 5.32 to 5.35**. However, accuracy study produced peculiar results. When BP1 was used as a reference in **Table 5.32**, gas mixture BP2 produced the best accuracy results with % differences of ≤ 0.187% for C_3H_8 and ≤ 0.154% for C_4H_6, followed by BP3, and BP4 with % difference of ≤ 2.636% for C_3H_8 and ≤ 15.369% for C_4H_6 respectively. When BP2 was used as a reference, the best accuracies were seen with BP1, followed by BP3, and then BP4. When BP3 was set as a reference, accuracy results ranged between 1.081% and 9.167% for both C_3H_8 and C_4H_6 in gas mixtures BP1, BP2 and BP4. And when BP4 was set as a reference, % difference results ranged from 1.360% to 16.742%. The high percentage differences between the gravimetric and verification amount fractions for gas mixtures BP3 and BP4 could be attributed to a leak in the filling system during the preparation process.

Table 5.32 Verification data for C_3H_8 and C_4H_6 using BP1 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)[1]**	**Standard deviation[2]**	**%RSD[3]**	x_{grav} **(%mol.mol^{-1})[4]**	x_{veri} **(%mol.mol^{-1})[5]**	**%Difference[6]**	**Sensitivity ratio[7]**	**Drift[8]**
BP2	C_3H_8	1243.067	3.078	0.248	3.949	3.956	0.187	1.002	-0.084
	C_4H_6	820.278	1.965	0.240	1.983	1.980	0.154	0.995	-0.077
BP3	C_3H_8	1253.375	2.069	0.165	4.023	3.972	1.259	0.990	0.160
	C_4H_6	785.808	1.289	0.164	2.002	1.875	6.352	0.943	0.162
BP4	C_3H_8	1215.800	2.213	0.182	3.949	3.845	2.636	0.958	-0.304
	C_4H_6	698.078	1.291	0.185	1.973	1.670	15.369	0.848	-0.295

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.33 Verification data for C_3H_8 and C_4H_6 using BP2 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)**[1]	**Standard deviation**[2]	**%RSD**[3]	x_{grav} **(%mol.mol^{-1})**[4]	x_{veri} **(%mol.mol^{-1})**[5]	**%Difference**[6]	**Sensitivity ratio**[7]	**Drift**[8]
BP1	C_3H_8	1260.067	4.093	0.325	4.011	4.002	0.237	1.002	0.287
	C_4H_6	824.867	2.746	0.333	1.985	1.987	0.083	0.995	0.364
BP3	C_3H_8	1254.950	2.242	0.179	4.023	3.986	0.914	1.008	0.266
	C_4H_6	784.167	1.494	0.191	2.002	1.896	5.301	1.053	0.349
BP4	C_3H_8	1399.767	2.270	0.162	3.949	3.855	2.369	1.004	0.161
	C_4H_6	795.983	1.344	0.169	1.973	1.691	14.288	1.166	0.097

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.34 Verification results for C_3H_8 and C_4H_6 using BP3 as reference.

Cylinder ID	Component	Average analyser response (Peak area)[1]	Standard deviation[2]	%RSD[3]	x_{grav} (%mol.mol^{-1})[4]	x_{veri} (%mol.mol^{-1})[5]	%Difference[6]	Sensitivity ratio[7]	Drift[8]
BP1	C_3H_8	1262.638	1.120	0.089	4.011	4.063	1.277	0.990	0.220
	C_4H_6	826.463	0.745	0.090	1.985	2.120	6.789	0.943	0.307
BP2	C_3H_8	1242.100	1.573	0.127	3.949	3.991	1.081	1.008	-0.006
	C_4H_6	817.633	1.044	0.128	1.983	2.097	5.770	1.053	0.121
BP4	C_3H_8	1398.883	3.860	0.276	3.949	3.903	1.146	1.013	-0.061
	C_4H_6	795.150	2.301	0.289	1.973	1.792	9.167	1.101	-0.034

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

Table 5.35 Verification results for C_3H_8 and C_4H_6 using BP4 as reference.

Cylinder ID	Component	Average analyser response (Peak area)[1]	Standard deviation[2]	%RSD[3]	x_{grav} (%mol.mol^{-1})[4]	x_{veri} (%mol.mol^{-1})[5]	%Difference[6]	Sensitivity ratio[7]	Drift[8]
BP1	C_3H_8	1265.833	0.923	0.073	4.011	4.188	4.229	0.958	0.364
	C_4H_6	828.480	0.652	0.079	1.985	2.341	15.226	1.044	-0.055
BP2	C_3H_8	1433.656	1.454	0.101	3.949	4.125	4.457	0.848	0.486
	C_4H_6	933.044	0.663	0.071	1.983	2.315	16.742	1.166	-0.034
BP3	C_3H_8	1444.144	1.692	0.117	4.023	4.078	1.360	1.013	-0.019
	C_4H_6	888.556	1.068	0.120	2.002	2.206	10.183	1.101	0.003

[1] **Average analyser response** of four (4) analytical response of component i

[2] **Standard deviation** of the four peak areas

[3] **% RSD** is the relative standard deviation given by **equation 4.14**

[4] x_{grav} is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142

[5] x_{veri} is the average verification amount fraction of 5 runs for component i

[6] **%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13**

[7] **Sensitivity ratio** is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[8] **Drift** is the measure of the changes in the instrument during analysis calculated using **equation 4.10**.

5.5.3. Internal consistency results of C_3H_8 and C_4H_6 in He multi-component pre-mixtures

The developed pre-mixtures of 4 %mol.mol^{-1} C_3H_8 and 2 %mol.mol^{-1} C_4H_6 in He internal consistency results are shown in **Table 5.36** and **Figures 5.24** to **5.25**. With ratios ranging from 0.002 to 1.004, all the samples showed good internal consistency for propane. Due to the significant dilution factor from high purity starting materials > 99% to 4% and 2% for C_3H_8 and C_4H_6, respectively, as well as the slightly higher analytical uncertainties attributed to the lower analysis response compared to the other pre-mixtures, the combined expanded uncertainties are noticeably larger than those of the previously discussed pre-mixtures. The overall uncertainty increases with an increase in the dilution factor and a decrease in the analysis response. BP1 was the gas mixture that was the most internally consistent, followed by BP4 and BP3. However, the internal consistency of 1,3-butadiene was only satisfactory for BP1 at 0.995. The sensitivity ratios for BP3 and BP4 were not satisfactory at 1.053 and 1.166, respectively. This dispersion of results for gas mixtures BP3 and BP4 was also observed during the verification of the mixtures, with extremely high % differences from their gravimetric amount fractions. Considering this, it can be concluded that gas mixtures BP3 and BP4 were the least internally consistent with the reference for 1,3-butadiene. The gas mixture BP2 and the reference mixture were more comparable. Therefore, it can be determined with certainty that mixtures BP1 and BP2 are the most suitable for dilution to the final low range refinery reference gas mixtures.

Table 5.36 Internal consistency results for C_3H_8 and C_4H_6 using BP2 as reference.

Cylinder ID	**Component**	**Average analyser response (Peak area)[1]**	x_{grav} **(%mol.mol^{-1})[2]**	**Sensitivity ratio[3]**	$U_{combined}$ **(%mol.mol^{-1})[4]**
BP1	C_3H_8	1260.067	4.011	1.002	0.461
	C_4H_6	824.867	1.985	0.995	0.471
BP3	C_3H_8	1254.950	4.023	1.008	0.254
	C_4H_6	784.167	2.002	1.053	0.270
BP4	C_3H_8	1399.767	3.949	1.004	0.231
	C_4H_6	795.983	1.973	1.166	0.239

[1] Average peak area of four (4) analytical response of component i

[2] x_{grav} is the gravimetric amount fraction for component i from the gravimetric preparation in accordance with ISO 6142

[3] Sensitivity ratio is the fraction of sensitivity of the sample and reference gas mixture calculated using **equation 4.11**

[4] $U_{combined}$ is the gravimetric and verification expanded uncertainty

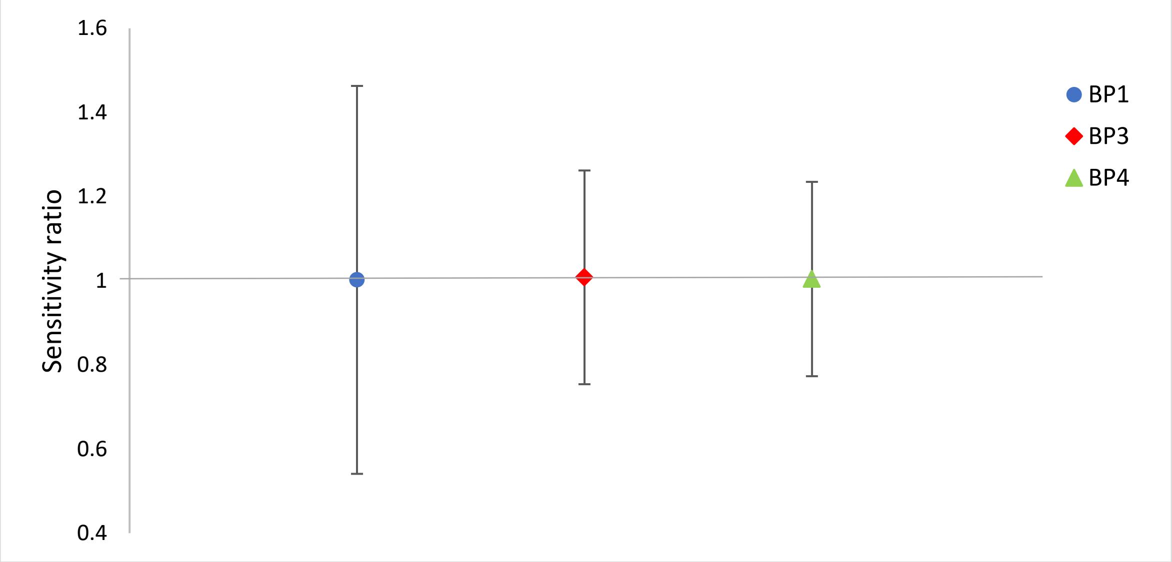

Figure 5.24 Internal consistency of C_3H_8 in C_3H_8 and C_4H_6 in helium pre-mixtures with BP2 as a reference.

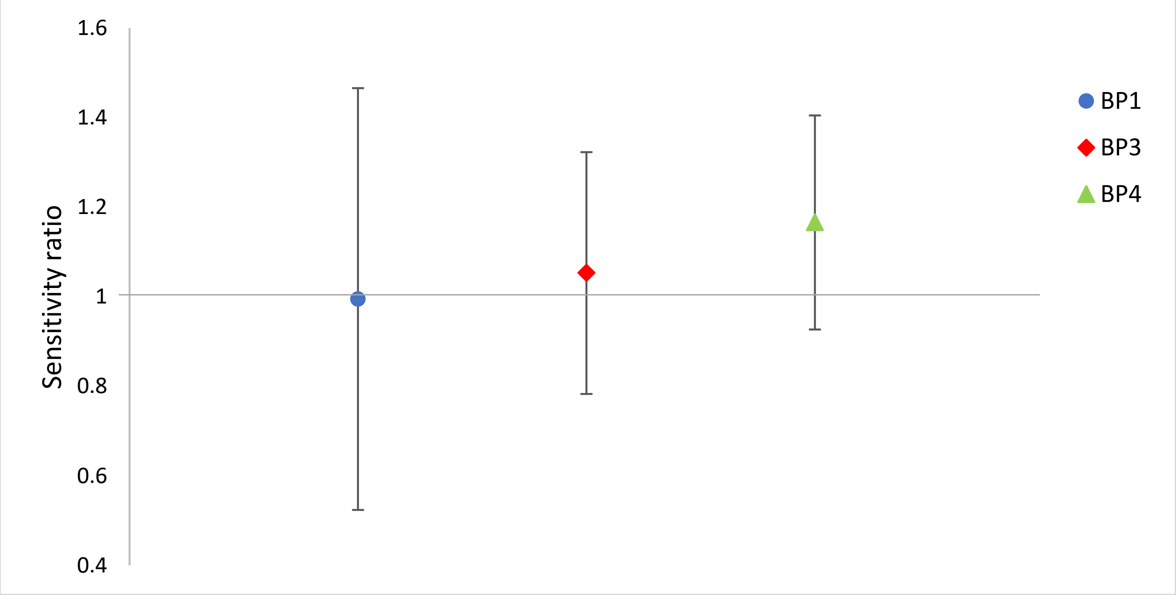

Figure 5.25 Internal consistency of C_4H_6 in C_3H_8 and C_4H_6 in helium pre-mixtures with BP2 as a reference.

5.6. Development of low range refinery reference gas mixtures results

5.6.1. Gravimetric preparation of low range refinery reference gas mixtures results

Four low range refinery reference gas mixtures were prepared using the gravimetric preparation method in accordance with ISO 6142 (ISO, 6142:2015). The three pre-mixtures prepared and verified in **sections 5.3–5.5** were used to prepare four low range refinery reference gas mixtures in 10 dm^3 cylinders at 11 MPa. The first pre-mixtures comprised nominal fractions of 10 $\%mol.mol^{-1}$ for CH_4, C_2H_6, and N_2 in He; the second pre-mixtures comprised of 4 $\%mol.mol^{-1}$ CO, 8 $\%mol.mol^{-1}$ CO_2, and 4 $\%mol.mol^{-1}$ O_2 in He; and the third pre-mixtures consisted of 4 $\%mol.mol^{-1}$ C_3H_8 and 2 $\%mol.mol^{-1}$ C_4H_6 in He. The final targeted nominal amount fractions of the low range refinery reference gas mixtures were 4 000 $µmol.mol^{-1}$ of N_2, 4 000 $µmol.mol^{-1}$ of CH_4, 4 000 $µmol.mol^{-1}$ of C_2H_6, 2 000 $µmol.mol^{-1}$ of C_4H_6, 4 000 $µmol.mol^{-1}$ of

C_3H_8, 1 000 µmol.mol^{-1} of O_2, 1 000 µmol.mol^{-1} of CO, and 2 000 µmol.mol^{-1} of CO_2 in He.

Table 5.37 shows the gravimetric amount fractions and their associated uncertainties for each component of interest in the gas mixtures. The prepared gas mixtures were labelled NM1, NM2, NM3, and NM4 for their unique identification. Detailed purity tables generated using GravCal software that include all the quantified impurities are tabulated in **Appendix C**. The calculated %REUs were ≤ 0.019% for all eight components of interest in the gas mixtures.

Table 5.37 Gravimetric amount fractions and associated uncertainties of the eight components of interest in the low range refinery reference gas mixtures.

