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A study of multicomponent gas mixtures using various analytical methods for stack emission measurements



Prelly Mohweledi Marebane

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

Johannesburg, 2017.

CANDIDATE'S DECLARATION

I declare that this dissertation is my own, unaided work. It is being submitted for the Degree of Masters 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 was conducted at the National Metrology Institute of South Africa's gas analysis laboratory.

……..

(signature of candidate)

……day of……20……in……

Supervisor:

Dr. James Tshilongo (National Metrology Institute of South Africa, Gas Analysis)

Co-supervisor:

Prof. Hlanganani Tutu (University of the Witwatersrand, Chemistry)

ABSTRACT

Multicomponent gas mixtures are inherently challenging to produce in the laboratory because of matrix effects, boiling points and reactivity amongst other factors. Therefore, methods must be continuously developed to control these challenges. The purpose of this work was to study these complex gas mixtures to improve their measurements with emphasis on the reduction of uncertainty. There are three critical steps to be followed in gas metrology for primary reference gas mixtures of the highest metrological level; purity analysis of source gases, gravimetric preparation and verification/validation which includes stability testing. Purity analysis of select source gases was quantified using various techniques. This methodology incorporated the use of molar masses and their uncertainties in order to obtain purity values for the chemical composition of gas mixtures. While many preparation methods such as permeation and dynamic methods are available, a static gravimetric method was used to prepare the complex stack and automotive gas mixtures following International Standard Organisation: 6142-1. For the mole fraction range of interest, four components (carbon dioxide, carbon monoxide, sulphur dioxide and nitric oxide) excluding propane, were obtained from analysis by non-dispersive spectroscopy techniques calibrated by several standard gas mixtures of different mole fractions. Propane was analysed by a gas chromatograph coupled with flame ionisation detection. Multipoint calibration was used to evaluate the linearity or nonlinearity of the detector.

The final results for the stack gas mixture components showed an achievement of 0.4% to 0.8% percentage relative expanded uncertainty and 0.4% to 1.3% for carbon dioxide depending on the matrix of the standard gas mixtures used, 0.5% to 1% for propane, 0.8% to 1.8% for nitric oxide, 2% to 6% for carbon monoxide and 0.3% to 2.3% for sulphur dioxide. One of the most important suppositions drawn was the incidence of synergistic effects associated with calibration by non-representative standard gas mixtures when these were used for analysis for some of the components of stack mixtures. To evaluate improvements in measurement capability, the results of the current work were compared to the data of the laboratory in 2008-2011 and there was an improvement in the measurement of

carbon dioxide, carbon monoxide, propane and nitric oxide. These improvements are attributed to rigorous purity analysis of starting materials, reduction of uncertainty and developments in measurement expertise. In this work, different measurement and calibration methods were used to analyse the components of the new stack gas mixtures. The stability of these components was evaluated by analysing them at different times and the statistical D-test was used to check for significant instability.

An unknown stack sample was compared with the standard gas mixtures prepared for this work. In combination with same matrix and same concentrations, single point calibration was found suitable for stack gas measurement. To reiterate the concept of matrix effect, the results of carbon dioxide in a mixture containing carbon monoxide and oxygen as well in nitrogen, were used to show how differences in matrix often give erroneous results and same conclusions cannot be made for different mixtures. While the data of this measurement was unsatisfactory, an improved method developed for this type of emission multicomponent was very successful.

Emission industries also require automotive primary reference gas mixtures. These are equally important and complex multicomponent mixtures measured and improved in this work. A very precise and repeatable single point method was developed for the analysis of the components of automotive mixtures. The repeatability of the gas chromatography method was 0.2% for oxygen, 0.1% for carbon monoxide, 0.5% for carbon dioxide and 0.3% for propane. The percentage relative expanded uncertainty was 0.4% for oxygen, 0.8% for carbon monoxide, 0.8% for carbon dioxide and 0.5% for propane. However, its limitation was the use of different calibration gases for each analysis. This led to inconsistencies in the calculated mole fractions, non-predictability and instability. A proficiency testing scheme was coordinated by the laboratory for automotive emission as part of this study. Given the complexity of the samples, the work aimed to check any improvements that could be made to the capability of measurement over the years. This new method using gas chromatography coupled with different detectors (residual gas analyser) was successful in verifying the gravimetric values very

accurately. Finally, the results of the stack gas mixtures were ≤1% relative except carbon monoxide and ≤1% for automotive mixtures. This work aimed to support the emission industry by providing it with representative and accurate reference gas mixtures, extend the accreditation scope of the laboratory and improve its calibration and measurement capability for multicomponent gas mixtures.

DEDICATION

To my daughter

Special thanks to the Marebane family, especially my parents, siblings and grandparents (Letlapa family as well) for their love.

ACKNOWLEDGEMENTS

First and foremost, I would like to thank God and my Lord for creating an opportunity for furthering my studies. I also thank the church for being my comfort during stressful times. It has not been easy, however, with the support I had I managed to finish this great feat. A million magnitude of gratitude to my two supervisors, Dr. James Tshilongo and Prof. Hlanganani Tutu. Dr. Tshilongo, thank you for not only allowing me to remain at the institution but for awarding me the opportunity to expand my education and your expertise as well. Prof, thank you for all the encounters that have left me feeling that you are one of the friendliest and genuine people I have ever known. Your sense of belief in me and my ability to carry this project, has picked me up many times.

Undoubtedly, one of the most stressful things I have been through was separation anxiety. Having left my daughter when she was only six months old, this degree saw many meltdowns. I am thankful for her for inspiring me to become better and push boundaries. This Master's degree brings us closer to staying together. I would like to specifically thank my parents, Surgeon and Alice Marebane, for all the support they gave me in every instance of my life, and most importantly for championing education. It is this very value that still drives me to this day. The idea that I can be whoever I want to be, by dedicating hard work and time in all the opportunities that come my way. Thank you to my brothers for consistently being my number one fans. It went such a long way. I would also like to appreciate the support of my aunts, their children and all my grandparents.

I want to take this opportunity to thank my colleagues at the gas analysis laboratory. I joined the institution with no prior knowledge of what you do, you welcomed me with open arms, and even with a few disagreements now and then, I am grateful for your support and knowledge. I wouldn't have gotten this far without your willingness to share your expertise. I have also have great friends in Pheladi and Sarah. Thank you for being my confidante always. You have been such great best friends. Thank you for all the encouragement when I left the lab late and was there on weekends with a non-existent social life. I thank Dineo Mokobodi for all his assistance when I needed it for all the gas chromatograph configurations.

Lastly but not least, I want to thank the National Metrology Institute of South Africa for giving me such a lifetime opportunity as well as the Department of Trade and Industry and the financial support throughout the two years of my bursary. I thank the National Research Foundation for their financial support as well. A successful completion of this degree symbolizes rainbows, light at the end of the tunnel and beautiful memories with my wonderful baby girl.

PRESENTATIONS IN CONFERENCES AND SEMINARS

1. National Association of Clean Air 2015 and 2016. Presenter – Dr. J Tshilongo
2. Oral presentation at the Department of Environmental Affairs National Research Seminar: 12 August 2016
3. Oral presentation at the South African Chemical Institute (SACI) Young Chemist' Symposium: 01 December 2016
4. National Metrology Institute of South Africa's Women in Science celebration 2017
5. National Metrology Institute of South Africa's Gas Analysis Technical Advisory Forum: 8 March 2017, Presenter – Dr J Tshilongo
6. National Laboratory Association Test and Measurement Conference: 31 July – 01 August 2017

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NOMENCLATURE

1. **APPA**	Air Pollution Prevention Act 45 of 1965
2. **AQA**	Air Quality Act 39 of 2004
3. **BIPM**	International Bureau of Weights and Measures
4. **CCQM**	Consultative Committee of Amount of Substance
5. **CENAM**	Centro Nacional de Metrologia
6. **CLD**	Chemiluminescence Detector
7. **CMC**	Calibration Measurement Capability
8. **DEA**	Department of Environmental Affairs
9. **FID**	Flame Ionization Detector
10. **FTIR**	Fourier Transform InfraRed
11. **GAWG**	Gas Analysis Working Group
12. **IPCC**	Inter-governmental Panel on Climate Change
13. **IPQ**	Instituto Portugues da Qualidade
14. **ISO**	International Standards Organization
15. **KRISS**	Korean Research Institute of Standards and Science
16. **NAAQS**	National Ambient Air Quality Standards
17. **NAEIP**	National Atmospheric Emission Inventory Project
18. **NDIR**	Non-Dispersive InfraRed
19. **NDUV**	Non-Dispersive UltraViolet
20. **NEMA**	National Environmental Management Act 108 of 1998
21. **NIST**	National Institute of Standards and Technology
22. **NMI**	National Metrology Institute
23. **NMISA**	National Metrology Institute of South Africa
24. **NPL**	National Physical Laboratory
25. **PDHID**	Pulsed Discharge Helium Ionization Detector

26. **PRGM**	Primary Reference Gas Mixture
27. **PSGM**	Primary Standard Gas Mixture
28. **SAAQIS**	South African Air Quality Information System
29. **SADC**	Southern African Development Community
30. **SAWS**	South African Weather Service
31. **SMU**	Slovak Institute of Metrology
32. **TCD**	Thermal Conductivity detector
33. **UNFCC**	United Nations Framework on Climate Change
34. **VNIIM**	D.I. Mendeleyev Institute for Metrology
35. **VSL**	Van Swinden Laboratorium
36. **WMO/GAW**	World Meteorological Organization/ Global Atmospheric Watch

CHAPTER ONE – INTRODUCTION

The central theme of this research dissertation is atmospheric emission management and measurement solutions in the South African context, drawing basis from its legislative framework and plausible mitigation efforts that were committed to. These solutions offered by gas metrology are provided by the availability of highly accurate reference materials for stack and automotive emission, very complex multicomponent mixtures inherent with difficulties. In this chapter, justification of this work, associated analytical challenges of these mixtures, research aim and objectives are discussed.

1.1 Overview of air pollution monitoring capability

Since the industrial revolution, South Africa has suffered from a heritage of non-effective environmental and emission management decrees to assist the administration with protection of the environment for its citizens. The Vaal-Triangle and Highveld regions, renowned for poor air quality, were professed national high priority areas owing to decades of unfortunate and ineffective practices. The Atmospheric Pollution Prevention Act (APPA) of 1965 for example, was inefficient in addressing the state's emission management issues and alleged to have contributed to the creation of the priority areas, Naiker et al., (2012). Emission compliance was not prioritised when industrialisation begun as well as consequent use of fossil fuels as energy resources. However, the enactment of the Constitution's Bill of Rights (108 of 1996), section 24a, provided a basis for a proper legal framework to address air pollution management. Section 24 states "the right of every citizen to a non-harmful environment that is also protected for future generations", van der Linde and Feris (2010). The exploitation of South Africa's mineral resources has been instrumental in its economic growth and development, however, there are negative environmental impacts associated with these activities, among them, land degradation, air and water pollution (Campbell et al., 2017). Poor air quality, as a direct result of emissions is also associated with respiratory-related health problems, climate change, global warming and rising sea levels.

The National Environmental Management Act (NEMA) 108 of 1998 was promulgated as a legislative framework to give effect to the enforcement of this basic human right. NEMA was later amended with other legislations addressing specific environmental areas. The NEM: Forest Act 84 of 1998 and NEM: Water Act 36 of 1998 serve as examples for specific protection of forests and water resources. For atmospheric pollution control, the NEM: Air Quality Act 39 0f 2004 repealed the APPA as the main legislative framework. This Act uses emission monitoring elements; cooperative governance, compliance standards, monitoring and reporting amongst others as tools to monitor the success of the Act, van der Linde and Feris (2010) and Naiker et al., (2012). As part of government's efforts to control pollution, it has also entered into agreements with other countries to reduce emissions such as the Kyoto Protocol of 1997, where commitment to reduce CO_2 emissions was made by South Africa. The country also hosted the Conference of the parties (COP 17) to the United Nations Framework Convention on Climate Change (UNFCCC) in 2011 in Durban where the green climate fund was established.

The Technical Guidelines for Monitoring, Reporting and Verification of Greenhouse Gas Emissions by Industry, (DEA, 2017) shows that currently emissions monitoring is mandated in South Africa and emissions are involuntarily reported through the Carbon Disclosure Project. This guideline was drafted with an intention to guide business on methods they can utilise to report their emissions and is based on the 2006 Inter-governmental Panel on Climate Change (IPCC) guidelines to estimate emissions in various areas. These emissions are then reported to the National Atmospheric Emissions Inventory System (NAEIS). Currently, stationary sources (stack emission) account for more than 60% of reported emissions and it is very critical to quantify those especially regarding the associated impact to air quality, DEA (2017). The IPCC guidelines are informed based on a three-level approach distinguished by the level of accuracy in estimations. Indirect observations are considered a more conservative approach, described by Tier 1 and Tier 2 is an intermediary approach. Direct sampling of stack gas, and the associated use of primary reference gas mixtures is implemented in Tier 3 with tools such as continuous emission monitoring.

The general methodology used by emission testers however, is based on indirect observations. Direct observation involving stack sampling of gas is not a very common practice and has its own limitations due to extreme stack conditions and availability of measurement methods compatible with these conditions. For example, infrared spectroscopy for carbon monoxide and carbon dioxide measurements suffers from moisture interference, Matshediso (2014). Additionally, questions on whether indirect observations are accurate can be posed.

Other internationally accepted standard methods used include the following from the International Standard Organisation (ISO); (1) ISO 12039:2001 Stationary source emissions – Determination of carbon monoxide, carbon dioxide and oxygen – Performance characteristics and calibration of an automated measuring method and, (2) ISO 10396: 2006 Stationary source emissions – sampling for the automated determination of gas concentrations.

To reiterate other challenges with emissions compliance, not related to measurement but infrastructure and technology, consider the contribution of coal emissions (discussed in detail below). The power utility of South Africa was not built with considerations of air pollution reduction and currently wet flue gas desulphurization is implemented to reduce sulphur oxides'emissions, Makgatho et al., (2017). This desulphurisation process however, is not hundred-percent efficient or environmental friendly and is flattered with other methods for full environmental compliance (Makgatho et al., 2017). The South African Air Quality Information System Information (SAAQIS) portal (last accessed 14 August 2017) also indicates that even though parts of Mpumalanga and Kwa-Zulu Natal are considered national high priority areas, these areas' Air Quality Management Planning (AQMP) is still under developed. In South Africa, emission inventories are not explicitly required by the NEM: AQA (Naiker et al., 2012) and there is no significant public-access data on stack and automotive inventories in South Africa.

Measurements performed by the monitoring framework are used to evaluate compliance to minimum emission standards or efficiency of current industrial technology in the reduction of pollution**.** Quality control, data reporting and compliance assessment are key elements of emissions compliance monitoring

systems, Matshediso (2014), and it is because of these requirements that emission primary reference materials are significant. At this point, it is pivotal to mention that a successful monitoring programme cannot be achieved without measurement science (gas metrology). Measurements of priority pollutants are dependent on the provision of accurate and reliable Primary Reference Gas Mixtures (PRGMs) for traceability and quality assurance of results. The availability of these PRGMs of the smallest uncertainties is limited to the measurement capability of the gas metrology laboratory of the National Metrology Institute of South Africa (NMISA) and while these may be found from local gas manufacturers, the accuracy at which these are produced may be lower with associated large uncertainties. Stack-sampling accreditation of stack testers is also dependent on the availability of emission PRGMs.

These important reference materials however, for stack and automotive emissions, and central to accurate emission management are not the easiest to produce. Chemical reactivity, adsorption, preparation techniques, condensation, pressure control amongst others, are extremely crucial factors to consider. These factors must be vigorously controlled to produce an accurate standard gas mixtures of the highest metrological level. Challenging standard gas mixtures are often those of a multicomponent nature (often interferent gases in a diluent gas in a single cylinder). The stack gas, which is the focus of this dissertation comprises a mixture of carbon monoxide, carbon dioxide, sulphur dioxide, nitric oxide and propane in nitrogen. Another important multicomponent mixture of the same gases for emission industries is automotive gas, and is a secondary focus of the dissertation. Mixtures of carbon dioxide, carbon monoxide and oxygen in nitrogen were also prepared for a proficiency testing scheme to evaluate the measurement capability of local industries related to the gas analysis laboratory of the institute.

In general, gas standards are prepared in a matrix of nitrogen, or air (nitrogen and oxygen) as compressed gases. A gas mixture composition can vary from two components to more than five components all in one cylinder. The accuracy of standard gas mixtures' requirement presents a challenge in the methodology used to prepare reference standards of high metrological quality. Highly accurate

methods must be developed to ensure excellent quality reference standards with very small uncertainties. To achieve the latter requirements preparation methods such as gravimetry, gas titrimetry and gas dilution systems are often used. The most common method is the preparation of gas mixtures in compressed cylinders, International Standards Organisation (ISO) 6142-1:2015, Milton et al., (2006).

Another challenge is a lack of analytical techniques and skills. Existing methods must be continuously improved while new methods are being innovatively explored to achieve the desired outcomes. The accurate analysis of any combination of a multicomponent mixture is therefore important, especially for industries which use these complex gases which are often susceptible to interferences due to matrix differences. This is especially important since the use of binary Primary Standard Gas Mixtures (PSGMs) has proven to give erroneous results unless the designer of the experiment compensates drift effects.

The main purpose of the work was to address a need for a comprehensive study (gravimetric preparation and analysis) of multicomponent mixtures to improve their preparative and value assignment capabilities and consequent implication in field measurements. The study also aimed to check the significance of differences in matrix on measurement results and the extent of their effects. This study further aimed to improve measurement equivalence of stack gas by comparing the results with those of the previous study to evaluate measurement capability. An upcoming international key comparison of automotive gas, CCQM.K3-xx (under the auspices of the CCQM Gas Analysis Working Group) was prepared for through this work. The mixtures prepared for this work will be used as standard gas mixtures during the key comparison. To evaluate the stability of stack and automotive gas components in the final homogeneous mixture, the behavior of the gas was indicated by using stability graphs and a statistical D test following the ISO 16664:2004 method. This method is a guideline for handling calibration gas mixtures and the statistical D test is used to check for significant instability in a mixture by comparing the results of two subsequent measurements.

1.2 Background

Air pollution, is defined as the emission of harmful substances into the ambient air that culminates into the degradation of the Earth's natural atmosphere, air composition and its chemistry and natural weather cycles. It is a global phenomenon associated with industrialisation and energy demands derived from combustion of fossil fuels (coal used to demonstrate the genesis of some emissions). Other activities that have been identified to contribute to air pollution including paper manufacturing and metallurgical industries were published in the standards and regulations edition of the NEM: AQA and these are discussed shortly in section **1.3**. In this dissertation, major focus centers around coal to highlight how the presence of trace impurities in South African coal of sulphides and nitrogen oxides result in emissions. Coal is also the main source of energy to other industries and power generation has been accounted for major contributions to air pollution. Therefore, it is used as demonstration for emission dialogue. Automotive emissions are profiled too in this section of Chapter 1 where the comparison of South Africa's emissions is made to Africa and the world's averages.

1.2.1 Coal use in South Africa

South Africa has an energy driven economy in which energy supports its industrialisation, global competitiveness and the livelihood of its citizens. With an over 51.8 million population *(PO301.4 – Census 2011, results),* the energy demand for former and present impoverished communities has risen for electricity access. http://www.statssa.gov.za/ last viewed 12 January 2017. It is the sixth (6^{th}) largest coal producer in the world and coal remains the main source of energy, Hancox and Gotz (2014), Wagner and Hlatshwayo (2005). It is also the only country that uses Coal to Liquid (CTL) technology to produce liquid fuels such as petrol and diesel. Coal mining in South Africa are distributed among at least sixteen coalfields (see **Figure 1.1** to see South Africa's major coalfields) and are distinguished by geological features such as; differences in type of sediment, origin, development, dispersal and value of coals, Hancox et al., (2014).



Figure 1.1: South African coalfields, Pinheiro (2000) extracted from Wagner and Hlatshwayo (2005).

The most popular ones are listed below as documented by Hancox et al., (2014)

- *Witbank coalfield*. Responsible for over 50% of the country's tradeable coal. Host to Kendal, Duvha, Komati and Arnot power stations.
- *Highveld coalfield*. Important to the CTL technology operated at the Sasol Synthetic fuels and Chemical industries plants. Host to Kriel, Matla and Tutuka power plants.
- *Ermelo coalfield*. Offers high quality coals compared to Witbank and Highveld coalfields. Camden, Hendrina and Majuba power stations are found here.
- *Free State coalfield*. This is the largest coalfield in SA, relatively untapped.
- *Vereeniging – Sasolburg coalfield*. Hosts the Lethabo power station
- *South Rand coalfield*. Low quality coals. Hosts the Grootvlei power station.
- *Waterberg coalfield*. Hosts the Matimba and Medupi power stations.

Energy security is central to the financial growth of South Africa and thus despite the environmental risks it poses, it will be prioritised. It supports business and the livelihood of its citizens. One of the largest projects by government to address the demands for energy security is the Medupi Eskom coal powered station (4800 megawatts) in Lephalale, Limpopo Province. The project aims to forge economic development by creating employment and fostering industrial competitiveness of companies in South Africa by supplying their energy needs. Moreover, 60% of the electricity in the Sub-Saharan region is provided by Eskom, and any shortfall will hinder the economic development of the Southern African Development Community (SADC) countries and thus the implementation of the project, Rafey and Sovacool (2011). Another project, the Kusile power station (4800 megawatts

generating capacity) near Witbank, Mpumalanga Province was undertaken shortly thereafter.

However, there are underlying implications associated with these activities, namely - climate change, global warming and air pollution. South Africa is reported as the thirteen (13^{th}) chief emitter of greenhouse gases in the world, Henneman et al., (2015) and has signed a pledge at the 2009 UNFCCC to reduce its carbon dioxide emissions. The treaty was designated as a move that formed part of its climate change mitigation policies. However, these recent developments suggest it might be challenging for the country to meet its obligations.

To illustrate how coal utilisation results in stack emissions of gaseous pollutants Hancox et al., (2014) used the processes of synthetic fuel plants to show how the end products often result in unwanted and harmful emissions. Synthetic fuel plants convert coal (with low or rich sulphur content) to crude synthesis gas. Part of the synthesis gas is led into a low temperature distillate apparatus and produces linear hydrocarbon products and paraffin. The remaining synthesis gas is led into a hot temperature reactor to produce carbon one to two hydrocarbons and synthetic crude oil. This gasification yields ammonia and sulphur among other trace elements and the chemical streams gives co-products such as ethylene and propylene; gases emitted by chemical processors.

1.2.2 Trace element impurities in coal - stack emission

The presence of trace elements (arsenic, cadmium, cobalt, chromium, mercury, manganese, nickel, lead and zinc amongst others) in South African coal, was studied by Wagner et al. (2005), to evaluate the quantity of these potential hazards from Highveld coals. A study by Jenner and Abiodun (2013), showed how brown haze pollution in Cape Town is attributed to sulphur emissions from the Highveld, a coal industry region. South Africa is also considered to have the second largest mercury emissions in the world from gold mining and coal processes processing. Combustion of coal vapourises mercury and it is emitted into the atmosphere together with inorganic and particle associated mercury, Dabrowski et al., (2008).

Sulphur dioxide, sulphuric acid and hydrogen sulphide, in atmospheric emissions are attributed to the presence of sulphur in coal. It is found in three forms in coal; sulphide, sulphate and organic sulphur. The amount of sulphur dioxide emissions by coal activities is dependent on the sulphur content in coal, release ratio, penetration and the removal efficiency of desulphurization techniques. Nitrogen is also found as a major component in coal, Hancox et al., (2014*).* The emission level of nitrogen oxides (NO_x) is dependent on factors such as differences in boilers and feed coal, unit magnitude, low NO_x burner technology and de-nitration facilities*,* Xiong et al., (2016).

1.2.3 Natural gas industry, the automotive sector and other emission industries.

The coal industry, used to demonstrate emission of priority pollutants is not the only trade sector associated with harmful atmospheric emissions. The discovery of gas reserves off the shores of the country and natural gas in neighbouring countries (Mozambique), has resulted in an ongoing development of the oil and gas market. These reserves were found in the Karoo basin offshore the Northern Cape Province*,* Altieri and Stone (2016*).* Compared to coal, it is associated with less carbon dioxide emissions. However, it still poses three major environmental risks; water pollution, methane leaks and land degradation, Yu (2014). New policies still need to be developed to mitigate the risks that a natural gas industry will have on South Africa's landscape. The correct determination of the composition of natural or shale gas is important for the determination of its economic value as well.

The South African Petroleum Industry Association in their 2014 annual report showed the extent of petroleum and diesel consumption in the country with an observable significant increasing trend. This trend ultimately gives off enough harmful vehicle emissions that are detrimental to air quality and its sustainability (SAPIA, 2014). These emissions owe to the presence of carbon dioxide, carbon monoxide, propane and other hydrocarbons in petroleum products. The extent of these emissions is determined by factors such as amount of fuel used, automobile

technology and fuel quality amongst others, Soylu, (2007) as cited by Thambiran and Diab (2011).

Automotive exhaust emissions are said to contribute 80% of the global emissions of carbon dioxide from the transportation sector (about 25% of carbon dioxide emissions). In South Africa, automotive emissions (crude oil imports) contribute approximately 9% of its greenhouse gas emissions. Lead and sulphur continue to be challenges in terms of air pollution control in the transportation sector, and lead based fuels were prohibited from year 2006 allowing technologies such as catalytic converters to be implemented, Thambiran et al., (2011). Statistics compiled on the average carbon dioxide emissions from automotive for Lesotho and South Africa showed that on average South Africa's CO_2 emissions are larger than the averages of Africa and international counterparts, Tongwane et al., (2015).

Other industrial sectors contributing to air pollution as identified by the Department of Environmental Affairs (DEA) include; Combustion installations, carbonization and coal processing, metallurgical and mineral processing, organic and inorganic chemicals industries, disposal of dangerous and general waste and animal matter processing. However, energy generation contributes the most atmospheric emissions than other industrial processes, as reported by Scorgie and Venter (2005).

Emission inventories have been developed in the past, however according to a comparison study by Seymore et al (2014) there were some inconsistencies in the data provided by International Energy Agency, Department of Energy and DEA. Seymore et al., (2014) suggests that the DEA's inventory underestimated emissions. With new developments in multicomponent automotive reference gas mixtures, perhaps other transportation not yet estimated can have their emissions measured.

1.2.4 Health, ecological and socioeconomic impacts of air pollutants

During the 10th annual Air Quality Lekgotla 2015, DEA presented a study on the health impacts of air pollutants in the national priority areas. The study indicated an associated risk of respiratory problems, including worsening of asthma and related illnesses due to exposure to particulate matter, sulphur dioxide and NO_X in these communities.

The geological impacts are as dire to human health and the sustainability of the environment. Elevated levels of sulphur dioxide and nitrogen oxides in the atmosphere are wet deposited to the Earth's surface through acid rain. Sulphur dioxide reacts with hydroxyl ($OH^{-)}$ radicals and moisture to form sulphuric acid and nitrogen oxide with OH^- group to form nitric acid. These acids corrode buildings, construction materials, steel and are deposited into the land soil and river streams during rainfall, consequently affecting aquatic systems and the agricultural sector. Marine life is jeopardized and food production becomes insufficient for regional and global demands.

Greenhouse gases such as methane and carbon dioxide have far much bigger implications in terms of climate change and global warming of the planet. Weather pattern changes and very extreme temperatures are attributed to these gases. Rising sea levels are consequently due to the impact exerted by the greenhouse gases as ice melts in regions like Antarctica.

The government declared three regions as national high priority areas owing to poor air quality associated with these areas; Highveld, Vaal Triangle and Waterberg-Bojanala regions encompassing the Mpumalanga, Gauteng, Northwest and Limpopo provinces. The South African Weather Service (SAWS) furnishes monthly reports on the air quality data observed for monitored parameters archived by the SAAQIS portal.

For example, in a September 2015 report for air quality information (last accessed 19 January 2017) the measurements of air pollutants over the Highveld were reported. The Highveld has five ambient air monitoring stations; Middleburg, Hendrina, Secunda, Ermelo and Witbank stations. Measured parameters are particulate matter (PM), SO_2, NO_X, ozone (O_3), CO, benzene, toluene,

ethylbenzene and xylene (BTEX). Metrological data such as wind speed and direction, ambient temperature (in °C), relative humidity (%RH), rainfall and barometric pressure are reported. This area with huge characteristic industrial activities (example, Columbus steel, Middleburg ferrochrome, Sasol plant near Secunda, coal transportation, industrial and mining emissions, use of domestic fuel etc.) was declared a priority area in 2007 (SAWS, 2015).

The Vaal Triangle has six (6) operated ambient air monitoring stations; Zamdela, Three Rivers, Sharpeville, Kliprivier, Sebokeng and Diepkloof. Amid these monitoring stations are the Eskom Lethabo station, steel production firms, Arcelor Mittal and domestic fuel burning activities *(*SAWS, 2015*)*.

The Waterberg-Bojanala districts were declared a priority area in 2012 (notice no. 35435 and no. 495 of 15 June 2012 national gazette). The area has three monitoring stations; Lephalale, Mokopane and Thabazimbi. Different from the latter and the former areas, it was declared a priority area based on government's strategy of a preventative approach. Waterberg-Bojanala districts is not a highly industrialised area, however it was identified to have a potential to become pollution hotspot because of planned future developments and the ongoing built of Medupi power station (DEA, 2015). This approach speaks of mitigation strategies that are discussed in the next section.

However, an overview of the state of the air reports (until 2015) shows that there hardly was exceedance of NAAQS in the past few years in the priority areas except small separate instances and particularly for particulate matter and ozone. However, the Highveld region among the three also shows the exceedance of sulphur dioxide limits periodically.

1.2.5 Regulations, laws and policies governing air quality

The Atmospheric Pollution Prevention Act (APPA) 45 of 1965 was the Republic's first official legislation to control sources of air pollution and their generated emissions. However, according to Naiker et al., (2012), the Act was inefficient in addressing its required objectives of air quality governance. It is suggested to have

contributed to the formation of the current national high priority areas. In 2004, a new legislation for air quality was promulgated by the South African government through the DEA to be a control measure of air pollution. The NEM: Air Quality Act was designed to provide a legislative framework to: "Prevent pollution and ecological degradation, promote conservation, secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development."

The Air Quality Act introduced approaches of emission licenses and air quality officers, such concepts that are intrinsically involved in making it a success. Establishment of air pollution monitoring stations was implemented directly from this legislation, as well as national, regional and local emission standards. SAAQIS was implemented also to act as a centralized database for all data reported from the monitoring network. Apart from the Air Quality Act there are other local and international strategies for pollution mitigation.

1.2.5.1 Local mitigation strategies and policies

Mitigation strategies formed and passed in parliament and international conventions includes declarations, amendments, new policies and policy changes to address this global challenge. One of these declarations is the declaration of greenhouse gases (carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons and sulfur hexafluoride) as priority air pollutants in an edition of the Air Quality Act (notice 172 of 2014) through which industries were then requested to submit their pollution prevention plan for approval by the DEA.

The Long-Term Mitigation Strategies (LTMS) technical report of 2007, is aimed at providing options which government and industry may consider to mitigate carbon dioxide emissions. Some of these plausible solutions includes energy efficiency, electricity generation from renewable resources, nuclear power and tax on carbon dioxide emissions. For automobile contributions to emissions, the government issued a Notice enforcing use of the fuels that have less than 10 µmol/mol sulphur content (EURO 5 standards), Henneman et al., (2015). Another mitigation strategy used by the government is the Integrated Resources Plan where

a pledge was made to utilize renewable energy sources up to 14% of total electricity generation by 2030.

The government amid all the catastrophe impacts of atmospheric emissions, also developed the National Climate Change Response White Paper of 2011 to communicate to the public and industry role players the diverse ways in which it wishes to address climate change and South Africa's influence to climate change. Among the priorities that the government aims to tackle are: (1) risk reduction and management where solutions that address immediate impacts to the environment and health of the citizens are prioritised, (2) mitigation actions with effective results, industry responses where they plan and prepare their pollution monitoring programmers and (3) enforcement of regulations.

The DEA as the custodian of air quality for all South Africans has formulated and established national minimum emission standards for compliance monitoring purposes to protect the livelihood of communities and sustain the environment, especially the atmosphere. At room temperature and atmospheric pressures, some of these emission standards are mentioned in **Table 1.1** for different gases. Atmospheric emission licenses were also introduced as part of the Air Quality Act compliance and enforcement mechanisms for effectively managing air pollution by industries. The inadequacy of such a control was a shortcoming of the APPA among others and was addressed in this manner, Naiker et al., (2012).

Table 1.1: National air quality standards for gas pollutants, Air quality Act (2004)

Pollutant	Instant peak (µmol/mol)	Hourly average (µmol/mol)	24-hour average (µmol/mol)	Monthly average (µmol/mol)	Yearly average (µmol/mol)
NO	1.4	0.8	0.4	0.3	0.2
NO_2	0.5	0.2	0.1	0.08	0.05
SO_2	0.19	-	1.8×10^{-5}	-	7.3×10^{-6}

1.2.5.2 International commitments regarding climate change

Several programmes are running on a global scale to study global atmospheric chemistry, distribution of gases and for planning international mitigation concerted efforts. These programmes include the World Meteorological Organisation Global Atmospheric Watch (WMO/GAW) programme, the Kyoto Protocol and European Trading Scheme.

The United Nations established an agency in 1950, the World Meteorological Organisation (formerly the International Meteorological Organization founded 1873). It is an organisation implemented with the objective of coordinating global activities that relate to climate, weather, and the Earth's atmosphere. At present, it has 191-member states including South Africa, WMO (2016).

The WMO/GAW programme is aimed at studying background conditions of measured parameters such as the amount of greenhouse gases in the atmosphere, reactive gases, aerosols etc. with assistance from monitoring stations across the globe. At the southern hemisphere one of the monitoring stations is in Cape Town South Africa, at Cape Point. The data measured here (Cape Point station) is archived at the World Data Centre for Greenhouse Gases (WDCGG). The WDCG makes one of the databases the measurements performed in South Africa reaches for global information access. http://ds.data.jma.go.jp/gmd/wdcgg/ last accessed 10 March 2016.

The Kyoto Protocol is an international agreement signed in 1997 but effected 2005 by member states of the Metre Convention as commitment to reduce greenhouse gas emissions. This treaty employs tools such as international emissions trading, clean development and joint implementation mechanisms to address its obligation. Member states are required to monitor and archive data of actual emissions and submit annual emission reports. South Africa agreed to the terms of the protocol at the 2009 UNFCCC to reduce carbon dioxide emissions between 30-40 % by 2025 *(*Henneman et al., 2015).

1.3 Metrology and its support role in mitigation efforts

While many regulations and efforts have been implemented on both local and global scale, there is a critical catalyst for the success of monitoring programmes gas mixtures are used to correctly determine the amount of gas pollutants with the highest accuracy, smallest uncertainties and traceability. They give confidence and credibility to reported measurement results. Therefore, to successfully measure stack and automotive emissions, accurate emission reference gas mixtures must be developed by metrology laboratories. To eliminate challenges of inaccuracies, and over/underestimations, reference gas mixtures are critical. This study employs metrology or measurement science to inform the feasibility of providing representative stack and automotive emission reference gas mixtures. It is also through metrology that measurement equivalence of countries can be assured for pollution reporting, especially for complex mixtures such as these.

A global demand for measurements that were independent of time and place is critical for successful importing and exporting. The Metre Convention of 1987, established the Bureau International des Poids et Mesures (BIPM), an organisation that coordinates measurement coherence around the globe. The BIPM was instrumental in establishing measurement standards for principal physical quantities, maintaining prototypes and coordinating comparisons of measurement activities. The measurement International System (SI) units used to date (metre, kilogram, mole, second, ampere, Kelvin and candela) were agreed upon in this convention. Since the subject of this dissertation falls under chemistry, only the official definition of the mole is given. The mole, the unit of measurement for amount of substance, was defined as; “amount of substance of a system which contains as many elementary entities as there are atoms in 0.012 kilogram of carbon 12.”

The BIPM consists of ten consultative committees that specialises in different areas of science and addresses varying measurement needs and demands. Of importance to this dissertation is the Consultative Committee for Amount of Substance (CCQM) and its Gas Analysis Working Group (GAWG). Member countries of the Metre convention treaty participate in the activities of the BIPM through national

metrology institutes. These in turn offer measurement traceability to industries in those countries to facilitate measurement excellence and equivalence for import/export. http://www.bipm.org/ 28 January 2017

South Africa is represented by the NMISA on this global scale of measurement coherence. It is through the activities of the BIPM that South Africa illustrates its measurement capability. CCQM K71 is a key comparison started in 2008 where global measurement comparability of stack gas measurements was evaluated. The challenge of this key comparison however, was the ability of the different participants to control cross-interferences between target gases. The NMISA participated in this study and while its results were not good, the laboratory aims to improve its capability. Therefore, this project is aligned with global measurement equivalence through this key comparison. If the new methods result in improved measurement, a subsequent key comparison will be very successful. Consequently, the measurements in emission industries will be improved and of the highest quality.