Cylinder ID	**Component**	x_{grav} **(μmol.mol^{-1})**^{1}	U_{grav} **(μmol.mol^{-1})**^{2}	**%REU**^{3}
NM1	CH_4	4389.532	0.516	0.012
	N_2	4012.455	0.618	0.015
	C_3H_8	3994.759	0.357	0.009
	C_2H_6	3952.424	0.490	0.012
	CO_2	2062.956	0.328	0.016
	C_4H_6	2006.145	0.257	0.013
	O_2	1016.600	0.168	0.017
	CO	1008.907	0.173	0.017
NM2	CH_4	4004.510	0.503	0.013
	N_2	4048.055	0.637	0.016
	C_3H_8	4025.922	0.368	0.009
	C_2H_6	3989.205	0.516	0.013
	CO_2	2302.603	0.356	0.015
	C_4H_6	1992.114	0.258	0.013
	O_2	1134.200	0.184	0.016
	CO	1124.499	0.189	0.017
NM3	CH_4	4055.521	0.647	0.016
	N_2	4116.981	0.647	0.016
	C_3H_8	4032.339	0.371	0.009
	C_2H_6	4031.919	0.526	0.013
	CO_2	2036.002	0.363	0.018
	C_4H_6	1995.289	0.259	0.013
	O_2	1003.320	0.184	0.018
	CO	995.725	0.188	0.019
NM4	CH_4	4486.101	0.519	0.012
	N_2	4100.076	0.617	0.015
	C_3H_8	3980.857	0.355	0.009
	C_2H_6	4039.378	0.493	0.012
	CO_2	2060.547	0.323	0.016
	C_4H_6	1999.163	0.256	0.013
	O_2	1069.167	0.174	0.016
	CO	992.479	0.169	0.017

[1] x_{grav} is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142

[2] U_{grav} is the expanded uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*)

[3] **%REU** is the percentage relative expanded uncertainty associated with the gravimetric amount fraction

5.6.2. Verification of low range refinery reference gas mixtures results

To assess their consistency with one another, the four low range refinery reference gas mixtures were compared to one another through analysis. **Equation 3.6** was used to determine the verification amount fractions for each sample using the substitution approach (A-B-A method). The mixtures were analysed on FID/TCD. The FID channel was used for analysis of the hydrocarbons using the CP-Sil 5 CB column, and the TCD channel had a series of two columns, Molecular Sieve 13X and ShinCarbon ST, for the separation of O_2, N_2, CO, and CO_2.

Table 5.38 shows repeatability results for gas mixtures NM1, NM2, and NM3 when gas mixture NM4 was set as a reference. The analysis results for repeatability (%RSD) were found to be less than 0.334% for CH_4, 0.318% for C_2H_6, 0.300% for C_3H_8, 0.285% for C_4H_6, 0.346% for O_2, 0.255% for N_2, 0.583% for CO, and 0.697 % for CO_2. The results show that NM1 is the most consistent gas mixture, with the lowest overall %RSDs, followed by NM3 and then NM2 relative to the reference gas mixture NM4.

The accuracy results for the prepared low range reference gas mixtures of CH_4, C2H_6, C_3H_8, and C_4H_6 are presented in **Table 5.39**, and those for O_2, N_2, CO, and CO_2 are presented in **Table 5.40**. The gravimetric amount fractions and the verification amount fractions were compared to assess accuracy. The verification results demonstrate that all the components of interest in the prepared gas mixtures had a percentage difference of less than 0.6%. Given that the absolute difference between the gravimetric and verification amount fractions is less than the calculated combined standard uncertainty in accordance with ISO 6143:2001's acceptable criteria stated in equation 3.7, each component of interest in the gas mixtures was also found to be reliable and validated.

Table 5.38 Data analysis of all components of interest in low range refinery gas mixtures using NM4 as a reference.

Cylinder ID	Component	Average analyser response (Peak area)[1]	Standard deviation[2]	%RSD[3]	x_{grav} (µmol.mol^{-1})[4]	x_{veri} (µmol.mol^{-1})[5]	Sensitivity ratio[6]	Drift[7]
NM1	CH_4	216.238	2.838	0.065	4389.532	4374.702	1.007	-0.197
	C_2H_6	382.638	3.229	0.082	3952.424	3938.880	1.007	-0.191
	C_3H_8	584.500	2.887	0.072	3994.759	3984.860	1.005	-0.197
	C_4H_6	382.463	0.957	0.049	2006.145	1999.653	1.037	-0.225
	O_2	540.658	3.525	0.346	1016.600	1018.867	1.002	-0.155
	N_2	1645.279	4.596	0.115	4012.455	4006.754	0.999	0.291
	CO	12146.250	5.921	0.583	1008.907	1015.206	1.006	-0.404
	CO_2	1283.978	0.125	0.006	2062.956	2074.505	1.006	-0.335
NM2	CH_4	198.275	13.394	0.334	4004.510	4006.441	0.997	0.158
	C_2H_6	388.175	12.690	0.318	3989.205	3991.491	0.997	0.169
	C_3H_8	591.388	12.093	0.300	4025.922	4028.274	0.997	0.206
	C_4H_6	384.013	5.636	0.285	1992.114	1977.816	1.013	0.242
	O_2	619.356	1.655	0.146	1134.200	1131.120	0.999	-0.136
	N_2	1684.756	10.307	0.255	4048.055	4043.752	0.997	-0.211
	CO	13487.905	14.054	1.241	1124.499	1132.476	1.007	-0.375
	CO_2	1439.011	16.065	0.697	2302.603	2304.243	1.001	-0.101
NM3	CH_4	200.563	2.960	0.073	4055.521	4051.418	1.000	-0.140
	C_2H_6	391.863	3.258	0.081	4031.919	4027.688	1.000	-0.145
	C_3H_8	591.713	3.117	0.077	4032.339	4027.698	1.001	-0.146
	C_4H_6	386.613	2.085	0.105	1995.289	1989.579	1.004	-0.102
	O_2	550.258	0.600	0.060	1003.320	1006.116	0.998	0.066
	N_2	1683.200	4.991	0.121	4116.981	4110.726	1.003	-0.036
	CO	12006.478	5.248	0.526	995.725	997.047	0.998	-0.572
	CO_2	1283.678	9.523	0.468	2036.002	2036.876	1.000	-0.871

Table 5.39 Verification results for the measurement of CH_4, C_2H_6, C_3H_8 and C_4H_6 in low range refinery reference gas mixtures.

Component	**Cylinder ID**	x_{grav} **(%mol.mol^{-1})**[1]	u_{grav} **(%mol.mol^{-1})**[2]	x_{veri} **(%mol.mol^{-1})**[3]	u_{veri} **(%mol.mol^{-1})**[4]	**Difference**[5]	**%Difference**[6]	$U_{combined}$ **(%mol.mol^{-1})**[7]	**%REU**[8]
CH_4	NM1	4389.532	0.516	4394.239	56.792	4.707	0.107	113.589	2.588
	NM2	4004.510	0.503	4006.321	34.930	1.811	0.045	69.867	1.745
	NM3	4055.521	0.647	4052.549	21.652	2.972	0.073	43.323	1.068
	NM4	4486.101	0.519	4482.381	72.189	3.720	0.083	144.382	3.218
C_2H_6	NM1	3952.424	0.490	3952.174	52.323	0.250	0.006	104.651	2.648
	NM2	3989.205	0.516	3987.945	33.747	1.260	0.032	67.502	1.692
	NM3	4031.919	0.526	4033.950	21.442	2.031	0.050	42.897	1.064
	NM4	4039.378	0.493	4039.270	66.269	0.108	0.003	132.542	3.281
C_3H_8	NM1	3994.759	0.357	4004.910	50.829	10.151	0.254	101.661	2.545
	NM2	4025.922	0.368	4027.438	35.789	1.516	0.038	71.582	1.778
	NM3	4032.339	0.371	4036.434	22.921	4.095	0.102	45.848	1.137
	NM4	3980.857	0.355	3970.724	63.665	10.133	0.255	127.332	3.199
C_4H_6	NM1	2006.145	0.257	1995.338	13.973	10.807	0.539	27.951	1.393
	NM2	1992.114	0.258	2000.394	12.624	8.280	0.416	25.253	1.268
	NM3	1995.289	0.259	1989.579	6.128	5.710	0.286	12.267	0.615
	NM4	1999.163	0.256	2001.031	3.114	1.868	0.093	6.249	0.313

[1]$\boldsymbol{x_{grav}}$ is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142, [2]$\boldsymbol{u_{grav}}$ is the standard uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*), [3]$\boldsymbol{x_{veri}}$ is the average verification amount fraction of 5 runs for component i, [4]$\boldsymbol{u_{veri}}$ is the standard uncertainty associated with the verification amount fraction for component i, [5]Difference between the gravimetric and verification amount fraction $|x_{grav} - x_{ver}|$, [6]%Difference between the gravimetric and verification amount fraction calculated using **equation 4.13,** [7]$\boldsymbol{U_{combined}}$ is the combined expanded uncertainty, [8] Percentage relative expanded uncertainty associated with the gravimetric amount fraction

Table 5.40 Verification results for the measurement of O_2, N_2, CO and CO_2 in low range refinery reference gas mixtures.

Component	Cylinder ID	x_{grav} (%mol.mol^{-1})[1]	u_{grav} (%mol.mol^{-1})[2]	x_{veri} (%mol.mol^{-1})[3]	u_{veri} (%mol.mol^{-1})[4]	Difference[5]	%Difference[6]	$U_{combined}$ (%mol.mol^{-1})[7]	%REU[8]
O_2	NM1	1016.600	0.168	1018.867	5.596	2.267	0.223	11.197	1.101
	NM2	1134.200	0.184	1131.120	2.646	3.080	0.272	5.305	0.468
	NM3	1003.320	0.184	1006.115	1.218	2.795	0.279	2.464	0.246
	NM4	1069.167	0.174	1067.820	5.452	1.347	0.126	10.910	1.020
N_2	NM1	4012.455	0.618	4006.754	14.574	5.701	0.142	29.174	0.727
	NM2	4048.055	0.637	4043.752	21.413	4.303	0.106	42.845	1.058
	NM3	4116.981	0.647	4110.726	6.641	6.255	0.152	13.345	0.324
	NM4	4100.076	0.617	4103.903	11.707	3.827	0.093	23.446	0.572
CO	NM1	1008.907	0.173	1010.459	3.977	1.552	0.154	7.962	0.789
	NM2	1124.499	0.189	1122.000	3.710	2.499	0.222	7.430	0.661
	NM3	995.725	0.188	996.866	3.123	1.141	0.115	6.257	0.628
	NM4	992.479	0.169	990.042	4.093	2.437	0.246	8.193	0.826
CO_2	NM1	2062.956	0.328	2074.505	31.402	11.549	0.560	62.807	3.045
	NM2	2302.603	0.356	2304.243	17.448	1.640	0.071	34.903	1.516
	NM3	2036.002	0.363	2036.876	14.474	0.874	0.043	28.957	1.422
	NM4	2060.547	0.323	2059.993	9.223	0.554	0.027	18.457	0.896

[1] $\boldsymbol{x_{grav}}$ is the gravimetric amount fraction for component i from the gravimetric preparation of the gas mixture in accordance with ISO 6142, [2] $\boldsymbol{u_{grav}}$ is the standard uncertainty associated with the gravimetric amount fraction for component i at 95% confidence level (*K=2*), [3] $\boldsymbol{x_{veri}}$ is the average verification amount fraction of 5 runs for component i, [4] $\boldsymbol{u_{veri}}$ is the standard uncertainty associated with the verification amount fraction for component i, [5] Difference between the gravimetric and verification amount fraction $|x_{grav} - x_{ver}|$, [6] %Difference between the gravimetric and verification amount fraction calculated using **equation 4.13,** [7] $\boldsymbol{U_{combined}}$ is the combined expanded uncertainty, [8] Percentage relative expanded uncertainty associated with the gravimetric amount fraction

Figures 5.26 and **5.27** show plots of gravimetric amount fractions against verification amount fractions of CH_4, C_2H_6, C_3H_8, C_4H_6, O_2, N_2, CO, and CO_2 for gas mixtures NM1, NM2, NM3, and NM3, respectively. Gas mixtures NM1, NM2, NM3, and NM4 are each represented by a different symbol: a blue diamond circle for gas mixture NM1, a red circle for gas mixture NM2, a black triangle for gas mixture NM3, and a green square for gas mixture NM4. A line through the origin with a 1:1 slope is shown in each figure to show the linearity relationship of the results. A good linear relationship between the gravimetric and verification amount fractions can be seen with the data point close to and on the linearity line for plots of CH_4, C_2H_6, C_3H_8, O_2, N_2, CO and CO_2 with % differences ranging from 0.003% and 0.286%. %Difference results for C_4H_6 for gas mixtures NM1 and NM2 have the largest and the second largest % differences during analysis at 0.539% and 0.416%, respectively.

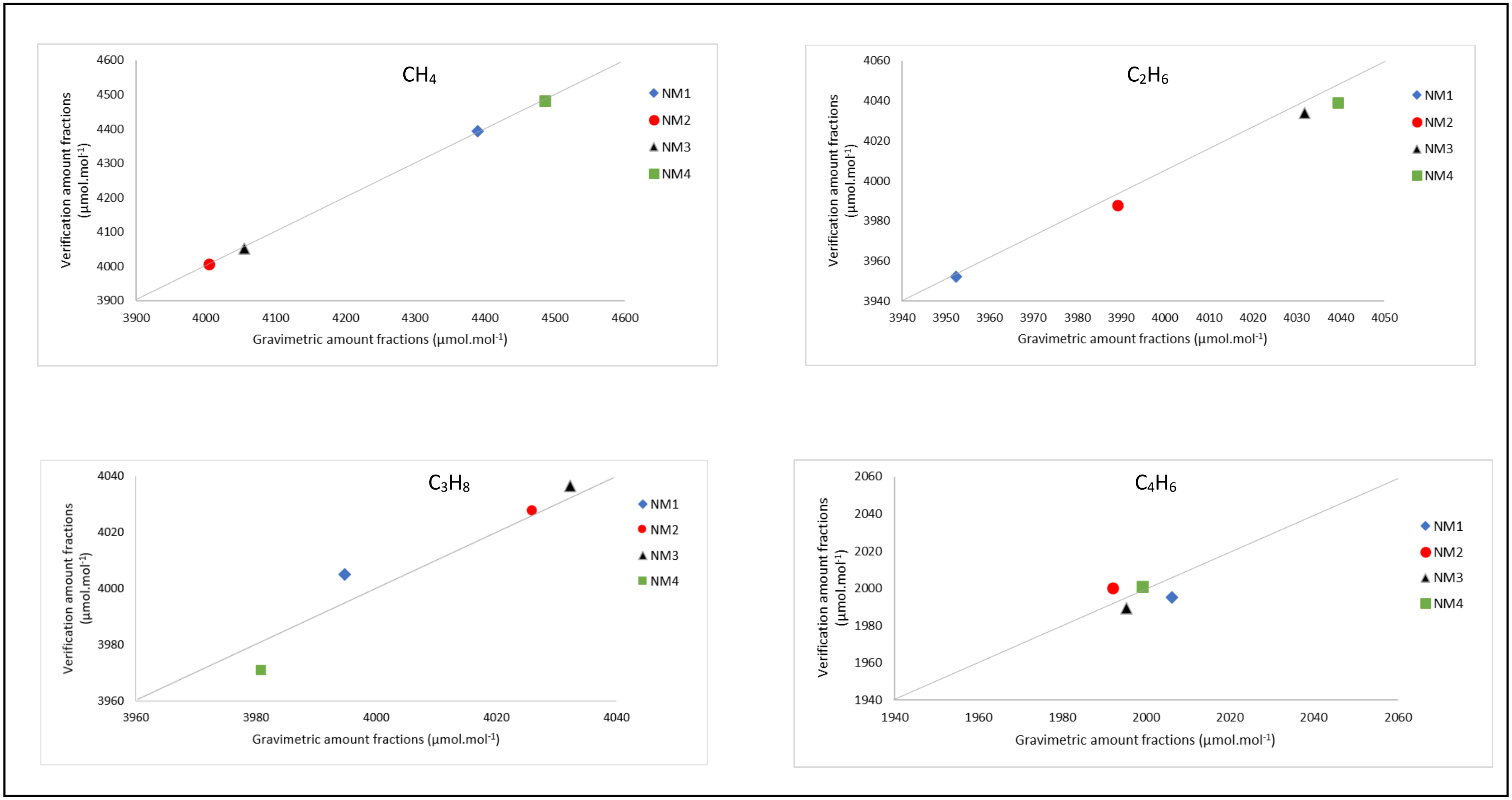

Figure 5.26 Scatterplot graphs of the gravimetric amount fractions against verification amount fractions of CH_4, C_2H_6, C_3H_8 and C_4H_6 in the low range refinery reference gas mixtures.

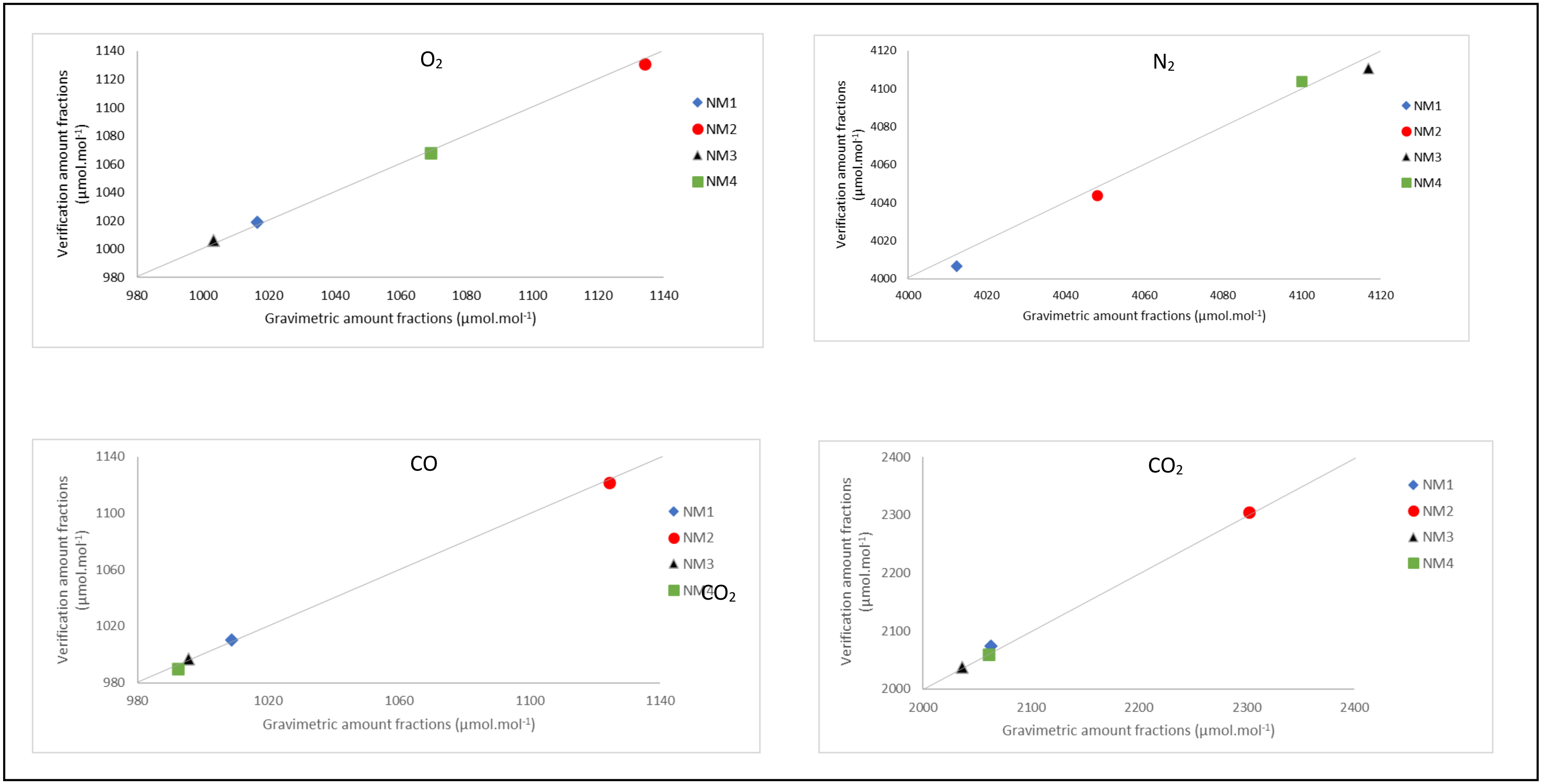

Figure 5.27 Scatterplot graphs of the gravimetric amount fractions against verification amount fractions of O_2, N_2, CO and CO_2 in the low range refinery reference gas mixtures.

5.6.3. Internal consistency results for low range refinery reference gas mixtures

Sensitivity ratios were used to perform an internal consistency evaluation of the low range refinery reference gas mixtures to determine whether they were comparable with one another. Gas mixtures NM1, NM2, and NM3 were used as samples, with gas mixture NM4 serving as a reference. The ideal sensitivity ratio to demonstrate internal consistency between the sample and reference gas mixtures is that which is close to one.

Figures 5.28 and 5.30 show the internal consistency of all the components of interest in the study. The overall sensitivity ratios are well within 1.000 ± 0.040. For gas mixture NM1, all the analysed component indicate good agreement to the reference gas mixture with sensitivity ratios in the range 0.999 to 1.007 with an exception of 1,3-butadiene with a ratio of 1.037 and percent difference > 0.5% from that of the gravimetric value. The sensitivity ratios for gas mixture NM2 demonstrated good agreement with the reference gas mixture for all of the components of interest, with values ranging from 0.991 to 1.013. Sample NM3 was the most consistent with the reference gas mixture, with sensitivity ratios for all the components of interest ranging from 0.998 to 1.004.

Of all the components of interest, 1,3-butadiene was observed to have the largest inconsistencies with the reference gas mixture. This may be due to 1,3-butadiene's autoxidation state in the presence of oxygen (Liang et al., 2022). With this being said, the low range refinery gas mixtures were successfully verified with an accuracy of < 1%.

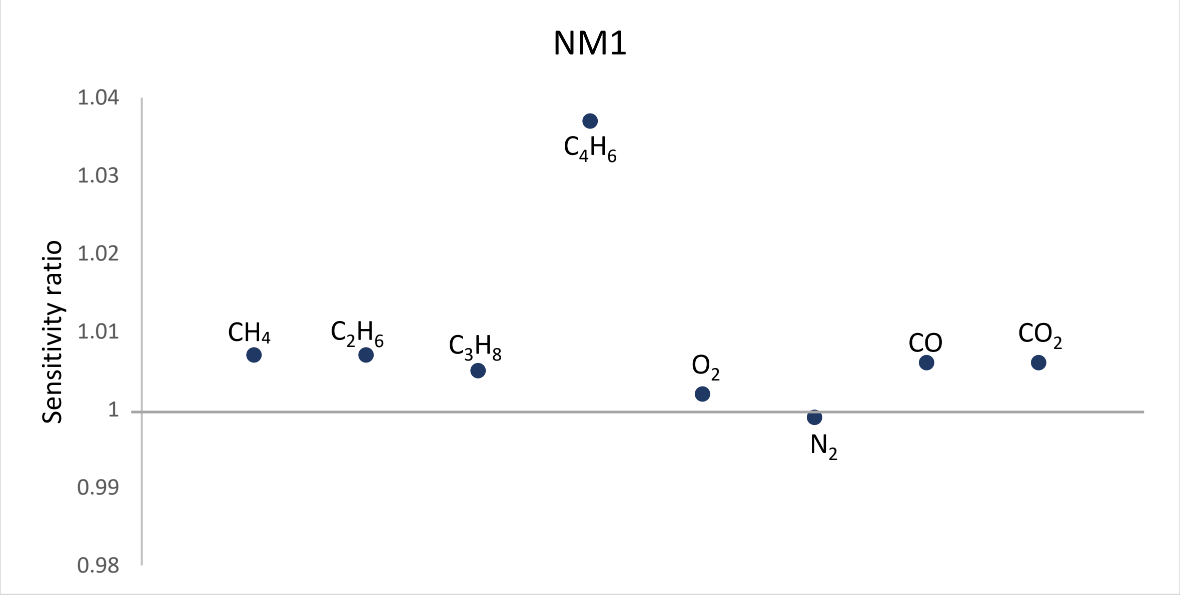

Figure 5.28 Internal consistency results for all eight components of interest in gas mixture NM1.

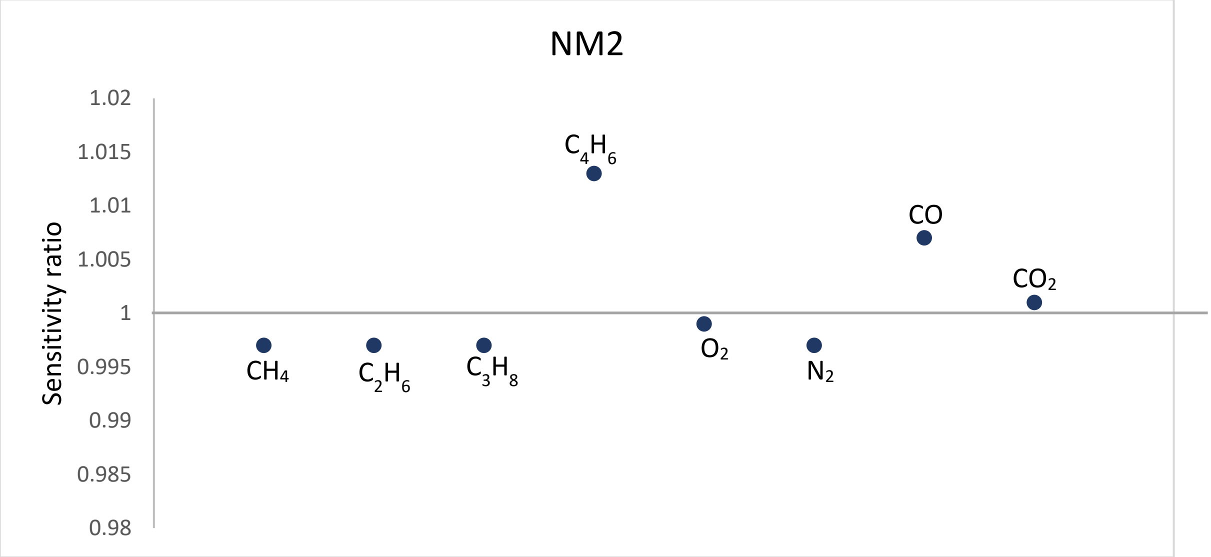

Figure 5.29 Internal consistency results for all eight components of interest in gas mixture NM2.

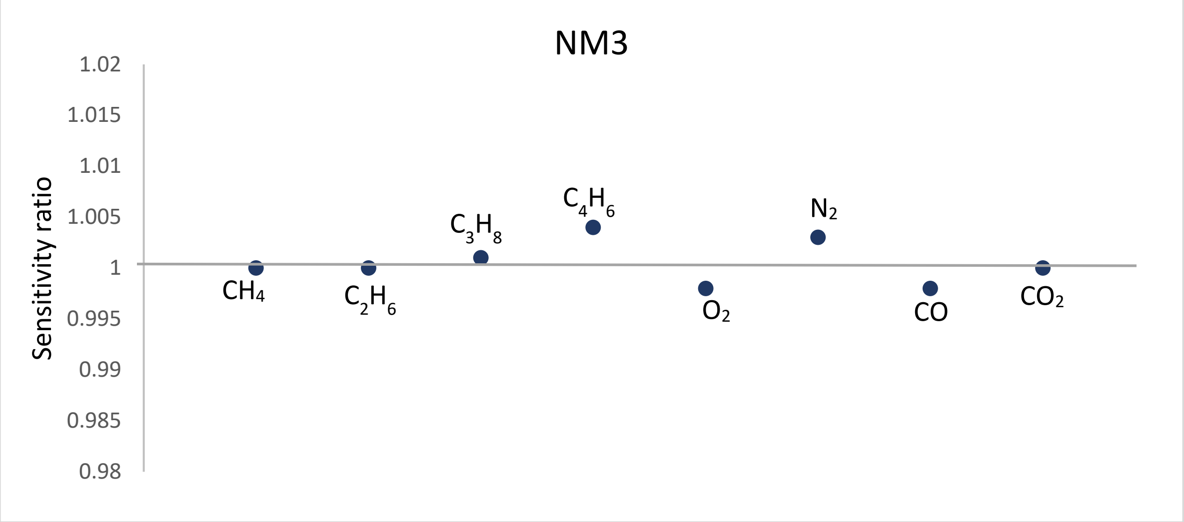

Figure 5.30 Internal consistency results for all eight components of interest in gas mixture NM3.

5.6.4. Measurement comparability test results

The measurement comparability test was done by comparing the developed refinery reference gas mixture NM1 against NPL-purchased certified reference material for the refinery reference gas standard (NPL-2) that had similar amount fractions on the FID/TCD. The gas standard purchased from NPL came with a certificate of calibration with expanded uncertainties based on standard uncertainties multiplied by a coverage factor where k = 2, at a 95% confidence interval.

Table 5.41 and Figure 5.31 show the results of the comparison between the developed refinery reference gas mixture NM1 and the NPL-2 gas standard. From the results, the overall absolute percentage difference between the gravimetric and verification amount fractions of all components of interest ranged from 0.049 to 1.395%. The results show an insignificant difference between the gravimetric and verification amount fractions, with measurement results lower than 2% demonstrating measurement equivalence between the developed refinery reference gas mixture NM3 and the NPL-2 refinery gas standard.

Table 5.41 Measurement results for comparison between cylinder NM1 against NPL-2 using gas chromatography.