1.4 Justification of research project

The improvement of preparative and value-assignment capabilities for any combination of multicomponent primary reference gas mixtures will result in the following outputs; technical knowledge, mitigation solutions, support of monitoring initiatives and improvement in measurement equivalence. Measurements undertaken by the National Ambient Air Quality Monitoring Network are supported by provision of appropriate reference materials. These measurements contribute towards the National Air Quality Officer's Annual report (2011, DEA) and therefore, critical national agendas will be supported by measurement results obtained through calibration with improved reference gas mixtures for emission monitoring and the consequent desired accuracy. National projects such as the National Atmospheric Emission Inventory Project (NAEIP) will be sustained by the provision and availability of representative standards to evaluate compliance to minimum emission standards. The NAEIP is a collaboration between the DEA and SAWS and it is aimed at orchestrating,

developing, testing and executing a national atmospheric emission inventory system for toxins and greenhouse gases.

The results of CCQM K71 for some of the component gases obtained in the comparison of stack gas were over 0.5 – 1.0% relative deviation. This previous work that has been conducted by NMISA and other organisations on stack gas measurements is discussed in detail in the literature review (**Chapter 2**) where the different methodologies used by the institutes are compared. An improvement by the current project will contribute towards a subsequent measurement comparison of stack gas and other combinations of gas mixtures. In the dissertation are results obtained from primary standard gas mixtures that will be used for a key comparison on automotive gas in 2018 (this is still a tentative date).

The need for accuracy and sample representativeness is also addressed by this work. The use of non-representative standard gas mixtures has proven to result in erroneous results dependent sometimes on the combination of gases. While there are inherent problems with standards that match sample, the project investigates the feasibility of offering emission testers standard gas mixtures similar in matrix to sample of automotive and stack emissions. Holistically, the project aims to support the mandate of the NMISA and environmental emission management as enforced by the Department of Environmental Affairs, and the rest of the monitoring framework.

1.5 Research aim and objectives

The main aim of the proposed research project was to study the feasibility of the provision of representative multicomponent gas mixtures for stack emission measurements and air pollution monitoring. This aim was realised through the following objectives;

1. Gravimetric preparation according to an international standard for producing standard gas mixtures, ISO 6142-1:2015, and subsequent analysis of multicomponent gas mixtures of gaseous components of interest, i.e. carbon monoxide, carbon dioxide, sulphur dioxide, nitric oxide, propane and oxygen, using different analytical methods.
2. Purity analysis of high pure source gases
3. Development of automotive reference gas mixtures in preparation of a 2018 (tentative) international key comparison
4. Studying the stability of the prepared gas mixtures over a period of time (short term e.g. within few hours to days to long-term e.g. more than three months)

CHAPTER TWO – LITERATURE REVIEW

This chapter discusses literature on different methods available for preparing standard gas mixtures and compares their effectiveness as reported by different authors. The analysis of gas mixtures by gas chromatography, non-dispersive infrared/ultraviolet and Fourier transform spectroscopy measurement techniques is also presented in detail. Gas mixtures can be prepared by gravimetry (weight-based) and titrimetry (pressure-based) among other methods. However, gravimetry is given preference because the subject of the dissertation is on gravimetry.

2.1 Reference materials in chemistry - prelude

The development of reference materials in chemistry was adopted from the 1888 International Congress of Chemists in Chicago were a resolution was passed to equate them to the roles of the metre (m) and kilogram (kg) in length and mass measurements respectively. The congress was held thirteen years after formation of the BIPM in 1875 to coordinate measurement standards independent on time or place to facilitate global trade. Therefore, reference measurements have been around for over a century and chemical metrology for over half a century. Primary reference gas mixtures contain known amounts of analyte in a balance gas (nitrogen, helium or argon) and are characterised by stable concentrations of these analytes. Depending on the composition, reference materials can also be classified into matrix or non-matrix reference gas mixtures, Slominska et al., (2014). There are three major steps for highest metrological quality reference gas mixtures, namely –purity analysis, preparation and validation of values obtained from preparation. These will be discussed as the main topics in the literature review.

2.2 Purity analysis of source gases

Purity analysis of ultra-pure gases is the first prerequisite for manufacture of accurate standard gas mixtures. The purity of a source gas is determined by using the subtraction method from ISO Guide 35:2006, Matsumoto et al., (2013). There are many studies that have been performed to quantify the amount of permanent

gases for example, in source gases. Methane, hydrogen, oxygen, nitrogen and carbon dioxide trace impurities were analysed in high pure carbon monoxide by gas chromatography with thermal conductivity detection by Matsumoto et al., (2013). These gases were separated by using a molecular sieve stationary phase and carbon dioxide by a PLOT U column at 50 ^{o}C oven temperatures. Methane, nitrogen, and oxygen trace impurities in noble gas xenon were analysed by using a novel reduction gas analyser and cold trap methods. Cold trap methods were used because the partial pressures of these impurities are high compared to the xenon. Therefore, liquid nitrogen was used to trap the gas as the impurities passed through and were separated, Leornard (2010).

Trubyanov et al., (2016) developed a novel method for the analysis of hydrogen, oxygen, nitrogen, methane, carbon monoxide and carbon dioxide in ammonia by using a multidimensional gas chromatography system attached with a pulsed discharge helium ionisation detector. The chromatogram of gases separated by the 1 m long 13x molecular sieve column of 2 mm internal diameter is shown below in **Figure 2.1**. Sufficient separation was observed between oxygen and nitrogen. In a multidimensional GC system, an analyst can simultaneously analyse gases which would need different gas chromatographs in conventional chromatography.

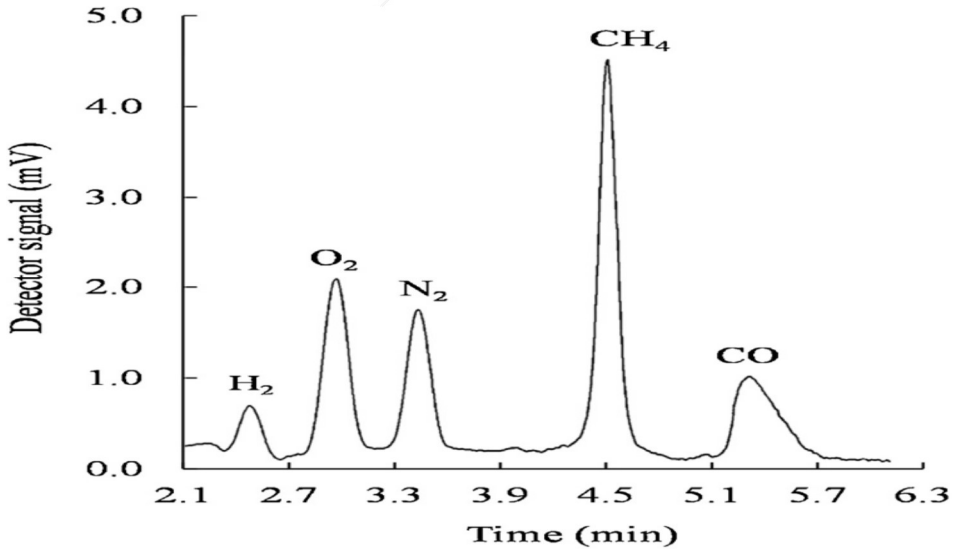


Figure 2.1: Hydrogen, oxygen and nitrogen separation for impurity analysis. Trubyanov et al., (2016).

The carbon dioxide was separated by use of a 4 m x 2 mm internal diameter Porapak Q column. Both columns were operated at 70°C oven temperature. For the determination of oxygen, nitrogen and hydrogen in high purity deuterium, 5A molecular sieve and alumina stationary phases were used at 30°C column temperature for the analysis of O_2 and N_2 and at -196°C for hydrogen. The gas chromatograph method was developed by Junbo et al. (2012). The use of molecular sieve packing materials is popular for the quantitative and qualitative measurements of permanent gases (except CO_2) in gas chromatography. Porous polymers were preferred for use as stationary phases for the separation of carbon dioxide from different matrices by most authors.

2.3 Gravimetric preparation of reference gas mixtures.

The gravimetric preparation of gas mixtures can be divided into two; static and dynamic methods. Some of the challenges often encountered to produce a standard gas mixture include; the demands of multicomponent mixtures, ability to quantify trace impurities, control of interferences and demands to measure lower mole fractions, Slominska et al., (2014).

Low uncertainties PRGMs of permanent gases in an inert balance are commonly prepared in accord with an international standard: *ISO 6142-1: 2015, Gas analysis -Preparation of Calibration gas mixtures, part 1: Gravimetric method for class I mixtures*. This method is used as a guide for coherence of methods along with other ISO methods for global comparability. These calibration gas mixtures are prepared from high purity grade gases purchased from gas manufacturers and other leading institutes. The source gases and pre-mixtures are diluted in a series of steps (multi-step dilution) in balance gas to the desired mole fraction (ambient, background etc.). The target mole fraction of a component in a sample mixture is derived by determining the target masses of both the pre-mixture and balance gas to be added using this equation;

$$m_i = \frac{x_i P_F V_{cyl} M_i}{RT_f} \qquad \textbf{2.1}$$

, where x_i= mole fraction, P_F = required final pressure, V_{cyl} is the volume of the cylinder, M_i is the molar mass of the major component, R is the gas constant (R= 8.31451 J/mol.K), T is the standard temperature (T= 294.15 K) and Z_f is the compression factor (Assume Z=1).

The static and dynamic mixing techniques (Dantas et al., 2014) of this widely used gravimetric method (Shuguo et al., 2013) are compared using **Table 2.1** as described by Slominska et al., (2014). The way in which a gas component is introduced into a balance gas distinguishes these two gravimetric methods. A measured small amount of gas is diluted in a large volume of balance gas in static methods and dynamic methods pertains to the combination of different gases continuously adjusting flow rates, Dantas, et al., (2014)

Table 2.1: Comparison of static and dynamic filling methods, Slominska et al., (2014)

	Advantages	Shortcomings
Static method	Simple, cost effective.	Time consuming, inaccurate, adsorption problems, stability problems, not suitable for NO_x and SO_2.
Dynamic method	Very accurate, no adsorption problems, stable mixtures	Control of flow rate of balance gases, necessity to have high pure gases

Whilst these two methods are conventional techniques used for many years, Shuguo et al., (2013) and Milton et al., (2006), there has been new developments in a quest to achieve better measurement capabilities, accuracy and improved preparation of gas mixtures with lower mole fractions. These new developments are derived from diffusion, permeation, thermal decomposition scientific principles and innovative improvements of analytical instruments.

Diffusion is normally used for preparation of volatile organic compounds gas mixtures (e.g. benzene, toluene, xylene etc.). Permeation is suggested to be able to allow preparation of multicomponent gas mixtures at low mole fractions (ppb). Thermal decomposition involves heating a surface for longer periods of time and

giving off the component gas which is consequently mixed with the stream of the balance gas, Slominska et al., (2014). Some of these other preparation techniques are compared in **Table 2.2 below**.

Table 2.2: New developments in PRGMs' preparation, Slominska et al., (2014)

	Diffusion	Permeation
principle	Controlled diffusion of target gas into a stream of balance gas	Controlled permeation of target gas into a stream of balance gas
factors	Total pressure, temperature, diffusion tube geometry, balance gas flow rate	Temperature, permeation of membrane and gas component.
Equation	$C = \frac{rK}{M}$ Where r is the diffusion rate, K is the gas constant and M is the molar mass of the sample gas.	$C = \frac{q_d 22.4M}{Q}$ Where q_d is the permeation rate, Q is the flow rate and M the molar mass.

2.3.1 Gravimetric preparation challenges

As simple as gravimetry seems, preparation of standard gas mixtures has its own inherent analytical difficulties. The preparation of a mixture involves mixing different gases (two or more) and presents challenges of relative volumes, diffusion and effusion phenomena and compressibility of component gases. Compressibility is a challenge especially with condensable gases which often results in changing "apparent' composition of a certified mixture over a period of time. Vigorous monitoring of temperature, pressure and flow rate is very critical to achieve accurate preparation. To overcome challenges such as these, Dantas et al. (2014) proposed an automated system for preparing gas mixtures with a suitable accuracy level for quantitative purposes. The practice of multistep dilution is also attributed with increasing the uncertainties associated with gravimetry, Shuguo et al., (2013). A gravimetric method utilising a small container before transfer to the sample

container is profiled below. It is used to overcome some of the challenges associated with traditional gravimetry.

2.3.2 Traditional gravimetry and multi-step dilution limitations

Primary reference gas mixtures of lower mole fractions (up to ppb level) are prepared in a multi-step dilution process from high pure source gases. At equilibrium filling pressure and volume of cylinder, the target mass is directly related to dilution steps. However, multi-step dilution is not only time consuming but susceptible to errors as well. When the number of dilution steps is reduced, the target mass of parent gas is also reduced, and it increases the relative error of weighing making it difficult to maintain a specific desired uncertainty. A minimum of 10 g is recommended to ensure acceptable weighing accuracy. An alternative method to decrease the uncertainty associated with weighing is described below by Shuguo et al., (2013);

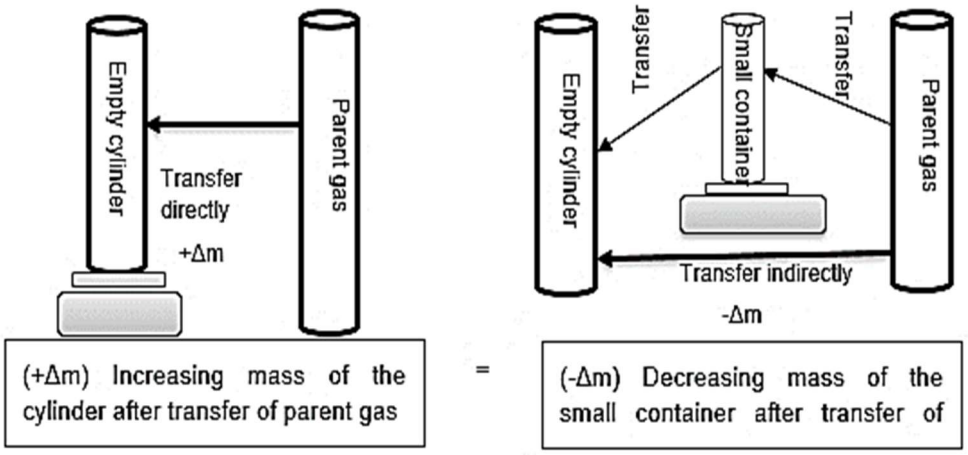


Figure 2.2: Comparison of traditional gravimetric method and TTG, similar to Shuguo et al., (2013).

Transfer Technique of small amount of Gas (TTG), is an indirect gas transfer method shown above in **Figure 2.2.** The small container used in TTG can be weighed by a balance of very high sensitivity and low capacity by measuring mass

loss. The advantages of this method over the traditional one include gas transfer without any loss and high precision of weighing, Shuguo et al., (2013).

Milton et al., (2011) also reiterate that the smallest target mass that can be weighed with an acceptable limits accuracy of PRGMs prepared by the static gravimetric method. Therefore, multi-step dilution of static gravimetry arises from the limitations posed by the requirements of acceptable uncertainty constraining mixtures that can be prepared in a sole step. Milton et al. (2011), described a mathematical relation for "developing optimal serial dilution strategies" to minimise uncertainties associated with the smallest mass that can be weighed.

2.3.3 Uncertainty contributions in gravimetric preparation

Assuming traditional methods of gravimetry and weighing the target component and balance in the same high-pressure cylinder, the uncertainty in the composition of a PRGM arises from; the weighing processes, purity analysis of high pure gases, stability molar masses of gaseous components. To illustrate the challenges associated with the weighing process in PRGM preparation Milton et al., (2011), used the following illustration; weighing a mass of between 20-1500 g with < 20 mg uncertainty in a cylinder weighing more than 100 times the mass of the gas. Such measurements use mass metrology principles of high accuracy mass determination for success. Influences of buoyancy of air is reduced by weighing the sample cylinder alternatively with an identical empty cylinder. However, buoyancy effects will not be reduced if the two cylinders have different temperatures. If the sample cylinder was recently filled with gas and is weighed immediately, this cylinder will weigh less than the actual mass. Thermal and vibration effects in balances also introduces uncertainty contributions but these are reduced by use of automated balances. Buoyancy corrections can be applied by developing a weighing equation (developed by Milton et al., (2011)) to describe the weighing process of a target component assuming the weighing of a sample cylinder against an identical tare cylinder. The apparent mass, r_i, is determined by the difference of the weighed cylinder at a particular weighing cycle and at vacuum. In terms of cylinder volumes and density the equation can be described as in **Equation 2.4**.

$$r_i = V_i(\rho_i^c - \rho_i^0) - V_T(\rho_i^T - \rho_i^0) \quad \textbf{2.4}$$

$$r_2 - r_1 = V_2(\rho_2^c - \rho_2^c) - V_1(\rho_1^C - \rho_1^0) - V_T(\rho_1^0 - \rho_2^0) \quad \textbf{2.5}$$

$$m_2 = V_2\rho_2^c - V_1\rho_1^c$$

$$m_2 = r_2 - r_1 - \Delta b_{12} + (V_2 - V_1)\rho_2^0 \quad \textbf{2.6}$$

The mass of the minor component is calculated from **Equation 2.5** The buoyancy correction term (**Equation 2.6**) results from the variance in the volume of the hollow cylinder and when the first/minor component gas has been added and corrects for the buoyancy variation owing to linear expansion. V_i and V_t refers to the volumes of the sample cylinder and the tare. ρ to the density of the sample cylinder (C), the tare (T) and air (air). r_1 refers to the vacuum weighing and r_2 to the weighing of the first/minor component in the same cylinder.

$$\Delta b_{12} = (V_1 - V_T)(\rho_1^0 - \rho_1^0) \quad \textbf{2.7}$$

Differential buoyancy (**Equation 2.7**) is triggered by variations in atmospheric density. The correction terms come together after the major component (balance) is added, m_3 and the mass fraction (w) of the given mixture is determined;

$$w = \frac{m_2}{m_2+m_3} = \frac{r_2-r_1-\Delta b_{12}}{r_3-r_1-\Delta b_{13}} C_1 \quad \textbf{2.8}$$

$$C_1 = \frac{1-K(\frac{Z_3^* RT}{M_3^*})\rho_3^0}{1-K(\frac{Z_2 RT}{M_2})\rho_2^0} \quad \textbf{2.9}$$

The linear expansion correction term (C_1) is given by **Equation 2.9**.

2.4 Analysis of multicomponent gas mixtures

The amount of gas in molar fraction is measured by Non-Dispersive Infrared/Ultraviolet spectroscopy (NDIR/UV), Gas Chromatography (GC), chemiluminescence detection, Fourier Transform InfraRed (FTIR) spectroscopy as reported by, Milton et al., (2011) and cavity ring-down spectroscopy, among other methods. Many studies have been done where analyses of multicomponent gas mixtures where performed, especially by gas chromatography and non-dispersive infrared spectroscopy. Gas chromatography is often preferred because certain compatible gaseous components can be analysed simultaneously, Luong et al., (2012), and Watanabe et al., (2008). For example, propane and carbon dioxide on a Porapak column under the same analytical conditions. However, only the permanent gases including hydrocarbons can be analysed by gas chromatography excluding nitric oxide and sulphur dioxide for the research project using specified research methods. The gas chromatography methods for these gases were not available for the period of this work. Challenges posed by complex multicomponent mixtures in a chromatographic experiment include the absence of a single stationary phase adequate for separation of all analytes and matrix effects.

Analytical difficulties posed by matrix gas of standard gas mixtures and emission samples are encountered in spectroscopy as well. For example, the results of an experiment were Fourier transform infrared spectroscopy was used to analyse a 10 μmol/mol methane in different matrix gases of nitrogen, argon and helium can be used to show discrepancies. The study was performed to assess the outcome of matrix differences on the results. Methane in nitrogen analysis results were 4% higher than the reference gravimetry mole fractions. The results of methane in argon and helium were 6% and 8% higher respectively, than true mole fractions, Geiger and Raynor, (2013). This example illustrates the impact that different matrices have on the analysis of target gases. Here, the discrepancy was resolved by performing span calibration using the 10 μmol/mol value to correct the deviations.

Matrix effects are not recent developments in the field of gas analysis. Carrier gas corrections were carried out to compensate for carrier gas effects during air

monitoring experiments by Griffith, (1982). Griffith reported that calibration of atmospheric carbon dioxide monitoring instruments by carbon dioxide-in-nitrogen standards to measure the concentration of carbon dioxide in sampled air that contained other gases such as argon and oxygen introduced some imprecision in the measurement 1% relative. A numerical spectral model was devised to correct for any shifts encountered. Matrix effects are also referred to as carrier gas shifts These were also determined using standards of carbon dioxide-in-nitrogen, carbon dioxide-in-air and carbon dioxide-in-argon mixtures. These were determined based on the assumption that differences in matrices implies differences in analyser responses. Carrier gas effects can be attributed to changes in pressure expansion in the sample cell.

Matrix effects are also encountered in industry. During the Air Quality and Emissions Show held during 2013 in Telford, England, leading gas manufacturer Air Products gave a presentation about "*Accreditation of stack gas calibration gas mixtures"* with special emphasis on cross interferences. They reiterated that calibrating analytical instruments that measure stack gas with binary mixtures can lead to erroneous results owing to cross sensitivity problems occurring within analysers. The cross interference was quantified in two ways. Firstly, by preparing several mixtures of the analyte and the possible interferent in different concentrations and ratios. Single component standard gas mixtures were used in this experiment and the cross interference calculated. In another way three independent mixtures of nitrogen, nitric oxide-in-nitrogen and carbon dioxide-nitrogen can be connected simultaneously and fed into a gas mixer then the analyser. The results of the study show an example of typical cross-interferences that are encountered when stack gas mixtures are analysed. The mole fraction of nitric oxide was kept constant and varying amounts of carbon dioxide were added into individual mixtures. The higher the concentrations of carbon dioxide in a stack gas cylinder, the higher the chances of synergistic effects.

Three common measurement techniques are profiled below from **2.4.1** to **2.4.3**.

2.4.1 Analysis of gas mixtures by non-dispersive infrared spectroscopy

The Non-Dispersive InfraRed (NDIR) spectroscopy technique was first used in the 1930's by the Germans and has since been widely used to measure gases, You-Wen et al., (2012). This measurement method is used for stack emission measurements, Sun et al., (2013), ambient air and pollution monitoring and has been considered reliable since the 1950s for measuring gas samples. However, its limitations include sensitivity, cross interferences and instrument drift which often declines the accuracy at which measurements are made. The sensitivity of an NDIR spectrometer for a specific gas is dependent on its absorption band. Therefore, a weaker absorption band often results in a decline in sensitivity. Cross interferences are also a limitation because of overlap of absorption bands of different target gases. These often make it an unreliable technique. Its advantages however, include its fast response and ease of maintenance, Wong and Anderson ((2012).

2.4.1.1 Principle of operation

Non-dispersive infrared spectroscopy is a form of an optical detection analytical tool based on wavelength absorption properties of gases in the middle infrared absorption band. Its principle of operation is based on the determination of the amount of radiation that is absorbed by a gas sample and on the Beer-Lambert law for monochromatic light, You-Wen et al., (2012) and Dinh, et al., (2016).

$$I = I_0 e^{-\alpha l} \qquad \textbf{2.10}$$

I refer to the radiation transmitted after absorption, I_0 the incident radiation, α the absorption coefficient and l the optical path length of a gas cell. A typical configuration of a non-dispersive infrared analytical system is shown in **Figure 2.2.**

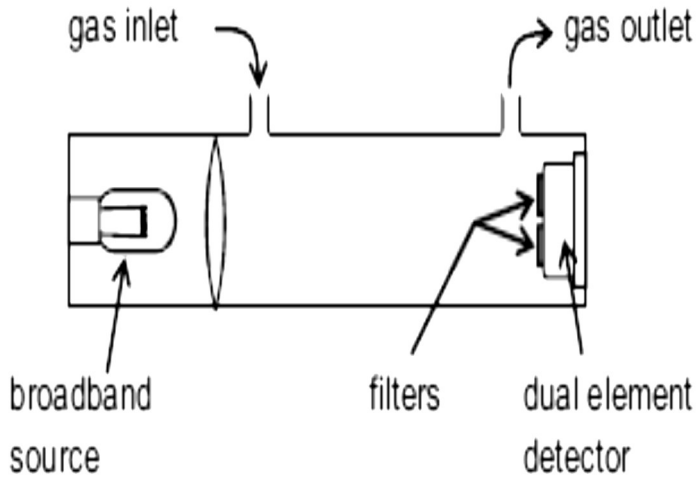


Figure 2.3: Typical non-dispersive infrared/ultraviolet spectrometer configuration, Hodgkinson et al., (2013).

Radiation from a broadband source passes through two optical filters for the active and reference channels where the gas samples are contained and it is absorbed. The active channel comprises the absorption band of the target gas species and a non-absorbed region for reference channel. The amount of radiation absorbed is determined in each channel using embedded algorithms.

2.4.1.2 Cross interferences in non-dispersive infrared spectroscopy

As successful as it has been for many years, and while simultaneous analysis can be achieved by use of multi-gas spectrometers, the technique is susceptible to interferences among target gases. Three of the major disadvantages of non-dispersive infrared spectroscopy measurements is cross-interference from moisture, Sun et al., (2013), and other target gases in complex gas mixtures and non-linear absorption, You-wen et al., (2012).

To correct interferences, reference filters for moisture, spectral correlators, interference matrices (applicable when linear absorption is certain) and cross correlation methods are used. You wen et al., (2012) developed a correction algorithm for interferences from target gases. Carbon dioxide, carbon monoxide and nitric oxide were analysed simultaneously by a non-dispersive infrared multi-

gas analyser with a light source generating infrared radiation in the wavelength range of 1.5 – 10 µm. The band pass filters were at 4.61 µm for carbon dioxide, 4.84 µm for carbon monoxide and 5.25 µm for nitric oxide. The extent of cross interference (interference function) of gas A to B was described by **Equation 2.11**.

$$\tau_{AB}(x) = \frac{1}{C_{max} - C_{min}} \int_{C_{min}}^{C_{max}} F_A(\tau) F_B(\tau + x) d\tau \qquad \textbf{2.11}$$

Where the response function of A is $F_A(x)$, $F_B(x)$ the response function of B and C_{min} and C_{max} are the lower and upper detection limits for A. The calibration curves were extrapolated by using the least square method of a third-order polynomial owing to the non-linear absorption phenomenon.

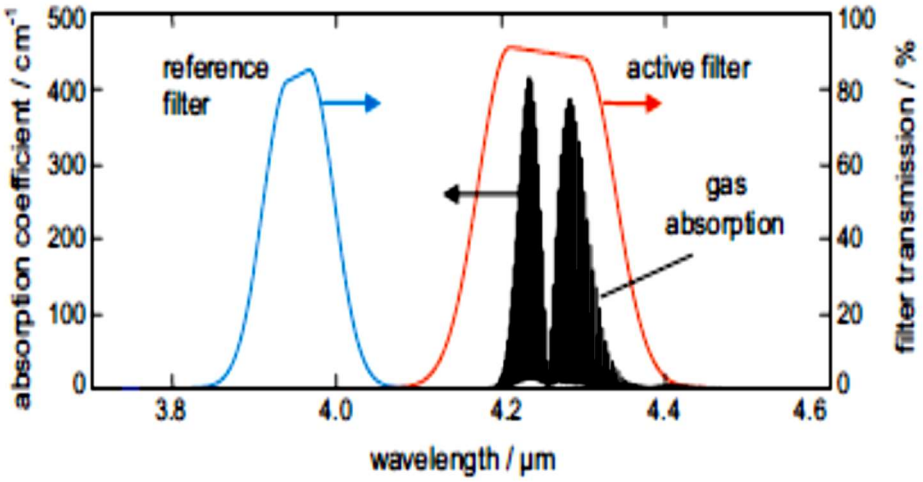


Figure 2.4: NDIR absorption spectrum of CO_2 with optical band filters at 4.26 and 3.95 µm, Hodgkinson et al., (2013).

An absorption spectrum for carbon dioxide is shown in **Figure 2.4** between 4.2 and 4.4 µm wavelength range. Hodgkinson et al., (2013) suggested that when CO_2 is measured by NDIR interferences can be kept minimal provided the filter bands of the reference and active channel are not overlapping with those of other target

gases. This principle can be applied to the measurement of other gases where filters can be incorporated into the instrument design to minimise interferences.

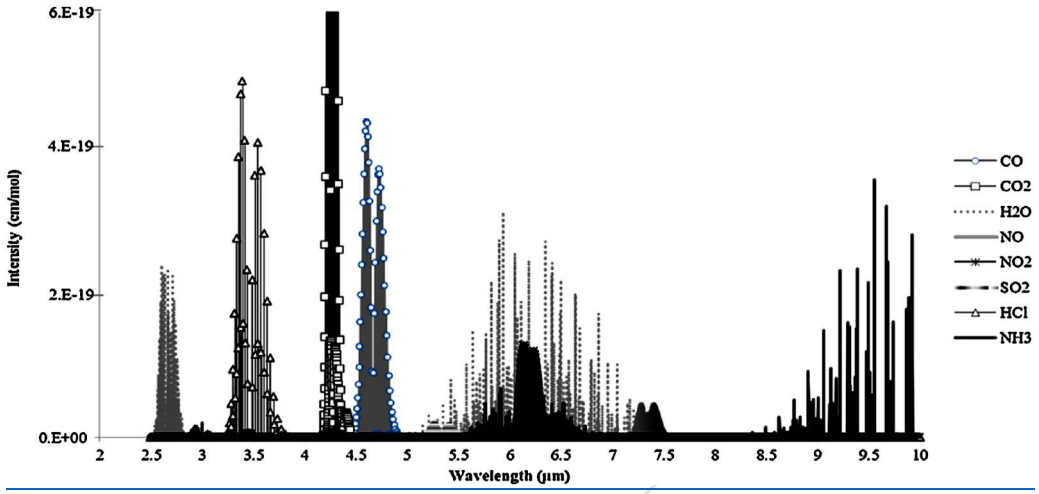


Figure 2.5: HITRAN spectrum of various gas components, Dinh et al., (2016).

A HIgh-resolution TRANsmission molecular absorption database (HITRAN) spectrum of carbon monoxide, carbon dioxide, nitric oxide, sulphur dioxide and other gases is shown in **Figure 2.5**. Notice how moisture absorbs in many regions of the bandwidth. Water vapour is such a critical interferent most especially in the measurement of stack gas where it is found in massive quantities and its presence has significant implications. It is important that water vapour interference is accounted for and corrected from results. It occurs mainly between 2 and 8 µm wavelength range where sulphur dioxide, nitric oxide, carbon monoxide and carbon dioxide absorb, Dinh et al., (2016).

Table 2.3: Absorption wavelengths in the mid infrared range of SO_2, NO, CO, CO_2.

Gas	Middle infrared absorption wavelength (μm)
SO_2	3.96
NO	3.4
CO	4.67
CO_2	4.26

Absorption wavelengths of some of the components of stack gas in the infrared bandwidth are shown in **Table 2.3**. Besides the use of optical filters, double beam samples cells coupled with several detectors similar to one developed by Warnke et al cited by Vingh et al., (2016) and response coefficients can be used to correct for water vapour interferences. Water vapour is also an undesired impurity in gas mixtures of reactive gases because it catalyses secondary aerosol formation.

2.4.2 Analysis of gas mixtures by gas chromatography

A German scientist Erika Cremer developed the first prototype of a gas chromatograph in the late 1940s. By 1953, industries in Europe have already started using the then new analytical technique, Poole, (2012). Other authors however, credit Runge F.F for the development of chromatography for his 1834 work of spot testing dye and plant extracts using paper and cloth. In 1850, he also successfully separated salt solutions on paper. Wilson J.N wrote the first publication on chromatography in 1940. Cremer is said to have introduced gas-solid chromatography only in 1951, Grob and Barry, (2004).

Gas chromatography is used for measurement of stack emission gas, exhaust emissions and air pollution control, Matsumuto et al., (2013) and is advantageous because of its rapidness, ability of simultaneous determination, separation of complex mixtures and simplicity amongst other features. Several types of detectors of varying sensitivity, linearity and stability exist for detection of various analytes by exploitation of their chemical/physical properties. The analysis of binary mixtures is routine, however, that of multicomponent gas mixtures can be extremely difficult.

2.4.2.1 Principle of operation

The principle of gas chromatography is introduction of sample (mobile phase) via automated switching valves into a steel tubing of solid adsorbent (column, stationary phase) and separation by partitioning. This stationary phase may be polar or non-polar or separating based on physical properties such as molecular weight and boiling point. The mobile gas is an inert gas (helium, nitrogen, argon and hydrogen) that must be free of oxygen and dry. The choice of carrier gases often depends on the desired outcome of the experiment and cost limitations. Helium is expensive and hydrogen is more efficient (resulting in overall short run times) but it's expensive. Nitrogen is used as matrix gas in most mixtures and therefore, not used as carrier gas. Both packed and capillary (open-tubular) columns are used in gas chromatography, Haskins (2013*).* Glass capillary columns used for gas analysis were manufactured by using materials such as soda lime, borosilicate, uranium glass, potash soda lead and fused silica. Packed columns are preferred in gas chromatography than open tubular columns. The unpopularity of open tubular columns arises from limited sample capacity and low carrier gas flow rates, which made the introduction of sample onto a column difficult. There are two ways of sample introduction in gas chromatography; split injection and split-less injection. In split injection, a part of the injected volume of sample passes through the analytical column while the other is vented. In split-less injection all the sample volume is kept.

Split injection has disadvantages of low bandwidths, incompatibility with less volatile samples, and difficulties in quantifying gases in dilute gas. Therefore, a split-less injection method was developed to overcome the inefficiencies of split injection. Split-less injection methods transfer relatively large samples very slowly over a longer period of time instead of venting some to waste, Poole (2012).

A Flame Ionization Detector (FID), fundamental to this project, is commonly used for hydrocarbons (CH-bond) that burn in the hydrogen/air flame. Thermal conductivity Detector (TCD) is based on the principle of varying thermal conductivity properties between a carrier gas and analytes of a gas mixture, Budiman et al., (2015). Gas chromatography is also a suitable choice due to the

high volatility of permanent gases and light hydrocarbons, Luong et al., (2013). The choice of carrier gas is made by use of a Van-Deemter plot depending on the efficiency an analyst requires.

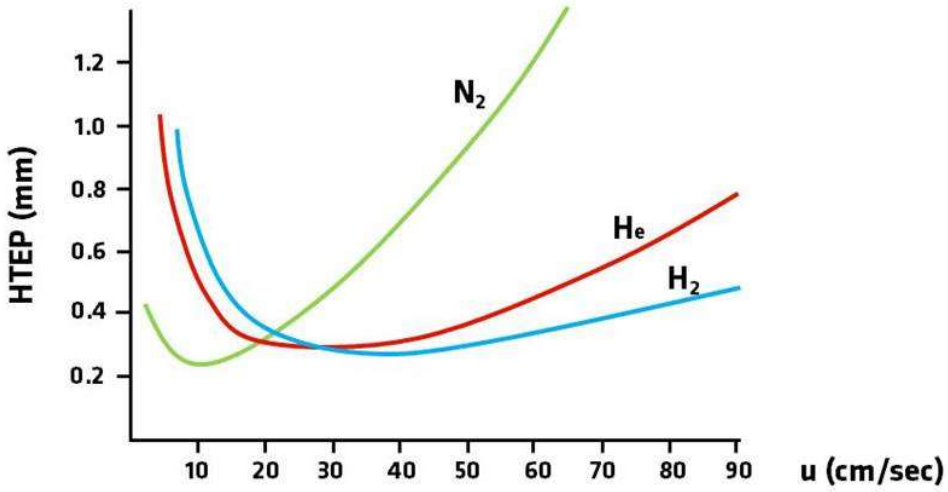


Figure 2.6: Van-Deemter plot for helium, nitrogen and hydrogen

A more economical choice of carrier gas in gas chromatography is the use of hydrogen. Its use significantly reduces analysis time and it permit the use of lower temperatures, increasing column lifetime. However, nitrogen offers a better resolution than hydrogen, (Peakscientific, 2017)

2.4.2.2 Multidimensional gas chromatography

The analysis of oxygen, nitrogen, carbon monoxide, carbon dioxide, methane and other light hydrocarbons by gas chromatography presents various challenges associated with the availability of stationary phases to the analyst. Whilst these analyses are important for pollution control, the simultaneous determination of these gaseous compounds has many constraints. The volatility of these gases makes gas chromatography an obvious choice for separation and quantification. However, not a single stationary phase exist that is adequate of sufficient separation for all

analytes. For example, divynl benzene (porous polymer) co-elutes oxygen, nitrogen and carbon monoxide almost perfectly; while a molecular sieve (zeolite stationary phase) column can efficiently separate hydrogen, oxygen, nitrogen, carbon monoxide and methane. The molecular sieve stationary phase adsorbs carbon dioxide and the heavier hydrocarbons. Moisture is also known to deactivate molecular sieve at percent concentrations. The separation between oxygen and nitrogen is also inadequate when a carbon molecular sieve is used. Reactivity of carbon molecular sieve with saturated hydrocarbons poses analytical difficulties (Luong et al., 2013).

The adsorption of carbon dioxide and thus plausible "deactivation" of the molecular sieve however, has been determined to be false. While the peak of the component hasn't been seen in the column chromatograms even when it is present in a sample, carbon dioxide only takes longer to accumulate then elute (that is it is strongly retained by the molecular sieve stationary phase). About 43% of deactivation can be achieved however, at 400 ml of CO_2, which is highly unlikely in practice. Under conditions for the quantification of nitrogen and oxygen separately, CO_2 elutes between 3 to 4 hours, Thompson (1977).

Chromosorb and Porapak columns can be used to separate carbon dioxide, propane and sulphur dioxide in the stack gas mixtures by using multi-detectors on the same gas chromatograph at 80 ^{o}C oven temperature and using He at 30 cc/min flow rate as carrier gas. The retention times (peaks) can be identified by binary standard gas mixtures or using the polarity of these gases and other chemical properties, Thompson (1977).

The absence of fitting stationary phases for the analysis of all gases at the same time is often compensated using a sequence of multi-port switching valves that transfer the effluent selectively from one column to another or can bypass specified columns at varying steps of the analysis cycle. The system however has drawbacks; excessive void volume can lead to degraded chromatography, lack of inertness and cross leakages from valve rotor wear. To address these drawbacks is a multidimensional gas chromatography system configuration developed by Luong

et al. (2013) for the analysis of oxygen, nitrogen, carbon monoxide, carbon dioxide and light hydrocarbons shown below:

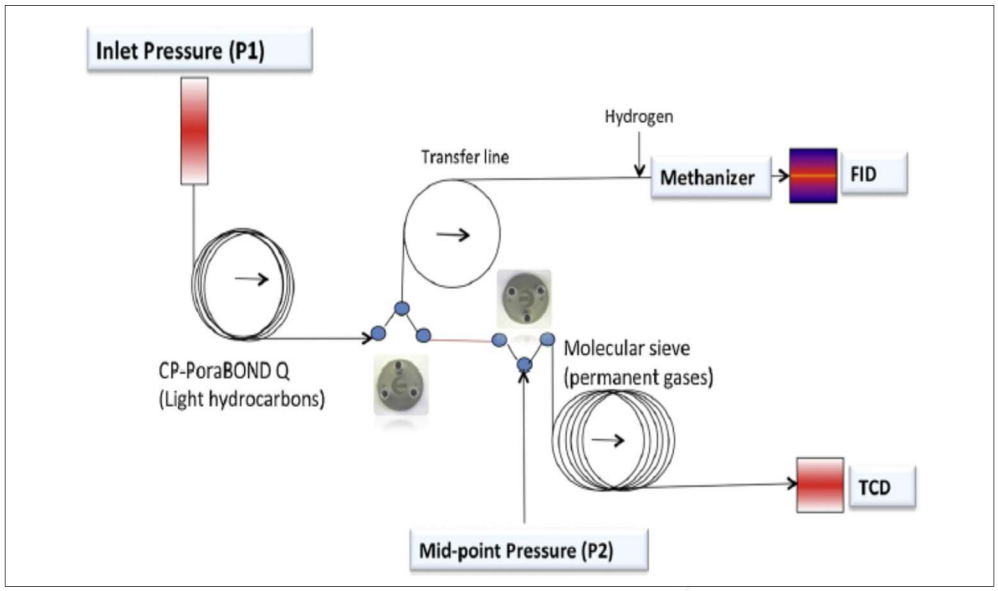


Figure 2.7: Multidimensional gas chromatography system, Luong et al., (2013)

This multi-detector system configuration includes the use of planar microfluidic devices in series with each other with built-in microfluidic gates and mid-point pressure source for column isolation and back-flushing; for determination of permanent gases and light hydrocarbons in one single analysis using flame ionization and thermal conductivity detectors operated at 250°C and 150°C respectively. A 50-m x 0.32 mm id x µm CP-PoraBOND Q column where the injection of sample is made retains and separates moisture and hydrocarbons, while a 15m 0.32 mm id x 25 µm CP-molecular sieve 5A separated the oxygen, nitrogen, etc. The midpoint pressure is then increased such to bypass the molecular sieve and the effluent is directed into the thermal conductivity detector. The methaniser (nickel catalyst) converts the carbon monoxide and carbon dioxide into methane and the hydrocarbons were separated by a divynl benzene column

Simultaneous analysis often requires multi-columns and detectors as illustrated by **Figure 2.7**. However, the Pulsed Discharge Helium Ionization (PDHID) detector can also be used to analyse organic and inorganic volatiles with a better sensitivity

than the thermal conductivity detector, van Rensburg et al., (2007) and Suzuki and Takahashi, (2012). PDHID is also used when analytes cannot be detected by the flame ionization detector. In a PDHID system comprising only a single column (micro packed ST, 2 m x 1.0 mm id) and detector, hydrogen, carbon monoxide, carbon dioxide and hydrocarbons were determined.

An analytical method was designed by Kaminiski et al., (2003), to determine small quantities of carbon monoxide, carbon dioxide and methane in air and refinery hydrogen gases using a flame ionization detector with two columns; a Porapak Q and molecular sieve 5A, with catalytic hydrogenation. The authors of this work suggest that multicolumn or multidimensional gas chromatography without catalytic hydrogenation is insufficient to determine trace amounts of these analytes. The novelty of the proposed analytical method is prior carbon monoxide and oxygen separation before introduction of carbon monoxide to the methaniser; using a Porapak Q column the order of elution is $CO/O_2/N_2/Ar$, H_2, CH_4, CO_2, C_2 etc. the co elution of oxygen and carbon monoxide makes for difficult quantification of carbon monoxide. The application of a short molecular sieve column allows for carbon monoxide peak elution between oxygen and methane peaks. The method is summarized as follows;

In this method, the Porapak Q and molecular sieve 5A columns and the nickel (methaniser) catalyst are connected in series. When the methane peak has eluted at retention time of approximately 3.6 minutes, the molecular sieve column is bypassed to elute carbon dioxide and other heavier hydrocarbons. This work is like work done by Luong et al., (2013).

The two-dimensional gas chromatography is advantageous over conventional gas chromatography due to increased peak capacity and sensitivity owing to various separations and analyte compression between these separations. Multidimensional gas chromatography with mass spectroscopy is also of huge interest since it allows direct identification of analytes, Gem et al., (2010).

2.4.2.3 Calibration methods for gas chromatography experiments

Different calibration methods are used in gas chromatography and a comparison is made of calibration techniques used for chromatography analyses reviews from **section 2.4.2.2**: No system calibration was mentioned by Luong et al., (2013). A mixture of methane/ethane/propane/carbon dioxide-in-helium was used to analyse oil field gas samples by a pulsed discharge helium ionization detector by Saito et al., (2012). These calibration gas mixtures were similar in matrix (representative) to samples. The column used for separation was a micro packed Shin Carbon ST (2 m x 1.0 mm internal diameter) with a maximum operating temperature of 330 ºC. The 250 µl sample was fed onto the column at 30 ml/min and 4.5 ml/min discharge (helium) and carrier gas (helium) flow rates. The oven was set at 40 ºC for 3 minutes and ramped to 300 ºC for 15 minutes for heavier molecules.

Kaminski et al., (2003) used $CO/CO_2/CH_2$-in-H_2 (matrix matched) standard mixtures for their analytical systems. In the last review, the calibration was performed using matrix matched standards as well. This suggests that using calibration gas mixtures representative of samples is a popular and preferred among chromatographers.

However, in contrast, a different calibration method for quantifying hydrocarbons was developed using a post column reaction capillary gas chromatography with a flame ionization detector, Watanabe at al., (2006). For adequate quantification calibration standards of each analyte should be used to calibrate the analytical instrument. However, the authors argue that this is an inefficient and costly practice when catalytic hydrogenation is used. To reduce the number of correction standards in their study, a system consisting of two micro-reactors to oxidize the analytes to carbon dioxide and reduce them to methane was developed. The target gases were separated and quantified as methane. Only one standard of methane was used for calibration. This calibration method is known as a primary ratio method and can be used as an alternative.

One other technique that can be used for analysis is FTIR whose main advantages above GC and NDIR measurements is total simultaneous determination. From the literature review of GC and NDIR only partial simultaneous determination were

done for components of stack gas. However, with FTIR all components of stack emission can be analysed at the same time similar to work done by Tshilongo et al., (2015). While its operation has been described below, the technique was not used in the study.

2.4.3 Fourier-Transform Infrared spectroscopy for the analysis of gas mixtures

2.4.3.1 Principle of operation

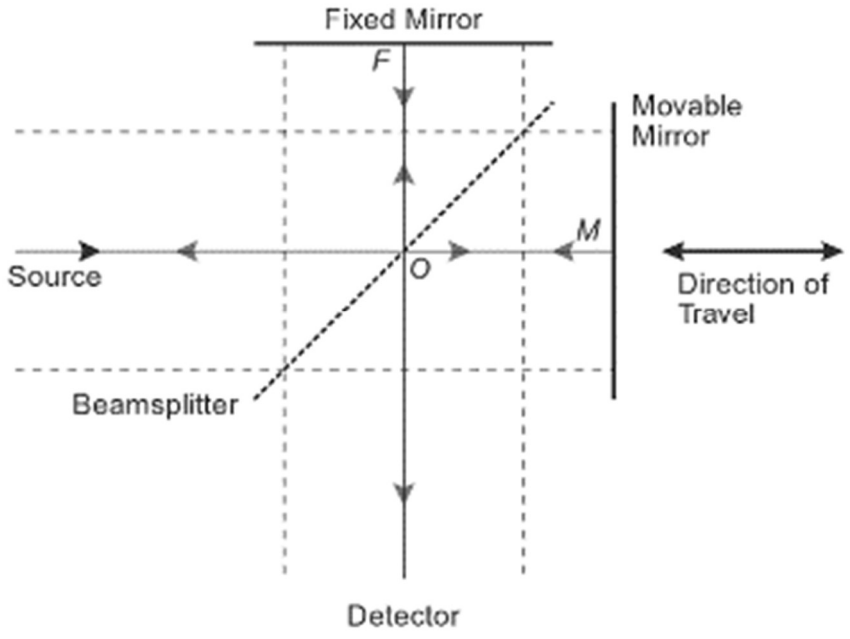


Figure 2.8: Michelson type interferometer, Griffiths et al., (2007).

The basic tool of FTIR measurements is an interferometer (**Figure 2.8**) similar to one designed by Michelson in 1891. The interferometer divides radiation beam into two and then recombines them after a path variance has been introduced. The beam splitter reflects a part of the beam onto the fixed mirror and transmits the remainder to the movable mirror. The spectral information is obtained from the variation of

intensities of the beam transitory to the detector and returning from an IR light source as a function of path variance, Griffiths and Haseth (2007)

Unlike non-dispersive instruments, the usage of Fourier-Transform InfraRed (FTIR) spectroscopy has many desirable advantages. Faster scanning, simultaneous determination of components, high sensitivity and speed are some of these advantages. The US Environmental Protection Agency (EPA) has even developed measurement protocols using the technique for air pollution monitoring (Chu et al., (1999). FTIR is used for both qualitative and quantitative purposes, to confirm or check the presence and amounts of unknown components in a variety of samples. To achieve the highest level of accuracy, quantitative analysis requires a spectral database for reference purpose. Some of the spectral database available include; US EPA library, High Resolution Transmission (HITRAN), cross section and infrared analysis. However, there are discrepancies that occur when these libraries are compared. More than 10% in differences have been observed in quantitative analysis of gases and the presence of impurity bands in spectra affects the correction of sample spectra, Chu et al., (1999), (EPA, 2017).

The metrology institute of America, National Institute of Standards and Technology (NIST), to overcome these challenges, developed their own spectral database, Chu et al., (1999). The database was developed based on the standard gas mixtures prepared by NIST and was obtained at 25 ^{o}C, and 1 atmospheric pressure (pressure broadened by nitrogen). The spectra were at 0.12 cm^{-1} resolution. Final absorption coefficients were corrected to 296 K and 1.013 x 10^{5} Pa using the ideal gas law. For calibration, the wavenumber scale was calibrated by moisture from 1200-1900 cm^{-1} and 3500-4000 cm^{-1} regions.

Background spectra is extracted in several ways depending on application. Valkova et al., (2011) evacuated the gas cell to pressures of approximately 10^{-5} and less when they used FTIR (Boomed MB 100 spectrometer) with a deuterated triglycine sulfate detector to assign the purity of source gases. Valkova et al., (2011) analysed carbon monoxide, carbon dioxide moisture and propane. Ultra-

high purity nitrogen gas is also flowed through the gas cell and the extracted spectra taken as background.

2.4.3.2 Challenges encountered in FTIR analyses

FTIR analysis of gases is also vulnerable to interferences. Carbon dioxide and moisture are two common interferences. The two molecules appear in broad bands of the infrared spectrum and their measurement is important to subtract their influence (effects) on the quantification of other components, Valkova et al., (2011) and Rothman et al., (2013).

A 2012 HITRAN compilation of the molecular absorption parameters at high resolution for moisture, carbon dioxide, carbon monoxide, methane, oxygen, nitric oxide, sulphur dioxide and other gases was compiled by Rothman et al. (2013). Here, there were also discrepancies associated with the HITRAN 2008 list and hence the evaluation of these differences. For example, a systematic error of 10-15% was observed for moisture lines in the range of 8000-9000 cm^{-1} using HITRAN 2008 for recent experiments. The measurement of complex gas mixtures is inherently difficult. The use of FTIR methods are susceptible to spectral overlap. Spectral overlap occurs when molecular structures of mixture components are closely similar. For example, both ethane and propane contain a $-CH_2$ group and their spectrums overlap when a gas mixture containing both species is analysed. However, there have been advances in algorithms for extraction of information from infrared spectra of complex multicomponent gas mixtures. Methods such as variable selection for multivariate calibration are also employed to determine the quantity of species that contain the same functional groups, Yu et al., (2011).

2.5 Stability of gas mixtures

The assurance of stability of any reference mixture is essential for long term monitoring purposes. To ensure stability of gas mixtures for a specified period of time, the mixtures are analysed over short intervals and then in three months, 6 months, 9 months etc. intervals (ISO Guide 34:2009). Stability testing is performed

to evaluate the behaviour of a component gas in a mixture. Three of the most critical factors that affects stability of gas mixtures are reactivity of component gases, impurities and total pressure of a mixture. For example, nitric oxide can react with the interior walls of the cylinder and other trace impurities in a mixture. Therefore, control of these impurities and precise gravimetric preparation is key to ensuring long term stability of components in any gas mixture, Chapman (1976).

To illustrate the way total pressure can affect the stability of a gas mixture, Miller et al., (2014) investigated the adsorption/desorption of carbon dioxide in aluminum chambers to evaluate the origin of carbon dioxide losses/gains. The study found that the concentration of carbon dioxide increases with a decrease in pressure. Therefore, an increase in pressure results in carbon dioxide loss.

Adsorption and desorption of reactive species also affect the stability of gas mixtures. Static mixing techniques introduce an error in sample mixtures containing nitrogen oxides and sulphur dioxide that readily adsorb on the surface of aluminum and stainless steel compressed cylinders. The quantity of loss of the component is dependent on the surface area of the cylinder and in a cylinder of specified dimensions, the % difference (error) in mole fraction increases as the concentration is reduced, Geiger and Raynor (2013). We can assume that the analysis of NOx and SO_2 molar fractions are inherently difficult at lower concentration levels and especially in complex mixtures.

Adsorption is an important subject in the studies of surface chemistry, and therefore chemistry of aluminum cylinder's interior surfaces is important. While monolayer adsorption on homogeneous surfaces has been extensively studied, and was described by Langmuir isotherm, multilayer adsorption had been challenging. Several models like the Frenkel-Halsey-Hill and Guggenheim-Anderson-de Boer however, have been proposed to explain the physical phenomenon. Adsorption on heterogenous surfaces and the approximation of adsorption of multicomponent gas mixtures is suggested to be difficult both theoretically and by experiment than the latter and former. However, an approximation model was developed that could describe the single component and multicomponent adsorption on homogenous surfaces and was extended to include heterogenous surfaces, Varreti et al., (2016).

2.6 Previous stack gas measurement key comparison

This section aims to compare the different methodologies used by various institutes for the CCQM K71. It is a critical source of literature for review of reference methods for improvements or successes in measurements of complex gas mixtures. Ten metrology institutes were involved in this key comparison that was coordinated by the Dutch institute

In general, gas chromatography was a more popular choice in the key comparison to analyse carbon monoxide, especially the use of flame ionization detection coupled with a methaniser. This choice however, was not available to the laboratory. The flame ionization detection coupled with a methaniser is used during routine analysis and to avoid deactivation of the methaniser by nitric oxide and sulphur dioxide this method was not exploited and it was still not exploited with this work. For the analysis of carbon dioxide, gas chromatography with thermal conductivity detection was the more popular choice, seconded by the use of non-dispersive infrared spectroscopy.

Chemiluminescence was preferred for the analysis of nitric oxide, followed by Fourier transform infrared spectroscopy. Ultraviolet fluorescence was used comparably with non-dispersive infrared/ultraviolet to measure sulphur dioxide in stack gas. In 2008-2011, the laboratory used UV fluorescence but non-dispersive ultraviolet spectroscopy was used in this work. The comparison is shown in results and discussion. The analysis of propane was performed exclusively by gas chromatography with flame ionization detection.

To reiterate the extent of the analytical challenges associated with stack gas measurement, the % relative deviations graphs are shown in **Annexure E** for all five components. A stack gas mixture, M93 7424, prepared by the coordinating laboratory was analysed by the laboratory, since the CCQM K71 was a value assignment comparison. The laboratory analysed C_3H_8 was by a gas chromatograph coupled with a Flame Ionization Detector (GC-FID). The separation was achieved by a 1.0m x 2.2 mm ID x 3.2 OD Molecular sieve 5A (40/60 mesh size) column at an oven temperature of 130 ºC. A helium carrier gas

at a pressure of 260 kPa. A sample volume of 2ml was injected, at a constant flow of 100 ml/min. The FID was set at 300 ºC. The significant difference of this method to the current one, is the choice of stationary phase and column pressures. On average, the measurement result was comparable with only one participant (VNIIM); the only two results furthest away from the reference value. However, the uncertainty associated with propane results was large for most participants.

The measurement of CO_2 achieved a less than 0.5% relative deviation from the reference value. However, the uncertainty needed to be reduced. A closer inspection of the graph however, reveals that compared to other laboratories, there existed a significant room of improvement in CO_2 measurements in stack gas. The measurement result of CO was off by 0.73% relative deviation from the reference value. Improvements in analytical methods and uncertainty reduction are critical following this key comparison. The measurement of NO was off by almost 1.0%. A significant relative deviation from any reference value. The results of sulphur dioxide were the most accurate by value assignment and the closest to the reference value compared to the other four components. The uncertainty however, can still be reduced

For calibration, NMISA reported all its measurements to have been performed using standard gas mixtures similar to the stack gas samples. Five other institutes used the same type of standards for measurement of carbon monoxide, however different analytical methods were used. These included non-dispersive infrared spectroscopy and gas chromatography flame ionization detector coupled with methaniser (GC-FID/meth), gas chromatography coupled with thermal conductivity detector and gas chromatography coupled with electron capture detector. The results of four of the above-mentioned participants were lower than the reference value compared with those using binary mixtures with GC-TCD/FID analytical system, suggesting that matrix has influence on the results.

Four institutes performed carbon dioxide analysis using matrix matched standards. These participants used gas chromatography with thermal conductivity detector and their results were lower than the reference value in comparison to those using single-component standard gas mixtures and the same analytical technique,

NMISA's result was higher than the reference value compared with the results of those of similar matrix (inconsistency) however similar to those using binary mixtures and the NDIR technique. The propane analysis was performed exclusively with gas chromatography coupled with flame ionisation detection for all the participants; six used stack gas measurement standards in which the results of four are higher compared to the two which are lower with comparison to reference values. In general, the results of the component are evenly spread and comparable, there is no suggestive evidence to suggest matrix effect. However other factors such as purity analysis of parent components, calibration methods and instrumental variation may have contributed to the differences.

Nitric oxide was measured by five participants using matrix matched standards, by two different techniques; Fourier Transform Infrared (FTIR) spectroscopy and Chemiluminescence detector (CLD). The results are evenly distributed even in comparison with those analysed using single-component standard gas mixtures. It is suggested that the analysis may have been affected similarly to propane. The analysis of sulphur dioxide gave results where five other participants used matrix matched with results evenly spread above and below the reference value, using three different techniques. The results of the participants using sulphur dioxide in nitrogen mixtures were lower with two different techniques, suggesting that matrix may have influence in the results.

The techniques used in the study above all have advantages and limitations. The analysis of some components using FTIR offers a wide spectrum of application where many infrared active components can be detected. However, it has limitations for hydrocarbon analysis because many of those absorb in similar regions (Tang et al., (2015). Moisture (H_2O) has absorption in many regions which inhibits the analysis of those components with single absorption region. Nitric oxide is analysed using NDUV where there could be synergistic effect due to sulphur dioxide and the chemiluminescent reaction chamber is poisoned by substantial amounts of carbon dioxide. Sulphur dioxide analysis using NDUV is prone to quenching effect by the presence of carbon dioxide. Leading expert participants mastered measurements of stack gas, however, the gas analysis

laboratory results were not satisfactory. There was a skill and understanding gap regarding complex gas mixtures such as stack gas. Therefore, the current project was initiated to improve the quantification of multicomponent gas mixtures at the highest metrological levels.

The literature shows that there are several ways that can be exhausted to produce highly accurate multicomponent gas mixtures. For preparation, the use of permeation tubes is the most accurate option for multicomponent mixtures up to parts per billion levels. However, these methods of preparation are not available to the laboratory and thus cannot be explored. Automated weighing systems can be used to minimise uncertainties associated with the static gravimetry method. This method could not be exploited as well since a new automated system was procured only after completion of this work. The design of the NDIR spectrometers in the laboratory also does not allow for moisture corrections or corrections of interferences from other gases. The use of multi-detectors was not available for all gases. The main gap identified in literature is comprehensive studies of stack mixtures and how they behave. There is no detailed literature on successful gravimetric preparation on these mixtures including automotive mixtures. Nor are there enough studies on analysis of these gases and all applied corrections and their algorithms. The lack of literature on how a combination of these gases behave, made this project very challenging. However, the methodologies followed by the CCQM K71 participants assisted in compiling a list of methods that work.

CHAPTER THREE – RESEARCH METHODOLOGY

The research methods and experimental design approach followed to conduct this work are described in this chapter.

3.1 Purity analysis

The highest pure source gases available were purchased from local and international gas manufacturers in various volumes. Upon receival, the pure gases were stored outside in a cage underneath an upper wall mounting to protect them from the harmful sun and rain. The effect of rain and the oxygen in the atmosphere rust, destroys cylinder exterior surfaces. Purity assignment was performed by use of a Varian CP-3800 gas chromatograph coupled with a thermal conductivity detector and a methaniser (Nickel/Zirconium catalyst) connected in series with a flame ionization detector, Van Rensburg (2007) shown on **Figure 3.1**. The GC TCD/FID (methaniser) system was used for the analysis of permanent gases (H_2, Ar/O_2, O_2) on the TCD by a molecular sieve column 13A (Restek). The measurement of hydrocarbons (CH_4, C_2H_6 etc.) was performed on the FID where the carbon-hydrogen bonds, Budiman et al., (2015), are burned in the air flame. The amounts of carbon monoxide and carbon dioxide as impurities in other pure gases are often very small and therefore, the sensitivity of the TCD is not high enough to detect the two gases. The methaniser in the presence of hydrogen converts the two gases into methane and then are detected on the FID. Porapak Q and Hayesep N were used to separate CO_2 and heavier hydrocarbons. Other measurements of permanent gases were performed on the gas chromatography – pulsed discharge helium ionization detector using capillary columns. The gas chromatograph system is shown in **Figure 3.2**. It is a 6-port valve configuration, with the sample loop connected at port 2 and 5. The gas sample was introduced into the inlet (port 3) and following its path past the capillary molecular sieve 13A column (Restek, USA) and the detector, it is vented out into the atmosphere from port 4.

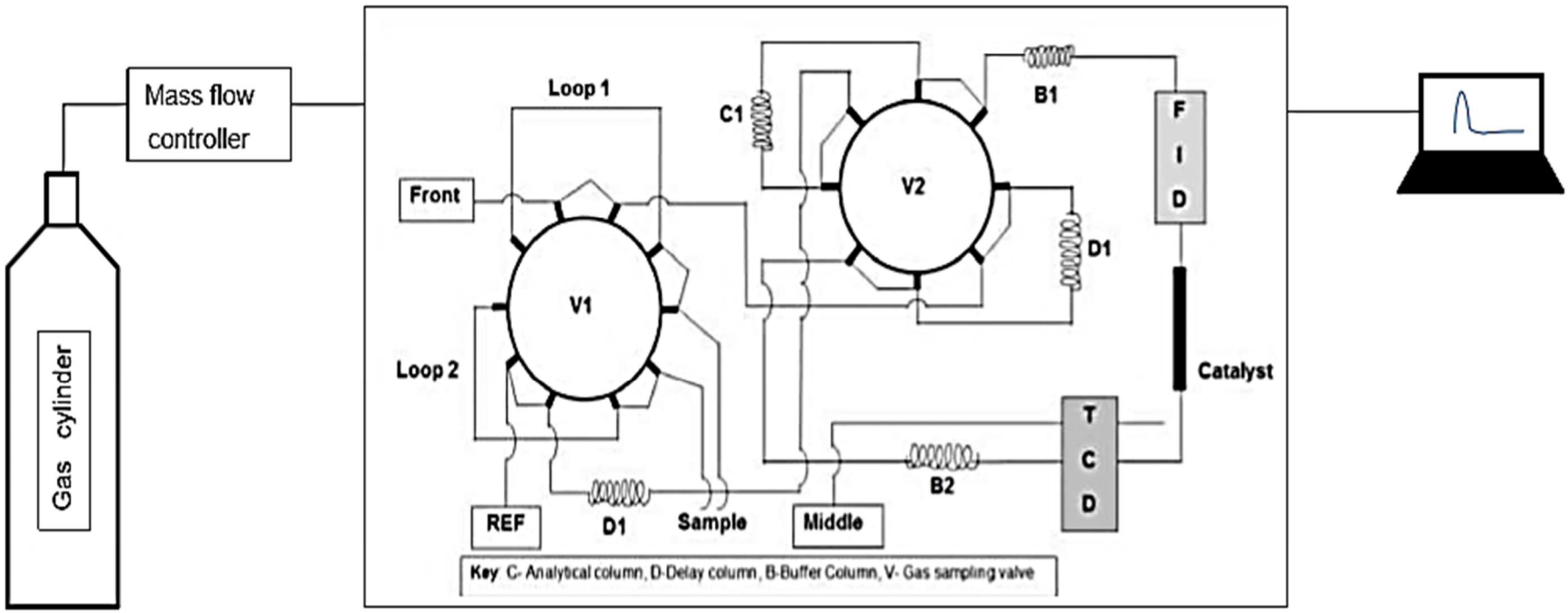


Figure 3.1: Configuration of the GC TCD/FID (methaniser) system used for purity analysis and propane measurement.

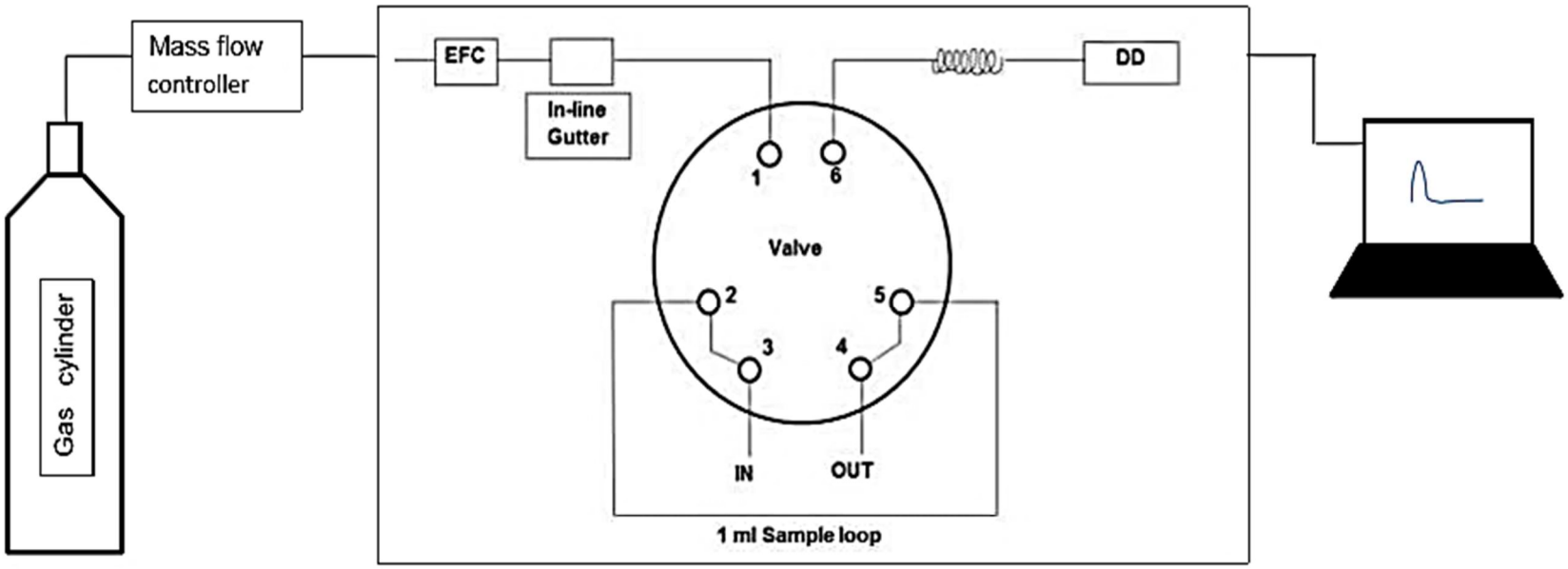


Figure 3.2: Gas chromatograph-pulsed discharge helium ionization detector system used for purity analysis.

3.2 Preparation of gas mixtures by gravimetry

ISO 6142-1:2015, for preparation of gas mixtures by gravimetry was used to prepare stack and automotive standard gas mixtures. The composition of these gases was expressed as μmol/mol. This molar expression can be changed to mg/m^3, Berezkin and Drugov (1991), a mass fraction unit. The principle of gravimetry is weighing of a mass of target gas added into a sample cylinder. Critical factors to be considered when a PRGM is prepared include; the volume of the cylinder (in litres), target pressures (kPa), pressures of pre-mixtures (Pa), a leak-free filling system, high sensitivity balances etc. These are important since a good preparation technique and analytical results often depend on them. This is especially true for complex multicomponent gases. For example, if cylinder *x* containing substance *c* with a pressure *y* is required to add *c* into cylinder *k* which already has contents *a* and *b*, the pressure of *x* should be high enough than the pressure of *k*. However, if it is comparable or low, a state of pressure equilibrium may be reached before the total mass of *c* is added. A lower mass of *c* will result in an erroneous concentration of *a*, *b* and *c* collectively. Consequently, an erroneous preparation and the mixture will be replaced.

Gravimetric preparation comprises evacuation, weighing, filling and homogenization. The evacuation of cylinders is necessary to remove residual gas and moisture and ensure no contaminants are left in the cylinder. To evacuate these, the cylinders were connected onto a turbo molecular pump and left until they reach $\leq 5.0 \times 10^{-6}$ Pa vacuum pressure. The vacuum was weighed using the substitution method using a tare cylinder to correct for buoyancy effects and air density variations, Milton et al., (2011). Pressure, relative humidity and temperature were monitored and recorded on the weighing sheet. The weighing system is shown below in **Figure 3.3** with its accompanying hanging balance.

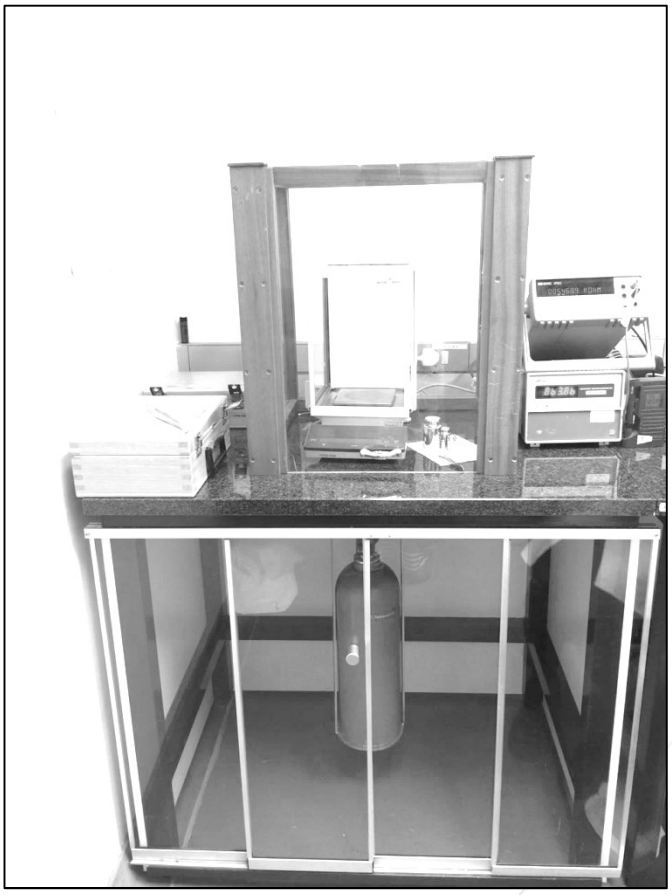


Figure 3.3: Mass comparator electronic balance used to weigh the cylinders during gravimetric preparation. Resolution = 1 mg and sensitivity = 1 g

To add a gas into a sample cylinder, both the pre-mixture and sample cylinders were connected on opposite sides of a special filling station shown by **Figure 3.4**. The gas lines were purged eight times to minimise any risk of cross-contaminations. A vent system is used to relive the pressure of the purging gas to the atmosphere. One of the most critical steps at this stage is leak checking. If there is a pressure drop in the station when a high pressure N_2 gas is within, it is often the direct result of a leak. Leak checks were performed by using a SNOOP solution. The presence of a leak is shown by foam bubbles in the connections where the leak is.

The mass of the added gas was determined as the difference between the mass of the empty cylinder and the mass at the subsequent weighing. During the preparation of stack gas mixtures, six weighing cycles of approximately 30 minutes each were performed for each mixture and five weighing cycles for each of the

eleven automotive gases. The weighing cycles alternate with the filling until all components are added into the sample cylinder. When the balance gas (N_2) is filled, the cylinders were left for a minimum of two hours to equilibrate to weighing room conditions. A mixture that is recently filled with nitrogen will be of a higher temperature than the tare and laboratory conditions. Therefore, it is left to settle to minimise effects of difference in air density and consequent inaccurate weighing, Milton et al., (2011). Following the weighing of the balance gas, the cylinders were rolled on a roller bench to homogenize contents of the mixtures.



Figure 3.4: Filling station in the gas analysis laboratory used for adding gas into the sample cylinder.

This gravimetric method was described in great detail by Milton et al., (2011) on "*Gravimetric methods for the preparation of standard gas mixtures*". The uncertainty of the gravimetry is also attributed to thermal effects and use of transfer containers.

3.3 Techniques used for the analysis of stack and automotive mixtures

The analyses of carbon monoxide, nitric oxide and sulphur dioxide were performed using non-dispersive infrared/ultraviolet spectroscopies. **Figure 3.5** shows a graphic depiction of the NDIR/UV spectrometers used for the analysis, Wong and Anderson (2012). The infrared/ultraviolet lamp, 1, is the source of the IR or UV light that travels to the gas chamber. The chopper wheel, filter and a pneumatic detector are represented by 2, 3 and 4 respectively. The NDIR/UV measurement technique is based on the chemical ability of gases to absorb IR or UV light.

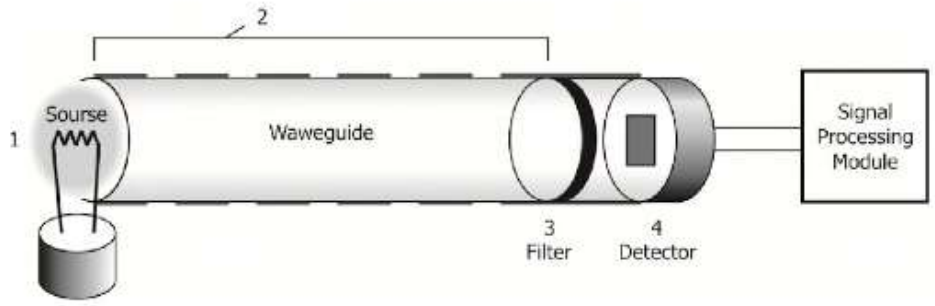


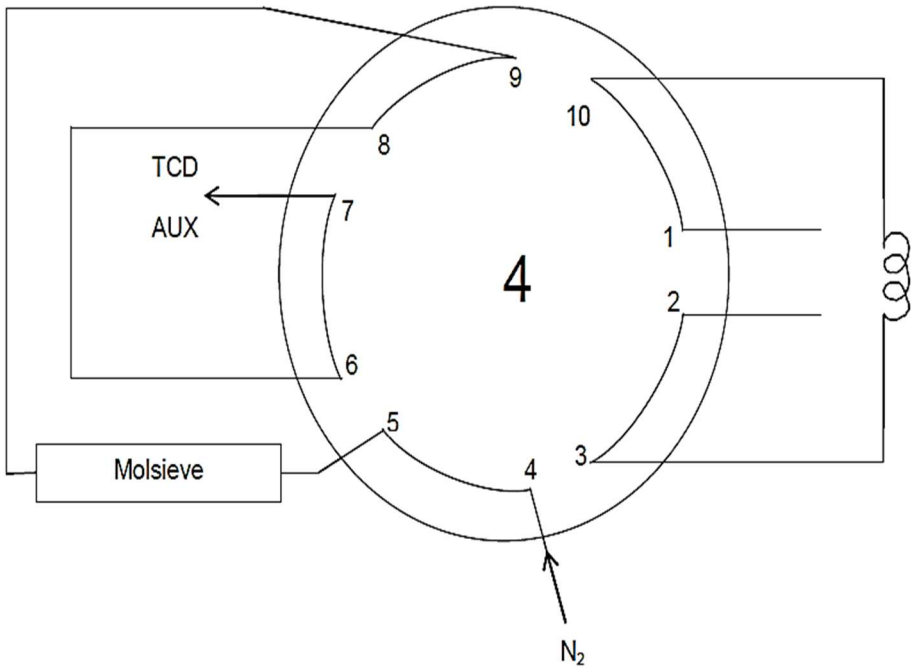
Figure 3.5: Simplified diagram of non-dispersive infrared or ultraviolet spectrometers, Wong and Anderson, (2012).