Cylinder ID	**Component**	x_{grav} **(µmol.mol^{-1})**[1]	u_{grav} **(µmol.mol^{-1})**[2]	x_{veri} **(µmol.mol^{-1})**[3]	u_{veri} **(µmol.mol^{-1})**[4]	**% Difference**[5]	**Combined expanded uncertainty** $(k = 2)$[6]
NM1	CH_4	4389.532	0.516	4381.978	19.030	0.172	19.058
	C_2H_6	3952.424	0.490	3947.199	16.751	0.132	16.780
	C_3H_8	3994.759	0.357	3992.817	13.556	0.049	13.575
	C_4H_6	2006.145	0.257	1978.162	8.893	1.395	8.908
	O_2	1016.600	0.168	1008.564	10.779	0.790	10.784
	N_2	4012.455	0.618	4022.656	21.918	0.254	21.953
	CO	1008.907	0.173	1013.156	11.884	0.421	11.889
	CO_2	2062.956	0.328	2058.547	14.985	0.214	14.999

[1] x_{grav} is the gravimetric amount fraction for component i from the gravimetric preparation in accordance with ISO 6142

[2] u_{grav} is the standard uncertainty associated with the gravimetric amount fraction for component i

[3] x_{veri} is the average verification amount fraction of 5 runs for component i

[4] u_{veri} is the verification standard uncertainty associated with the verification repeatability measurement

[5] %difference between the gravimetric and verification amount fraction calculated using **equation 4.13**

[6] Combied expanded uncertainty of the gravimetric and verification uncertainties ($U = 2\sqrt{(u_{grav})^2 + (u_{veri})^2}$

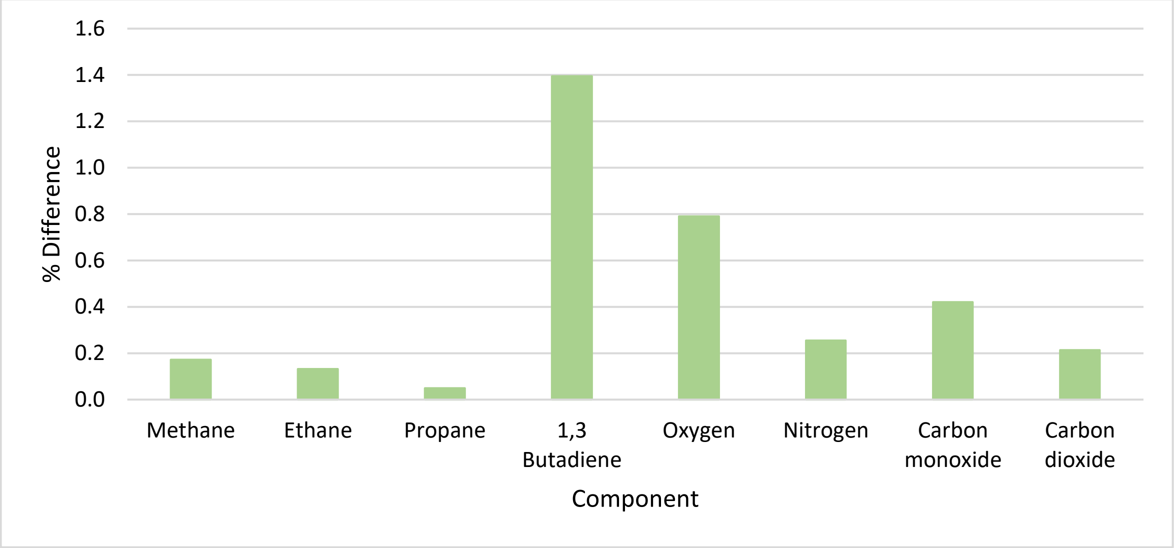

Figure 5.31 Calculated percentage difference of the eight components of interest in the developed low range refinery gas mixtures.

5.6.5. Stability assessment of low range refinery reference gas mixtures

The NM3 gas mixture containing all nine components of interest was initially analysed six days after preparation and then eight times over a period of 359 days. Six consecutive sample injections of the gas mixture to the GC-FID/TCD were made following a single-point calibration method using an A-B-A sequence for the analysis of the mixture. During the first sets of measurements, four replicate sets of the A-B-A sequence were taken. Later, measurements were reduced to 2 - 3 sets to conserve the gas mixture.

The results of testing the stability of low range refinery reference gas mixtures at amount fractions of 4 000 µmol.mol^{-1} for CH_4, C_2H_6, C_3H_8, and N_2, 2 000 µmol.mol^{-1} for C_4H_6, and CO_2 and 1 000 µmol.mol^{-1} for O_2, and CO are graphically represented in **Figures 5.32 to 5.39**. The graphs aid in assessing the ability of a measurement system to yield consistent results when the same sample is analysed over time. The gravimetric amount fractions are represented by a green line, the verification amount fractions are represented by black diamonds, with the verification uncertainty represented by the error bars, and the upper and lower limits of 2% of the gravimetric amount fraction are indicated by the red lines (*k* = *2* at 95% confidence level) in the figures below. The gravimetric amount fraction was taken as the reference value.

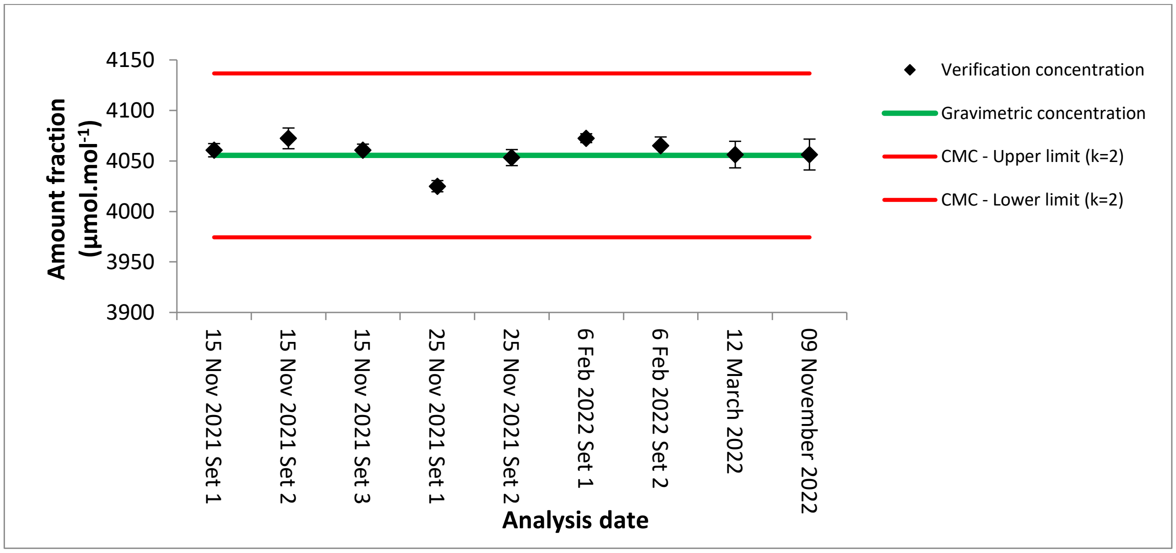

Figure 5.32 Stability results of methane in low range refinery reference gas mixtures.

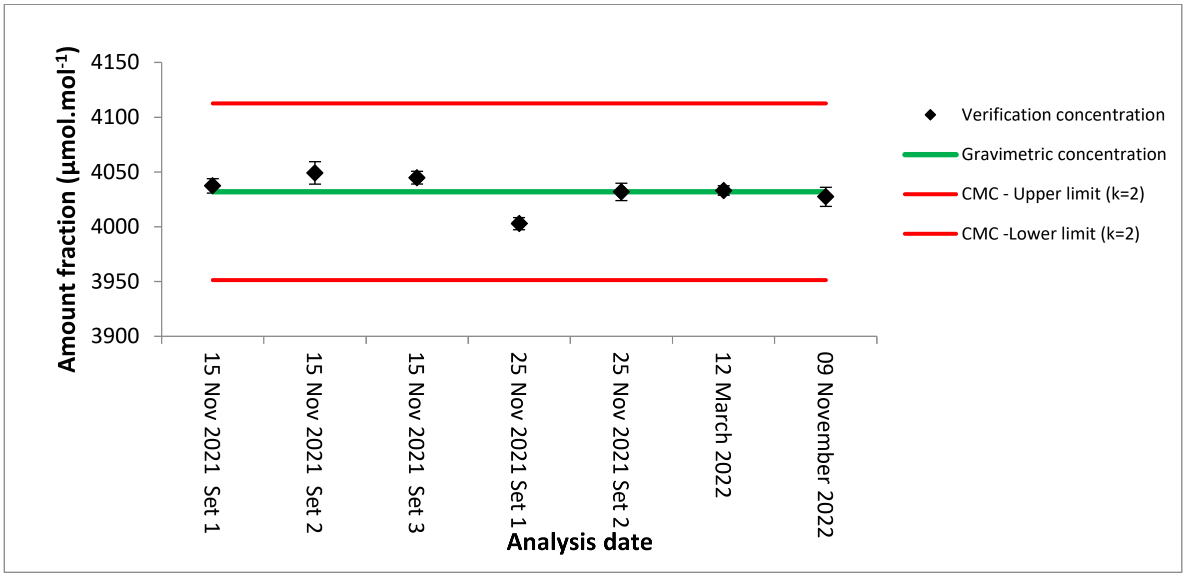

Figure 5.33 Stability results of ethane in low range refinery reference gas mixtures.

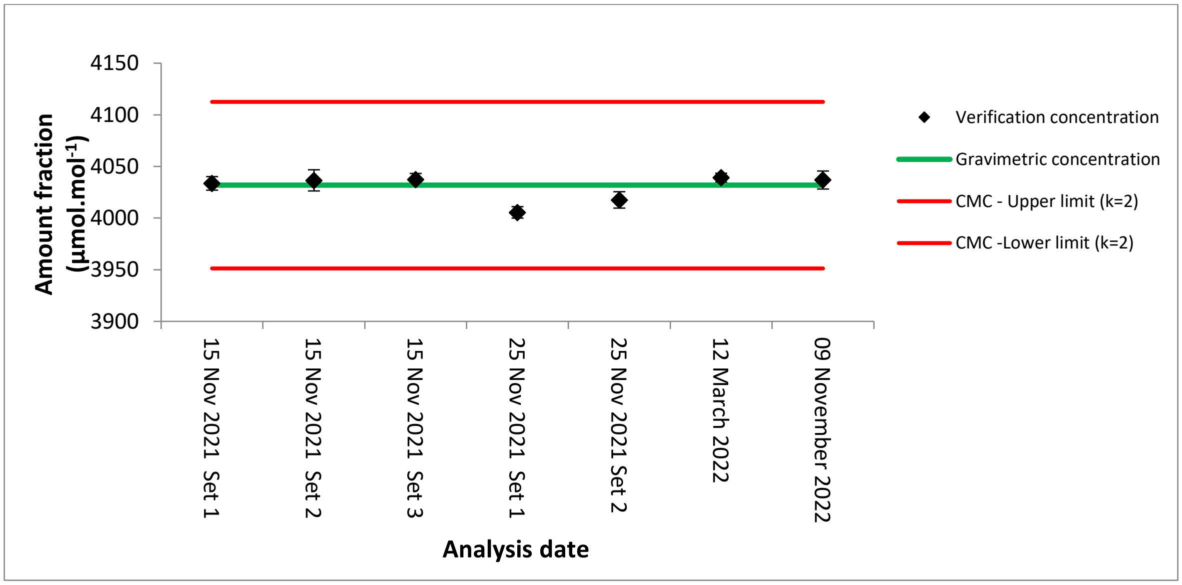

Figure 5.34 Stability results of propane in low range refinery reference gas mixtures.

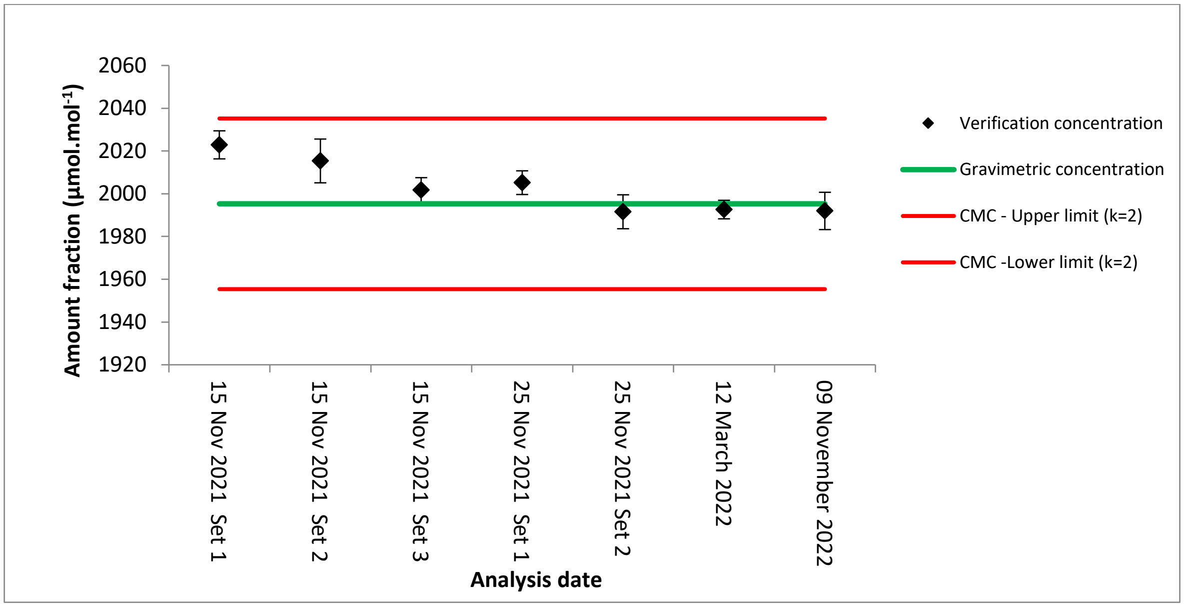

Figure 5.35 Stability results of 1,3-butadiene in low range refinery reference gas mixtures.

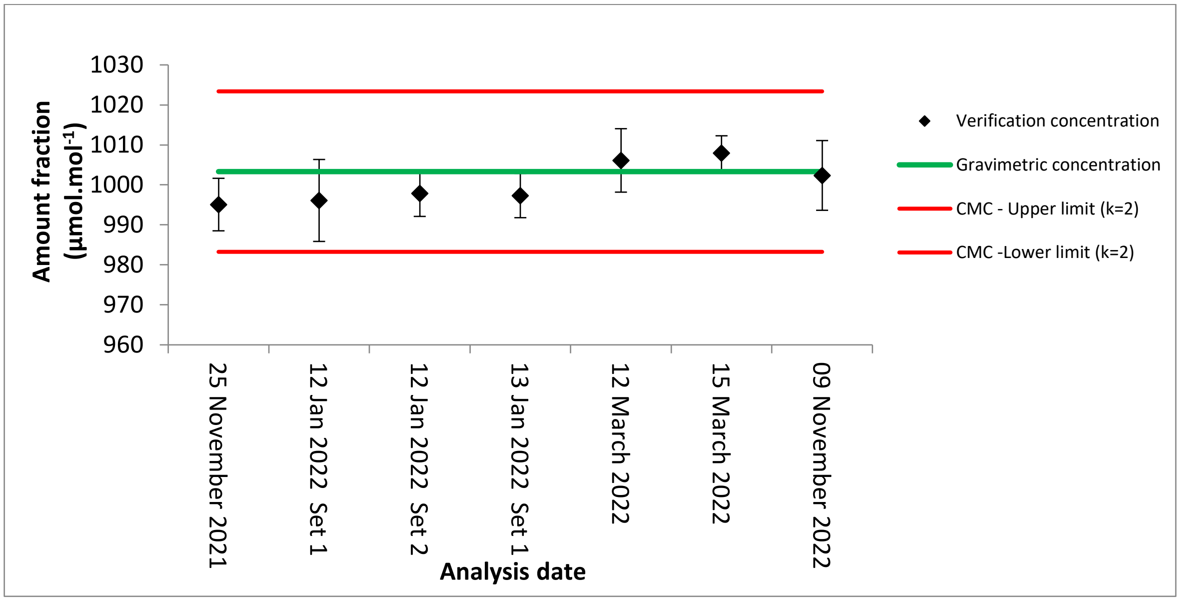

Figure 5.36 Stability results of oxygen in low range refinery reference gas mixtures.