The cylinders were connected on the NDIR/UV spectrometers in the manner shown below in **Figure 3.6** in random positions. The analysis of propane was performed by a gas chromatograph shown on **Figure 3.1** using only the flame ionization detector. Carbon dioxide was also performed using non-dispersive infrared spectroscopy. However, for measurements of a PRGM, the CO_2 was analysed by gas chromatography as well. To evaluate the discrepancies by matrix effect, use of binary standard gas mixtures when measurements of stack gas are performed, the analysis results were compared with those of use by stack gas standard gas mixtures.



Figure 3.6: Non-dispersive ultraviolet analyser for nitric oxide measurement

For measurement of gas emissions from automotive industries, a multidimensional gas chromatograph (Agilent 7890, USA) was used to analyse oxygen, carbon monoxide, carbon dioxide and propone simultaneously. Its three different channels are shown In **Figures 3.7-3.9**.



*AUX auxiliary

Figure 3.7: Hydrogen channel of the multidimensional 7890B Agilent gas chromatograph

Shown by **Figure 3.7** is the auxiliary thermal conductivity detector which during analysis of automotive samples was configured to analyse hydrogen. The TCD was connected to a ten-port valve. The sample enters the instrument on port 1, goes through the sample loop and leaves the valve at port two. The carrier gas (nitrogen) enters the valve at port 4 and together with the injected sample passes through a molecular sieve 13x column (Agilent, USA) where hydrogen is separated and detected by the TCD. Valve 4 was switched off after four minutes and sample flow redirected to valves 1, 2, 3 and 5. On the next page is **Figure 3.8**, with the second thermal conductivity detector. This channel was used for the detection of other permanent gases beside hydrogen. The carrier gas for this configuration was hydrogen. To separate the oxygen/nitrogen peak, a different carrier gas was need to identify this peak in the chromatogram. Initially the oxygen/nitrogen peak was identified as one peak. To separate them, the temperature was lowered from 75ºC to 30ºC.

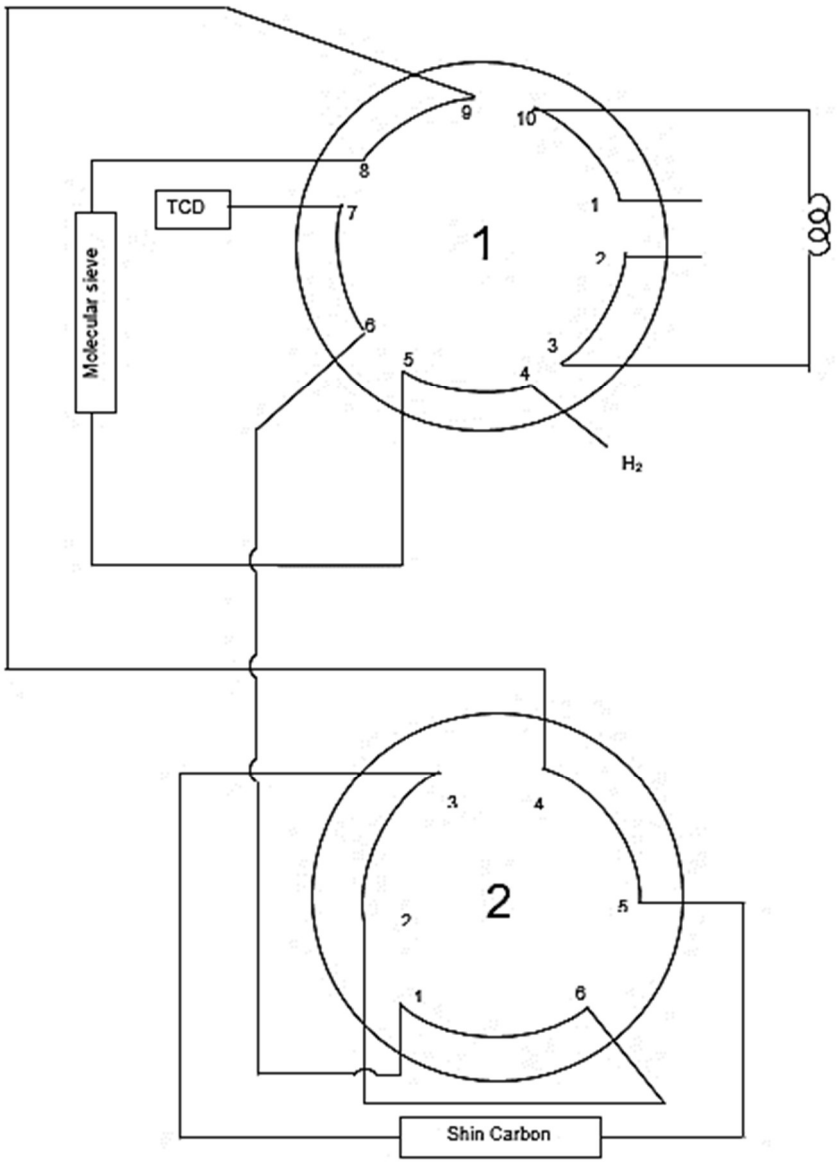


Figure 3.8: Permanent gas channel of the multidimensional 7890B Agilent gas chromatograph for oxygen, nitrogen, carbon monoxide and carbon dioxide.

The flame ionisation detector channel is comprised of two 6-port valves (**Figure 3.9).** The separation of propane was achieved by a HP-AL-KCL 50m length x 0.320 mm internal diameter PLOT column (Agilent, USA).

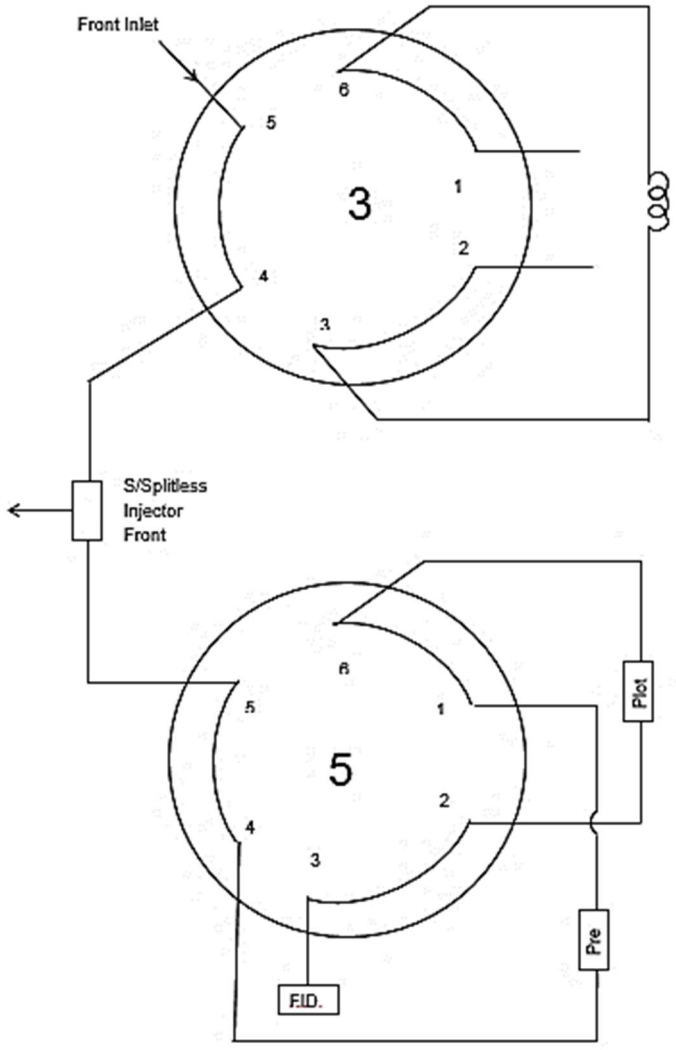


Figure 3.9: Flame ionisation channel of the 7890B Agilent gas chromatograph for propane measurement.

3.4 Stability evaluation

Stability testing was performed to evaluate the behavior of all the components in the stack gas and automotive mixtures. This is done by evaluating the comparability and precision of measurement results. A D-test from the ISO 16664:2004 was also applied to check for significant instability in components of stack mixtures. This ISO method provides guidelines on the handling of standard gas mixtures.

3.5 Internal uniformity of gas mixtures

The sensitivity ratio factors were used to evaluate the internal uniformity of the concentration of each component of automotive mixtures to specific reference gas mixtures.

3.6 Uncertainty calculations

To prepare primary reference gas mixtures of the highest metrological value by gravimetry, all uncertainty contributions, minor and major were identified and quantified. Large uncertainty contributions can be attributed to the weighing process, purity of starting materials and analysis. The XLgenline used for raw data manipulation and calculations used polynomial functions of the order two for regression analysis when non-linearity was assumed. It was also used for estimation of uncertainties for all stack components. An example of a polynomial function is shown below.

$$y = a\ ^2 + bx + c \qquad \textbf{3.1}$$

, where x is a solution and a, b and c are constants.

The uncertainty associated with weighing from **Figure 3.10** includes uncertainty in the resolution, and sensitivity of the weighing balance, its precision and pressure, temperature and relative humidity measurements. Other major uncertainty contributions include; the stability of the specific components in the mixture and their molar mass.

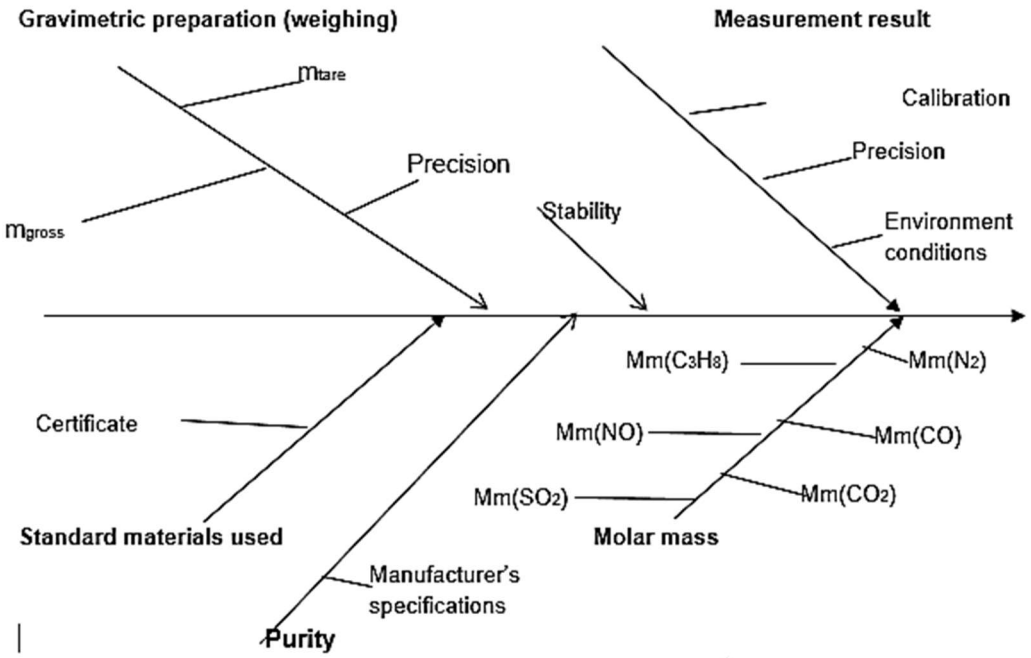


Figure 3.10: Fishbone diagram for uncertainty contributions associated with the preparation of gas mixtures by gravimetry.

3.7 Accuracy

Accuracy was determined by a measure of bias, also referred to as % difference or % relative deviation from the true value.

$$\%difference = \frac{|\mu_{grav} - x_i|}{\mu_{grav}} * 100 \qquad \textbf{3.2}$$

where μ_{grav} refers to the gravimetric mole fraction of a certain component and x_i refers to the calculated mole fraction.

3.8 Precision

% relative standard deviations were used as measures of precision.

$$\%RSD = \frac{\sigma}{\bar{x}} * 100 \qquad \textbf{3.3}$$

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

3.9 Linearity

The correlation coefficients of calibration curves were used to evaluate linearity.

3.10 Calibration models

Two types of calibration models were used; single point and multipoint calibration. For multipoint calibration, a polynomial calibration curve was used to calculate unknowns and for single point calibration the following equation was used.

$$C_{samp} = \frac{C_{ref}}{A_{ref}} * A_{sample} \quad \textbf{3.4}$$

, where C_{sample} refers to the concentration of the sample, C_{ref}, the concentration of the reference mixture, and A, the area peak.

CHAPTER FOUR – EXPERIMENTAL PROCEDURE

In this chapter, the experimental procedures of all analyses performed are outlined, together with all starting materials and instrumentation. It serves as a step-to-step archive of all processes followed for reproducibility purposes.

4.1 Starting materials

High pure gases Built-in-Purifier (BIP^{TM}) N_2 with a purity grade of 5.0, SO_2 (3.8), CO and CO_2 (4.7 and 4.5 respectively), C_3H_8 (3.5) and CH_4 (4.5) purchased from Air Products and Air liquide (South Africa), and NO from Mathenson TriGas (Japan) were used as starting materials for gravimetric preparation of all mixtures. Approximately 7 kg aluminum cylinders of 5 litres water capacity with a 30 000 kPa maximum pressure threshold from Luxfer (United Kingdom) were used as containers for the gas mixtures. Stainless steel tubing and regulators from Swagelok (United States of America) were used to make connections between cylinders and analytical instruments including those used for gravimetric preparation.

4.2 Analytical instrumentation

A Varian 3800 CP gas chromatograph was used for the analysis of carbon monoxide, carbon dioxide, hydrocarbons and purity analysis. Another gas chromatograph (Agilent 7890B, United States) was used for the analysis of the component gases of automotive reference gas mixtures. A PR 1003 mass comparator electronic balance with a sensitivity of 1g and resolution of 0.001 g from Mettler Toledo (Switzerland) was used to weigh sample and identical tare cylinders during gravimetric preparation. Mettler Toledo mass pieces were used to balance the weights of the two cylinders during a weighing cycle.

During the filling process, SB12001 electronic target balances with a sensitivity of 1 g and resolution of 0.001 g from the same manufacturer were used to target the amount of pre-mixture needed. The filling stations used consisted of a DCU 110 pressure indicator and an MVP 040-2 vacuum pump from Pfeiffer Vacuum

(Germany) with a special vent system to release the purging gas to the atmosphere. Two evacuation stations with internal turbo charge molecular pumps from Pfeiffer Vacuum were used to evacuate the cylinders before gravimetric preparation. Two Limas 11 non-dispersive ultraviolet spectroscopy measurement instruments from ABB (Germany) were used for nitric oxide and sulphur dioxide analyses and two Uras 26 non-dispersive infrared analysers from the same manufacturer for carbon monoxide and carbon dioxide.

4.3 Software used during gravimetry, analysis and for data processing

Even though manual calculations can be used following the ISO 6142-1:2015 method, software was used to estimate target masses and complemented by a spreadsheet tool developed by the laboratory since it is quicker. The NPL developed GravCalc Version 2.03.001 was used to estimate the amount of pre-mixtures and balance gas needed to get desired concentrations. A visual basic software (in-house developed) was used to control the weighing cycle while ABB data converter was used to retrieve raw data after analysis on the NDIR/NDUV instruments. The Xlgenline V1.1 was used to extrapolate linear calibration curves and retrieved results using a linear regression model. Lab view software replaced the ABB data converter V.1 however, these work similarly. The Agilent chemstation was used to control the analyses by the Agilent 7890B gas chromatography instrument.

4.4 Purity assessment

The purity of source gases was assigned by a Varian CP-3800 dual system gas chromatograph and GC-PDHID shown by **Figures 3.1** and **3.2**. The uncertainties were calculated by assuming a normal probability distribution. However, where a limit of detection approach and manufacturer specifications were used, rectangular distribution assumption was made.

$$LOD = 3 \times \frac{a}{H} \quad \textbf{4.1}$$

Limit of detection (LOD) is calculated by using signal-to-noise ratio (a) and the peak height (H). Standard gas mixtures (1µmol/mol $CO/CO_2/CH_4/C_2H_6$ in N_2 and $Ar/N_2/O_2$ in He) were prepared by gravimetry. Initially 1 µmol/mol mole fractions are used to check the impurities. When the amount of impurities was significantly lower, these PSGMs were diluted to 100 ppb mole fraction levels. These standard materials and source gases were connected randomly on the gas chromatograph. The sample flow rate was set at 100 ml/min. The lines were purged by venting the sample at-least three times. Different high pure gases of the same component have the same impurities but in different amounts. Therefore, a badge analysis is not always efficient. Where carbon monoxide, carbon dioxide, methane and ethane impurities may be present, the GC-FID with methaniser was used to determine the small impurities. For the analysis of oxygen, nitrogen and carbon dioxide, carbon monoxide and methane were analysed simultaneously. A 13x molecular sieve (45/60 mesh size) column was used. CO elutes at approximately 1.20 min and CH_4 slightly before that at 0.86 min. Temperature programming was employed where initially the oven was 50ºC for 2.50 min and increased to 150ºC at a rate of 50ºC/min and held for 5 min to push the peak of CH_4 closer to CO and reduce total run time. The FID was set at 300ºC.

For CO_2 and C_2H_6, a Porapak Q (3 m x 1/8-inch internal diameter, 80/100 mesh size packing material) column was used. CO_2 adsorbs on the molecular sieve packing material and hence could not be separated simultaneously with CO and CH_4. The FID was also set at 300 ºC. No temperature programming was applied. The oven was set at 100 ºC for 3 min. Argon, nitrogen, oxygen and hydrogen were separated using a 6-inch length x 1/8-inch inner dinner diameter molecular sieve 5A column with a 45/6 mesh size packing material. These were analysed on the TCD, at small oven temperatures of approximately 30ºC and TCD at 180ºC. For propane, nitrogen was analysed with an oven temperature of 120ºC and TCD at 190ºC. The analysis of nitrogen in sulphur dioxide and nitric oxide were performed on the GC-PDHID Varian CP-3800 by a molecular sieve 5A column.

4.5 Cylinder pre-treatment and handling

The cylinders were cleaned using paper towel, an acetone solution and a paint thinner to remove any dust particles or grease residue accumulating during storage. The cylinders were then connected to a turbo charge molecular pump and evacuated to very low pressures of ≤5.0 x10E-8 kPa, to remove any residual gas and moisture contamination. When the desired pressures were reached, the cylinders were disconnected and stored in the weighing room for them to reach the same environmental conditions (humidity and temperature) as an identical cylinder used for comparison during the weighing process. Identical cylinders were of the same manufacturer's specifications (shape, volume, etc.)

4.6 Balance calibration

Mass measurements were performed by a system consisting of; (1) a mass comparator electronic balance with a resolution of 0.001 g, a sensitivity of 1 g and a capacity of 10 kg, (2) an accompanying hanging balance that can support one cylinder and (3) a computer with a Visual Basic software to control the weighing process. The electronic balance sits in an isolated glass container to minimise negative effects of fluctuations and vibrations, Tshilongo et al., (2015).

4.7 Preparation of gas mixtures

Mass estimations were made by assuming ideal gas behaviour where the state of gas can be described using its temperature, volume and pressure. The ideal gas law is given by **Equation 4.2** below;

$$pv = n \qquad \textbf{4.2}$$

, where P is pressure of the gas in kPa, V is the volume of the occupied space in dcm^{-3}, n is the number of moles of gas in mol, R is the gas constant defined as R=

8.314 L kPa K^{-1} mol^{-1} and T is the temperature measured in Kelvin (K). This approximates the target masses of pre-mixtures to dilute in a balance gas

Empty sample cylinders were weighed by the substitution method and during each weighing process, the temperature (^{o}C), relative humidity (%r.h) and pressure (mbar) were recorded. After weighing the empty cylinders, the components of stack and automotive gas were added by using a filling station described in **section 3.2** and shown in **Figure 4.5**. The sample and pre-mixture cylinders were connected on opposite ends of the station. The filling station was purged several times (x8) with the pre-mixture before adding it to the sample cylinder. Purging cleans the system and remove any residual gas to avoid cross-contamination. After purging, the target balance was tared to zero at the target pressure prior to adding the component. When the balance reads zero, the pressure was released and the components were added.

$$P_{target} = \frac{C_{required}}{C_{premixture}} \text{ x } P_{required} \qquad \textbf{4.3}$$

After filling, the mass of the gas added is determined as a difference of the mass of the cylinder before and after filling. If the added mass was smaller or larger than desired, the mass of the major component (normally N_2) is re-calculated. When the balance gas has been added, the gas mixtures were left for a minimum of 2 hours to settle and for the mixtures to equilibrate to laboratory environment conditions. For a multicomponent mixture, filling and weighing alternates until the balance gas has been weighed. After weighing the last component, the gas mixtures were put on a roller bench for a minimum of 2 hours to homogenize the contents of the mixture. A typical production diagram is shown on **Figure 4.1**. The preparation was similar for all mixtures except for differences in number of dilution steps, pre-mixtures used and amounts of gas added.

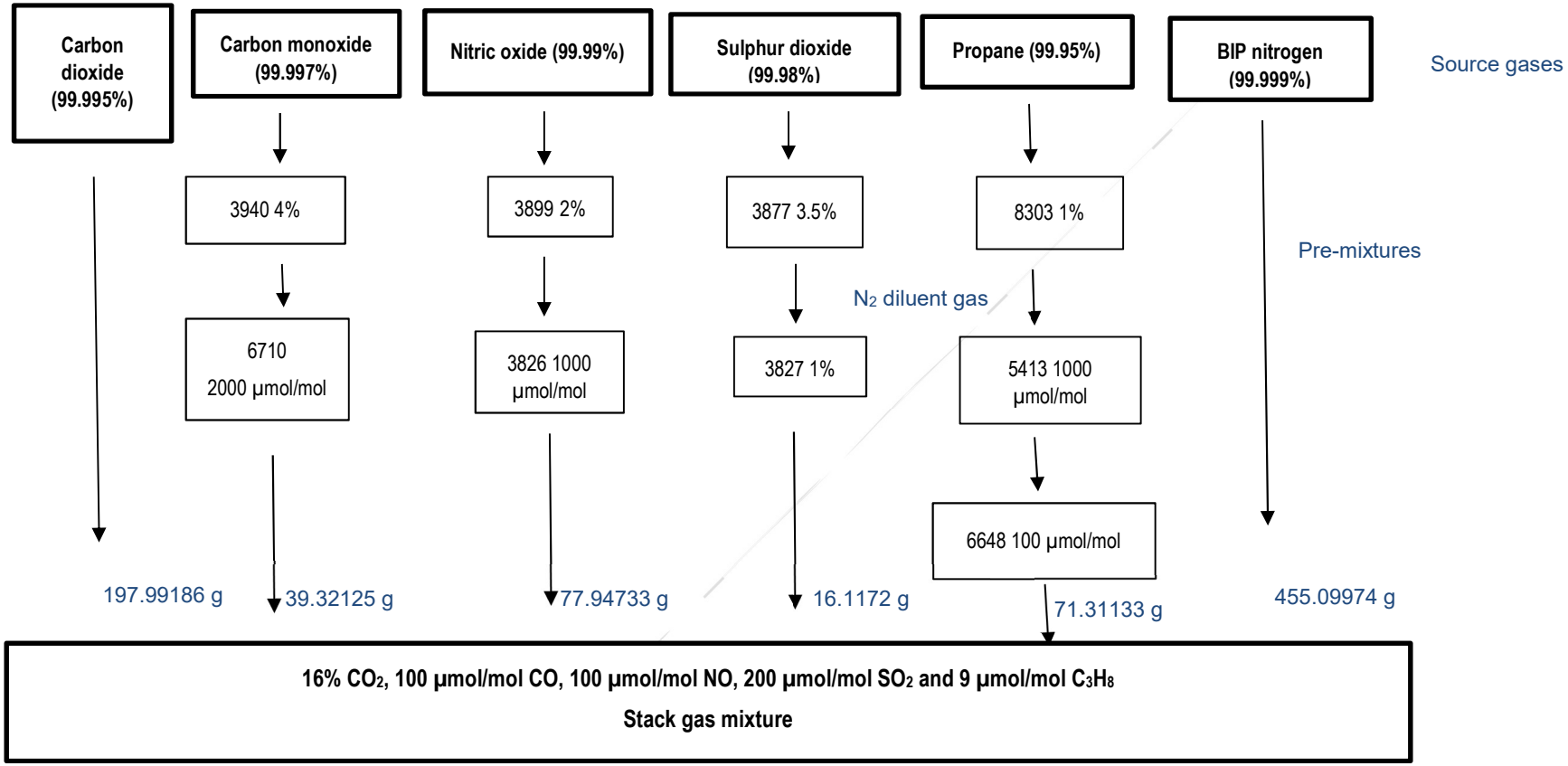


Figure 4.1: Production diagram of stack gas mixture 6633 from source gases to required composition. µmol/mol can be expressed as mg/m3

The cylinder was evacuated by a turbo molecular vacuum pump (**5.2**), and disconnected when the pressure was 5.0 x 10-8 kPa. The vacuum weighing was performed at the average temperature of 21.4ºC, 87 kPa average atmospheric pressure and a relative humidity of 51.4% r.h. Following purging of the gas filling system several times with high pure CO_2, 198 g of the gas was added to the mixture cylinder. At a slightly higher temperature of 21.5 ºC, 87 kPa and 56.4% r.h the first component was weighed. The CO_2 was followed by 39 g of CO and subsequent weighed at 22ºC, 86 kPa and 56% r.h. 78 g of NO was added and weighed at 22ºC, 86 kPa and 55% r.h. Then 16 g of SO_2 was added and weighed at 21ºC, 87 kPa and 52% rh. 71 g of C_3H_8 was added and weighed at 22ºC, 86 kPa and 54% r.h. Finally, 455 g of nitrogen was added and weighed at 21ºC, 86 kPa and 52% r.h. In average, the environmental conditions of the laboratory remained constant during the preparation of the gas mixture. Pressure and temperature affect the amount of gas in a constant volume according to the ideal gas law and these two factors need to be vigorously monitored. Relative humidity also affects preparation of gas mixtures by negatively affecting the weighing process. If the relative humidity is too high, the moisture adsorbs to the cylinder surface and its weight will be larger than is true. Therefore, resulting in errors during the weighing process. Purity tables showing the composition of the gas mixtures were obtained and are shown from **Table 6.2**. Composition was expressed in molar factions (µmol/mol) for this work. However, it can be expressed in mass fractions by using the following equation:

$$\frac{mg}{m^3} = \frac{\mu mol}{mol} \cdot \frac{M_i}{M_v} \qquad \textbf{4.4}$$

, where M_i is the molar mass of the gas and M_v its molar volume, Berezkin and Drugov (1991). To validate the gravimetric values, analyses were performed using different measurement techniques and analytical conditions. These are described shortly.

4.8 Non-dispersive infrared/ultraviolet spectroscopy measurements

Sample and standard gas mixtures were connected to a sampling box that is integrated onto the ABB Limas 11 and Uras 26 non-dispersive infrared and ultraviolet spectrometers. Prior to that, cylinders were purged several times to clean the stainless-steel valves. The Swagelok pressure regulators were connected to the valves to regulate sample pressure. Each cylinder was opened and closed three times to purge the sampling lines. A constant flow of gas was set by using a mass Bronkhorst flow controller (Netherlands). Just before any individual measurement was started, each mixture was checked to confirm whether analyser responses corresponds with expected values. Zero and span calibrations were performed to calibrate the measuring instrument. Nitrogen was used as zero gas. The analyses for each gas were performed separately. **Table 4.1** shows the analytical parameters. The analytical conditions were determined during prior method validations.

Table 4.1: Analytical conditions of the NDIR/UV measurements for carbon monoxide, carbon dioxide, sulphur dioxide and nitric oxide.

Gas component	Sample time(s)	cycles	No. of sample readings	No. of pressure readings	Sample flow
CO	60	3	30	30	100
CO_2	30	3	30	30	200
NO	30	4	60	30	250
SO_2	30	4	60	30	250

4.9 One-point calibration method for propane and carbon dioxide

To measure carbon dioxide and propane of the stack gas primary reference gas mixture for a company X from the air pollution monitoring framework, a Varian CP-3800 gas chromatograph coupled with flame ionization (methaniser) and thermal conductivity detection systems similar to the one shown in **Figure 3.1** was used. A 3-m x 1/8-inch inner diameter, 80/100 mesh size of packing material Porapak Q column was used for separation. The column was set at 150ºC oven

temperature with front column pressure at 240 kPa at and middle column pressure at 250 kPa both at 100 ml/min flow. The thermal conductivity detector for carbon dioxide detection was set at 175ºC and flame ionization detector for propane at 300ºC. A 20 µl sample loop was used, with a constant sample flow of 100 ml/min. Seven injections were made. These results were obtained by using only matrix matched PSGMs and one-point calibration.

4.10 Automotive mixtures' measurements

These mixtures were also purged several times before connecting to the spectrometer to remove any contaminants on the opening of the valve. Then pressure regulators were connected. The regulators were purged several times too by opening and closing the cylinder valve. For this experiment, the mixtures were connected one at a time and analysed following the method below:

The gas chromatograph coupled with three detectors (two TCDs and one FID) shown in **Figures 3.7, 3.8 and 3.9**, was used to analyse the CO_2/CO/C_3H_8/O_2 components in N_2 samples. O_2, CO and CO_2 were detected by the front TCD, and C_3H_8 on the FID. The sample was injected and loaded at 0.5 min. The oven temperature was set at 30°C at an equilibration time of 0.1 min. The maximum oven operating temperature is 250°C. The temperature programming was set at 30°C initial temperature for 2 min for light eluents, and increased to 85°C for 3 min at 30°C/min for the more retained eluents to elute quicker and shorten the run time to 6.833 min. From the second experiment, this was shortened to 6.003 min.

The spilt-spilt less inlet was heated to 150°C, at a pressure of 87.824 kPa, total flow of 23.927 ml/min and a standard septum purge flow at 3 ml/min. the split ratio was 5:1 at 17.44 ml/min flow.

On the front TCD a 13x molecular sieve column of 80/100 packing material size and 1 m x 1.00 mm internal diameter and a Shin Carbon ST 100/120 mesh size column were connected. A Helium (He) carrier gas at a 30°C oven was connected and running at 5 ml/min flow and 102.9 kPa. Before the auxiliary TCD, another molecular sieve column of the same dimensions was connected, with Heat 5

ml/min flow at 115.5 kPa pressure. On the back-FID channel, a 50-m x 320 µm x 8 µm PLOT was connected and H_2 set at 3.4879 ml/min flow, 87.824 kPa pressure, 55.132 cm/sec average velocity and 1.5115 min hold up time.

The mass flow controller was set at 30 ml for first experiment and 40 ml/min for other experiments. The permanent gas and H2 channels used 100 µl sample loops and 1ml for the FID channel. 1000 µl of sample is injected.

The front TCD was heated to 175°C, with the reference and make up flow at 10 and 5 ml/min flows respectively. The auxiliary TCD was heated to the same temperature, same make up flow but a 15 ml/min reference flow. The FID was set at the same temperature with 400 ml/min air flow, 30 ml/min H_2 fuel flow and 25 ml/min make up flow (N_2).

A supplement analysis was made to compare the TCD and FID for automotive measurement capability. **Table 4.2** shows the experimental conditions of the measurements of carbon monoxide and carbon dioxide in automotive mixtures on the Varian 3800. The supplement work was performed to evaluate differences in accuracy and precision of the two methods.

Table 4.2: Analytical conditions for CO and CO_2-in-automotive mixtures using Varian CP-3800 GC FID

Varian CP 3800 GC chromatograph	**CO_2**	**CO**
Column:	Porapak Q 80/100 mesh	Molecular sieve 5A
Column oven:	150°C	same
Column pressure:	Front at 240 kPa at 100 ml/min	same
	Middle at 150 kPa at 100 ml/min	same
Detectors:	TCD at 175°C, FID at 300°C and methaniser at 380°C	same
Sample loop:	100 µl	same
Sample flow:	100 ml/min	same
Injections:	7	Same
Run time:	3 min	7 min
Carrier gas	Helium	Same
Flame gas	Synthetic air	same

4.11 Proficiency testing scheme

The carbon monoxide measurement was performed using the 7890B Agilent micro electron capture and flame ionization detectors gas chromatograph with the following conditions. The mixtures were purged several times and then connected to pressure regulators. The regulators were also purged to remove residual air and contaminants. The mixtures were then connected to the sample lines of the gas chromatographs. The measurements of oxygen and carbon dioxide were performed separately as shown on **Table 4.3**. The oxygen was separated by a molecular sieve stationary phase and a Shin Carbon was used to separate the carbon dioxide from the matrix.

Table 4.3: Analytical conditions for the automotive emission proficiency testing scheme's mixtures

	CO_2 and O_2 (RGA with 2x TCD and FID)	CO (Micro electron capture detector GC)
Column:	1 m x 1.00 internal diameter 13x molecular sieve and Shin Carbon ST	2 m Shin Carbon ST
Column oven:	35°C for 4.5 min and 30°C/min rate to 85°C for 4 min 5 ml/min column flow	100°C
Detectors:	Front and Aux TCD at 175°C	FID at 300°C
Sample loop:	250 µl	2 ml
Sample flow:	40 ml/min helium carrier gas	35 ml/min (carrier gas N_2) 87.5 ml/min MFC
Injections:	7	7
Run time:	10.2	4.5 min
Gases	Front (Reference flow 10 ml/min and make up (H_2) at 5 ml/min) Aux (reference flow at 15 ml/min and make up (H_2) as 10 ml/min	H_2 (40 ml/min), Air (450 ml/min) and make up (9ml/min)

CHAPTER FIVE - PURITY ASSIGNMENT AND GRAVIMETRIC PREPARATION

In this chapter, the results of purity analysis and the composition of the prepared gas mixtures are presented. The mole fraction quantities in µmol/mol are reported along with associated uncertainties for all stack and automotive gas mixtures.

5.1Preface

Impurities expected in the high pure N_2 gas were O_2, H_2O, CO, CO_2 and CH_4. By assuming a rectangular distribution and using manufacturer's specifications, the high pure nitrogen was estimated to be ≥99.99% pure. Expected impurities in CO_2 were oxygen, moisture and hydrocarbons according to specifications. Estimating the purity at a 100% and subtracting the sum of all impurities, yielded a purity of ≥ 99.99%. Other air composition constituents such as argon and hydrogen are expected impurities in high pure carbon monoxide. These impurities also include oxygen, nitrogen, moisture and hydrocarbons. The argon impurity was expected to be higher than the others. The purity of carbon monoxide was estimated at ≥99.99%.

Moisture, oxygen, carbon dioxide, hydrogen and nitrogen were expected impurities in high pure propane. However, there were no hydrocarbon impurities expected. The purity of propane was estimated to be ≥99.99%. The expected impurities in nitric oxide were nitrous oxide, nitrogen, carbon dioxide and moisture. These impurities were present in very large quantities, significantly reducing the purity of high pure nitric oxide. The concentration of moisture, though not very large, may result in the formation of aerosols. The purity was estimated at ≥99.89%.

Generally, there was an O_2, N_2 and H_2O impurity in most high pure gases. These may result from production processes but also owes to their presence in the atmosphere as major air constituents. Significant impurities in sulphur dioxide

were sulphur trioxide, moisture and non-volatile residues. The amount of moisture may result in the formation of sulphuric acid, another impurity.

5.2 Purity assignment by gas chromatography

Table 5.1 shows the results of high pure carbon dioxide purity analysis. The purity analysis was performed by using the gas chromatograph shown in **Figure 3.1**. The nitrogen impurity was the largest at 364 µmol/mol. However, comparison with specifications assumes that there should not be a nitrogen impurity in high pure CO_2 or it is not a critical impurity. The results contradict the specifications. The uncertainties associated with the amount impurity of argon, nitrogen, carbon monoxide, methane and hydrogen were calculated as type A uncertainties (normal/Gaussian distribution). The impurity of high pure CO_2 (cylinder 280695) was estimated to be ≥ 99.96%.

The differences in the presence and amount of nitrogen, including the purity of carbon dioxide of cylinder 280695 shows discrepancies in the purity of gases reported by manufacturers. The Ar impurity was 0.09 µmol/mol, CO 0.19 µmol/mol, CH_4 20 µmol/mol, C_2H_6 0.01 µmol and H_2 0.66 µmol/mol. The purity of different gas mixtures of the same component is also not always similar. Same manufacturer and production process does not equal similar amount of impurity. Therefore, batch analysis for the gravimetric preparation of primary reference gas mixtures is not advised. Below (**Tables 5.2 and 5.3**) are other high pure carbon dioxide cylinders. These were analysed using similar methods as cylinder 280695. However, the amount of specific impurities was not the same.

For example, the amount of nitrogen in cylinder 09122 is 472 µmol/mol and 823 µmol/mol in APL1002961. The amount of methane is 10 and 4.3 µmol/mol respectively. The total purity was also different. The purity of 09122 was estimated at ≥99.95% and only ≥99.91% for APL1002961.

Table 5.1: Purity table of carbon dioxide (gas chromatography)

Component	Analysis Value (µmol/mol)	Distribution	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol)	Expanded Uncertainty (µmol/mol)
Ar	0.09	Normal	0.09	0.01	0.01
N_2	363.6	Normal	363.6	18	36
CO	0.19	Normal	0.19	0.03	0.06
CH_4	21	Normal	21	3.1	6.3
C_2H_6	<0.01	Type B rectangular	0.006	0.003	0.01
H_2O	<0.05	Type B rectangular	0.03	0.02	0.03
H_2	0.66	Normal	0.66	0.03	0.07
		Total impurities	385.4		
			0.9996	18	37
CO_2		**%mol/mol**	**99.9614564243**	**0.00184**	**0.004**

Table 5.2: Purity table of carbon dioxide (gas chromatography)

CO_2 09122 purity table					
Component	**Analysis Value (µmol/mol)**	**Distribution**	**Mole fraction (µmol/mol)**	**Standard Uncertainty (µmol/mol)**	**Expanded Uncertainty (µmol/mol)**
Ar	0.24	Normal	0.24	0.01	0.02
N_2	472.9	Normal	472.9	23.6	47
CO	0.05	Normal	0.05	0.01	0.01
CH_4	10.1	Normal	10.1	1.5	3.0
C_2H_6	<0.01	Type B rectangular	0.01	0.003	0.01
H_2O	<0.05	Type B rectangular	0.01	0.01	0.0
H_2	0.06	Normal	0.06	0.003	0.01
		Total impurities	483.4		
			0.9995	**23**	**47**
CO_2		**% mol/mol**	**99.9516646207**	**0.002**	**0.01**

Table 5.3: Purity table of carbon dioxide (gas chromatography)

CO_2 APL1002961 purity table					
Component	**Analysis Value (µmol/mol)**	**Distribution**	**Mole fraction (µmol/mol)**	**Standard Uncertainty (µmol/mol)**	**Expanded Uncertainty (µmol/mol)**
Ar	0.22	Normal	0.22	0.01	0.02
N_2	823.4	Normal	823.4	41	82
CO	<0.04	Type B rectangular	0.02	0.01	0.03
CH_4	4.3	Normal	4.23	0.64	1.3
C_2H_6	<0.01	Type B rectangular	0.01	0.003	0.01
H_2O	<0.05	Type B rectangular	0.03	0.02	0.03
H_2	0.04	Normal	0.04	0.002	0.004
		Total impurities	828.0		
			0.9992	**41**	**82**
CO2		**% mol/mol**	**99.9171997282**	**0.00412**	**0.01**

Table 5.4: Purity analysis of oxygen

O_2 UHP purity table					
Component	**Analysis Value (µmol/mol)**	**Distribution**	**Mole fraction (µmol/mol)**	**Standard Uncertainty (µmol/mol)**	**Expanded Uncertainty (µmol/mol)**
N_2	No separation				
CO	0.20	Normal	0.20	0.03	0.06
CO_2	0.23	Normal	0.23	0.04	0.07
CH_4	<0.01	Type B rectangular	0.01	0.003	0.01
C2H6	<0.01	Type B rectangular	0.01	0.003	0.01
H_2O	Not analyzed	Type B rectangular	0.01	0.006	0.01
		Total impurities	0.45		
			1.0000	**0.05**	**0.09**
O2		**% mol/mol**	**99.9999548000**	**0.00000**	**0.000**

Table 5.5: Purity table of nitrogen

BIP N_2 purity table 3166101						
Component	**Specifications**	**Analysis Value (µmol/mol)**	**Distribution**	**Mole fraction (µmol/mol)**	**Standard Uncertainty (µmol/mol)**	**Expanded Uncertainty (µmol/mol)**
Ar	Not specified	54.99154594	Normal	54.99155	2.750	5.499
CO	<0,025		Type B rectangular	0.01750	0.010	0.020207
CO_2	<0,025		Normal	<0,025	0.005	0.009
CH_4	<0,013		Type B rectangular	0.00650	0.004	0.008
C_2H_6	<0,010		Type B rectangular	0.00500	0.003	0.006
C_2H_6	<0,010		Type B rectangular	0.00500	0.003	0.006
O_2	<0,01		Type B rectangular	0.00500	0.003	0.006
H_2O	<0,02		Type B rectangular	0.01000	0.006	0.012
H_2	<1		Type B rectangular	0.50000	0.289	0.577
			Total impurities	55.541		
				0.9999	**2.765**	**5.529**
N_2			**% mol/mol**	**99.9944459454**	**0.00028**	**0.001**

There was no separation achieved of nitrogen from oxygen in the purity analysis of high pure oxygen. When a matrix gas is separated before an analyte, the peak is hardly resolved. Therefore, the amount of the nitrogen impurity was not reported. Other gases were present in very small amount in high pure oxygen. The results are reported in **Table 5.4.** The argon impurity was the largest in high pure nitrogen. Other impurities were present in very tiny amounts.

5.3 Summary - preparation

Carbon dioxide liquid condensation during gravimetric preparation is a challenging phenomenon. CO_2 is a permanent gas however at very high pressures it is condensed into a liquid. If the gas is filled at a higher pressure or too quickly into a sample mixture cylinder, the steel tubing will show frozen liquid on the outside, an indication of the condensed CO_2. This is not a desired effect because the condensation may result in loss of mole fraction of the CO_2. A change in mole fraction of CO_2 will effect change in other components, resulting in an inaccurate and erroneous gravimetric preparation. There is also uncertainty of the time required for the liquid CO_2 to become gas phase and form a homogeneous mixture.

In total, ten stack gas mixtures were prepared by the ISO 6142-1 gravimetric method. See **annexures A and B** for production diagrams which details the dilution steps, pre-mixtures and target masses. There are many analytical, if not mathematical challenges, associated with producing a multicomponent gas mixture, and those can be attributed to atmospheric chemistry, cross interferences, chemical properties of individual target gases (for example, reactivity) and their purity. For example, depending on the purity, the addition of an x amount of carbon monoxide gas effects a change in carbon dioxide gas mole fraction. **Table 5.6a** shows how an estimated 53.8 g carbon monoxide from a pre-mixture will be required to prepare approximately 60 µmol/mol of the gas in a multicomponent mixture containing carbon dioxide.

Table 5.6a: Multicomponent mixture's target mass estimations from an in-house developed spreadsheet.

CO	CO	0.99991	28.0109	0.9991	100.0
m=	53.8	g p=	9.34 bar		
	premixture	(%n/n) or µmol/mol			
	CO_2	120951.6			
	CO	59.6			
	O_2	100878.1			
	N_2	778044.6			

In **Table 5.6b**, 55 g of CO has been added. Notice how the CO_2 concentration decreased by with an increase in CO. Accurate preparation techniques must be employed to ensure accurate preparation of the desired mole fractions. Therefore, adding the target mass accurately is very critical.

Table 5.6b: Change in mixture's mole fractions

CO	CO	0.99991	28.0109	0.9991	100.0
m=	55.0	g p=	9.34 bar		
	premixture	(%n/n) or µmol/mol			
	CO_2	120753.7			
	CO	60.8			
	O_2	100713.1			
	N_2	778406.2			

5.4 Stack gas mixtures

The composition of the stack gas mixtures is shown by **Tables 5.7** and **5.8**.

Table 5.7: Composition of the gravimetrically prepared stack mixtures

Amount of impurity (µmol/mol)							
Component	**Mixture (cylinder number)**						
	6633	6634	M9 3885	M9 3878	M9 3970	M51 8141	M51 8268
H_2	0.43	0.44	0.46	0.41	0.45	0.44	0.35
O_2	0.41	0.33	0.24	0.46	0.29	0.30	0.36
N_2	839088	869360	906773	819005	887317	879853	858436
Ar	71	76	79	72	78	50	53
HC	0.41	0.33	0.24	0.45	0.29	0.30	0.36
CH_4	0.006	0.006	0.006	0.005	0.006	0.002	0.003
C_2H_6	0.005	0.005	0.006	0.005	0.005	0.002	0.004
C_3H_6 (propene)	0.0009	0.0005	0.0008	0.0007	0.0006	0.0002	0.0004
C_3H_8	**9.1**	**5.1**	**8.3**	**7.1**	**5.8**	**2.2**	**4.4**
CO	**100**	**41**	**20**	**30**	**10**	**40**	**81**
CO_2	**160423**	**131418**	**92955**	**180823**	**112496**	**120011**	**141189**
H_20	0.33	0.27	0.20	0.37	0.24	0.25	0.29
N_2O	0.001	0.0006	0.0009	0.0002	0.0002	0.0003	0.001
NO	**99**	**41**	**60**	**10**	**10**	**20**	**81**
NO_2	0.001	0.0006	0.0009	0.0002	0.0002	0.0003	0.001
SO_2	**201**	**56**	**101**	**50**	**80**	**20**	**152**
SO_3	0.005	0.001	0.003	0.001	0.002	0.0005	0.004

*6633 composition determined by GravCalc not ISO 6142 software.

The impurities of stack gas mixtures include H_2, O_2, N_2, Ar and CH_4; major constituents of air composition. Whereas their presence as impurities was expected, their concentrations are very small and almost negligible with the exception of Ar. However, Ar is not problematic owing to its noble gas characteristics. An undesirable impurity is often larger amounts of oxygen which

react with NO and SO_2 to form nitrogen dioxide and sulphur trioxide respectively. Another is the impurity of water vapour which results in aerosol formation when it interacts chemically with NO and SO_2. The amounts of individual impurities are relatively equal across the first five mixtures, with few exceptions for M51 8141 and M51 8268 especially for Ar, CH_4, C_2H_6 and C_3H_6.

Table 5.8: Composition of the gravimetrically prepared stack mixtures: Stack PRGM for company X.

Component	**Amount of impurity (µmol/mol)**		
	Mixture (cylinder)		
	M51 8260	M51 9528	M51 8173
H_2	0.43	0.43	0.41
O_2	0.31	0.31	0.44
N_2	878334	878086	827012
Ar	78	77	70
HC	0.33	0.33	0.46
CH_4	0.006	0.006	0.007
C_2H_6	0.01	0.01	0.02
C_3H_6 (propene)	0.006	0.006	0.009
C_3H_8	**60**	**60**	**86**
CO	**60**	**90**	**63**
CO_2	**120461**	**120679**	**172105**
H_20	0.26	0.26	0.36
N_2O	0.006	0.006	0.0009
NO	**402**	**402**	**60**
NO_2	0.006	0.006	0.0009
SO_2	**602**	**601**	**599**
SO_3	0.02	0.02	0.02

Three reference gas mixtures were prepared to provide an air pollution monitoring consultancy company with a stack gas PRGM. The composition of the three

mixtures is shown above in **Table 5.8.** The preparation of M51 8173 was not very accurate compared to the other two with respect to the concentrations of C_3H_8, CO and CO_2, whilst M51 9528's concentration of CO was higher. M51 8260 was well prepared. The composition tables suggested that the impurities of these stack gas mixtures are the same independent of differences in concentrations when **Tables 5.7** and **5.8** were compared. The presence of O_2 and H_2O is very little to have any significant effect.

5.5 Automotive gas mixtures

In total, eleven automotive samples were prepared by gravimetry in the proposed nominal fraction range of CCQM.K3-2018 (tentative date); an upcoming international key comparison.

Carbon monoxide 0.5 – 2 %mol/mol

Carbon dioxide 2-5 %mol/mol

Propane 100-300 µmol/mol

Oxygen 1-4 %mol/mol

The composition of these standard gas mixtures is tabulated in **Tables 5.9** and **5.10**.

Table 5.9: Composition of automotive mixtures analysed using A-B-A substitution method

Component	**Amount of impurity (µmol/mol)**				
	Mixture (Cylinder number) M51				
	8269	9512	8091	8183	8186
H_2	0.55	0.57	0.55	0.55	0.55
O_2	**30051**	**30001**	**29355**	**30028**	**29940**
N_2	920037	919554	916676	919758	919907
Ar	81	81	81	81	81
HC	0.09	0.10	0.10	0.09	0.09
CH_4	0.008	0.008	0.008	0.008	0.008
C_2H_6	0.01	0.02	0.01	0.01	0.01
C_3H_6 (propene)	0.01	0.01	0.01	0.01	0.01
C_3H_8	**100**	**97**	**99**	**100**	**100**
CO	**19824**	**19963**	**23525**	**20069**	**19977**
CO_2	**29903**	**30299**	**30260**	**29960**	**29992**
H_20	0.13	0.13	0.13	0.13	0.13

The first five mixtures that were prepared have almost similar concentrations for use of the substitution method for calibration. The impurities are largely the constituents of air composition, some C1-C3 hydrocarbons and moisture. The amounts of these impurities are the same for the five mixtures, and this suggests a purely similar matrix as intended.

An interesting trend is shown by **Table 5.10.** The amount of impurities, H_2 and Ar, decrease with an increase in O_2 mole fraction and consequent decrease in N_2. Hence, the H_2 and Ar impurities are not the same throughout these mixtures. The moisture impurity presence is not significant.

Table 5.10: Composition of automotive mixtures analysed using multipoint calibration.

Component	**Amount of impurity (µmol/mol)**					
	Mixture (Cylinder number) M51					
	9535	8156	8158	9517	8121	8193
H_2	0.58	0.47	0.46	0.46	0.60	0.45
O_2	**9832**	**24805**	**31037**	**36947**	**14883**	**40506**
N_2	964866	928688	915169	899893	958679	888339
Ar	61	56	56	51	63	51
HC	0.06	0.09	0.10	0.11	0.06	0.13
CH_4	0.004	0.02	0.02	0.02	0.004	0.03
C_2H_6	0.02	0.01	0.01	0.02	0.02	0.03
C_3H_6 (propene)	0.01	0.02	0.02	0.02	0.01	0.03
C_3H_8	**120**	**180**	**200**	**250**	**148**	**300**
CO	**5000**	**11071**	**14765**	**17452**	**6084**	**20283**
CO_2	**20118**	**35198**	**38771**	**45404**	**20138**	**50519**
H_20	0.07	0.12	0.14	0.16	0.07	0.18

CHAPTER SIX – STACK GAS MEASUREMENT

In this chapter, the results for the validation of gravimetric values, stability and any improvements or need for it are reported. Each component of stack gas is presented separately from **6.1**. A stack gas PRGM's results using a different calibration method are reported as well.

6.1 Carbon dioxide in stack gas

6.1.1 Accuracy and linearity

Table 6.1: Relative deviation results of CO_2 by NDIR: matrix matched

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	% difference	% REU
6634	131418.1	5.0	131889.2	0.36	0.5
M9 3885	92955.4	5.9	93134.0	0.19	0.8
M9 3970	112496.8	3.8	112697.9	0.18	0.4
M51 8268	141189.8	14.3	141572.6	-0.27	0.4
M51 8141	120011.7	7.7	120184.5	0.14	0.5

*Xi gravimetric/reference mole fraction

U(xi) uncertainty of Xi

REU Relative expanded uncertainty

The results of carbon dioxide are shown in **Table 6.1**. In the nominal fraction range of 100 – 160 mmol/mol, the concentration of CO_2 was determined with relative deviations from the reference value (gravimetric) of 0.4% and less. The measurement of CO_2 in stack gas by the NDIR method using CO_2/stack gas PSGMs can be considered an accurate method fit for purpose. The uncertainty associated with the measurement at 95.45% level of confidence, coverage factor (k) of 2 and infinite degrees of freedom, is at 0.5% and less. However, this observation excludes the measurement of M9 3885. From the three measurements performed, it is suggested that the uncertainty of a CO_2 measurement decreases with each subsequent analysis. Repeated measurements (see stability graphs) also increased the precision and accuracy of results.

Table 6.2: Relative deviation results of CO_2 by NDIR: CO_2/N_2 PSGMs

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	%difference	% REU
6634	131418.1	5.0	131715.3	0.23	0.5
M9 3885	92955.4	5.9	93134.4	0.19	1.3
M9 3878	180823.0	5.1	180937.1	0.06	0.6
6633	160423.5	12.5	160440.9	0.01	0.5
M9 3970	112496.8	3.8	112675.0	0.16	0.7
M51 8268	141189.8	14.3	131230.9	0.02	0.4
M51 8141	120011.7	7.7	120026.9	0.01	0.6

Using single component PSGMs, the results in **Table 6.2** above shows that % relative deviations of 0.2% and less were achieved at expanded uncertainties of 1.3% and less. The accuracy observed in this method was better compared to results from **Table 6.1**. Therefore, we can assume that the use of CO_2/N_2 standard gas mixtures has a comparable accuracy to matrix matched standard materials representative of samples. The matrix effect here is negligible. The larger concentration of CO_2 is not affected by lower concentrations of possible interferents such as NO, SO_2 and CO absorbing in the mid-infrared wavelength.

To evaluate the linearity of the measurement and whether the measurement absorption is linear or not, the calibration curves of the first measurements are presented. **Figures 6.1** and **6.2** follow.

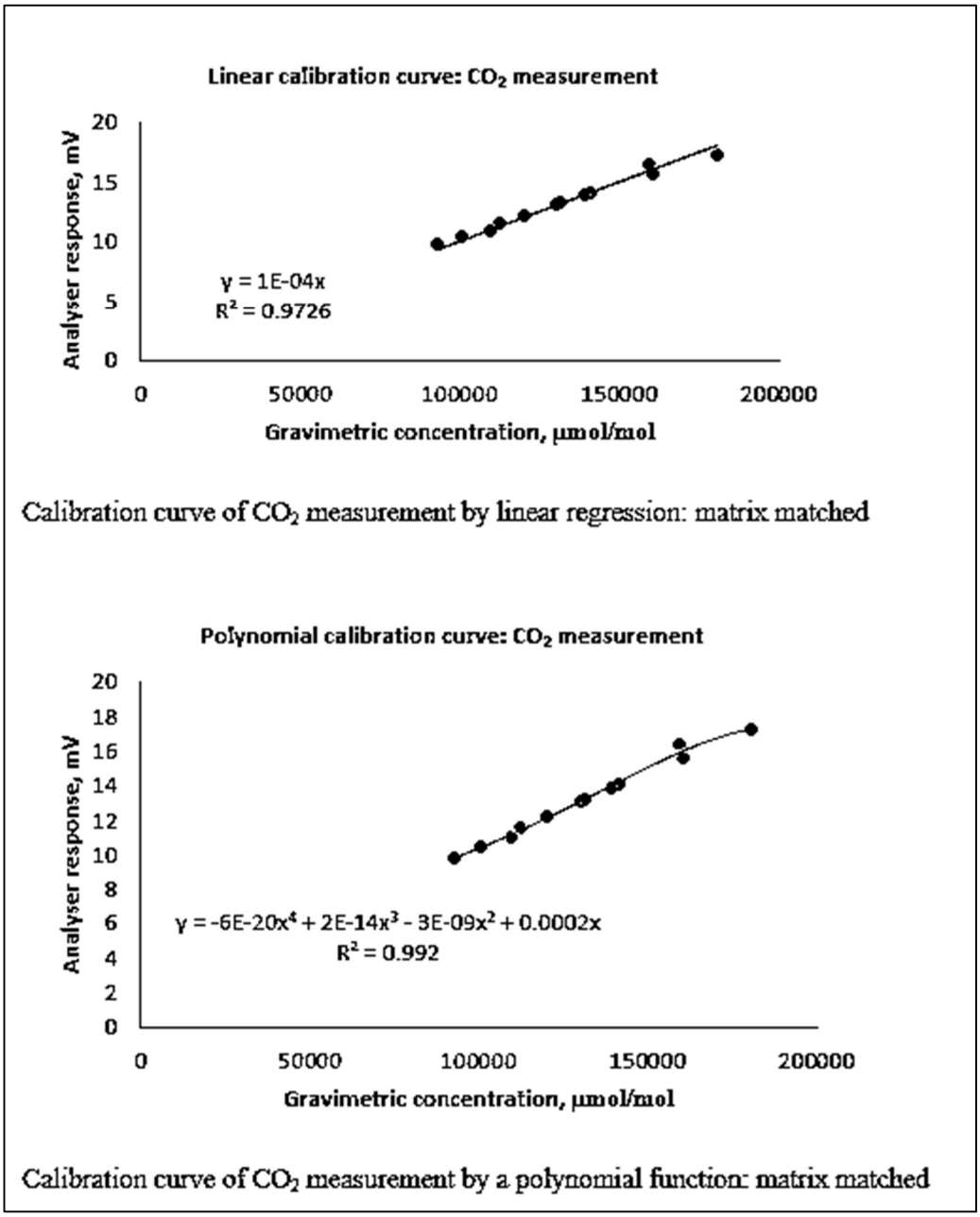


Figure 6.1: Linear and polynomial calibration curves of CO_2 measurement when multicomponent stack mixtures were used for calibration

The calibration curves shown by **Figure 6.1**, indicate that the absorption of CO_2 of a stack gas mixture is non-linear. The correlation coefficient (R^2) of the polynomial function is larger than the linear fit. Therefore, the measurement of CO_2 in stack gas is best described by polynomial functions of the order of four (4). The

following two figures evaluates if the same conclusion is similar for use of CO_2/N_2 standard gas mixtures.

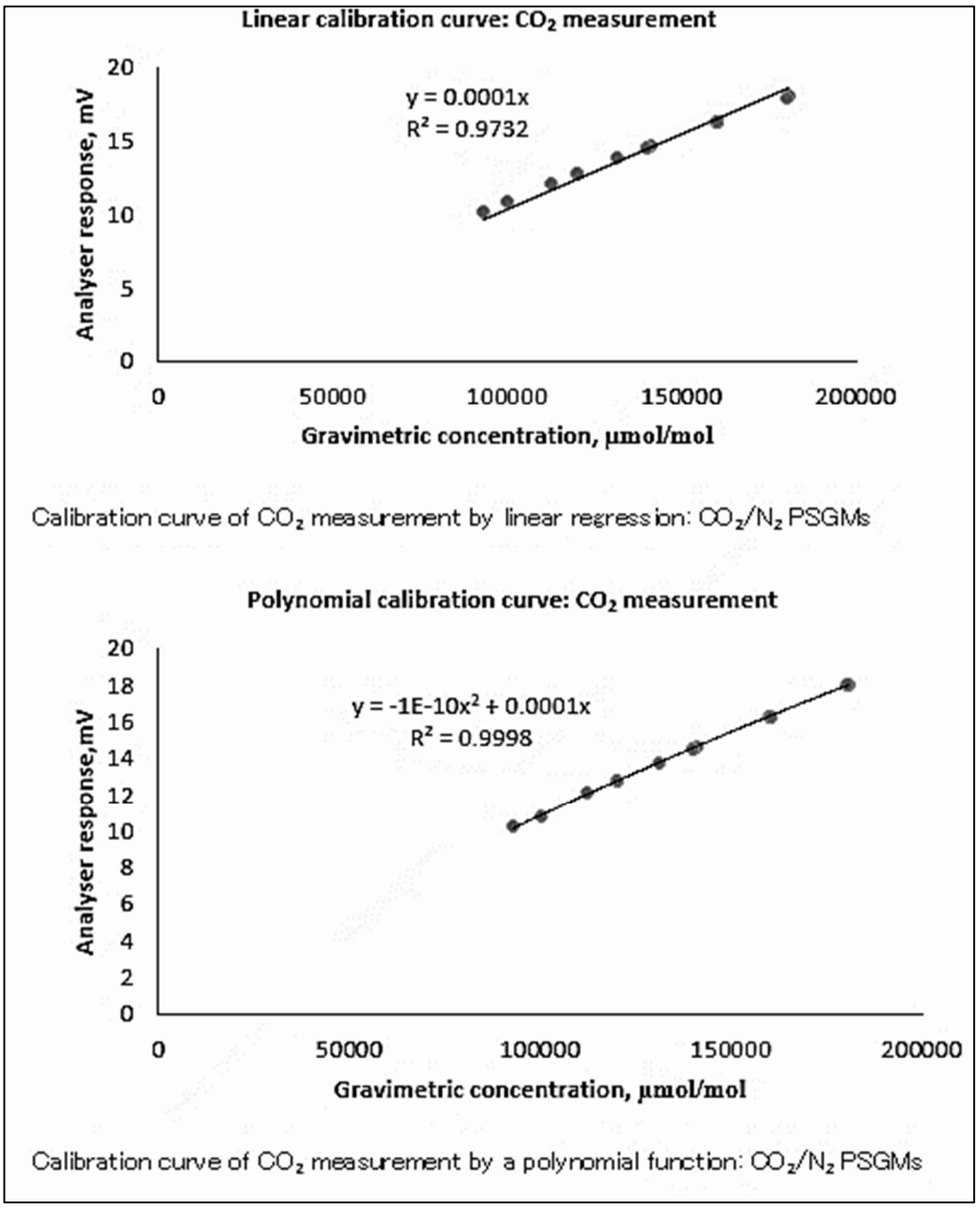


Figure 6.2: Linear and polynomial calibration curves of CO_2 measurement when CO_2 in N_2 mixtures were used for calibration

The absorption of CO_2 in a stack gas mixture is less non-linear than when the sample is a binary mixture of CO_2 in N_2. The correlation coefficients of the CO_2-in-N_2 standard gas mixtures' method are larger than the matrix matched method. However, a polynomial function of order two (2) is more preferred to describe the measurement equation over a linear regression model for the binary method. In

general, the results of CO_2 indicate non-linear absorption. However, results by linear regression models are not inaccurate and are within a 1% accepted relative deviation from the reference values. Matrix effect is also negligible in this nominal fraction range for the measurements of CO_2 in stack gas.

6.1.2 Comparison to CCQM K71 - improvements

Using the new stack gas standards, the old standard gas mixtures used for the analysis of the CCQM K71 sample were analysed to check if the new methods will result in a better accuracy. These gas mixtures were D19 4921 and D19 4899. There are problems inherent to this analysis of over eight-years stack gas among them; stability, pressure effects and chemical reactions. At higher mole fraction however, the stability can be assured for a longer period. However, some significant instability can exist when the sample is a complex gas mixture like stack gas as shown below.

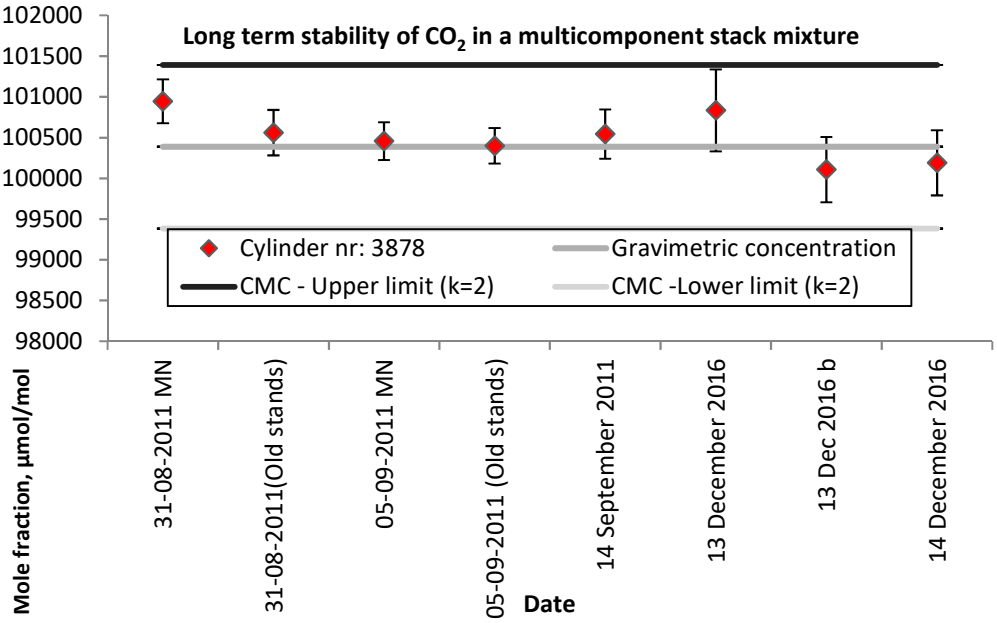


Figure 6.3: Stability graph of a CCQM K71 standard - D19 4899 comparing the stability of CO_2 in 2011 and 2016.

Stability of a mixture is often assured by analysing it more than three times and comparing the variation of the calculated mole fractions. The first and second

measurements may display instability as shown from **Figure 6.3** from analyses performed in 2011 and 2016. This plot also shows that a stack gas reference mixture can be used over an 8-year period (prepared in 2008) to still measure emissions. There was no statistically significant difference ($p > 0.5$) between the results obtained at the various times. A cost-effective tool and economical.

To evaluate whether there were significant improvements of measurements of stack gas by the project to the previous study, the results of the same mole fraction are presented below. The error bars represent the uncertainties associated with analysis. **Table E1** presents the measurement equivalence of the laboratory to other leading institutes. Out of other participants, the laboratory was only better than two other laboratories. There was a 0.17% relative deviation from the results reported by the laboratory from the reference value. The same analytical method was used to measure CO_2 in stack gas of sample M93 7424.

Table 6.3: Improvements in CO_2-in-stack gas measurements

Mixture	Gravimetric mole fraction (µmol/mol)	U(gravimetry) (µmol/mol)	Determined (analysis) (µmol/mol)	U(analysis)(µmol/mol)	% Difference
M9 3970	120011.7	7.7	120184.5	528.4	**-0.14**
M93 7424	119970	12	120170	120.0	**0.17**

A measurement of sample M9 3970 at 120 mmol/mol saw a % relative deviation from the reference value of 0.14% as shown by **Table 6.3**. The improvement made was not large, but nonetheless a significant difference in the increase of accuracy to measure CO_2 in stack gas. The accuracy to measure CO_2 in stack gas was improved. The associated uncertainty was also reduced. **Table 6.3** compares the results of M93 7424 from a previous study of 2008 and measurements of M9 3970 (2016). The measurements shown here are of the matrix matching method.

6.1.3 Short-term stability of CO_2-in-stack gas

The stability graph is a plot to assist in visualizing the behaviour of a component in a mixture of gas over a period of time. The green line represents the gravimetric mole fraction and red and blue lines, the upper and lower limits of the mole fraction (1% relative).

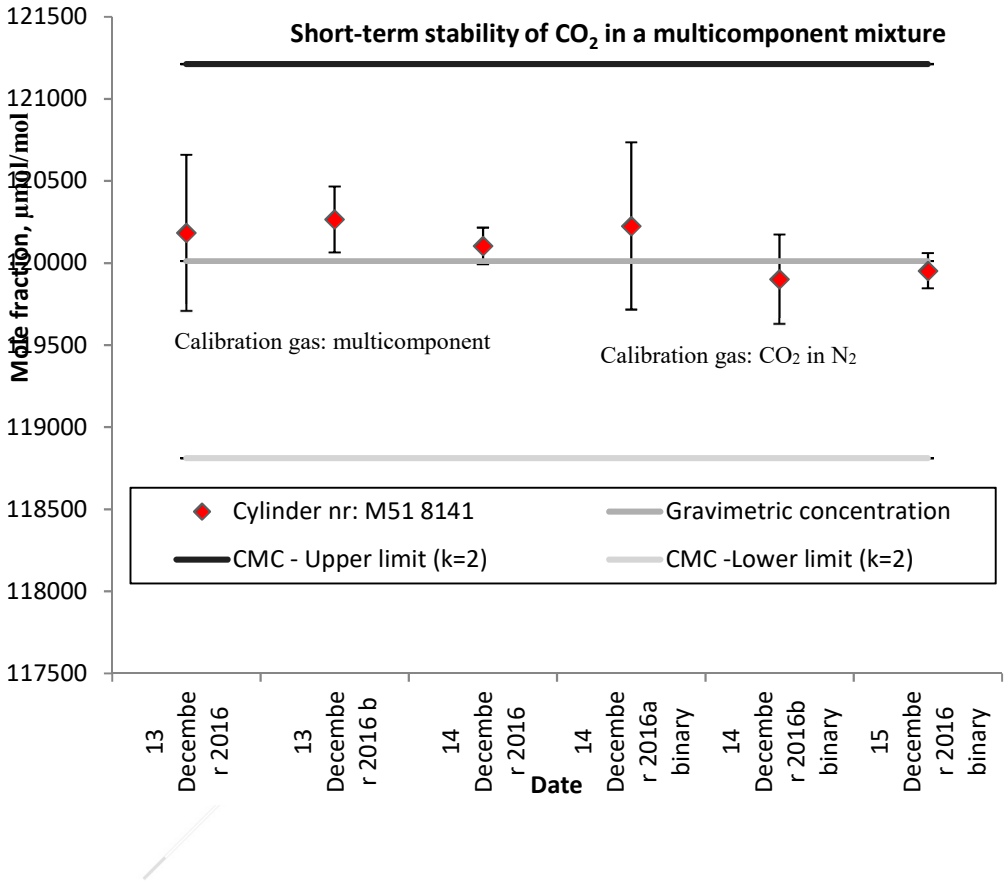


Figure 6.4: CO_2 stability graph of sample M51 8141 comparing stability attained from calibration by binary and multicomponent gas mixtures.

The stability of CO_2 is sufficient as shown by **Figures 6.4** and **6.5**, the measurement results are gathered around the reference value. Six measurements were performed by using the two different methods (matrix matching and CO_2/N_2 PSGMs). The results also show that repeated measurements will bring results closer to the reference value.

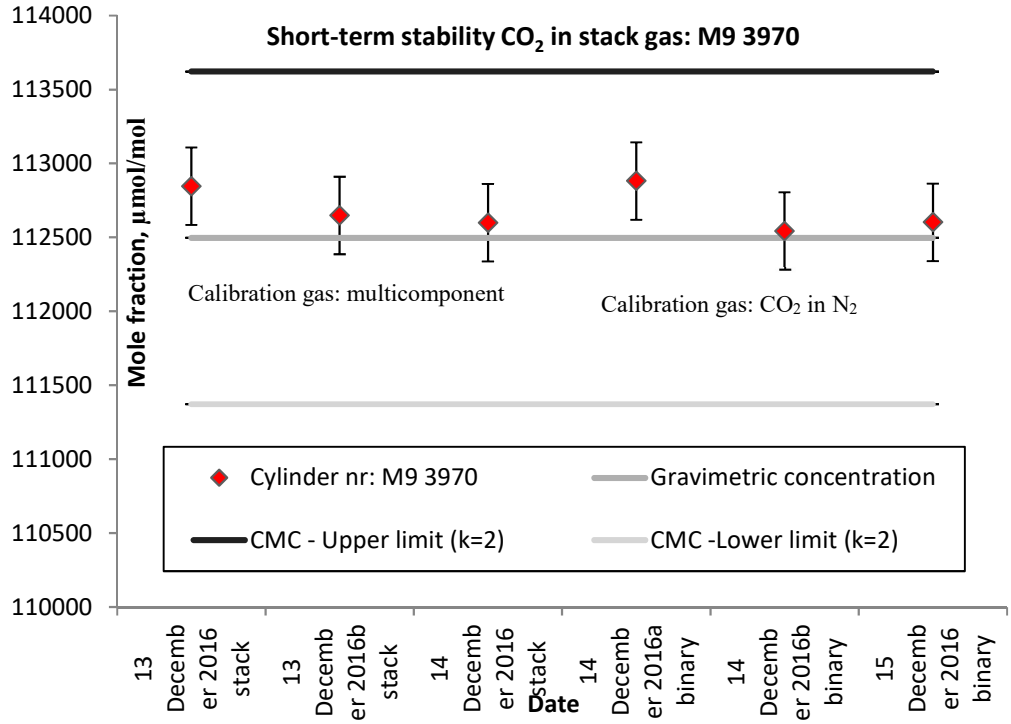


Figure 6.5: CO_2 stability graph for M9 3970 comparing stability attained from calibration by binary and multicomponent gas mixtures.

The stability of CO_2 in stack gas mixture M9 3970 was determined to be satisfactory. However, there is an indication of a slight positive bias in the measurement results. The stability of components can also be checked by following the ISO 16664: 2004 guideline for stability. Assume x_0 is the first measurement with its standard uncertainty $u(x_0)$, and x_1 is the measurement following x_0 with its uncertainty $u(x_1)$. Then the stability is determined by calculating the D test using the following equation;

$$D = \frac{|x_0 - x_1|}{\sqrt{u^2(x_0) + u^2(x_1)}} \qquad \textbf{7.1}$$

If $D \leq 2$ no significant instability

If D is greater than 2 there is significant instability. **Table 6.4** confirms that no significant instability was observed for carbon dioxide in the stack gas samples.