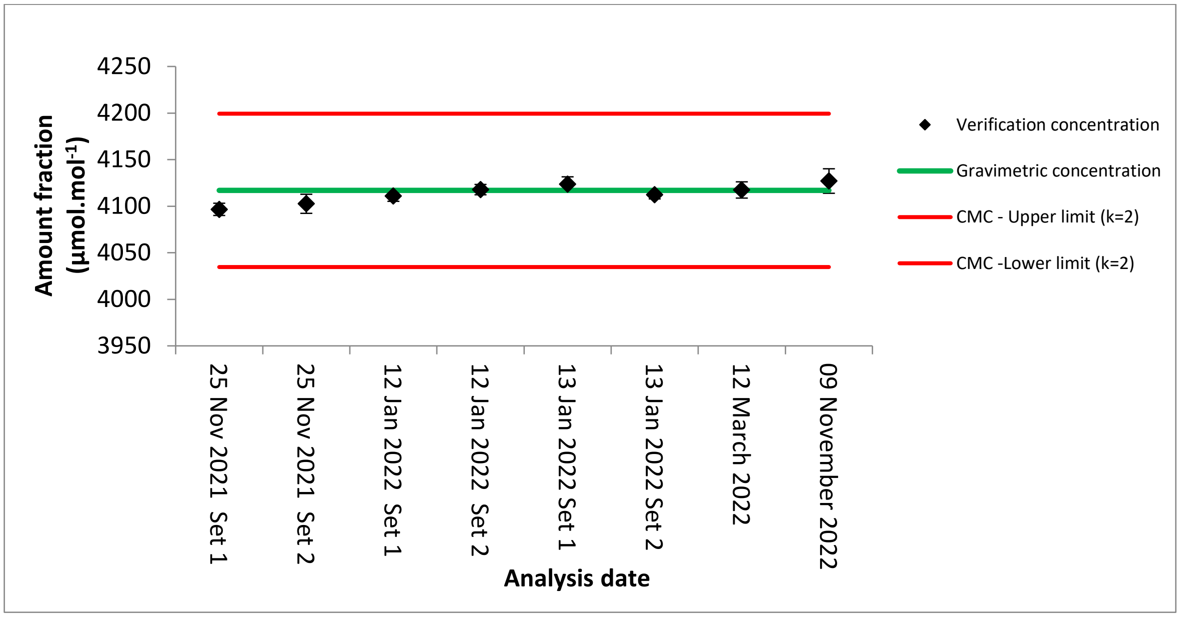

Figure 5.37 Stability results of nitrogen in low range refinery reference gas mixtures.

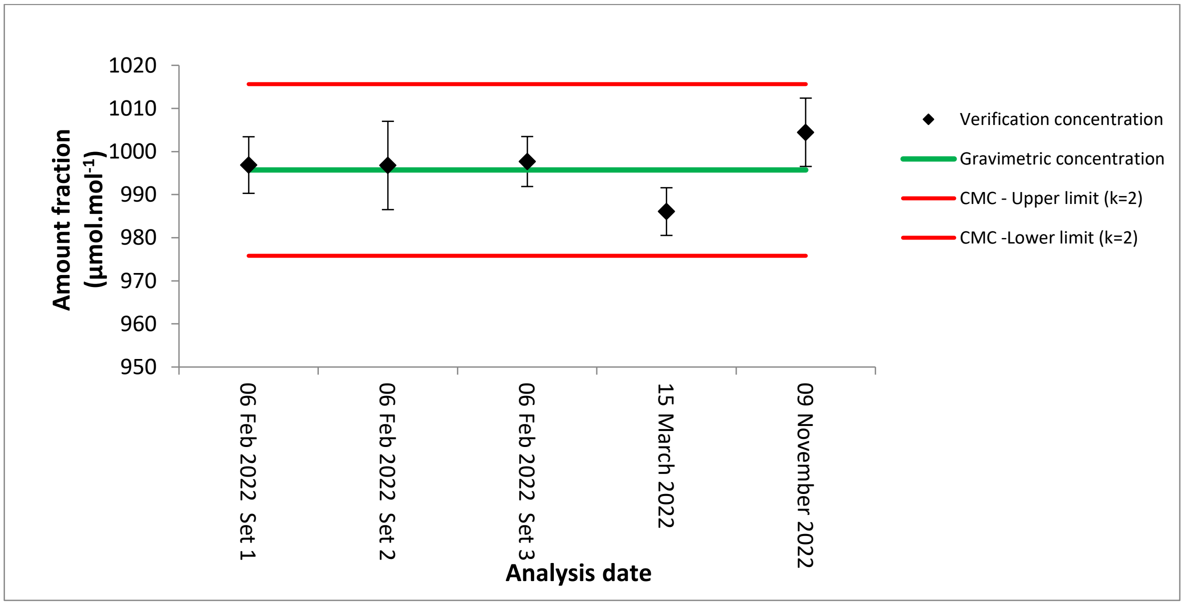

Figure 5.38 Stability results of carbon monoxide in low range refinery reference gas mixtures.

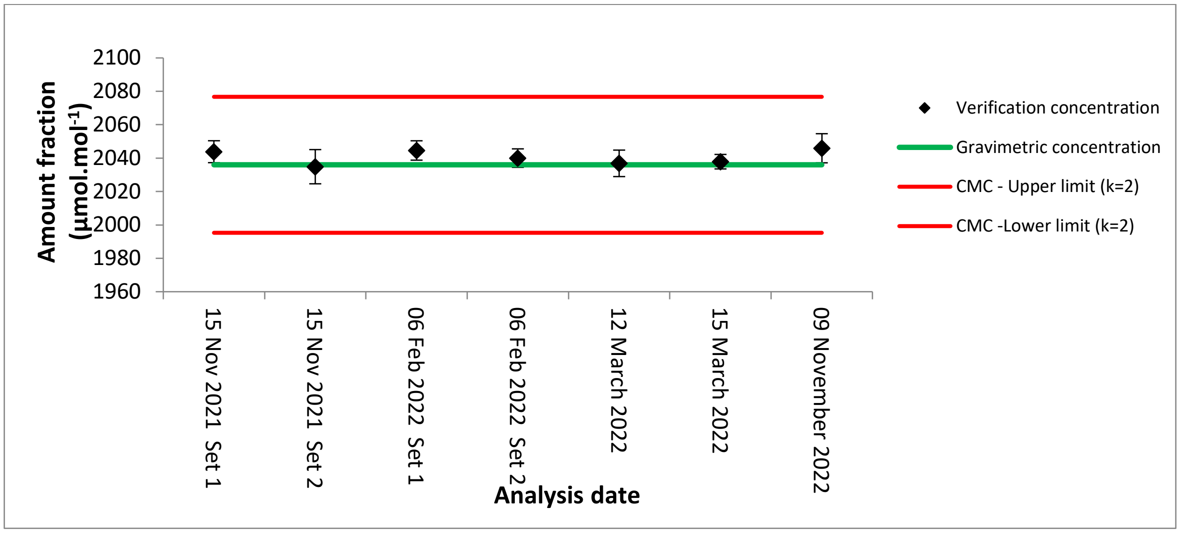

Figure 5.39 Stability results of carbon dioxide in low range refinery reference gas mixtures.

From the graphs above, it can be concluded that there was no significant change between the gravimetric and verification amount fractions because all the verification amount fractions, and their associated uncertainties fell within the 2% measurement uncertainty. This further suggests that the cylinder treatment prevented aluminium oxide from permeating into the gas mixtures (Rhoderick and Lin, 2013).

The stability of the gas mixtures was also investigated using the D statistical test at a 95% confidence interval and on the assumption of a normal distribution. **Equation 5.1** was used to calculate the D value. A D value of less than 2 indicates no substantial instability, while a D value of more than 2 indicates severe instability.

Table 5.42 Statistical D test for stability assessment for the nine components of interest in the low range refinery reference gas mixtures.

Component	$\boldsymbol{D}$ $\boldsymbol{x_1, x_2}$	$\boldsymbol{D}$ $\boldsymbol{x_2, x_3}$	$\boldsymbol{D}$ $\boldsymbol{x_3, x_4}$	$\boldsymbol{D}$ $\boldsymbol{x_4, x_5}$
Methane	0.4282	0.1694	0.3132	0.0001
Ethane	0.4996	0.0825	0.0147	-
Propane	0.6562	0.0267	0.0206	-
1,3-butadiene	0.6965	0.1121	0.0176	-
Oxygen	0.0135	0.0219	2.7642	0.7621
Nitrogen	0.0665	0.2472	0.0172	0.0253
Carbon monoxide	0.8730	0.5338	0.1248	-
Carbon dioxide	0.0395	0.0168	0.0163	0.0975

$\boldsymbol{D}$ is the test statistic measurement, $\boldsymbol{x_1}$ is the first analysis results, $\boldsymbol{x_2}$ is the second analysis results, $\boldsymbol{x_3}$ is the third analysis results, $\boldsymbol{x_4}$ is the fourth analysis results and $\boldsymbol{x_5}$ is the fifth analysis results.

It can be seen from the results presented in **Table 5.42** that there was no detectable instability during the 12-month stability study period for all the components of interest in the study, with results ranging from 0.0001 to 0.8730 except for the third result for oxygen at 2.7642. This observed significant difference is due to a change in the reference gas mixture used during verification, which contributed to the significant change in the verification amount fraction. This is because the reference's amount fraction is directly proportional to the amount fraction of the sample mixture. Although this significance was observed, the oxygen verification data still falls within the measurement uncertainty of 2%.

5.7. Method validation for analysis of refinery reference gas mixtures using GC FID/TCD

5.7.1. Method validation preface

The performance characteristics of any developed method must be evaluated to demonstrate its fit-for-purpose application in the laboratory (Barwick, 2016). This translates into the requirement for technical methods to satisfy the need for accurate and low uncertainty refinery reference gas mixtures. This section is aimed at demonstrating that the measurement method used for analysis of the primary refinery reference gas mixtures using GC-FID and TCD is fit for purpose through evaluation and conclusive statements on the following parameters: accuracy, precision, selectivity, robustness, measurement comparability, and measurement uncertainty. The Eurachem Guide performance parameters served as the framework for the method validation criteria shown in **Table 5.43** (Magnusson and Örnemark, 2014).

Table 5.43 Method validation criteria.

Validation parameters	Criteria
Accuracy (%difference)	< 2
Repeatability (% RSD)	< 2
Reproducibility (%RSD)	< 2
Measurement uncertainty (%REU)	< 5
Selectivity	No interference desired

5.7.2. Accuracy results

The accuracy evaluation was done through the comparison of the true value and the measured value for each component of interest contained in the refinery reference gas mixture NM3. Single-point calibration method was used to assess the accuracy of the analytical method. The gas mixture NM3 was analysed on three different days using three different gas standards with comparable amount fractions. The analysis results were averaged, and the accuracy was calculated by evaluating the absolute percentage difference (%difference). **Table 5.44** shows the gravimetric amount fractions as the true value and the averaged measured analytical values of refinery reference gas mixture NM3 for all eight components of interest. The calculated % differences between the eight components of interest ranged from 0.052 to 0.314%. The %difference observed was well within the 2% limit for the analytical method, thus the requirement for accuracy in the measurement method was satisfied.

Table 5.44 Accuracy results for refinery references gas mixture NM3.

Component	x_{grav} **(%mol.mol^{-1})^{1}**	x_{veri} **(%mol.mol^{-1})^{2}**	**%Difference^{3}**
C_4H_6	1995.289	2001.556	0.314
CO_2	2036.002	2033.053	0.145
CO	995.725	995.173	0.055
C_2H_6	4031.919	4035.354	0.085
CH_4	4055.521	4061.587	0.150
N_2	4116.981	4114.856	0.052
O_2	1003.320	1006.115	0.279
C_3H_8	4032.339	4035.000	0.066

$^{1}x_{grav}$ is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142, $^{2}x_{veri}$ is the average verification amount fraction over three different days for component i and ^{3}**%Difference** between the gravimetric and verification amount fraction calculated using **equation 4.13.**

5.7.3. Precision

5.7.3.1. Repeatability

The closeness of the results obtained under the same measurement conditions is defined as a measuring instrument's repeatability. Repeatability was performed to assess the method’s ability to consistently produce precise measurements. It was determined using refinery reference gas mixtures NM1 and NM3. Three analytical measurement replicates for both gas mixtures were taken by the same personnel, on same day under the same environmental conditions. **Tables 5.45** and **5.46** show the repeatability results of the analytical method on refinery reference gas mixtures represented by %RSD. The set criteria for repeatability of the analytical method were % RSD of less than 2%. The % RSD for the measurements of all the components of interest lie between 0.006% and 0.346%, satisfying the validation criteria.

Table 5.45 Measurement results for the repeatability test using gas mixtures NM1.

NM1								
Number of replicates	**1,3-butadiene**	**Carbon dioxide**	**Carbon monoxide**	**Ethane**	**Methane**	**Nitrogen**	**Oxygen**	**Propane**
Experiment 1 (µmol.mol^{-1})	1995.443	2074.368	1008.555	3958.786	4397.292	4013.404	1020.929	4006.263
Experiment 2 (µmol.mol^{-1})	1995.233	2074.615	1007.020	3956.512	4393.500	4010.455	1014.797	4003.760
Experiment 3 (µmol.mol^{-1})	1999.653	2074.530	1009.523	3950.378	4387.867	4010.806	1020.874	3996.641
Average[1]	1996.776	2074.505	1008.366	3955.226	4392.886	4011.555	1018.867	4002.221
Standard deviation[2]	2.493	0.125	1.262	4.349	4.742	1.611	3.525	4.992
%RSD[3]	0.125	0.006	0.125	0.110	0.108	0.040	0.346	0.125

Table 5.46 Measurement results for the repeatability test using gas mixtures NM3.

NM3								
Number of replicates	**1,3-butadiene**	**Carbon dioxide**	**Carbon monoxide**	**Ethane**	**Methane**	**Nitrogen**	**Oxygen**	**Propane**
Experiment 1 (µmol.mol^{-1})	2019.892	2036.872	996.779	4035.202	4057.883	4116.490	1006.207	4031.756
Experiment 2 (µmol.mol^{-1})	2023.701	2033.463	998.928	4036.198	4059.715	4112.703	1006.664	4032.616
Experiment 3 (µmol.mol^{-1})	2015.347	2033.795	996.215	4040.438	4064.195	4117.627	1007.936	4036.552
Average[1]	2019.647	2034.710	997.307	4037.279	4060.597	4115.607	1006.936	4033.641
Standard deviation[2]	4.182	1.880	1.432	2.781	3.247	2.578	0.896	2.557
%RSD[3]	0.207	0.092	0.144	0.069	0.080	0.063	0.089	0.063

[1]**Average** obtained using four analytical responses for each measurement, [2]**Standard deviation** of the measurement results calculated using equation 4.8 and [3]**Percentage relative standard deviation (%RSD)** calculated as a measure of repeatability using equation 4.14.

5.7.3.2. Reproducibility

Another type of precision is reproducibility, which refers to the variability of measurement results across different measurement conditions. It was calculated by averaging three daily analytical measurement replicates of gas mixtures (NM1 and NM3) for three different days. The method validation criteria define the reproducibility parameter as %RSD ≤ 2%. **Table 5.27, Table 5.28,** and **Figure 5.40** show reproducibility results following analysis of the study's target components over three different days. The reproducibility %RSDs for 1,3-butadiene, carbon dioxide, carbon monoxide, ethane, methane, nitrogen, oxygen, and propane lie between 0.023% and 0.662%, demonstrating that the method met the criteria for reproducibility.

Table 5.47 Measurement results for the reproducibility test using gas mixture NM1.

	NM1							
Day of analysis	**1,3-butadiene**	**Carbon dioxide**	**Carbon monoxide**	**Ethane**	**Methane**	**Nitrogen**	**Oxygen**	**Propane**
Day 1 (μmol.mol^{-1})	1995.338	2058.259	1011.127	3957.649	4381.193	4007.287	1025.721	4005.011
Day 2 (μmol.mol^{-1})	1996.776	2074.505	1008.366	3955.226	4392.886	4011.555	1018.867	4002.221
Day 3 (μmol.mol^{-1})	1999.653	2064.234	1005.019	3938.88	4374.702	4007.011	1026.694	3991.126
Average^1	1997.256	2065.666	1008.170	3950.585	4382.927	4008.617	1023.760	3999.453
Standard deviation^2	2.197	8.217	3.059	10.209	9.215	2.548	4.266	7.345
%RSD^3	0.110	0.398	0.303	0.258	0.210	0.064	0.417	0.184

Table 5.48 Measurement results for the reproducibility test using gas mixture NM3.