Table 6.4: Statistical D test results for stability assurance – carbon dioxide in stack gas

	STACK GAS MIXTURES													
	6633		6634		M9 3885		M9 3878		M9 3970		M51 8141		M51 8268	
Measurements	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2
D (binary)	0.19	0.34	0.53	0.90	0.43	0.01	0.10	0.04	0.59	0.16	0.56	0.18	0.72	0.75
D (matrix match)	-	-	0.67	0.46	0.44	0.21	-	-	0.63	0.24	0.16	0.70	0.60	0.69

* x_0 first analysis

x_1 second analysis

x_2 third analysis

6.2 Propane in stack gas

6.2.1 Accuracy and linearity

The measurement of C_3H_8 was performed on the GC-FID/TCD system shown on **Figure 3.1** by using matrix matched standard gas mixtures only. However, special focus was placed on the improvements of C_3H_8 analysis from the previous study.

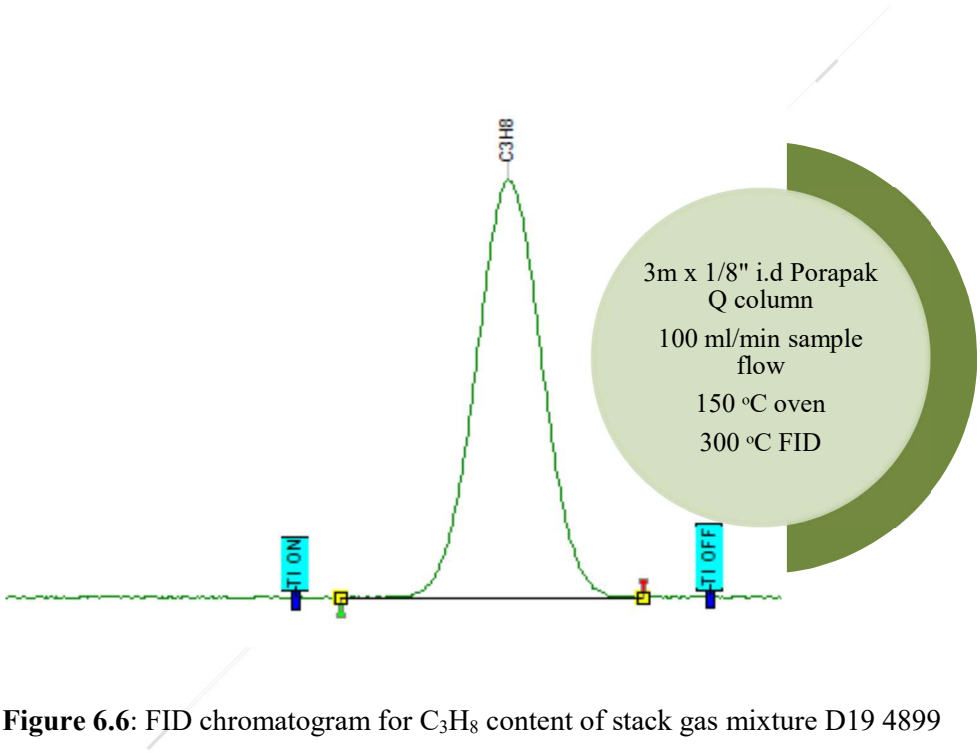


Figure 6.6: FID chromatogram for C_3H_8 content of stack gas mixture D19 4899

A chromatogram of one of the standards used during the CCQM K71 is shown in **Figure 6.6** where a Porapak Q column was used to separate the propane and FID used to detect its signal. The nominal fraction range of propane in this work was 1-10 µmol/mol. Lower levels are inherently difficult to prepare and analyse. However, the analysis of these samples was simple. Using the method described in **Chapter 4.9**, the separation of the propane was very good from the rest of the eluents. No tailing or peak broadening were observed.

Table 6.5: Relative deviation results of C_3H_8 by GC FID: matrix matched

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	%difference	%REU
M9 3885	8.3	0.005	8.4	0.89	1.00
M9 3970	5.840	0.003	5.843	0.05	0.51
M51 8268	4.37	0.004	4.42	1.2	**51**
M51 8141	2.20	0.002	2.21	0.33	0.91

Table 6.5 presents the accuracy of the analytical method to measure propane in stack gas. The uncertainties associated with mixtures M9 3885 and M51 8141 during the first measurement were very large, increasing the combined uncertainty to more than 1.0% for both. For M51 8268, it was the third measurement that was associated with a large uncertainty, resulting too in a larger uncertainty. The former mixtures were determined to an accuracy of 0.9% and 0.3% respectively, however, the accuracy of M51 8268 was larger than a 1% desired limit. The large uncertainty at the beginning can be attributed to instrumental drift since the GC instrument has not been operated for some time. These mixtures were at very low concentrations, nominal fraction range 1 – 10 µmol/mol, hence the larger uncertainty of measurement observed. To evaluate whether the measurement of C_3H_8 in stack gas is linear or non-linear a calibration curve was plotted and shown in **Figure 6.7**.

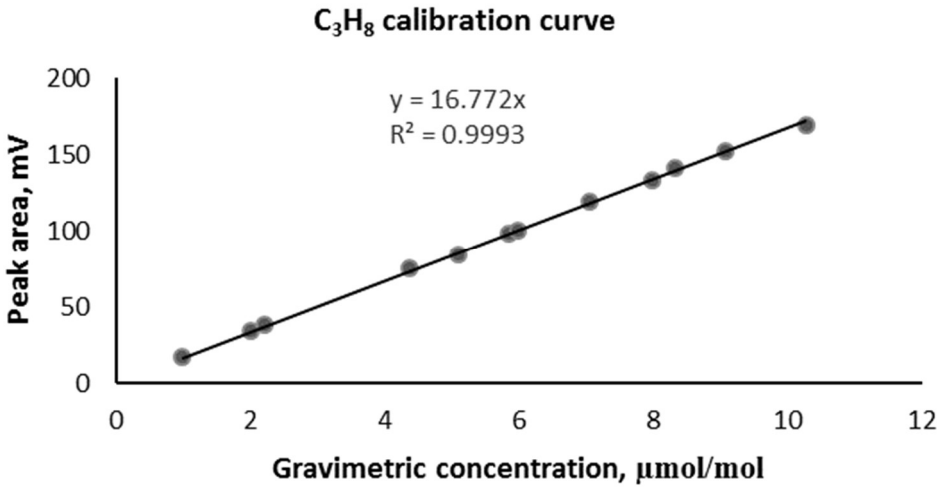


Figure 6.7: Linear calibration curve of C_3H_8 measurement when multicomponent stack gas mixtures were used for calibration use original plots

The measurement of C_3H_8 in stack gas by GC-FID can be considered linear. The correlation coefficient of the calibration curve was greater than 0.99. One-point calibration techniques can be used to measure C_3H_8 in stack gas by GC-FID.

6.2.2 Comparison to CCQM K71 – improvements

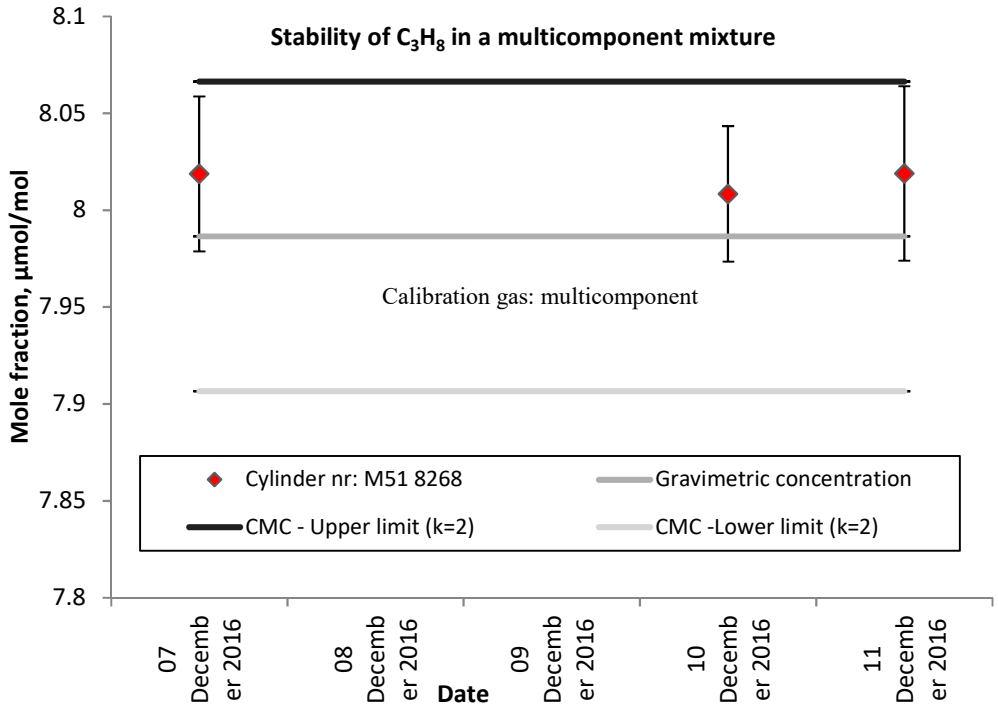


Figure 6.8: Stability of C_3H_8 analysed by GC-FID and attained by calibration with multicomponent stack gas mixtures

D19 4899 was prepared in 2008 for the key comparison. Information was not available to compare its previous measurement with the current one. However, the measurements shown in **Figure 6.8** show improvements in measurement capability. The new method of propane analysis resulted in a very accurate quantification of propane in stack gas. The relative deviation measured from the gravimetric value was only a 0.36%. This data also shows that propane in stack gas is stable for more than 5 years. D19 4921 data could not be calculated because at 1µmol/mol, it was the only one at that mole fraction and is not bracketed by any other standards on the calibration curve for analysis.

The laboratory was better than only one participant in the previous key comparison. **Table E2** shows the global equivalence of C_3H_8 in stack gas measurements. Compared to the reference value, the laboratory's measurement of C_3H_8 was off by a 1.2% relative deviation using GC FID, same measurement technique as experiments performed in 2016.

Table 6.6: Improvements in C_3H_8-in-stack gas measurements

Mixture	Gravimetric mole fraction (µmol/mol)	U(gravimetry) (µmol/mol)	Determined (analysis) (µmol/mol)	U(analysis) (µmol/mol)	% Difference
M9 3970	5.840	0.003	5.843	0.02	**0.05**
M93 7424	5.98	0.004	6.048	0.006	**1.20**

A mixture (same mole fraction) used for comparison with CCQM K71 showed an improvement in the accuracy of measurement from 1.2% to 0.05% relative deviation from reference value at 0.5% combined uncertainty. The comparison of measurement results of M93 7424 and M9 3970 show that both the uncertainty and % relative deviation was improved in the measurement of C_3H_8. The measurement capability of propane in this complex mixture.

6.2.3 Short-term stability of C_3H_8-in-stack gas

The stability graphs of C_3H_8 in stack gas are plotted below to show the behavioural trends of the component in a brief period of time.

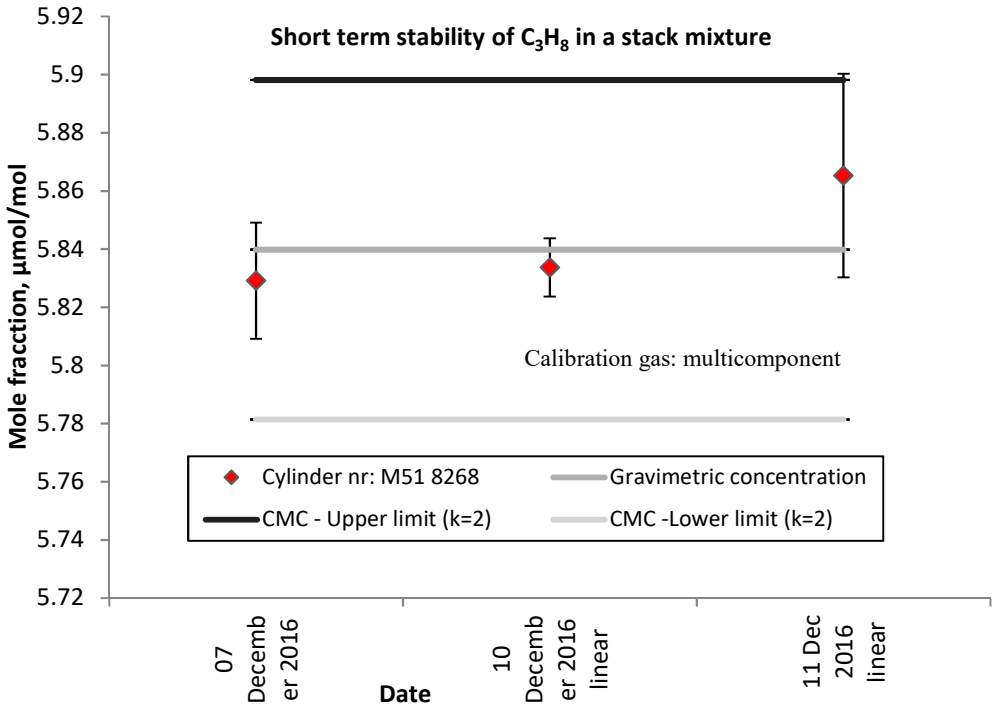


Figure 6.9: C_3H_8 short-term stability for sample M9 3970 attained by using only multicomponent gas mixtures for calibration.

The stability of C_3H_8 in stack gas for sample M9 3970 shown by **Figure 6.9** was adequate but not satisfactory, no bias indicated by the results.

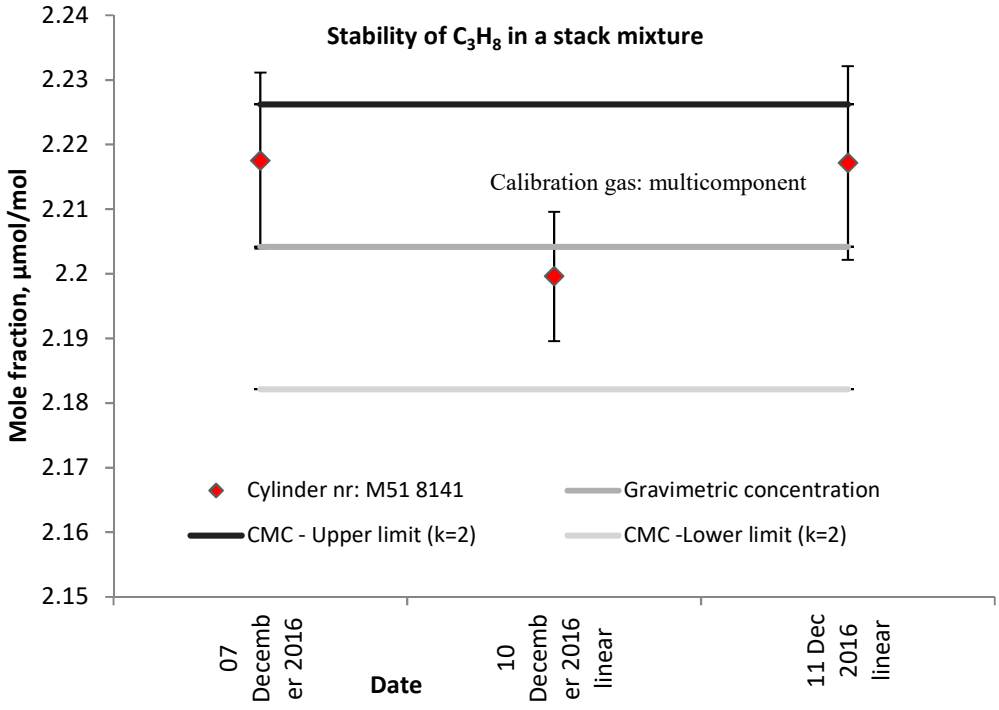


Figure 6.10: C_3H_8 short-term stability for sample M51 8141 attained by using only multicomponent gas mixtures for calibration.

There was no bias in the measurement of C_3H_8 in stack gas, the concentrations were adequately stable as shown by the stability graph of M51 8141.

The results of the D-test from **Table 6.7** indicate significant instability of the propane component in the four stack samples. Most of the D values were above the limit of 2. Instability is caused mainly by changes in composition of a mixture but it may also be attributed to instrumental drift. This multipoint method however, did not measure drift.

Table 6.7: Statistical D test results for stability assurance – propane in stack gas

	STACK GAS MIXTURES							
	M9 3885		M9 3970		M51 8141		M51 8268	
Measurements	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2
D (matrix match)	6.4	2.5	0.31	4.4	1.3	7.9	5.7	0.01

6.3 Nitric oxide in stack gas

6.3.1 Accuracy and linearity

Table 6.8: Relative deviation results of NO by NDUV: matrix matched

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	%difference	%REU
6633	99.6	0.13	**100.1**	**0.46**	0.74
M9 3885	60.5	0.02	**61.0**	**0.82**	1.0
M9 3878	10.0	0.01	11.1	10.7	13
M9 3970	10.0	0.01	-	-	Not conclusive
M51 8268	81.5	0.05	**81.8**	**0.42**	1.8

The NO results where stack gas PSGMs were used, indicate that NO in stack gas can be measured with at-least 0.4% relative deviation. However, this behaviour is not the same for all mole fractions; deviations from the reference value of more than 1% are observed. Lower concentrations (10 ppm) inherently are the most challenging to analyse. A relative deviation of more than 10% was observed for sample M9 3878. The stability of individual results was a challenge for NO especially for M9 3970.

Table 6.9: Relative deviation results of NO by NDUV: NO/N_2 PSGMs

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	%difference	%REU
6634	41.0	0.01	41.6	-1.4	9.0
M9 3885	60.5	0.02	62.8	3.9	2.8
M9 3878	10.0	0.01	11.2	11.8	17
M9 3970	10.0	0.01	11.5	14.3	9.0
M51 8268	81.5	0.05	84.4	3.6	2.1
M51 8141	20.2	0.01	20.7	2.2	5.1

Using single component PSGMs, not a single mixture was determined accurately within the desired uncertainty. Relative deviations of more than 1% were observed. This low accuracy was more significant for 10 ppm concentrations. The binary PSGMs have a synergistic effect on the amount of NO in stack gas.

Another challenge observed for NO measurement is large uncertainties up to 17 % relative expanded uncertainty and 13% relative expanded uncertainty for binary PSGMs and matrix match methods respectively. Even though the uncertainties at which the results are obtained for a matrix match are lower than for binary standard gas mixtures, these are still higher than is desired.

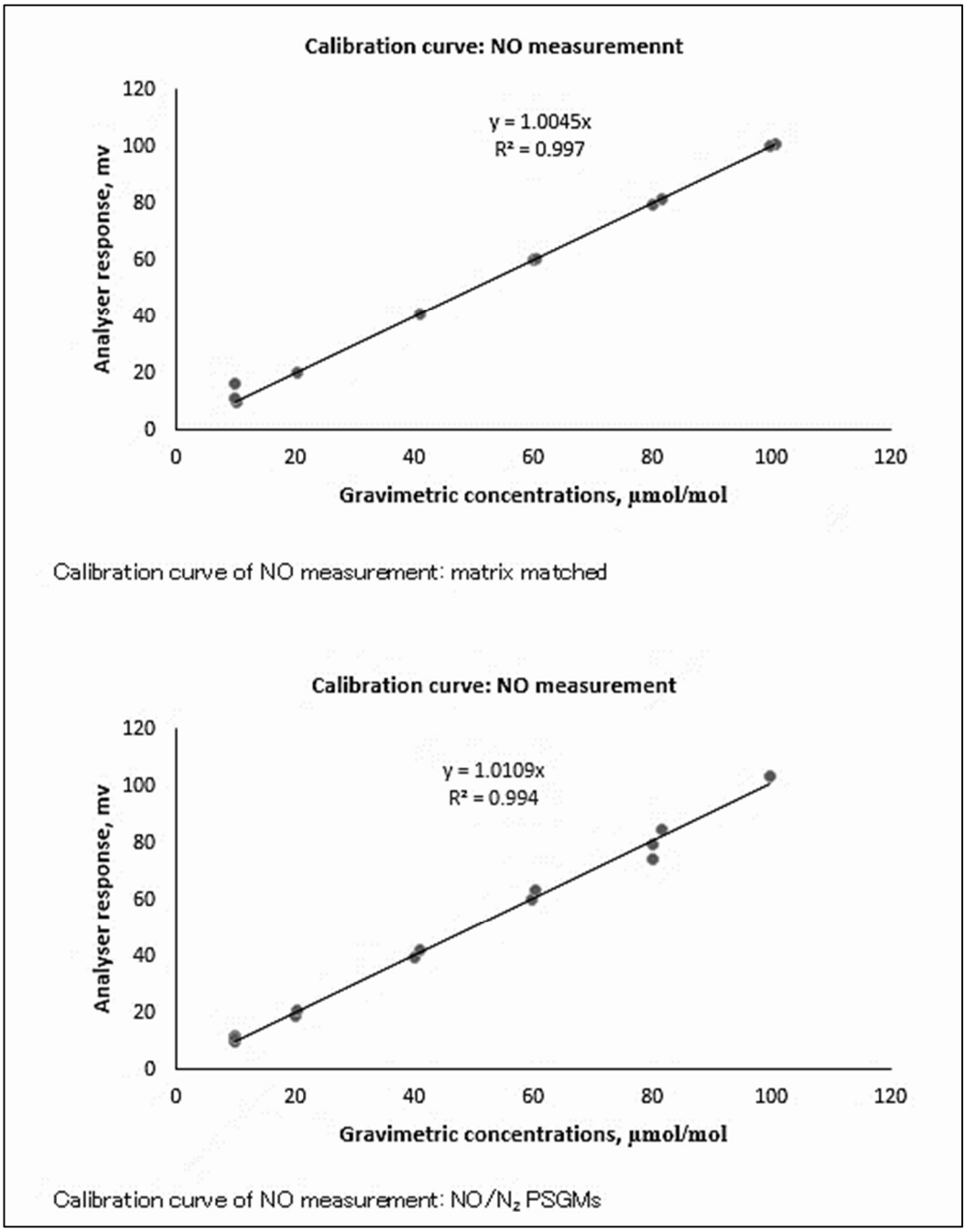


Figure 6.11: Linear calibration curves for nitric oxide measurement comparing use of standard mixtures with different matrices.

The absorption of nitric oxide can be considered linear and linear regression can be used to determine the concentration of NO-in-stack gas. The absorption follows the Beer-Lambert law. When nitric oxide in nitrogen standard gas mixtures were used, the method showed to be less linear than stack gas calibration. However, the linear regression models to calculate unknowns can still be used.

6.3.2 Comparison to CCQM K71 - improvements

For nitric oxide, a reactive gas, the analysis of the old CCQM K71 standards was not satisfactory. Comparison of the pervious data and current worked showed that while accuracy was very poor at that period, there still needs not be significant developments even currently. The results of D19 4899 are still well outside the desired 1% accuracy. However, it is critical to note that at 10 µmol/mol, the mole fraction is very low and therefore inherently difficult. This can be compared to the data of another stack gas mixture at 100 µmol/mol.

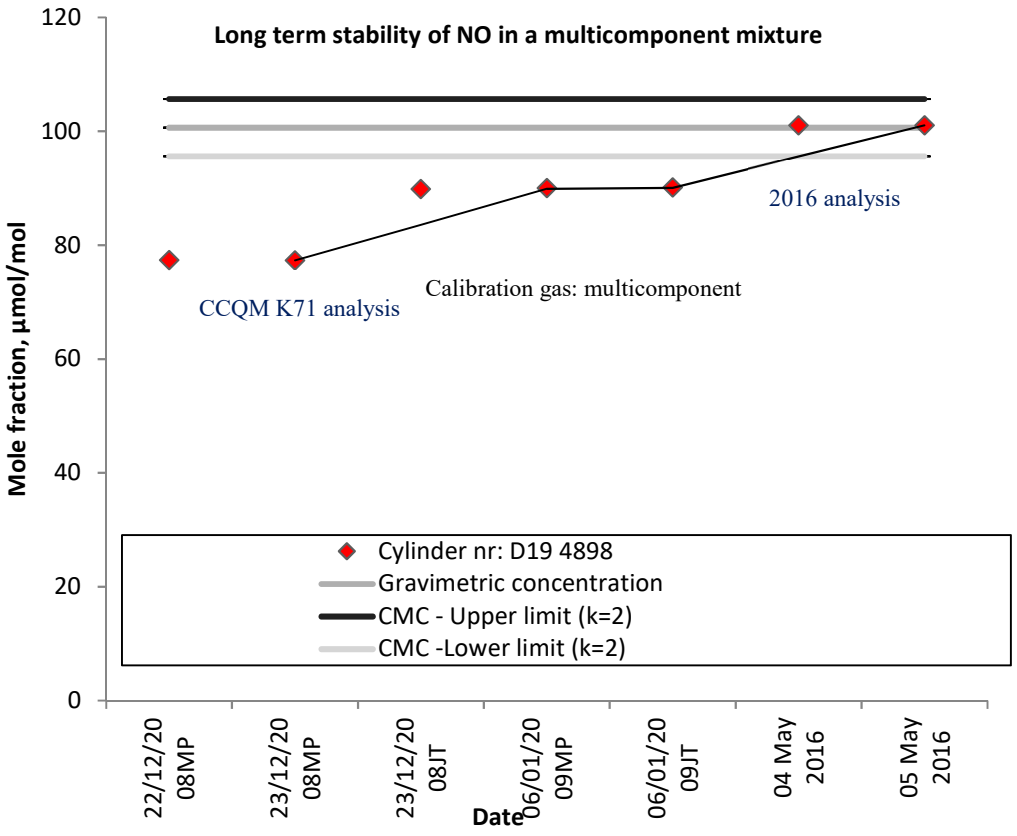


Figure 6.12: Stability of NO in a stack gas mixture comparing the analysis of 2008 and 2016, signifying improvements in capability.

The new method (non-dispersive ultraviolet spectroscopy) saw an increase in the accuracy to measure nitric oxide at 100 µmol/mol. The NO content was measured previous in December 2008 and January 2009 using the chemiluminescence

method and the results thereof were not good. The current method was very precise. Its limitations however, is the analysis of very low mole fractions of nitric oxide which must still be improved. The stability of the NO was very poor in 2008 but the results of the current work showed very good stability.

The results of nitric oxide from CCQM K71 are presented in **Table E3**, and those of the laboratory are presented below to evaluate whether there has been an improvement in the measurement of nitric oxide in stack gas. The laboratory result was better than the result of one other participant. The measurement during the CCQM K71 was 0.90% relative from the reference value using chemiluminescence technique for NO.

Table 6.10: Improvements in NO-in-stack gas measurements.

Mixture	Gravimetric mole fraction, µmol/mol	U(gravimetry), µmol/mol	Determined (analysis), µmol/mol	U(analysis), µmol/mol	% Difference
M51 8268	81.5	0.05	81.8	1.2	0.42
M93 7424	80.1	0.05	79.4	0.008	0.90

An improvement of 0.4% was achieved from 0.9% as shown on **Table 6.10** when the analysis results of CCQM K71 were compared with the current 80 µmol/mol sample. These two measurements are by two different techniques; however, key-comparisons only compare relative deviations from reference values of given samples, that is, measurement capability. Even though the relative accuracy was increased, the associated uncertainty has increased for the current measurement of nitric oxide in stack gas. Therefore, we can assume that using current PRGMs, the NO in stack gas can be measured accurately but the uncertainties will be larger than desired. The uncertainty of measurement needs to be reduced.

6.3.3 Short-term stability of NO-in-stack gas

Two different stability graphs are presented for NO. On average, nitric oxide is one of the challenging gas analytes to encounter. Their reactivity often means that they interact with other gases and results may often be erroneous in comparison to reference values. It also means the behaviour of nitric oxide may be unpredictable. Reactive gases are also known to adsorb on the interior surface of cylinders.

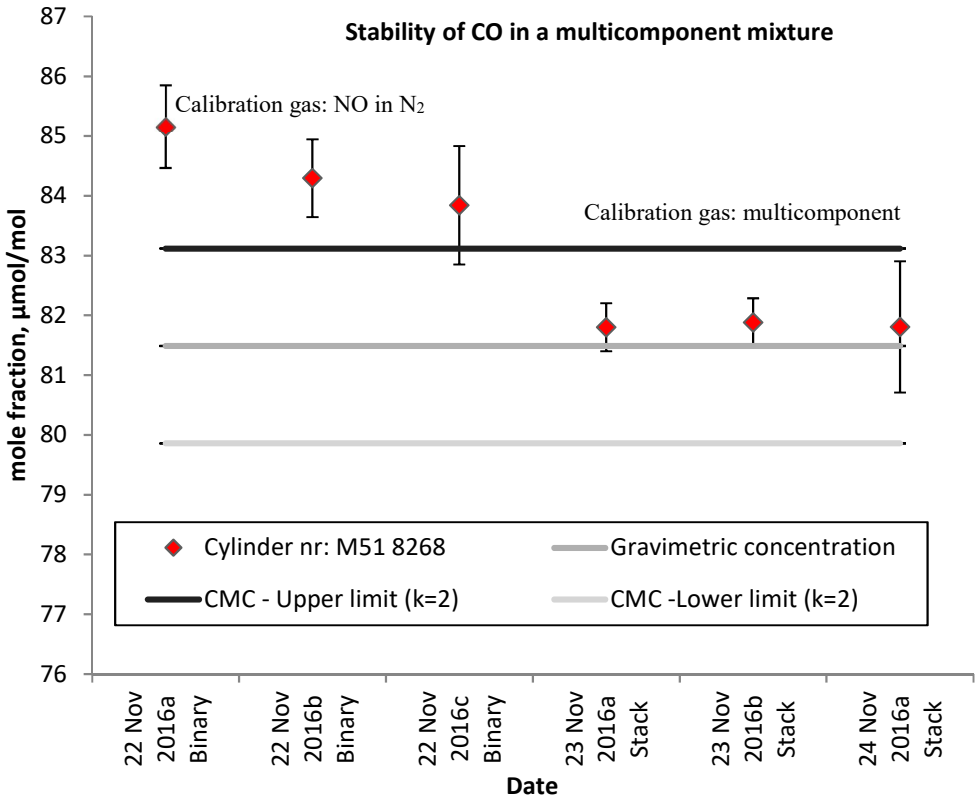


Figure 6.13: NO short-term stability for sample M51 8268 showing the discrepancies in the use of nitric oxide in nitrogen mixtures for stack gas mixtures.

By visual inspection of the stability plot, the concentration of NO does not appear stable. However, if only one of the two methods (matrix matched or use of binary standard gas mixtures) is considered, it is the latter that indicates non-stability. The use of multicomponent gas mixtures to analyse the mole fraction of nitric oxide in multicomponent mixtures by NDUV proves the NO content to be stable for

calibration uses. The limitations of the NO in N2 standard gas mixture is shown above on **Figure 6.13**.

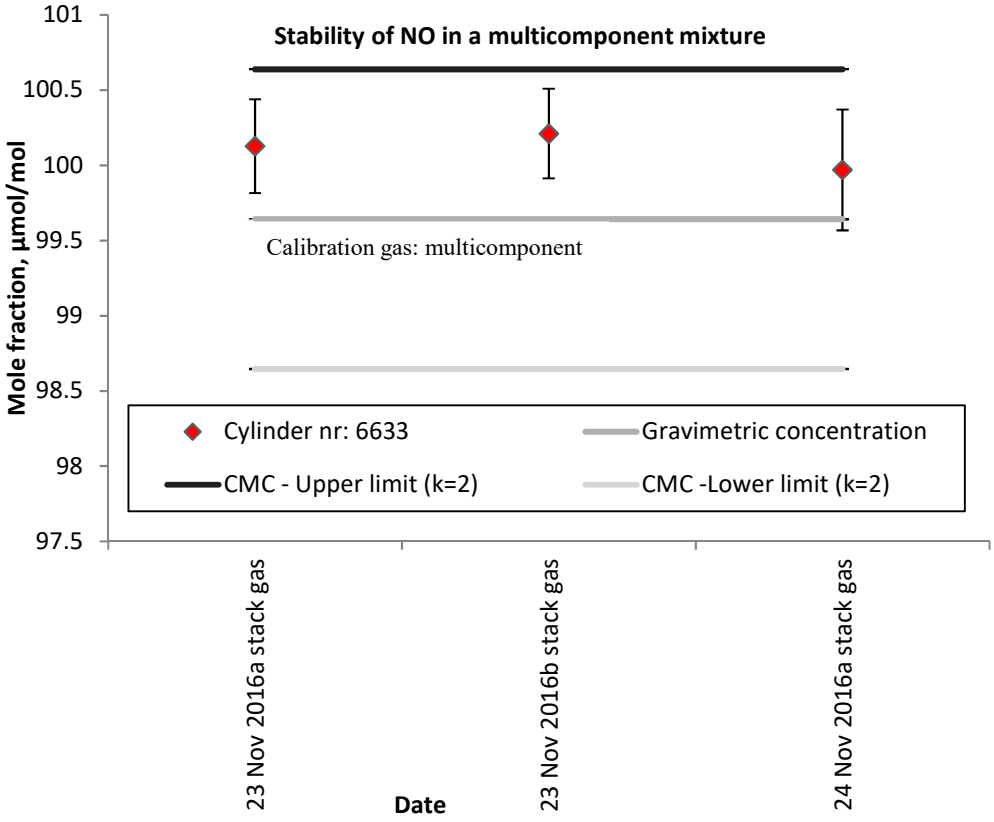


Figure 6.14: NO short-term stability for sample 6633 where calibration was done using multicomponent stack gas mixtures only.

The stability of nitric oxide in the multicomponent gas mixture 6633 shown on **Figure 6.14** was satisfactory for short term uses when the multicomponent calibration gas method is used for determining its mole fraction. The D test results on **Table 6.11** also shows that there is no significant instability associated with this final homogeneous mixture.

Table 6.11: Statistical D test results for stability assurance – nitric oxide in stack gas

	STACK GAS MIXTURES													
	6633		6634		M9 3885		M9 3878		M9 3970		M51 8141		M51 8268	
Measurements	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2
D (binary)	0.20	0.48	0.27	0.44	0.91	0.11	0.22	0.06	0.19	0.10	0.20	0.20	0.91	0.38
D (matrix match)	-	-	1.94	0.05	0.28	0.41	0.02	0.15	0.48	1.0	-	-	0.14	0.06

6.4 Carbon monoxide in stack gas

6.4.1 Accuracy and linearity

Carbon monoxide was one of the challenging components in stack gas. The results of carbon monoxide follow to demonstrate its measurement in stack gas by non-dispersive infrared spectroscopy.

Table 6.12: Relative deviation results of CO by NDIR: matrix matched

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	%difference	%REU
6633	100.1	0.07	100.5	0.31	5.8
6634	41.6	0.01	41.5	0.10	4.2
M9 3885	20.4	0.01	**19.6**	**4.1**	2.3
M9 3878	30.3	0.01	**31.5**	**-4.2**	4.5
M9 3970	10.1	0.01	**-**	**Not stable**	-
M51 8268	81.03	0.02	**79.1**	**2.4**	5.4
M51 8141	40.5	0.01	**41.0**	**-1.2**	4.2

Table 6.12 shows that analysis of carbon monoxide by stack standard gas mixtures was associated with large uncertainties. Measurement capability also declined with the analysis of lower fractions (10-30 µmol/mol). The overall accuracy of determining the correct mole fractions was not satisfactory. However, 6634 and 6633's CO amount were measured at 0.10% and 0.3% respectively. More work still needs to be done to improve the measurement of CO-in-stack gas.

Table 6.13: Relative deviation results of CO by NDIR: CO/N_2 PSGMs

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	%difference	%REU
6633	100.1	0.07	**107.4**	**7.3**	9.6
6634	41.6	0.01	**45.3**	**9.1**	6.3
M9 3885	20.4	0.01	**21.0**	**6.3**	13
M9 3878	30.3	0.01	**35.6**	**17**	12
M9 3970	10.1	0.01	**14.6**	**44**	47
M51 8268	81.0	0.02	**86.8**	**7.1**	6.4
M51 8141	40.5	0.01	**43.1**	**6.5**	4.1

It was observed however, that using binary standard gas mixtures results in even larger relative expanded uncertainties of measurement as shown by **Table 6.13**. Of the seven (7) mixtures, none was determined to within a 1% accuracy limit. Although in general, the stack gas experiment was not accurate, it showed to be better than the traditional method.

To evaluate the linear or non-linear absorption of carbon monoxide, calibration curves were extrapolated to compare the correlation coefficients.

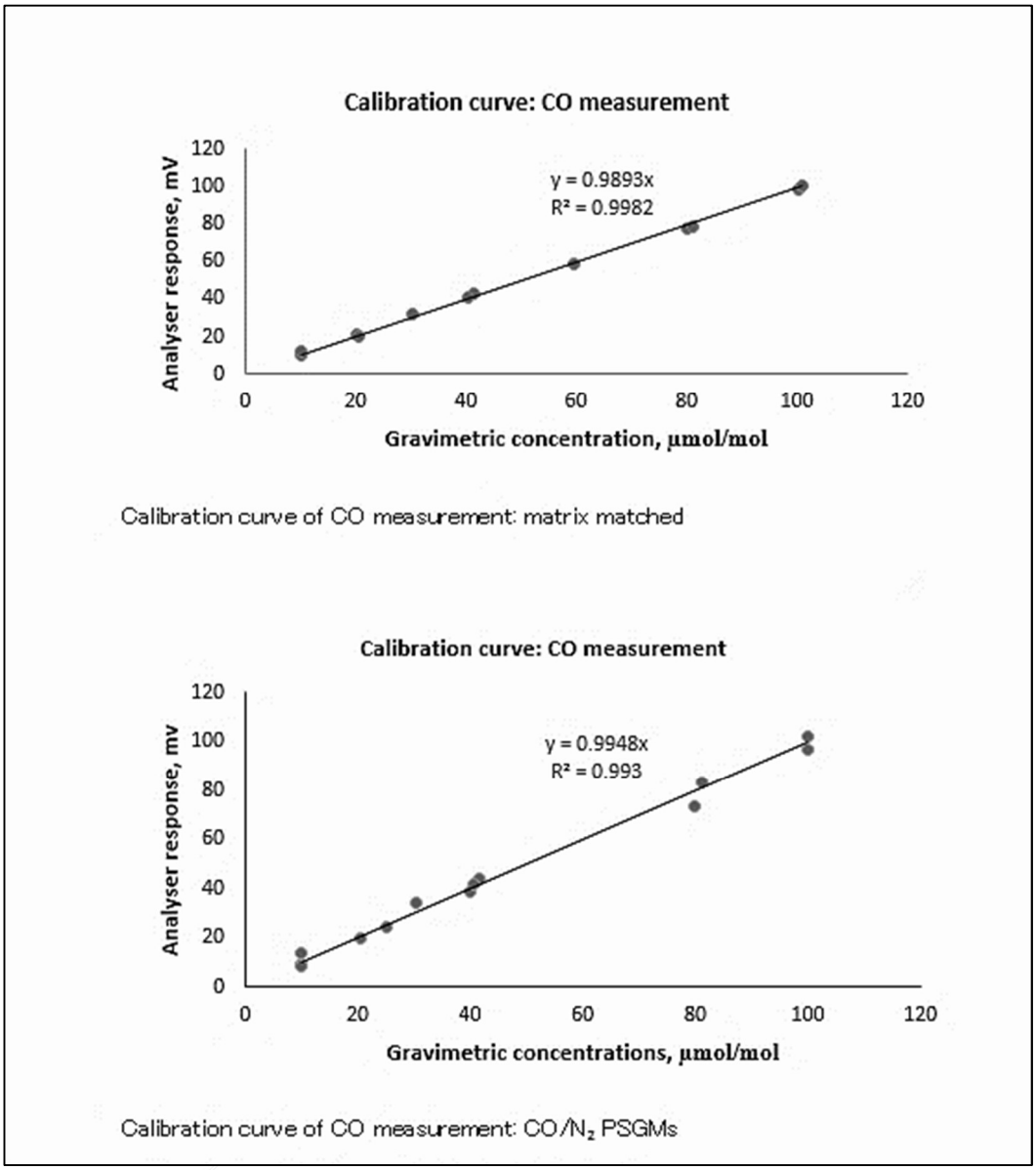


Figure 6:15: Calibration curves of carbon monoxide comparing calibration from binary and multicomponent gas mixtures

The absorption of carbon monoxide is linear (correlation coefficient almost 1). Therefore, linear regression can be used to calculate the amount of CO-in-stack gas by calibration using matrix matched standards. In comparison, the linearity of the calibration curve where binary standard mixtures were used was relatively poor compared to the matrix-matched experiment. However, significant linear absorption was observed. The correlation coefficient was 0.993.

6.4.2 Comparison to CCQM-K71: improvements

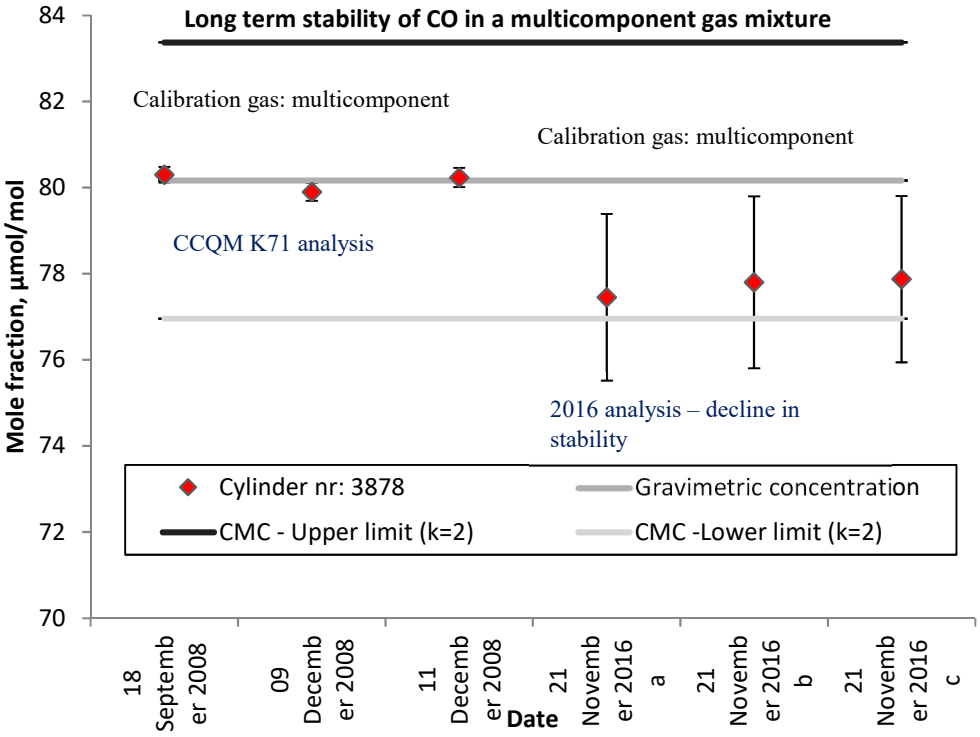


Figure 6.16: Stability of CO in a stack gas mixture - D19 4899 comparing 2008 and 2016 results.

The analysis of the old standard for the CO mole fraction was not satisfactory. As a reactive gas, the stability was expected to be a problem. There was a decline in the stability of the mole fraction when 2008 results and 2016 results were compared. However, the overall independent stability of the calculated mole fraction for each method was good. The accuracy of the current work however, was unsatisfactory. If its only stability-decline, this analysis may have been good.

The results of any improvements carbon monoxide are presented below, with special emphasis on % relative deviations from reference values (measure of accuracy). The laboratory's results were better than only two other laboratories. The measurement was 0.73% deviated from the reference value during CCQM K71 on CO measurement.

Table 6.14: Improvements in CO-in-stack gas measurement

Mixture	Gravimetric mole fraction, µmol/mol	U(gravimetry), µmol/mol	Determined (analysis), µmol/mol	U(analysis), µmol/mol	% Difference
6634	41.6	0.01	41.5	1.5	0.01
M93 7424	40.1	0.03	39.8	0.06	0.73

By using an approximately 40 µmol/mol stack mixture for comparison, the current measurement resulted in a 0.10% relative difference from the reference value, significantly lower than the measurements performed in 2008 as shown by **Table 6.14**. The % relative deviation was improved to measure CO-in-stack gas, However, the uncertainty associated with this measured has increased and needs improvement.

6.4.3 Short-term stability of CO-in-stack gas

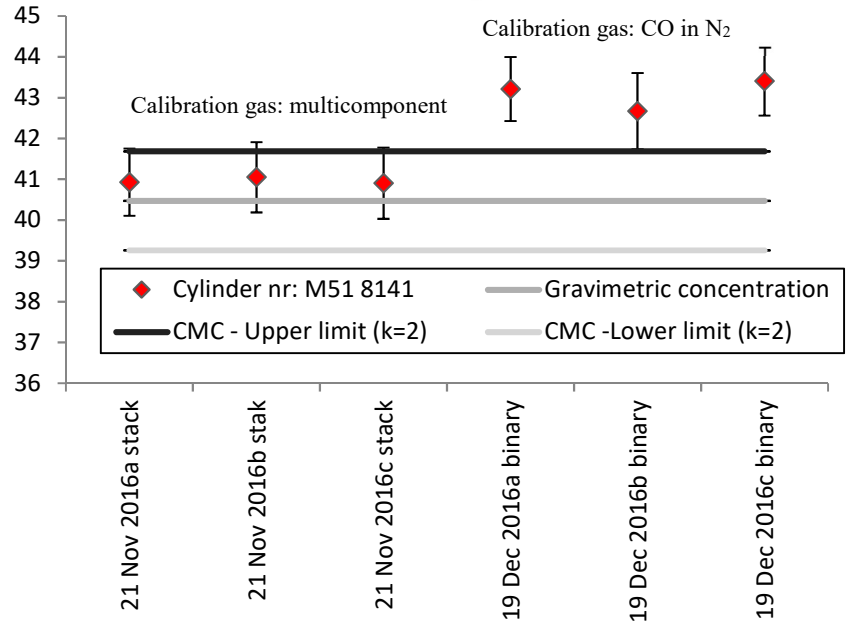


Figure 6.17: CO short term stability for stack mixture M51 8141 attained by calibration with different types of standard gas mixtures.

To evaluate the short-term behaviour of carbon monoxide in stack gas, the stability graphs were plotted to examine it. The gravimetric mole fraction of M51 8141 was accurate within 3%. The overall stability of the carbon monoxide's content in the multicomponent gas mixture (stack) when the instrument was calibrated with a standard similar to the sample was satisfactory. The stability of the content of CO when the single component CO in N2 gas was used showed a slight inconsistency for the second measurement. However, this observed stability was not significant. See the results of the D test below. The stability graph also confirms clearly the conclusions of **Table 6.13**.

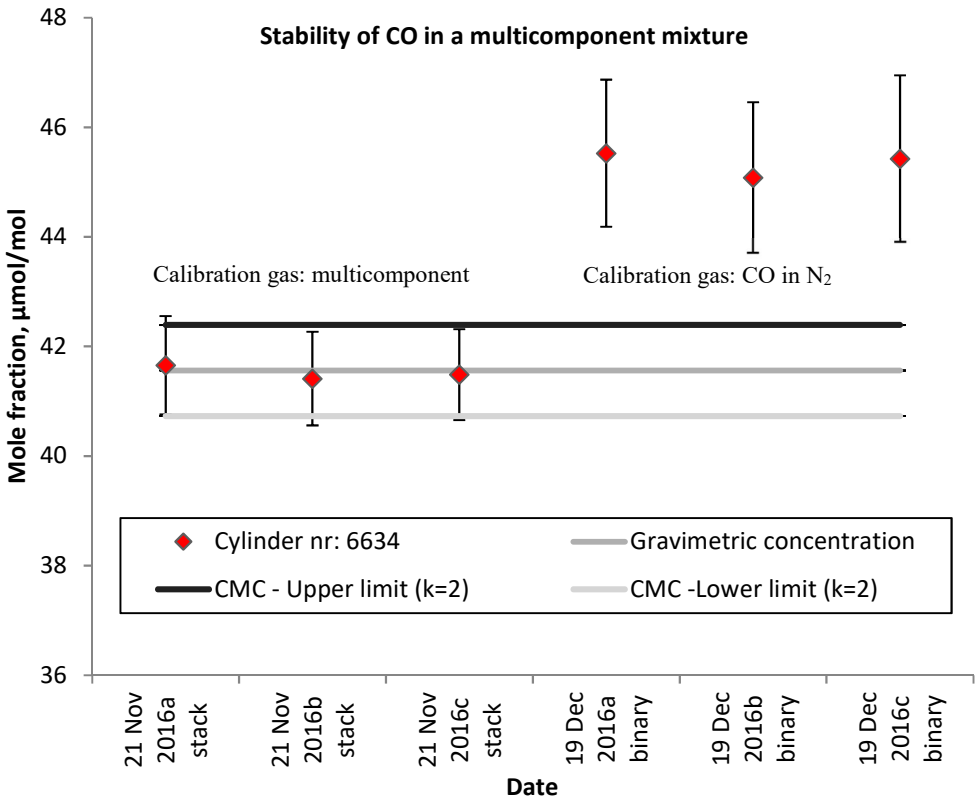


Figure 6.18: Stability of CO in a stack gas mixture for 6634 showing discrepancy associated with binary standard gas mixtures

Adequate short-termstability was observed and is guaranteed as well for the carbon monoxide content of 6634 as shown by **Figure 6.18**. The limitations of the single-component calibration gas mixtures however, are clearly made visible by this trend

plot. The use of multicomponent calibration gas mixture, non-dispersive infrared spectroscopy and calibration curve methods however results in accurate analysis and good stability by visual inspection of behaviour. Using the D-test, **Table 6.15** indicates that there was no significant instability associated with the gas. All D values are less than 2.

Table 6.15: Statistical D test results for stability assurance – carbon monoxide in stack gas

	STACK GAS MIXTURES													
	6633		6634		M9 3885		M9 3878		M9 3970		M51 8141		M51 8268	
Measurements	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2
D (binary)	0.003	0.05	0.23	0.17	0.02	0.23	0,05	0.08	0.07	0.05	0.44	0.58	0.28	0.07
D (matrix match)	0.09	0.24	0.20	0.06	0.13	0.15	0.16	0.68	-	-	0.10	0.12	0.10	0.06

6.5 Sulphur dioxide in stack gas

6.5.1 Accuracy and linearity

The accuracy of using standard gas mixtures similar to the sample or single component standards for calibration, is compared in **Tables 6.16** to **6.17**. The comparison is done using % relative deviations from reference values (gravimetry). These help us to understand the level of deviation from true values in our measurement results. Ideally, % relative deviation of 0.5% and less are desired.

Table 6.16: Relative deviation results of SO_2 by NDUV: matrix matched

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	%difference	%REU
6634	56.2	0.02	**54.6**	**2.8**	2.5
M9 3885	101.7	0.02	**103.2**	**1.5**	3.3
M51 8268	152.5	0.03	**155.7**	**2.2**	2.5

The analysis of sulphur dioxide was the most analytically challenging of the five components of stack gas. The measurement results of four mixtures could not give goodness of fit less than two from the calibration curves. Hence only three results are reported in **Table 6.16**. The % differences relative to the gravimetric concentration are suggested to be indicative of the effect of matrix (and how sulphur dioxide interacts with the contents of the stack gas) as well as cross-interferences of other target gases. This behaviour however was not expected. See **Table 6.17**.

Table 6.17: Relative deviation results of SO_2 by NDUV: SO_2/N_2 PSGMs

Mixture	X_i, µmol/mol	$U(x_i)$, µmol/mol	Result, µmol/mol	%difference	%REU
6633	201.6	0.19	201.3	0.13	0.52
M9 3885	101.7	0.02	100.5	0.32	2.3
M51 8268	152.5	0.03	125.1	0.21	0.33
M51 8141	20.08	0.01	20.07	0.09	1.5

It was assumed that the use of standard gas mixtures similar to the sample in matrix results in a better precision and accuracy. However, the measurement results of sulphur dioxide rejected the hypothesis.

Table 6.17 above shows that the use of sulphur dioxide in nitrogen standard gas mixtures resulted in a better accuracy and comparably lower uncertainties. A relative deviation of 0.09% was achieved by binary standards for the concentration of M51 8141. However, there were some outliers in the average behaviour. These were 6634 and M9 3970.

The calibration curves from two different methods are used to evaluate the linearity of the absorption of sulphur dioxide in stack gas;

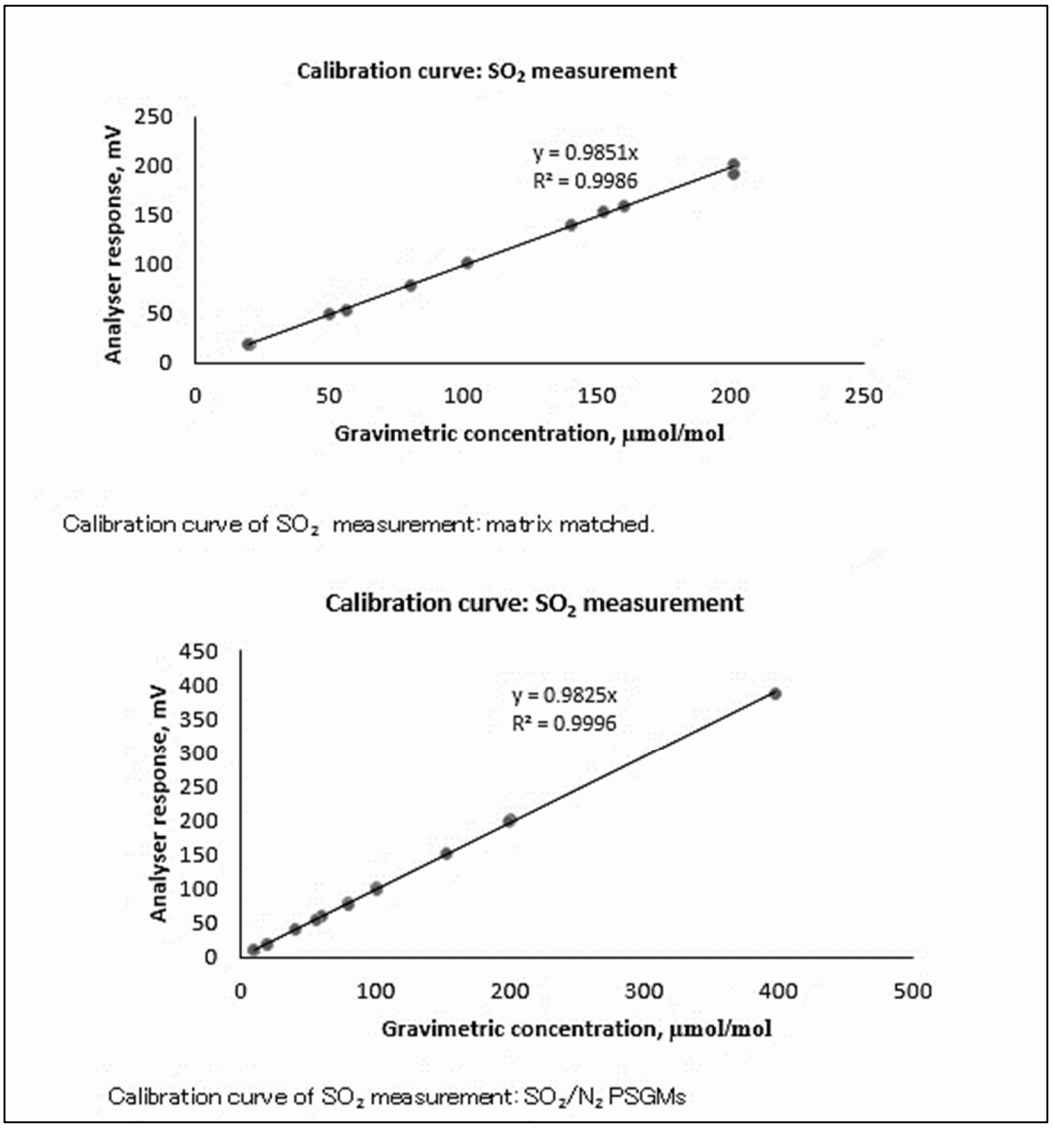


Figure 6.19: Linear calibration curves for the measurement of SO_2 using both types of standard gas mixtures.

The correlation coefficient was determined to be 0.9986 from the calibration curve attained by analysis with stack standard mixtures. The absorption of sulphur dioxide was linear. Within this range, the mole fraction of an unknown sample can be determined accurately by linear regression using this method. The correlation coefficient was 0.9996 for method were binary mixtures were used to calibrate the spectrometer, relatively larger than when standard gas mixtures of similar matrix were used. However, the linearity is comparable. Sulphur dioxide absorption can be considered linear in both methods and linear regression can be used with confidence.

6.5.2 Comparison to CCQM-K71: improvements

The analysis of the CCQM K71 standards for sulphur dioxide by similar matrix standards was the most challenging experiment. This phenomenon was similar to the analysis of the new samples by the same method. The calibration curves' goodness of fit was more than the desired 2. Therefore, the results are not reported. It can be assumed however, that use of single component standard gas mixtures may result in more accurate

Table 6.18: Improvements in SO_2-in-stack gas measurements.

Mixture	Gravimetric mole fraction, µmol/mol	U(gravimetry), µmol/mol	Determined (analysis), µmol/mol	U(analysis), µmol/mol	% Difference
M9 3970	80.3	0.01	78.1	0.26	2.8
M93 7424	80.0	0.05	80.1	0.08	0.13

Sulphur dioxide registered the best measurement capability and the laboratory the best of all participants. Relative to the reference value, the laboratory's result deviated by 0.13% for SO_2 in stack gas measurement using UV fluorescence. **Table 6.18** shows the results of the current project. Compared to the results of the key comparison, there was no improvement observed, but a decline in accuracy to measure SO_2 in stack gas. There was an associated decline in the measurement of sulphur dioxide in stack gas graphically. The uncertainty of measurement however was reduced.

6.5.3 Short term stability of SO_2-in-stack gas

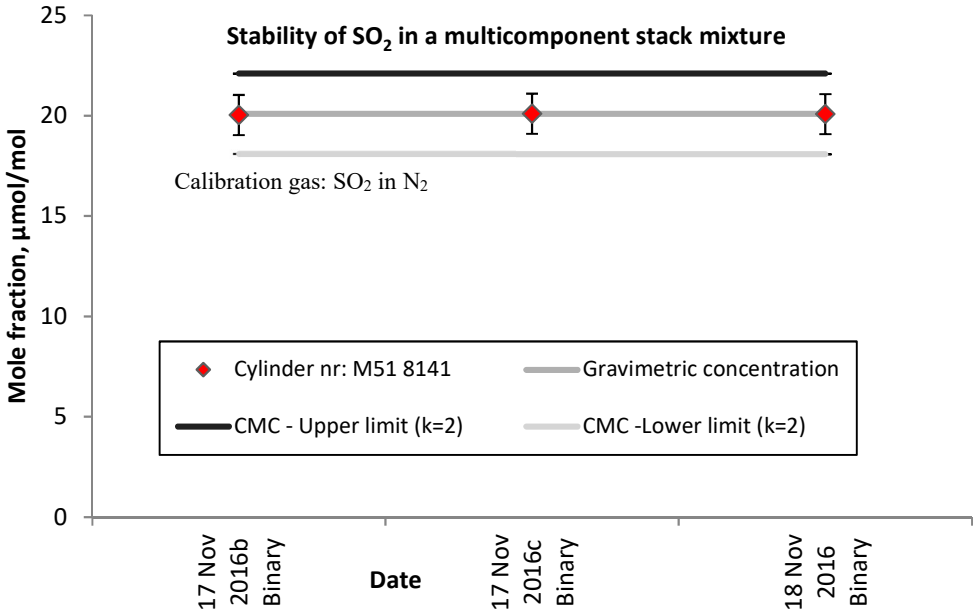


Figure 6.20: Short term stability of sulphur dioxide for M51 8141 were calibration was done using sulphur dioxide in nitrogen standard mixtures.

Sufficient stability was observed for the sulphur dioxide content of M51 8141 as shown in **Figure 6.20**. Here the method used to acquire this stability was use of single-component sulphur dioxide in nitrogen calibration standards. The short term behaviour of the sulphur dioxide gas was very consistent when the 20 µmol/mol was analysed by non-dispersive ultraviolet spectroscopy. The use of multicomponent mixtures for calibration resulted in inconclusive data.

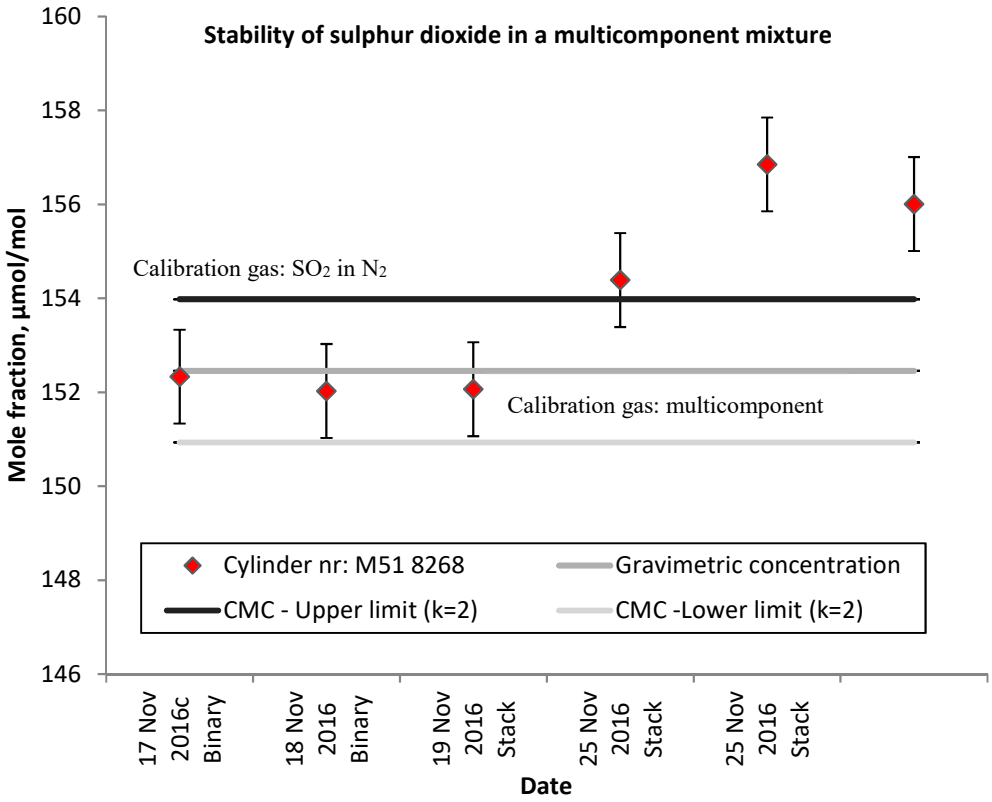


Figure 6.21: Short term stability of sulphur dioxide for M51 8268 showing the discrepancies of using multicomponent stack gas mixtures for calibration

The stability of sulphur dioxide in M51 8268 was adequate when calibration was completed using the binary standard gas mixtures method. However, instability was observed with the other method by visual inspection of the trend. The instability may be attributed to drift and instrument poor conditioning. There results on **Table 6.19** for the statistical D test indicate that no significant instability exists of the sulphur dioxide in stack gas.

Table 6.19: Statistical D test results for stability assurance – sulphur dioxide in stack gas

	STACK GAS MIXTURES											
	6633		6634		M9 3885		M9 3970		M51 8141		M51 8268	
Measurements	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2	x_o,x_1	x_1,x_2
D (binary)	0.39	0.06	1.1	0.22	1.9	0.71	0.46	0.31	0.27	0.22	0.76	0.42
D (matrix match)	-	-	1.2	0.55	1.7	0.83	-	-	-	-	0.88	0.27

6.6 Stack gas primary reference gas mixture - results

In addition to the work conducted in this project, a stack gas PRGM requested by a client X from the air pollution monitoring framework was prepared with two other PSGMs at; 60 µmol/mol carbon monoxide, 12% carbon dioxide, 400 µmol/mol nitric oxide, 600 µmol/mol sulphur dioxide and 60 µmol/mol propane.

6.6.1 Results for carbon dioxide and propane

The results of carbon dioxide and propane are shown below in **Tables 6.20** and **6.21**. These measurements were performed simultaneously. The method used was repeatable at 0.7% and 0.6% relative standard deviations for measurements of CO_2 and C_3H_8 respectively. However, there were drift problems encountered during experiment which resulted in poor reproducibility of the response for the standard. Conditioning the instrument before analysis or analysis for longer periods may assist in solving the problem. Drift can also be attributed to pressure changes during experiment. The atmospheric pressure was not monitored and therefore the extent of its effect is not known. The internal consistency of the sample in comparison to the reference gas mixture was adequate. A relative deviation of 0.5% and less was achieved for CO_2 and 0.6% and less for C_3H_8. Therefore, gas chromatograph can be used for the analysis of the CO_2 as a complementary method for NDIR. This repeatable and very accurate method can be used confidently for the determination of C_3H_8 in stack mixtures in the mole fraction range of 10 – 100 µmol/mol. From these results, we can exempt these components from the list of challenging stack gas analytes. At similar concentrations CO2 was analysed by two different methods successfully. However, the success of propane may largely depend on concentration.

The criteria used for a good preparation technique and measurement is for the analytical results to be determined within a 1% relative accuracy. For 12.0462 % mol/mol, that is ± 0.120462 %mol/mol. Only data lying within the range 11.925738 – 12.166662 % mol/mol are accepted. This criterion was also used for the propane measurement. These measurement results were accepted and met this criterion. In general, the laboratory can achieve a combined uncertainty of 1% and better for propane and carbon dioxide by use of gas chromatography with flame ionisation and thermal conductivity detection. The use of flame ionisation for carbon dioxide however, could not be exploited.

Table 6.20: Carbon dioxide gas chromatograph results for the primary reference gas mixture

Mixture	M51 9528	M51 8260	M51 9528	M51 8260	M51 9528	M51 8260	M51 9528	M51 8260	M51 9528	M51 8260	M51 9528
Average	93.46	93.5	94.68	94.74	94.64	93.76	93.5	94.3	93.48	93.5	93.74
Standard deviation	0.15	0.34	0.11	0.05	0.55	0.63	0.1	0.46	0.22	0.14	0.05
%RSD	0.16	0.36	0.12	0.06	0.58	0.67	0.11	0.49	0.23	0.15	0.06
ESDM	0.07	0.15	0.05	0.02	0.24	0.28	0.04	0.21	0.10	0.06	0.02
Sensitivity	7.7	7.8	7.8	7.9	7.8	7.8	7.7	7.8	7.7	7.8	7.8
Corr. Sensitivity		7.8		7.8		7.8		7.7		7.8	
Concentration	12.0679	12.0462	12.0679	12.0462	12.0679	12.0462	12.0679	12.0462	12.0679	12.0462	12.0679
Calculated concentration		**11.99478**		**12.0781**		**12.02813**		**12.17246**		**12.05372**	
Drift			-1.3		0.04		1.2		0.02		-0.28
Ratio		0.995731		1.002648		0.9985		1.010481		1.000624	
% difference		0.43		-0.26		0.15		-1.0		-0.06	

Table 6.26: Flame ionisation detector propane results for the primary reference gas mixture

Mixture	**M51 9528**	**M51 8260**	**M51 9528**	**M51 8260**	**M51 9528**	**M51 8260**	**M51 9528**	**M51 8260**	**M51 9528**	**M51 8260**	**M51 9528**
Average	164.04	162.86	166.24	165.38	165.9	164.26	164.28	163.72	164.62	163.22	164.56
Standard deviation	0.13	0.84	0.32	0.28	0.87	0.97	0.31	0.61	1.5	0.59	0.11
ESDM	0.06	0.37	0.14	0.12	0.39	0.43	0.14	0.27	0.66	0.26	0.05
%RSD	0.08	0.51	0.19	0.17	0.53	0.59	0.19	0.37	0.90	0.36	0.07
Sensitivity	2.7	2.7	2.8	2.8	2.8	2.8	2.7	2.7	2.7	2.7	2.7
Corr. Sensitivity		2.7		2.7		2.7		2.7		2.7	
Concentration	60.406115	59.791829	60.40612	59.79183	60.406115	59.79183	60.406115	59.79183	60.406115	59.79183	60.406115
Calculated concentration		**59.57212**		**60.15514**		**60.10242**		**60.13797**		**59.90331**	
Drift			-1.3		0.20		0.99			0.31	
Ratio		0.9963254		1.006076		1.005195		1.005789		1.001865	
% difference		0.37		-0.60		-0.52		-0.58		-0.19	

6.6.2 Short-term stability of carbon dioxide and propane

To evaluate the stability of the two components in stack gas, the results of the three measurements performed were compared to check for inconsistencies.

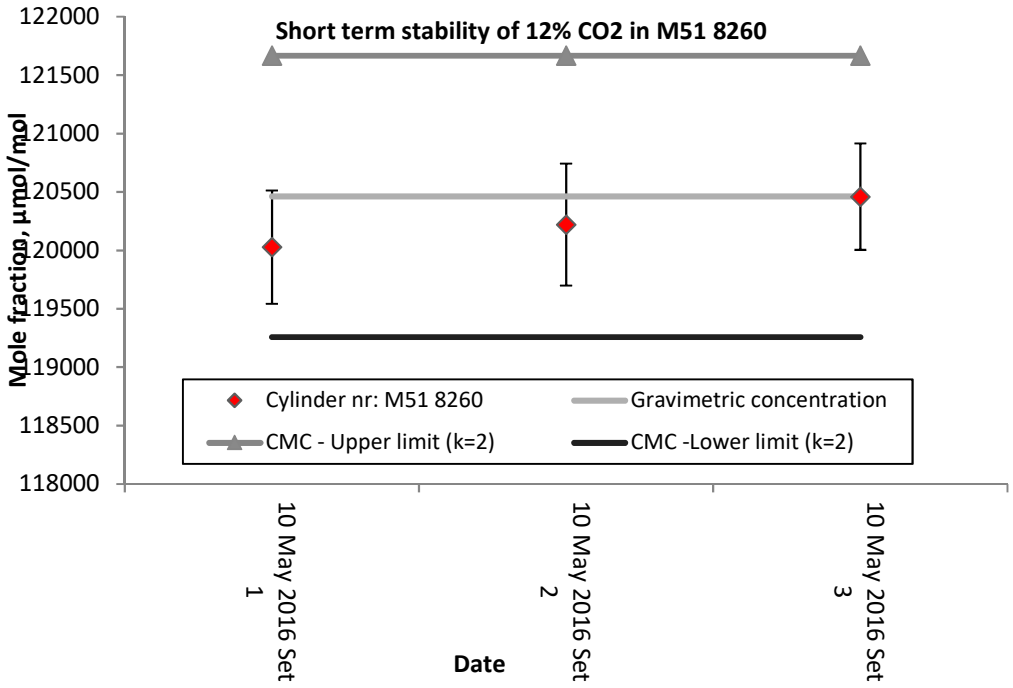


Figure 6.22: Carbon dioxide in a stack gas mixture's stability graph for M51 8260

Figure 6.22 shows the stability of the CO_2 mole fraction in the M51 8260 sample. The CO_2 mole fraction was stable in this stack gas mixture to satisfaction. However, there was an increasing trend observed as well. This trend may be attributed to instability of the chromatograph, changes in environmental conditions and drift.

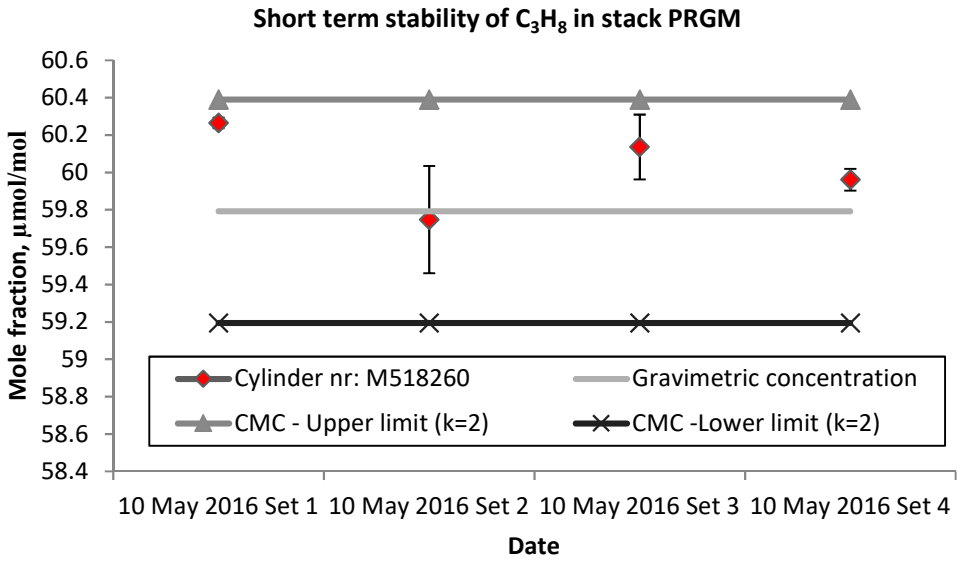


Figure 6.23: Stability of propane in a stack gas mixture for M51 8260

The stability of the propane was unsatisfactory as shown by **Figure 6.23**. The gas chromatograph was not in use for some time, therefore, drift and improper conditioning may be attributed to the instability. There was a slight positive bias observed more than twice.

6.6.3 Chromatograms

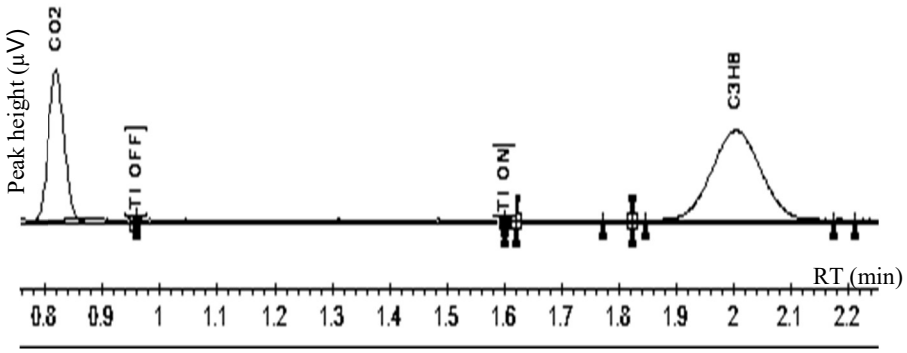


Figure 6.24: FID and TCD chromatograms of the primary reference gas mixture M51 8260

The carbon dioxide was separated at a retention time of 0.8 min, and the propane at 2 min retention time. These peaks were well resolved and sharp enough for correct integration.