	NM3							
Day of analysis	**1,3-butadiene**	**Carbon dioxide**	**Carbon monoxide**	**Ethane**	**Methane**	**Nitrogen**	**Oxygen**	**Propane**
Day 1 (μmol.mol^{-1})	2019.647	2037.806	996.703	4037.279	4060.597	4111.004	996.103	4033.641
Day 2 (μmol.mol^{-1})	1998.168	2036.876	998.709	4049.125	4072.349	4121.266	998.156	4049.379
Day 3 (μmol.mol^{-1})	1995.381	2037.216	991.488	4027.688	4051.418	4111.440	1006.115	4027.698
Average^1	2004.399	2037.299	995.634	4038.031	4061.455	4114.570	1000.125	4036.906
Standard deviation^2	13.278	0.470	3.727	10.738	10.492	5.803	5.289	11.203
%RSD^3	0.662	0.023	0.374	0.266	0.258	0.141	0.529	0.278

^{1}**Average** obtained using four analytical responses for each measurement, ^{2}**Standard deviation** of the measurement results calculated using equation 4.8 and ^{3}**Percentage relative standard deviation (%RSD)** calculated as a measure of repeatability using equation 4.14.

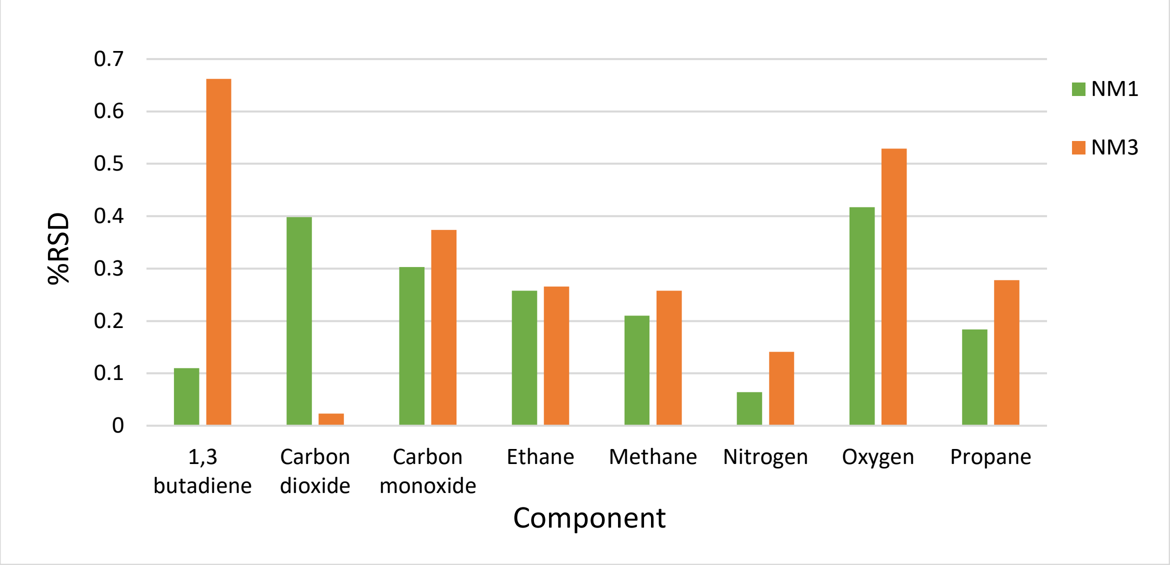

Figure 5.40 Measurement results for reproducibility taken over three days.

5.7.4. Selectivity/ specificity

The primary reference gas mixtures in this study were analysed on a gas chromatograph with a flame ionisation detector and a thermal conductivity detector. Methane, ethane, propane, and 1,3-butadiene were separated using the FID channel, while oxygen, nitrogen, carbon monoxide, and carbon dioxide were separated using the TCD channel. The selectivity of the method was investigated by examining its’ capacity to precisely identify the signal produced by the target component despite the presence of other components in a sample matrix. The analytical response data was used to determine the amount fractions for methane, ethane, propane, 1,3-butadiene, oxygen, nitrogen, carbon monoxide, and carbon dioxide using the single-point calibration method.

Hydrocarbons elute according to increasing C-H bonds in gas chromatography. This order of elution on the FID channel was such that the component with the fewest C-H bonds would elute first and components with more C-H bonds would elute last. Therefore, in the prepared refinery gas mixture, methane eluted first at a retention time of 5.989 minutes, ethane followed at 6.489 minutes, propane at 7.662 minutes and 1,3-butadiene at 10.300 minutes, as shown in **Figure 5.41**. A CP-Sil 5 CB column with a stationary phase made entirely of dimethylpolysiloxane (PDMS) was used to achieve this separation. Although methane, ethane, and propane were prepared at similar amount fractions of 4 000 µmol.mol^{-1}, it is apparent in **Figure 5.41** that their analytical responses are not identical. The difference in peak area is attributed to the components' sensitivity towards the flame ionisation detector due to the number of C-H bonds available. Methane, ethane, and propane have four, six, and eight C-H bonds, respectively, and because sensitivity increases with an increase in C-H bonds, their visual analytical response also increases (Van Santen, 2009).

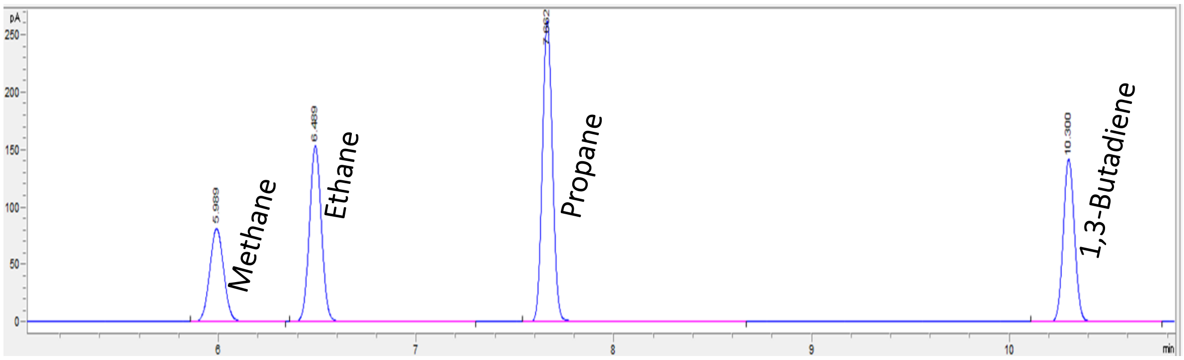

Figure 5.41 GC-FID chromatogram of primary reference gas mixture NM3.

To ensure good resolution of the oxygen and nitrogen peaks on the TCD channel, the oven temperature was set at 35 °C for the first three minutes. The temperature was then ramped up to 180 °C to allow for the elution of carbon monoxide and carbon dioxide within an adequate amount of time, as can be seen in **Figure 5.42**. The good separation of these gases on the TCD can be attributed to the Molecular Sieve 13X and ShinCarbon ST columns used. The columns are known to provide good separation of these components because the separation process of the Molecular Sieve 13X is dependent on the size and shape of the molecule (Rother and Fieback, 2013), while the ShinCarbon ST column is a high surface area carbon molecular sieve (~1,500 m2/g) ideal for separating permanent gases and light hydrocarbons without cryogenic cooling (Shade, 2022).

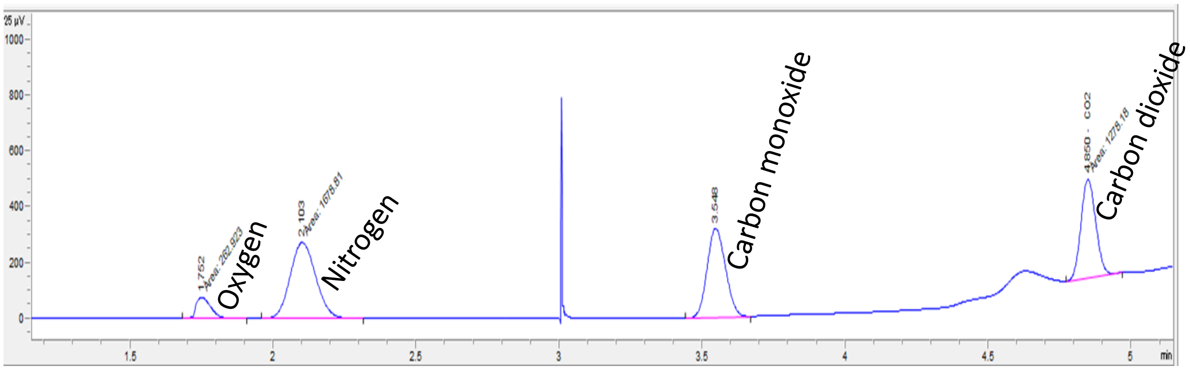

Figure 5.42 GC-TCD chromatogram of primary reference gas mixture NM3.

5.7.5. Ruggedness/ extreme conditions test

Ruggedness is a measure used to evaluate the consistency of results when external environmental conditions are varied, in this case, temperature. Gas mixture NM3 was analysed on three different occasions after being subjected to varying temperatures of 21.5 °C at first, then 36 °C, and lastly 2 °C as described in **Chapter 4 Section 4.12.4**. In order to investigate any change in the verification amount fraction of each component of interest in the mixture despite temperature changes, the percentage differences between the verification amount fractions and the gravimetric reference value were determined. The calculated % differences shown in **Table 5.49 and Figure 5.43** for the eight components of interest in the gas mixture ranged from 0.005% to 1.221%, which is well within the 2% accuracy criteria for the analytical method. Therefore, it can be concluded that temperature variations between 2 °C and 36 °C have no significant effect on the integrity of refinery reference gas mixtures.

Table 5.49 Percentage difference of eight components of interest in gas mixture NM3 at varying temperatures.

Component	**% Difference**[1]		
	Ambient (21.5 °C)	**Sun (36 °C)**	**Fridge (2 °C)**
1,3-butadiene	1.221	0.144	0.005
Carbon dioxide	0.089	0.043	0.060
Carbon monoxide	0.098	0.300	0.426
Ethane	0.133	0.427	0.105
Methane	0.125	0.415	0.101
Nitrogen	0.145	0.104	0.135
Oxygen	0.719	0.515	0.279
Propane	0.032	0.423	0.115

[1] **%Difference** between the gravimetric and verification amount fraction at each temperature calculated using **equation 4.13.**

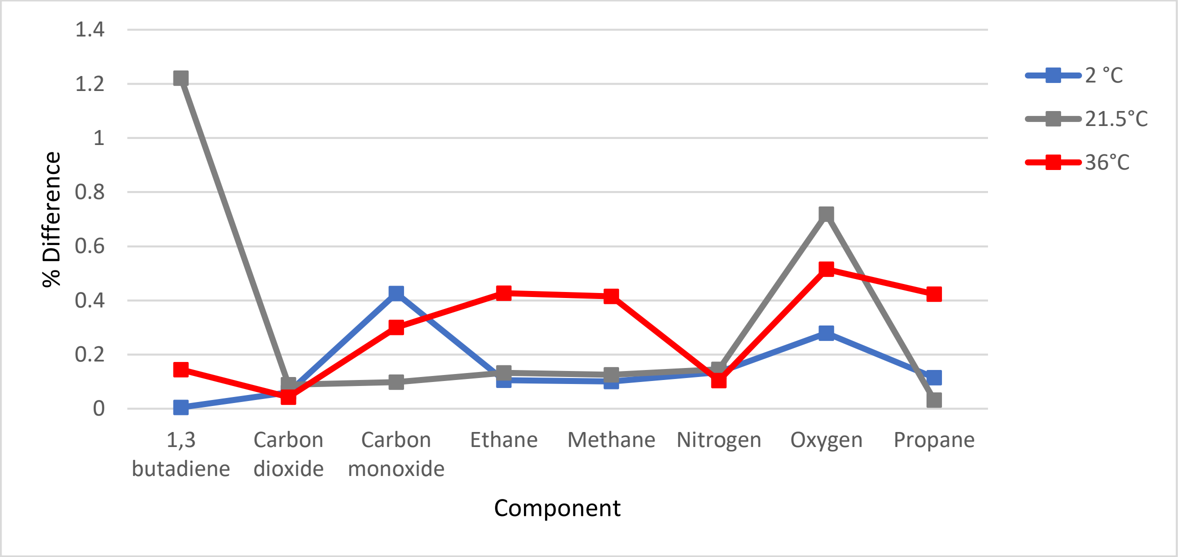

Figure 5.43 Extreme condition test results for eight components of interest in gas mixture NM3 2 °C, 21.5 °C, and 36 °C.

Figure 4.43 demonstrates that while components like nitrogen and carbon monoxide do not exhibit any bias with respect to exposure to different temperatures, ethane, methane, and propane show more uniformity the more the mixture is exposed to low temperatures. Whereas the percentage differences in oxygen and 1,3-butadiene were the smallest at 2 °C and the highest at 21.5 °C.

5.7.6. Measurement uncertainty evaluation

Measurement uncertainty is critical in analytical chemistry as it indicates the confidence of results. This parameter specifies a range, with a specified level of confidence (95.45% in this case), within which the value of the quantity being measured is anticipated to fall. It describes how much of the target analyte's unknown value is known after measurement, taking into consideration the information provided from the measurement. A list of uncertainty sources considered and quantified in the production of refinery primary reference gas mixtures is given and compiled from ISO-Standards, ISO-6142-1:2015 and ISO-6143:2001. The uncertainty contributors associated with the value assignment of refinery reference gas mixtures amount fractions were as follows:

a. Gravimetric uncertainty
b. Verification uncertainty (repeatability)
c. Short-term stability of the refinery reference gas mixtures (estimated standard deviation of the mean)

5.7.6.1. Gravimetric uncertainty

Gravimetric uncertainties are caused by a variety of factors. The purity of the starting materials, the molar masses of the components of interest in the mixture, and the mass comparator balance employed in the weighing process are significant sources of gravimetric uncertainty. The gravimetric amount fraction uncertainty calculations have degrees of freedom of infinity (∞) and multiplying the uncertainty result by a coverage factor of 2 results in a result with a level of confidence of 95.45%.

The uncertainty associated with the weighing process emanates from the accuracy of the automated weighing system connected to a mass comparator balance. This uncertainty considers the balance's linearity and calibration, as well as the impact of environmental moisture and dust on the cylinder's exterior surface, the repeatability of the balance's readings, and any inaccuracies caused by the cylinder's placement on the balance. Potential uncertainty sources, such as the buoyancy effect, were minimised by weighing by difference with a reference cylinder and are therefore insignificant in the weighing process. The uncertainty associated with the purity of the starting material and parent gas is obtained from the purity analysis results (ISO 6142, 2015), and the uncertainty of the molar masses of the components of interest in the mixture is found in the ISO 14912:2003, "*Gas analysis — Conversion of gas mixture composition data"* (Brown, 2009).

The gravimetric uncertainties for each component in the prepared gas mixtures were calculated using the Gravcalc software. **Table 5.50** lists the gravimetric standard uncertainty for each component in the gas mixture, the expanded uncertainty with the coverage factor (K) of 2 at 95,45% level of confidence and the relative uncertainty (%REU) associated with the gravimetric preparation of the NM3 gas mixture.

Table 5.50 Measurement uncertainty associated with the gravimetric preparation of NM3

Component	x_{grav} (µmol.mol^{-1})^{1}	u_{grav} (µmol.mol^{-1})^{2}	U_{grav} (µmol.mol^{-1})^{3}	%REU^{4}
C_4H_6	1995.289	0.259	0.518	0.026
CO_2	2036.002	0.363	0.726	0.036
CO	995.725	0.188	0.376	0.038
C_2H_6	4031.919	0.526	1.052	0.026
CH_4	4055.521	0.516	1.032	0.025
O_2	1003.320	0.184	0.368	0.037
N_2	4116.981	0.647	1.294	0.031
C_3H_8	4032.339	0.371	0.742	0.018

$^{1}\boldsymbol{x_{grav}}$ is the gravimetric amount fraction for each component from the gravimetric preparation in accordance with ISO 6142, $^{2}\boldsymbol{u_{grav}}$ is the standard uncertainty associated with the gravimetric amount fraction for component i, $^{3}\boldsymbol{U_{grav}}$ is the expanded uncertainty associated with the gravimetric amount fraction for component i and $^{4}\%\boldsymbol{REU}$ is the relative uncertainty given by the equation $\%REU = \frac{U_{grav}}{x_{grav}} \times 100$

5.7.6.2. Verification uncertainty

An evaluation of measurement uncertainty for the verification was obtained from the repeatability results of the GC-FID response for 1,3-butadiene, methane, ethane, and propane and the GC-TCD response for oxygen, nitrogen, carbon monoxide, and carbon dioxide. The uncertainty contributions were identified from the measurement's single-point calibration model used to calculate the unknown amount fractions given by **equation 4.6**.

$$x_{Sample} = \frac{y_{Sample}}{y_{Reference}} \times x_{Reference} \qquad \textbf{4.6}$$

Where x_{sample} and y_{sample} are the amount fraction and GC response of the sample gas mixture, and $x_{ref}$and y are the amount fraction and GC response of the reference gas mixture respectively.

The verification uncertainty for each component considers the standard deviation of repeated measurements and the number of measurement repeats (ISO 6143, 2001). The calculation is done using **equation 5.2**.

$$u_c(x_{veri}) = \sqrt{\sum_{i=1}^{n}[c_i u(x_i)]^2} \qquad \textbf{5.2}$$

Where $u_c(x_{veri})$ is the combined standard uncertainty for the verification measurements, c_i is the sensitivity coefficient for input i and $u(x_i)$ is the uncertainty estimates for input x_i.

The sensitivity coefficient demonstrates the relationship between each individual uncertainty component $(u(x_i))$ and the standard deviation of the output value. The Guide to the Expression of Uncertainty in Measurement (GUM) explains sensitivity coefficients as partial derivatives used to describe how output estimate of x_{veri} varies with changes in input estimates x_i using **equation 5.3**.

$$c_i = \frac{\partial f}{\partial x_i} \qquad \textbf{5.3}$$

Each component of the mixture's calculated verification standard uncertainty expanded uncertainty and the relative uncertainty related to the verification of NM3 reference gas mixture are tabulated in **Table 5.51**.

Table 5.51 Measurement uncertainty associated with the verification measurements of NM3

Component	x_{veri} **(µmol.mol^{-1})^1**	u_{veri} **(µmol.mol^{-1})^2**	U_{veri} **(µmol.mol^{-1})^3**	**%REU^4**
C_4H_6	2001.556	4.568	9.136	0.456
CO_2	2033.053	7.593	15.185	0.747
CO	995.173	3.477	6.953	0.699
C_2H_6	4035.354	8.407	16.813	0.417
CH_4	4061.587	6.633	13.265	0.327
O_2	1006.115	3.553	7.106	0.706
N_2	4114.856	3.216	6.432	0.156
C_3H_8	4035.000	7.577	15.155	0.376

$^1\boldsymbol{x_{veri}}$ is the average verification amount fraction of the analytical measurement results for component i, $^2\boldsymbol{u_{veri}}$ is the standard uncertainty associated with the verification amount fraction for component i, $^3\boldsymbol{U_{veri}}$ is the expanded uncertainty associated with the verification amount fraction for component i and $^4\%\boldsymbol{REU}$ is the relative uncertainty given by the equation $\%REU = \frac{U_{grav}}{x_{grav}} \times 100$.

5.7.6.3. *Short-term stability*

The uncertainty associated with the short-term stability was taken over four months using the estimated standard deviation of the mean (ESDM). The ESDM describes the closeness of the average verification data as an estimate of the true population. **Table 5.52** lists the calculated average verification values obtained during a four-month period, the associated standard deviations, and the estimated mean standard deviation for each of the components of interest in the study.

Table 5.52 Measurement uncertainty associated with the short-term stability of NM3.

Component	x_{veri} (µmol.mol^{-1})^1	$stdv_{veri}$ (µmol.mol^{-1})^2	$ESDM$ (µmol.mol^{-1})^3
C_4H_6	2001.556	15.626	5.524
CO_2	2033.053	3.480	1.230
CO	995.173	5.900	1.967
C_2H_6	4035.354	10.376	3.459
CH_4	4061.587	10.288	2.495
O_2	1006.115	14.225	5.029
N_2	4114.856	6.405	1.776
C_3H_8	4035.000	9.192	2.654

$^1\boldsymbol{x_{veri}}$ is the average verification amount fraction of the analytical measurement results for component i, $^2\boldsymbol{stdv_{veri}}$ is the standard deviation of the verification results for component i and $^3\boldsymbol{ESDM}$ is the estimated standard deviation of the mean associated with the verification results for component i.

5.7.6.4. Combined uncertainty

The combined uncertainty ($u_c(y)$) is a combination of all the uncertainty contributors calculated as square root of the sum of squared standard uncertainties of each given by equation 4.15 (JCGM 100:2008)

$$u_c(y) = \sqrt{u_{grav}^2 + u_{veri}^2 + ESDM^2} \tag{5.4}$$

Where $u_c(y)$ is the combined standard uncertainty, $\boldsymbol{x_{grav}}$ is the gravimetric uncertainty, $\boldsymbol{x_{veri}}$ is the verification uncertainty, $ESDM$ is estimation standard deviation of the mean.

The combined expanded uncertainty (U) is calculated using equation **5.5** where $K = 2$ at a level of confidence of 95,45%.

$$U = u_c(y) \times 2 \tag{5.5}$$

The percentage relative expanded uncertainty (%REU) is calculated using equation **5.6**.

$$\%REU = \frac{Combined\ expanded\ uncertainty}{Gravimetic\ value} \times 100 \qquad \mathbf{5.6}$$

Table 5.53 lists the standard uncertainty of the three major uncertainty contributors, the combined expanded uncertainties at a level of confidence of 95,45% where $K = 2$ and the %REU for each component of interest in the study. The acceptance criterion for uncertainty measurement is %REU of less than 5%. For each of the eight components of interest in the gas mixture, the %REU was determined to be between 0.18 and 1.22%, indicating results within the acceptance criterion.

Table 5.53 Combined uncertainty evaluation of NM3 refinery reference gas mixture in the matrix of helium.

Component	Uncertainty source x_i	Evaluation Type (A or B)	Assumed distribution	Standard uncertainty $u(x_i)$,(µmol.mol^{-1})	Combined Expanded Uncertainty, U (k=2) (µmol.mol^{-1})	% REU
1,3-Butadiene	Gravimetric	Type B	Normal	0.259	13.34	0.67
	Verification	Type A	Normal	4.568		
	Stability	Type A	Normal	5.524		
Carbon dioxide	Gravimetric	Type B	Normal	0.363	15.40	0.76
	Verification	Type A	Normal	15.185		
	Stability	Type A	Normal	1.230		
Carbon monoxide	Gravimetric	Type B	Normal	0.188	8.00	0.81
	Verification	Type A	Normal	3.477		
	Stability	Type A	Normal	1.967		
Ethane	Gravimetric	Type B	Normal	0.526	18.21	0.45
	Verification	Type A	Normal	8.407		
	Stability	Type A	Normal	3.459		
Methane	Gravimetric	Type B	Normal	0.516	14.21	0.35
	Verification	Type A	Normal	6.633		
	Stability	Type A	Normal	2.495		
Oxygen	Gravimetric	Type B	Normal	0.184	12.32	1.22
	Verification	Type A	Normal	3.553		
	Stability	Type A	Normal	5.029		
Nitrogen	Gravimetric	Type B	Normal	0.647	7.46	0.18
	Verification	Type A	Normal	3.216		
	Stability	Type A	Normal	1.776		
Propane	Gravimetric	Type B	Normal	0.371	16.17	0.40
	Verification	Type A	Normal	7.577		
	Stability	Type A	Normal	2.654		

5.7.7. Method validation conclusion

Method validation is a crucial analytical tool to ensure the accuracy and precision of analytical procedures. The validation results have demonstrated that the analytical method deployed for the analysis of refinery reference gas mixtures for the quantification of methane, ethane, propane, 1,3-butadiene, oxygen, nitrogen, carbon monoxide, and carbon dioxide is fit for purpose with reliable, consistent, and accurate results obtained. The summary of the validation results is shown in **Table 5.55**.

Table 5.54 Summary of the method validation results.

Validation parameters	Criteria	Method performance
Accuracy (%difference)	< 2	0.052 to 0.314
Repeatability (%RSD)	< 2	0.063 to 0.207
Reproducibility (%RSD)	< 2	0.023 to 0.662
Measurement uncertainty (%REU)	< 5	0.18 to 1.22
Selectivity	No interference desired	No interference observed

CHAPTER SIX – CONCLUSIONS AND RECOMMENDATIONS

This chapter concludes the outcomes for the development of refinery reference gas mixtures and highlights the study's performance in relation to the aims, objectives and research questions expressed in the preceding chapters. Additionally, this chapter offers recommendations for improvements in future work.

6.1. Conclusion

This study was successful in the development, quantification, and validation of multi-component refinery reference gas mixtures containing methane, ethane, propane, 1,3-butadiene, oxygen, nitrogen, carbon monoxide, and carbon dioxide as the components of interest in the balance of helium at two amount fraction ranges of 1 000 to 4 000 µmol.mol^{-1} (low range) and 1 to 22 %mol.mol^{-1} (high range). These traceable reference gas mixtures were created to provide measurement solutions for South Africa's carbon trading schemes in the energy industry. The aims and objectives of the study were achieved by performing purity analysis on the starting materials, gravimetric preparation and verification of the gas mixtures, stability assessment, measurement comparability testing, adsorption studies, matrix effect studies, and validation of the method developed.

Purity analysis of the high purity starting materials was done in accordance with ISO 19229:2015 as the initial step in the development of refinery reference gas mixtures. This was done to establish the gas composition of the high purity gas starting materials by accurately identifying and quantifying trace-level impurities present in the high purity starting materials. GC-FID was used for the quantification of trace-level CO, CO_2, CH_4, and C_2H_6; GC-PDHID was used for the quantification of trace-level H_2, N_2, Ar and O_2 and GC-TCD was used for the quantification of trace-level He. The impurities quantified using manufacturer specifications were assumed to have a rectangular distribution. The final compositions of the starting materials were successfully quantified at > 99.99 %mol.mol^{-1} for C_2H_6, C_4H_6, and C_3H_8, and > 99.999 %mol.mol^{-1} for CH_4, CO, CO_2, O_2, N_2, and He.

The gravimetric preparation of the gas mixtures was successfully done in accordance with ISO 6142-1:2015. The high range refinery reference gas mixtures were prepared directly from high purity starting material following a single-step dilution. The low range refinery reference gas mixtures were prepared by employing a multi-step dilution. The multi-step dilution included the preparation and verification of three pre-mixtures of 10 %mol.mol^{-1} CH_4, C_2H_6, and N_2 in He for mixture 1, 4 %mol.mo^{-1} CO, 4 %mol.mo^{-1} O_2 and 8 %mol.mo^{-1} CO_2 in He for mixture 2, and 4 %mol.mo^{-1} C_3H_8 and 4 %mol.mo^{-1} C_4H_6 in He for mixture 3 before dilution to the low range refinery reference gas mixtures. Both high and low range refinery reference gas mixtures were prepared at a relative expanded uncertainty below 0.021% for all components of interest in the study.

Successful analysis of refinery reference gas mixtures was achieved using GC-FID/TCD. The FID channel was used for the quantification of CH_4, C_2H_6, C_3H_8, and C_4H_6; and the TCD channel was used for the quantification of O_2, N_2, CO, and CO_2. Single-point calibration method was deployed for the verification of these matrix-matched reference gas mixtures. The differences between the gravimetric and verification amount fractions were found to be < 1% with relative expanded uncertainties of ≤ 2.0388% for high range and ≤ 3.218% for low range refinery reference gas mixtures at a 95% confidence level for all components of interest in both high and low range refinery reference gases. Good measurement precision was achieved with % RSD ranging between 0.006 and 1.841% at instrumental drift of < 1. Furthermore, with sensitivity ratios of 1.000 ± 0.020, all components of interest demonstrated satisfactory internal consistency, with the highest deviations observed on C_4H_6 in both the low and high range refinery reference gas mixtures.

The developed method was further validated by studying its accuracy, precision, selectivity, robustness, and measurement uncertainty using the low range refinery reference gas mixtures. The accuracy of the method was found to range between 0.052 to 0.314%. The precision results had relative standard deviations of less than 0.207% and 0.66% for repeatability and reproducibility, respectively. Successful peak identification for all components of interest was achieved by programming the oven temperature to allow for peak separation. These findings lead to conclude that the method deployed for the verification and validation of the prepared gas mixtures was fit for purpose.

The high range gas mixtures were used for the study of adsorption and matrix effect. The results lead to the conclusion that there is no adsorption observed for CH_4, C_2H_6, C_3H_8, C_4H_6, O_2, N_2, CO, and CO_2 on the inner surface of the aluminium cylinders at amount fractions ranging from 1 to 22% mol.mol^{-1}. However, matrix effects results obtained showed that the use of binary standards resulted in ion suppressions in the multi-component refinery reference gases with %MEs ranging from 13.38 to 40.31% for all components of interest, indicating a decreased ionisation efficiency for components of interest in the matrix of other components in the refinery reference gas mixtures.

Finally, stability assessments were conducted to monitor the behaviour of the gas over long periods of time. The stability of the high range refinery reference gas mixtures was analysed over a nine-month period, while that of the low range refinery reference gas mixtures was analysed over a twelve-month period. Each component of interest in the gas mixtures was stable within 2% of their gravimetric amount fractions.

6.2. Recommendations

This study effectively met its objectives heavily focusing on the development of refinery reference gas mixtures. While the matrix effect and adsorption on high-range refinery gas mixtures were investigated, further research on these parameters for low range refinery gas mixtures could provide a more comprehensive understanding of the behaviour of these matrix gases relative to their amount fractions by developing mathematical models for these interference corrections.

Participation in the upcoming international key comparison (CCQM-K77.2023) for refinery and synthesis gas will assist South Africa to establish its measurement capabilities as a global benchmark while monitoring gas stability. It is recommended that further development of refinery reference gas mixtures include components of interest such as hydrogen, ethylene, and butene. The development of these refinery gases should expand to include balance gases of nitrogen or hydrogen since they are among the most frequently requested balance gases to support the Southern African energy sector.

Measurement capabilities for refinery reference gas mixtures pave the way for collaboration between the gas analysis laboratory and the energy sector. These relationships could open doors for continuous improvement in refinery measurements and provide valuable measurement solutions to the industry.

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Appendix A. CCQM-K77 results

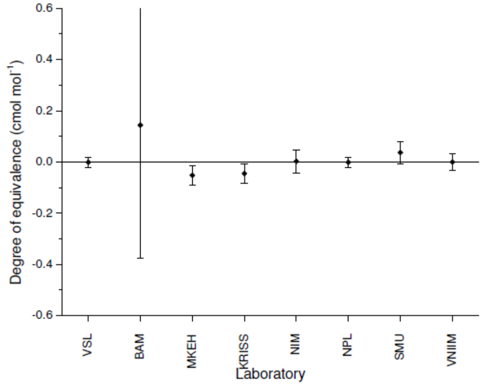

Figure 1: Degrees–of–equivalence for methane

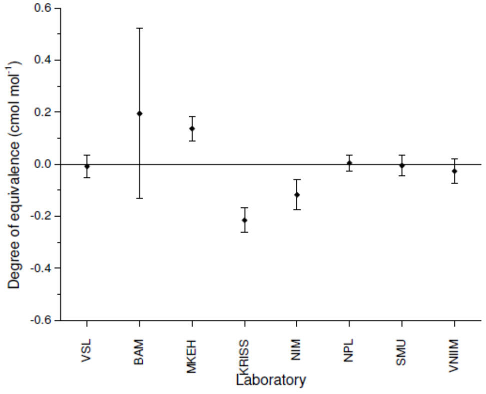

Figure 2: Degrees–of–equivalence for ethene

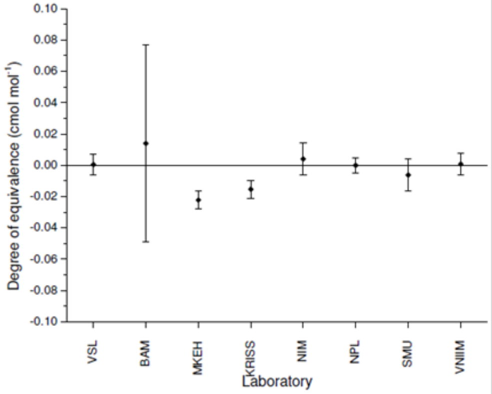

Figure 3: Degrees–of–equivalence for ethane

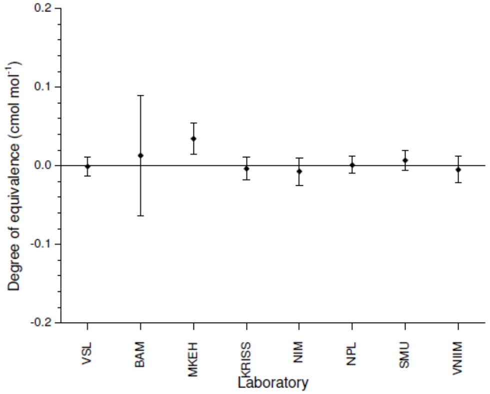

Figure 4: Degrees–of–equivalence for propene

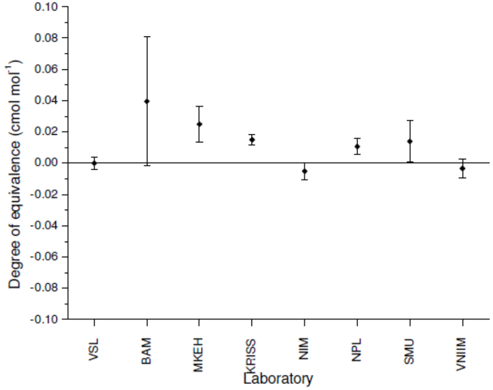

Figure 6: Degrees–of–equivalence for 1,3-butadiene

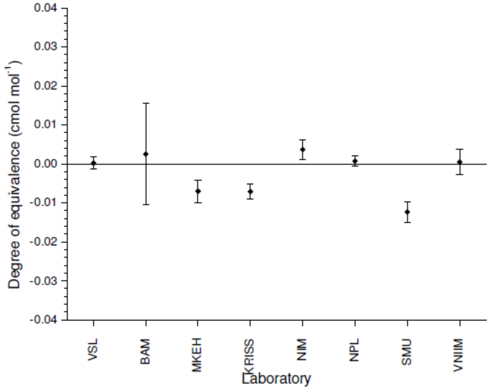

Figure 5: Degrees–of–equivalence for propane

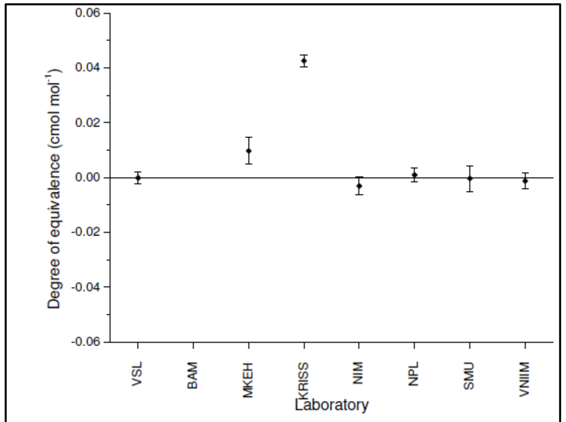

Figure 7: Degrees–of–equivalence for 1-butene

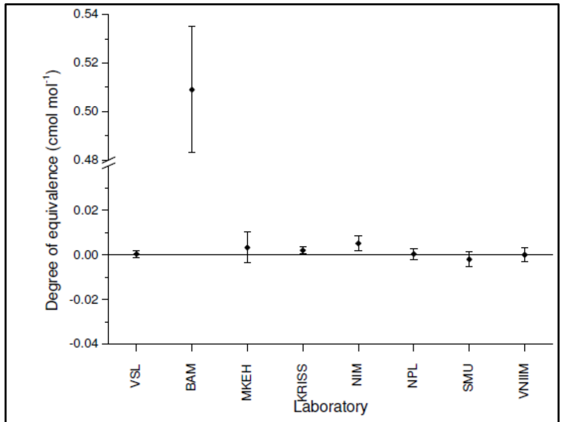

Figure 8: Degrees–of–equivalence for iso-butene

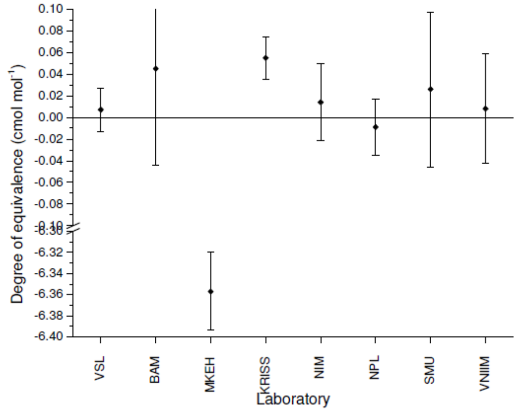

Figure 9: Degrees–of–equivalence for hydrogen

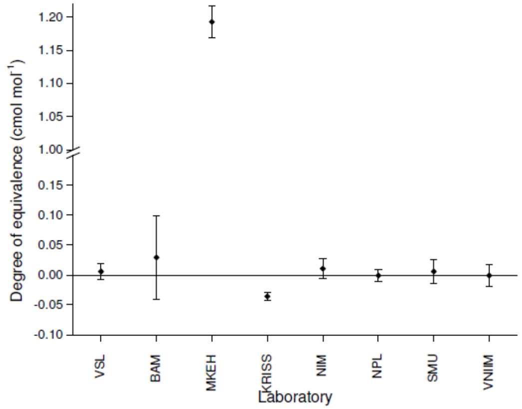

Figure 10: Degrees–of–equivalence for nitrogen

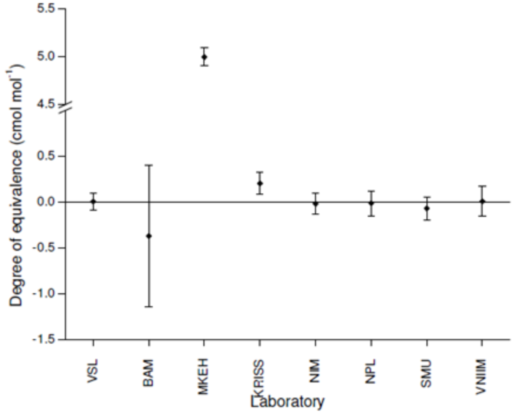

Figure 11: Degrees–of–equivalence for helium

Appendix B. Purity tables for high range refinery reference gas mixtures

Table B1. Purity table for mixture DM1

Component	**Amount fraction μmol.mol^{-1}**	**Standard uncertainty μmol.mol^{-1}**	**%REU (%u/c)**
He	427983.1997	9.37471466	0.002
N_2	217537.8132	5.97600196	0.003
CO	99991.6363	4.11124354	0.004
CO_2	80375.60747	2.73096956	0.003
CH_4	58224.41963	4.78470379	0.008
C_3H_8	49371.45723	3.43333895	0.007
C_2H_6	40980.52826	4.87728472	0.012
C_4H_6	14849.74014	1.73987718	0.012
O_2	10694.19848	1.75434733	0.016
C_2H_4	7.17337838	4.13941593	57.705
H_2	5.38312088	0.06802722	1.264
Ar	3.72524540	0.17105688	4.592
H_2O	0.72959842	0.17883378	24.511

Table B2. Purity table for mixture DM2

Component	Amount fraction µmol.mol^{-1}	Standard uncertainty µmol.mol^{-1}	%REU (%u/c)
He	426187.7727	9.56103507	0.002
N_2	218280.5517	6.04908999	0.003
CO	98883.68412	4.10917342	0.004
CO_2	80894.19104	2.76674216	0.003
CH_4	59783.30221	4.89639427	0.008
C_3H_8	49573.14515	3.45792218	0.007
C_2H_6	41736.39295	4.96703742	0.012
C_4H_6	14905.2792	1.75725671	0.012
O_2	9764.226714	1.78771079	0.018
C_2H_4	7.30568793	4.21576601	57.705
H_2	5.42281253	0.06826358	1.259
Ar	3.73800679	0.17164182	4.592
H_2O	0.73443793	0.18020963	24.537

Table B3. Purity table for mixture DM3

Component	Amount fraction µmol.mol^{-1}	Standard uncertainty µmol.mol^{-1}	%REU (%u/c)
He	427949.9782	9.43775786	0.002
N_2	218464.4796	6.00712827	0.003
CO	99506.01374	4.10846507	0.004
CO_2	79898.57969	2.72758843	0.003
CH_4	57472.31066	4.77704347	0.008
C_3H_8	49745.15356	3.45993678	0.007
C_2H_6	40909.93334	4.87685623	0.012
C_4H_6	14819.07113	1.74311321	0.012
O_2	11243.22577	1.77142346	0.016
C_2H_4	7.16102114	4.13228511	57.705
H_2	5.38984059	0.06819717	1.265
Ar	3.74104283	0.17178424	4.592
H_2O	0.72729240	0.17803200	24.479

Table B4. Purity table for DM4

Component	**Amount fraction μmol.mol^{-1}**	**Standard uncertainty μmol.mol^{-1}**	**%REU (%u/c)**
He	424068.7023	9.57036726	0.002
N_2	221283.8578	6.07026464	0.003
CO	100850.2324	4.16749913	0.004
CO_2	80445.74803	2.75764605	0.003
CH_4	59359.23872	4.88566312	0.008
C_3H_8	49569.30045	3.45843308	0.007
C_2H_6	40191.49228	4.81743630	0.012
C_4H_6	14703.01439	1.74359408	0.012
O_2	9537.233363	1.79181801	0.019
C_2H_4	7.03526216	4.05971510	57.705
H_2	5.37631353	0.06840528	1.272
Ar	3.78897494	0.17400490	4.592
H_2O	0.73093279	0.17971301	24.587

Appendix C. Purity tables for low range refinery reference gas mixtures

Table C1. Purity table for NM1

Component	**Amount fraction µmol.mol^{-1}**	**Standard uncertainty µmol.mol^{-1}**	**%REU (%u/c)**
He	977555.7525	1.62184028	0.000
CH_4	4389.531833	0.51583756	0.012
N_2	4012.454697	0.61780252	0.015
C_3H_8	3994.758726	0.35658202	0.009
C_2H_6	3952.424441	0.48978527	0.012
CO_2	2062.955727	0.32763319	0.016
C_4H_6	2006.144592	0.25713075	0.013
O_2	1016.600153	0.16798666	0.017
CO	1008.907269	0.17263414	0.017
H_2	1.40509596	0.03821355	2.720
C_2H_4	0.69184565	0.39921699	57.703
Ar	0.07259151	0.00315189	4.342
H_2O	0.05138145	0.01188432	23.130

Table C2. Purity table for NM2

Component	**Amount fraction µmol.mol^{-1}**	**Standard uncertainty µmol.mol^{-1}**	**%REU (%u/c)**
He	977378.4336	1.67783254	0.000
N_2	4048.055341	0.63667528	0.016
C_3H_8	4025.922333	0.36790050	0.009
CH_4	4004.510386	0.50285584	0.013
C_2H_6	3989.205485	0.51602315	0.013
CO_2	2302.603268	0.35639849	0.015
C_4H_6	1992.114183	0.25799802	0.013
O_2	1134.200297	0.18356738	0.016
CO	1124.499333	0.18851985	0.017
H_2	1.40268643	0.03807768	2.715
C_2H_4	0.69828395	0.40293189	57.703
Ar	0.07320376	0.00317908	4.343
H_2O	0.05132965	0.01170788	22.809

Table C3. Purity table for NM3

Component	**Amount fraction** **μmol.mol^{-1}**	**Standard uncertainty** **μmol.mol^{-1}**	**%REU (%u/c)**
He	977732.4311	1.71418296	0.000
N_2	4116.980648	0.64745587	0.016
CH_4	4055.521122	0.51574476	0.013
C_3H_8	4032.338904	0.37066594	0.009
C_2H_6	4031.918855	0.52594228	0.013
CO_2	2036.001981	0.36251645	0.018
C_4H_6	1995.289242	0.25917318	0.013
O_2	1003.320101	0.18441150	0.018
CO	995.7248276	0.18831835	0.019
H_2	1.40420864	0.03824154	2.723
C_2H_4	0.70576067	0.40724620	57.703
Ar	0.07435170	0.00323284	4.348
H_2O	0.05073345	0.01171058	23.083

Table C4. Purity table for NM4

Component	**Amount fraction** **μmol.mol^{-1}**	**Standard uncertainty** **μmol.mol^{-1}**	**%REU (%u/c)**
He	977271.7396	1.62355648	0.000
CH_4	4486.101287	0.51856266	0.012
N_2	4100.075568	0.61727360	0.015
C_2H_6	4039.37775	C0.49327988	0.012
C_3H_8	3980.857098	0.35484907	0.009
CO_2	2060.546983	0.32323380	0.016
C_4H_6	1999.163275	0.25605929	0.013
O_2	1069.166505	0.17386655	0.016
CO	992.4794745	0.16852150	0.017
H_2	1.40747812	0.03818523	2.713
C_2H_4	0.70706630	0.40799981	57.703
Ar	0.07408921	0.00322089	4.347
H_2O	0.05181255	0.01200633	23.173