The results shown by the two previous tables show the effectiveness of use of representative standard gas mixtures. The use of carbon dioxide in nitrogen and propane in nitrogen standard gas mixtures needed to be evaluated as well. The laboratory does not keep propane standard gas mixtures of the range 10-100 µmol/mol however; the analysis of carbon dioxide was done. The results of the test experiment follow to check if there existed any difference in the analysis of carbon dioxide by matrix-matched standards and by binaries.

Table 6.22: Multicomponent sample mixtures in an analysis using a binary as a calibration gas for CO_2 determination

	M9 6662	**M51 9528**	**M9 6662**	**M51 8260**	**M9 6662**	**M51 8260**	**M9 6662**
Average	92.74	93.32	93.04	93.58	93.08	93.42	93.02
Standard deviation	0.05	0.16	0.05	0.04	0.04	0.04	0.08
%RSD	0.06	0.18	0.06	0.05	0.05	0.05	0.09
Sensitivity	7.7	7.7	7.7	7.8	7.7	7.7	7.7
Corr. Sensitivity		7.7		7.7		7.7	
Concentration	12.0110	12.0679	12.0110	12.0679	12.0110	12.0679	12.0110
Calculated concentration		12.0666		12.0781		12.0588	
Drift			0.32		0.04		-0.06

Table 6.22 shows the raw data the experiment obtained under similar analytical conditions as the matrix match method. The % differences achieved for three independent results were 0.01, 0.08 and 0.08% respectively. The relative deviation from the true value was less than 0.1%. This is one of the highest accurate determinations made for carbon dioxide measurements by the laboratory. We can assume from these results that the results of carbon dioxide in stack gas in the

nominal fraction range of the study are independent of matrix differences. However, this may be due to the relatively large concentrations independent of matrix when it is measured by GC TCD and NDIR.

Previous studies have shown that in other type multicomponent mixtures, the results of carbon dioxide may be dependent of matrix. Consider this; A Fischer Rosemount non-dispersive infrared analyser was used to determine the concentration of several multicomponent mixtures of carbon dioxide, carbon monoxide and oxygen in nitrogen. The results of D95 8407 are presented from **Table 6.23.**

Table 6.23: Verification data of CO_2 by using binary standard gas mixtures

Date	Verification concentration	Gravimetric concentration	Gravimetric uncertainty
11/09/2014	99110.9	100006.6	8.6
11/09/2014	99242.8	100006.6	8.6
16/09/2014	99326.9	100006.6	8.6
16/09/2014	99371.2	100006.6	8.6
23/09/2014	98975.3	100006.6	8.6
23/09/2014	99021.7	100006.6	8.6
30/03/2015	98984.1	100006.6	8.6
30/03/2015	99175.6	100006.6	8.6
11/04/2015	98968.3	100006.6	8.6
11/04/2015	99208.8	100006.6	8.6
22/04/2015	99191.0	100006.6	8.6
22/04/2015	99231.4	100006.6	8.6
05/05/2015	99054.7	100006.6	8.6
05/05/2015	99304.5	100006.6	8.6

Comparison of the concentrations from analysis and the true values from gravimetry indicate that there was a negative bias associated with the results when carbon dioxide in nitrogen standard gas mixtures were used.

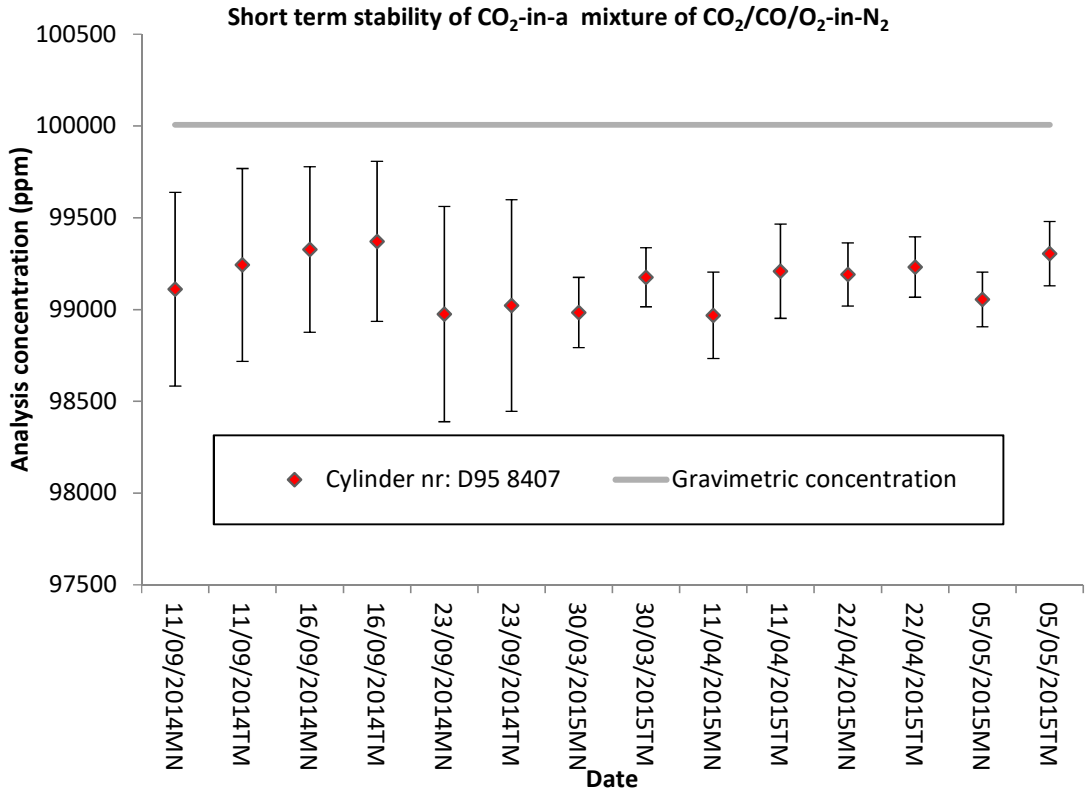


Figure 6.25: Stability graph for CO_2 measurement of D95 8407 – a mixture of CO, CO_2 and O_2 in N_2.

Even though, the concentration was determined lower than it should be, the overall measurement however, was stable as shown by **Figure 6.25**. Therefore, we can suggest that a binary standard gas mixture may or may not give the correct results, depending on the type of multicomponent system. The discrepancy here at this stage may be attributed to the presence of oxygen. The analysis performed here was for a method were CO_2 in N_2, CO in N_2 and O_2 in N_2 gas references were used. The use of CO/CO_2/O_2 in N_2 still needs to be investigated. The analytical challenges can be attributed to the presence of O_2 in the mixture. Qualitative and quantitative analysis of stack gas components was performed to evaluate the performance of the FTIR to measure this complex mixture.

6.6.4 Results for nitric oxide

The NO analysis for the stack gas PRGM was also performed using a different method for calibration: single-point calibration, but same analytical technique.

Table 6.24: NO results for the stack gas PRGM

Average	397.28	397.28	397.16	397.28	397.12	397.16	397.10	397.18	397.13	397.13	396.94
Standard uncertainty	0.63	0.52	0.55	0.58	0.50	0.57	0.56	0.53	0.56	0.59	0.55
Gravimetric mole fraction, µmol/mol	402.48	402.08									
Cylinder no.	M51 9528	**M51 8260**	M51 9528	**M51 8260**	M51 9528	**M51 8260**	M51 9528	**M51 8260**	M51 9528	**M51 8260**	M51 9528
Calculated concentration, µmol/mol		402.54		402.63		402.53		402.55		402.57	
% Difference		-0.11		-0.14		-0.11		-0.12		-0.12	
%RSD (precision)		0.07		0.06		0.04		0.07		0.01	

*reference M51 9528

Sample M51 8260

The results of this method showed that the use of the ABA method to calibrate the instrument is very precise and accurate for the measurement of NO in a multicomponent stack gas mixture. The precision of this method was between 0.01 to 0.07 %RSD. The accuracy is determined by how much the calculated mole fraction differs from the gravimetric value in percentages. The maximum % relative deviation measured for these measurements was 0.14%. This data suggests that on the 100 -1000 µmol/mol range, the measurement capability can be regarded as ≤0.2% for nitric oxide in this complex stack gas mixture. The precision however, was not significantly higher than the multipoint calibration method. The precision of the instrument remained almost similar. However, the accuracy associated with these methods differs significantly. The results are shown on **Table 6.24**. The precision of the method was 0.07% RSD or less.

6.6.5 Results for carbon monoxide

Table 6.25: 60 µmol/mol CO results for a multicomponent PRGM – ABA calibration method

	Measurements, µmol/mol	**% difference**	**%RSD (precision)**
M51 8260	60.37	-0.05	≤0.55
60.33 µmol/mol	60.31	0.04	≤0.81
	60.65	-0.52	≤0.82

The accuracy of the single point calibration with only the sample and one reference gas mixture far exceeds the accuracy with which CO in the 10 – 100 µmol can be determined by multipoint calibration with several gas mixtures of different concentrations. The measured %relative deviation from the true mole fraction was less than 0.6%. The repeatability here, however, was not satisfactory at over 0.5 %RSD.

6.6.6 Results for sulphur dioxide

Table 6.26: SO_2 results for multicomponent PRGM

Average	**601.78**	**604.92**	**601.63**	**604.87**	**601.63**	**605.01**	**601.68**
Standard uncertainty	0.40	0.49	0.41	0.41	0.43	0.43	0.38
Gravimetric mole fraction µmol/mol	601.64	602.31					
Cylinder no.	M51 9528	**M51 8260**	M51 9528	**M51 8260**	M51 9528	**M51 8260**	M51 9528
Calculated concentration, µmol/mol		604.77		604.88		605.02	
% Difference		-0.41		-0.54		-0.56	
% RSD (precision)		0.04		0.04		0.02	

This method was less accurate for sulphur dioxide determination. However, at relative deviation of less than 0.6% it is still regarded of high metrological capability. The precision of this method was very good with %RSD of 0.04 and less.

CHAPTER SEVEN – AUTOMOTIVE GAS

In this chapter, the results of one of the most critical emission gases is discussed. This chapter deals with the development of a new standard for pollution monitoring, measurement capability and measurement equivalence. The work performed here for a new standard of carbon monoxide, carbon dioxide, propane and oxygen in nitrogen will contribute towards outputs of a key comparison.

7.1 Results

The composition of the eleven prepared mixtures is shown in **Chapter 5**. These were mainly analysed by gas chromatography coupled with thermal conductivity and flame ionization detectors, and by non-dispersive infrared spectroscopy for carbon monoxide only. Initially the mixtures of carbon monoxide, carbon dioxide, propane and oxygen in nitrogen were analysed to predict peak retention times in the multicomponent automotive samples. These were 1 %mol/mol carbon monoxide in nitrogen, 1 %mol/mol carbon dioxide in nitrogen, 1000 µmol/mol propane in nitrogen and 3 %mol/mol oxygen in nitrogen.

The carbon dioxide was detected at 5.281 min retention time by the front thermal conductivity detector. After 1.424 and 1.692 min are oxygen and nitrogen peaks respectively. The carbon monoxide separated from the stationary phase after 3.275 min and expected at an approximate retention time in the multicomponent sample. The peaks at 1.425 and 1.693 min are oxygen and nitrogen. The peak of propane is identified at 4.457 min in the flame ionization detector chromatogram. The flow in the flame ionization detector channel was increased to shorten the retention time of the molecule and the overall run time.

Initially the method was adequate for separation of CO, CO_2 and C_3H_8 but the O_2 and N_2 separation was not achieved. Three analytical conditions can be exploited to split peaks; temperature, pressure and flow rate. However, there is some difficulty associated with separating the two components, including argon. The oven temperature was lowered from 75°C to 30°C. The oxygen and nitrogen separation was achieved, and the flow rate was reduced to push these two peaks further apart. The higher the temperature, pressure and sample flow, the closer peaks are brought closer. The converse does the opposite and separates peaks. Temperature programming was employed to reduce the retention time of later eluting peaks (carbon dioxide and propane). The higher ramp temperature makes heavier molecules elute faster.

In this experiment, three 1 ml sample loops were connected initially for all three channels, however, in the auxiliary and front thermal conductivity detectors, the chromatogram peaks were broad. At 3 %mol/mol carbon dioxide and 2 %mol/mol carbon monoxide, the system was fed too much sample and the sample loops were changed to 2 x 250 µl size sample loops. The peaks were tailing (especially O_2), and these were changed to 2 x 100 µl size sample loops. 100 µl is a smaller loop, and a sharper peak is expected; not broad and tailing. The flow in the FID channel was increased such that the C_3H_8 elutes before the CO_2. The flow was reduced from 100 ml/min to 50 ml/min and then to 30 ml/min. From the second experiment (data) the analyses were conducted at an optimum 40 ml/min. Before quantitative analysis, the position of the peaks was confirmed by comparing the retention times of the binary and automotive samples.

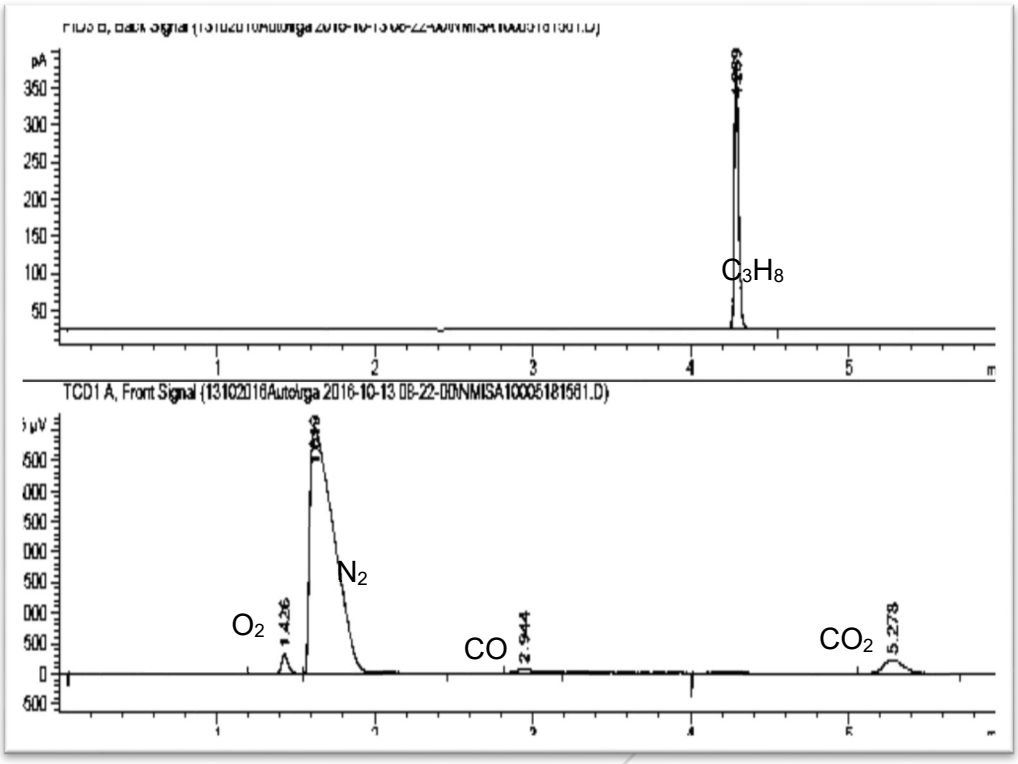


Figure 7.1: Chromatograms for the automotive gas mixtures

A slight shift in retention time was expected in the multicomponent sample as a result of the interactions of each component gas and other target gases. The permanent gases; carbon monoxide, carbon dioxide, oxygen and nitrogen were all detected by the thermal conductivity detector and the propane by the hydrocarbon sensitive flame ionization detector as shown by **Figure 7.1**. In the thermal conductivity detector, the order of elution for the permanent gases was $O_2/N_2/CO/CO_2$.This experiment was designed in such a way to investigate the repeatability, reproducibility (drift), sensitivity, accuracy and internal consistency of the first five (mixtures*).*

7.2 Discussion

When M51 8183 was used to determine the concentrations of the other four mixtures, the repeatability (**Tables 7.1-7.4**) of the method was determined as follows. 0.1 %RSD and less was achieved for O_2, 0.3 %RSD and less for CO with 0.1 %RSD and less for CO_2 excluding the results of M51 8269. The results of this sample are excluded in the approximation because the instrument signal was not stable (inconsistent) in comparison to the other results. The repeatability of the C_3H_8 measurement and was determined at 0.3 %RSD. The reference was changed to M51 8269 and the repeatability measured again. 0.2 %RSD and less was achieved for O_2, 0.08 %RSD and less for CO for three mixtures excluding M51 9512, 0.3% and less for CO_2 and ≤0.2 %RSD for C_3H_8. When M51 9512 was used to calibrate the method, ≤.0.1 % RSD was achieved for O_2 and CO, ≤0.3 %RSD for CO_2 and ≤0.2 %RSD for C_3H_8. When M51 8091 was used, ≤0.2 % RSD was achieved for O_2 and CO, ≤0.5 %RSD for CO_2 and ≤0.3 %RSD for C_3H_8. The last reference was M51 8186 where ≤0.2 %RSD was achieved for O_2 and CO, ≤0.3 % RSD for CO_2 and ≤0.2 %-RSD for C_3H_8.

The repeatability of the developed method for the measurement of these multicomponent gas mixtures was very good. However, the results also suggest that gas chromatograph is susceptible to drift at the initial stages of an analysis **Tables 7.1** to **7.4** shows the relative deviations from the reference values obtained from this method. These were presented to assess the accuracy of the method to measure the components of automotive gas. The associated uncertainties of these measurements are also shown.

Table 7.1: Results for the measurement of oxygen in automotive mixtures

Mixture	Gravimetric value	Analysis	% difference	% relative expanded uncertainty
M51 8183	30028.3	30006.2	0.07	0.44
M51 8186	**29940.0**	**30970.8**	**-3.4**	**0.35**
M51 8091	29355.9	29259.3	0.33	0.24
M51 9512	30001.2	30083.0	-0.27	0.21
M51 8269	30051.6	30071.5	-0.07	0.17

Without considering the results of M51 8186, the results in **Table 7.1** indicate that the measurement of oxygen in automotive gas was very precise and accurate. The developed method separated oxygen from nitrogen and allowed its accurate quantification. % differences of ≤0.3% were achieved.

Table 7.2: Results for the measurement of carbon monoxide in automotive mixtures

Mixture	Gravimetric value	Analysis	% difference	% relative expanded uncertainty
M51 8183	20069.9	20058.6	0.06	0.66
M51 8186	19977.2	19862.6	0.57	0.47
M51 8091	23525.6	23547.2	-0.09	0.28
M51 9512	19963.2	19981.6	-0.09	0.82
M51 8269	19824.8	19864.2	-0.20	0.75

The measurement of carbon monoxide was very accurate. The % differences from the gravimetric values was 0.6% and less as shown by **Table 7.2**.

Mixture	Gravimetric value	Analysis	% difference	% relative expanded uncertainty
M51 8183	29961.0	30073.6	0.06	0.44
M51 8186	29992.9	29945.4	0.16	0.78
M51 8091	30260.3	30229.4	0.10	0.28
M51 9512	30299.5	30292.8	0.02	0.45
M51 8269	29903.2	29909.8	-0.02	0.63

Table 7.3: Results for the measurement of carbon dioxide in automotive mixtures

The method also gave high accuracy with % relative deviations of less than 0.2% for carbon dioxide. Carbon dioxide results are shown in **Table 7.3**.

Table 7.4: Results for the measurement of propane in automotive mixtures

Mixture	Gravimetric value	Analysis	% difference	% relative expanded uncertainty
M51 8183	100.2	100.7	0.06	0.54
M51 8186	100.3	100.1	0.21	0.36
M51 8091	99.5	99.4	0.08	0.53
M51 9512	97.6	97.6	-0.05	0.29
M51 8269	100.1	100.4	-0.33	0.52

The maximum % relative deviations from true values achieved for propane as shown by **Table 7.4** were similar to the results of oxygen at 0.3% and less. In general, the developed method is very accurate for measurement of the components of automotive gas. The repeatability of this method is shown by **Tables 7.5-7.8** for oxygen, carbon monoxide, carbon dioxide and propane.

Table 7.5: Repeatability of oxygen in automotive gas measurements

	%RSD (measurement 1)	%RSD (measurement 2)	% RSD (measurement 3)	%RSD (measurement 4)	%RSD (measurement 5)
M51 8183	reference	0.05	0.05	0.09	0.08
M51 8186	0.10	0.22	0.07	0.16	reference
M51 8091	0.03	0.06	0.02	reference	0.10
M51 9512	0.03	0.16	reference	0.02	0.18
M51 8269	0.09	reference	0.13	0.04	0.07

Table 7.6: Repeatability of carbon monoxide in automotive gas measurements

	%RSD (measurement 1)	%RSD (measurement 2)	% RSD (measurement 3)	%RSD (measurement 4)	%RSD (measurement 5)
M51 8183	reference	0.08	0.11	0.09	0.11
M51 8186	0.03	0.06	0.10	0.11	Reference
M51 8091	0.10	0.07	0.06	reference	0.16
M51 9512	0.10	**0.96**	reference	0.06	0.16
M51 8269	0.25	reference	0.07	0.15	0.06

Table 7.7: Repeatability of carbon dioxide in automotive gas measurements

	%RSD (measurement 1)	%RSD (measurement 2)	% RSD (measurement 3)	%RSD (measurement 4)	%RSD (measurement 5)
M51 8183	reference	0.25	0.04	0.52	0.14
M51 8186	0.12	0.05	0.27	0.10	reference
M51 8091	0.05	0.07	0.11	reference	0.17
M51 9512	0.09	0.09	reference	0.10	0.10
M51 8269	0.94	reference	0.07	0.11	0.26

Table 7.8: Repeatability of propane in automotive gas measurements

	%RSD (measurement 1)	%RSD (measurement 2)	% RSD (measurement 3)	%RSD (measurement 4)	%RSD (measurement 5)
M51 8183	reference	0.19	0.05	0.18	0.12
M51 8186	0.28	0.14	0.23	0.25	reference
M51 8091	0.17	0.01	0.12	reference	0.16
M51 9512	0.09	0.24	reference	0.12	0.11
M51 8269	0.11	reference	0.21	0.14	0.21

7.3 Internal uniformity study

The sensitivity ratio is a factor used to investigate the internal uniformity of the five (5) mixtures relative to each other. A perfect uniformity is shown by a ratio equal to 1. The comparison was made by comparing the sensitivity ratios along with the uncertainties from analysis on a plot. From the results when M51 8183 gas mixture was used as a reference, the following internal consistencies were plotted for oxygen, carbon monoxide, carbon dioxide and propane.

$$\text{sensitivity} = \frac{\bar{x}}{\mu_{\text{gravimetry}}} \qquad \textbf{7.2}$$

$\bar{x}$ is the average of instrument response and $\mu_{\text{gravimetry}}$, the gravimetry mole fraction. If we assume that the consistency of the reference to itself is equal to one, then'

$$\text{ratio(consistency)} = \frac{\text{sensitivity(sample)}}{\text{sensitivity (standard)}} \qquad \textbf{7.3}$$

In general, an ideal consistency is of ratio(consistency)=1.00. However, where gravimetry or composition is significantly different, the ideal assumption will deviate.

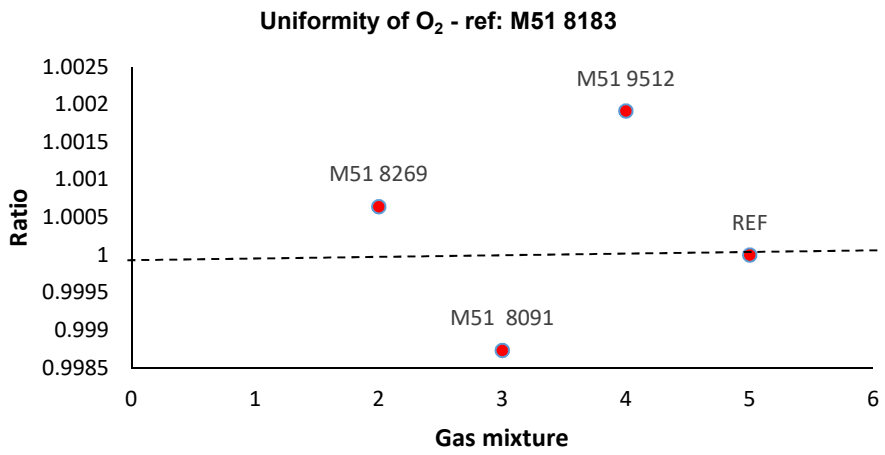


Figure 7.2a: Internal uniformity of oxygen in automotive gas mixtures

Generally, the internal consistency of oxygen was not satisfactory for all reference comparison. However, from the results shown **Figure 7.2a** the internal consistency of M51 8269 was the most comparable with the standard gas mixture.

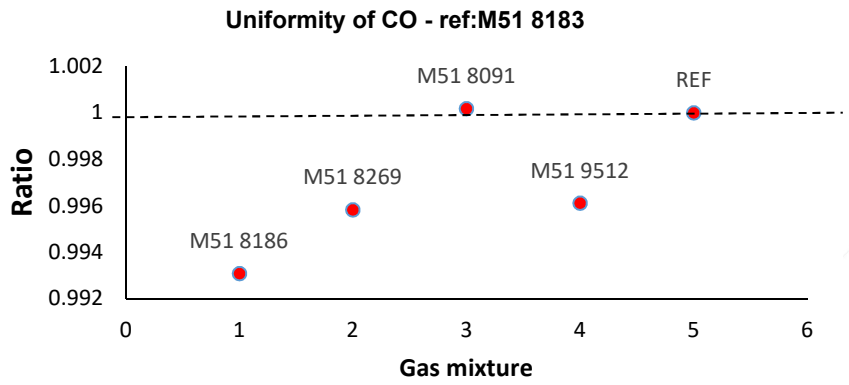


Figure 7.2b: Internal uniformity of carbon monoxide in automotive gas mixtures

Good internal consistency of carbon monoxide was observed for the samples. The most consistent with the standard gas mixture used was M51 8091, and the least consistent was M51 8186

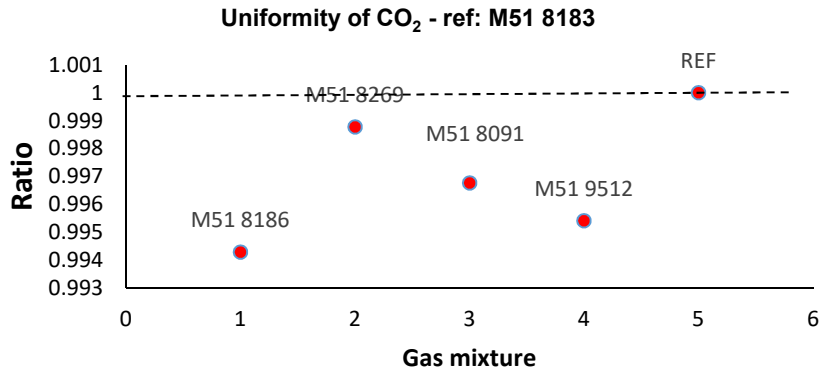


Figure 7.2c: Internal consistency of carbon dioxide in automotive gas mixtures

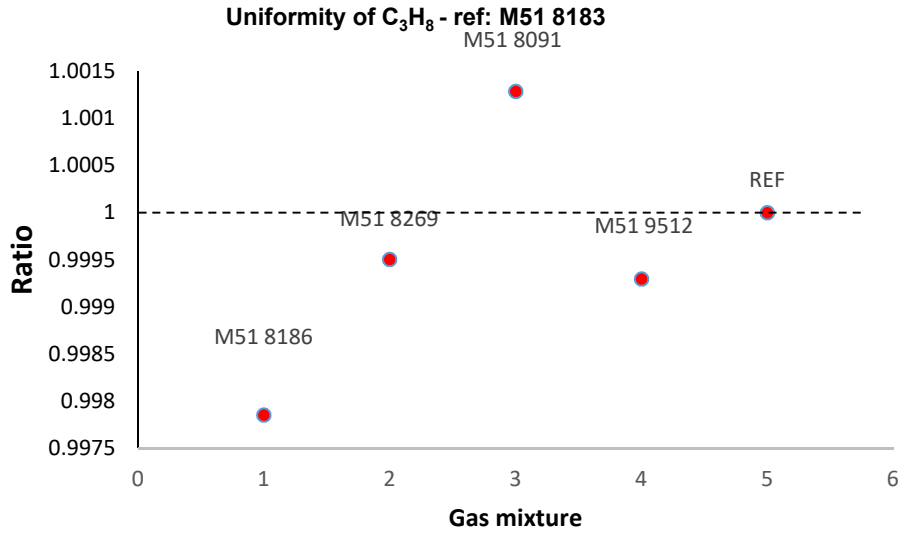


Figure 7.2d: Internal uniformity of propane in automotive gas mixtures

The amount of carbon dioxide and propane in the automotive mixtures were consistent with the amount in the reference. However, there is a large dispersion or variation observed in metrological terms. M51 8186 was the least consistent with the reference mixture for propane and carbon dioxide as well. Therefore, a conclusion can be made that M51 8186 was the least internally consistent with the reference. The reference mixture was more consistent with the standard gas mixture was M51 8269.

Baseline allocation was employed to re-integrate the individual peak areas of the four components that were suspected as outliers. This method is often used to improve the repeatability of the experiment. The oxygen measurements are repeatable, however at other measurements the difference between calculated and gravimetric preparation was over 3%. To develop a new national measurement standard of automotive gas, a newly developed method should meet the most stringent pre-requisites for it to be adopted for the validation of that reference gas mixture and its ability to produce the lowest uncertainties of measurement.

7.4 Stability of automotive gas components

To evaluate the behaviour of oxygen, carbon monoxide, carbon dioxide and propane in nitrogen, stability graphs were plotted. These are presented on **Figure 7.3**.

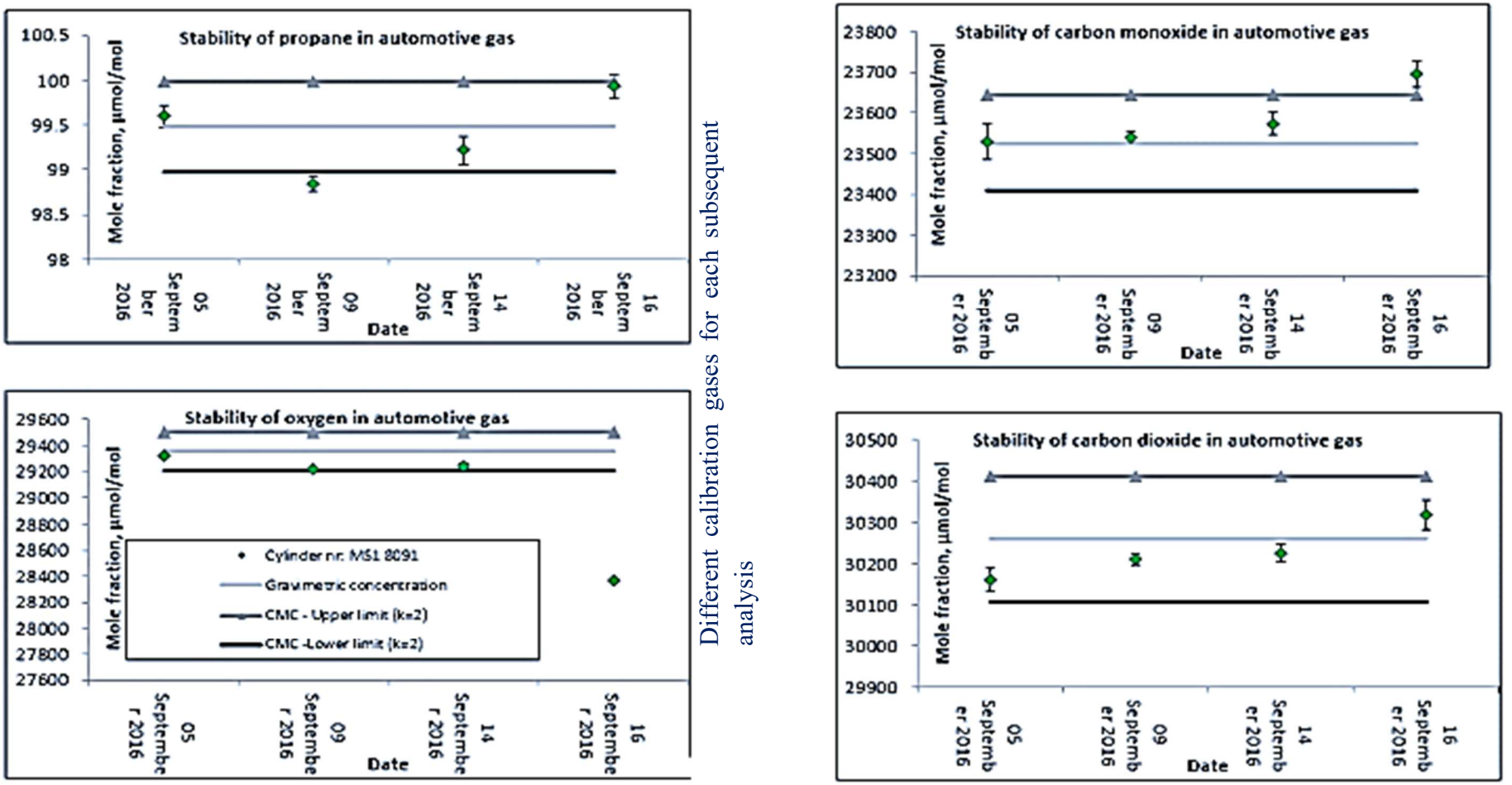


Figure 7.3: Short term stability study results of oxygen, carbon monoxide, carbon dioxide and propane for M51 8091

Figure 7.3 shows the stability of oxygen. Generally, oxygen was the least stable of the four components. Its stability was very poor. Even though the method had been proved slightly precise for oxygen, the oxygen has very poor stability.

The evaluation of stability for carbon monoxide in automotive gas shows that the gas has poor stability. The amount of carbon monoxide was not homogeneous or the preparation technique was inaccurate. Significant instability can be observed. The stability of carbon dioxide in automotive gas was not satisfactory. Generally, the stability graphs indicate that there is poor stability associated with the component gases. This effect may also be attributed to the presence of oxygen, however, that must be extensively studied. Different standard gas mixtures were used for each result, and this may have had a negative effect on the stability of oxygen, carbon monoxide, carbon dioxide and propane. In previous experiment, the analysis of CO, CO_2 and O_2 was not accurate. Whereas, the problem was solved here, the stability remains a challenge.

7.5 Uncertainty budget for borda substitution method

The uncertainty budgets of the results from **7.1** were determined by following the following approach. The uncertainty contributions were identified from the model equation used to calculate the unknown mole fraction

$$C_{unknown} = \frac{C_{known}}{\text{Peak area}_{known}} \text{Peak area}_{unknown} \qquad \textbf{7.4}$$

Table 7.9: Uncertainty budget for oxygen measurement of M51 8091 (M51 8183 as reference)

Parameter	Value	Standard uncertainty	Uncertainty	Distribution	Sensitivity coefficient	Uncertainty contribution (µmol/mol)
C_{known}	30028.3	8.4 µmol/mol	Type B	Gaussian	0.98	8.2
A_{known}	1082.8 25µV	0.29 25µV	Type A	Gaussian	-27	-7.9
$A_{unknown}$	1057.3 25µV	0.18 25µV	Type A	Gaussian	28	5.0
$C_{unknown}$	29318.8 ± 12.4 µmol/mol					

Table 7.9 was used to show how the uncertainties are calculated for the analysis results where ABA calibration method was used, similarly to the previous experiment.

7.6 Multipoint calibration method

The results **from 7.2** to **7.5** were extracted from the first of two experiments, where linearity of the instrument was assumed. In this next experiment, no linearity was assumed and calibration standards of different concentrations in the nominal fraction range of CCQM.K3-2018 were used to calculate concentrations of unknown samples (M51 9535 and M51 9517).

In this experiment, all components were analysed on the gas chromatography instrument coupled with flame ionization detector and two thermal conductivity detectors, similar to the first experiment. Using non-dispersive infrared spectroscopy only the analysis of carbon monoxide was performed. The carbon dioxide analyser was not working properly. Six more automotive reference gas mixtures were prepared for a multipoint calibration technique exercise. The first results are for non-dispersive infrared spectroscopy and then gas chromatography.

Table 7.10: Non-dispersive infrared spectroscopy results for carbon monoxide in automotive mixtures

Measurements	Mixture	% relative standard deviation	Result	% difference
1	M51 9535	0.01	5004.06	-0.08
2		0.01	5002.70	-0.05
3		0.01	5003.09	-0.06
1	M51 9517	0.01	17503.15	-0.29
2		0.003	17502.95	-0.29
3		0.03	17503.17	-0.29

The results on **Table 7.10** clearly indicate a very repeatable (high-precision) method for the measurement of carbon monoxide in automotive gas by gas chromatography. The % relative standard deviations were ≤0.01%. The non-dispersive infrared spectroscopy method for the measurement of carbon monoxide is also very accurate. The % differences of the analysis results from the gravimetric values were ≤0.3%. Therefore, we can suggest that the measurement of the component gas by this method is a highly precise and accurate measurement.

To evaluate the linearity of carbon monoxide absorption, the linear calibration curve of the first measurement is plotted below in **Figure 7.4**. the linearity was evaluated by use of the correlation coefficient.

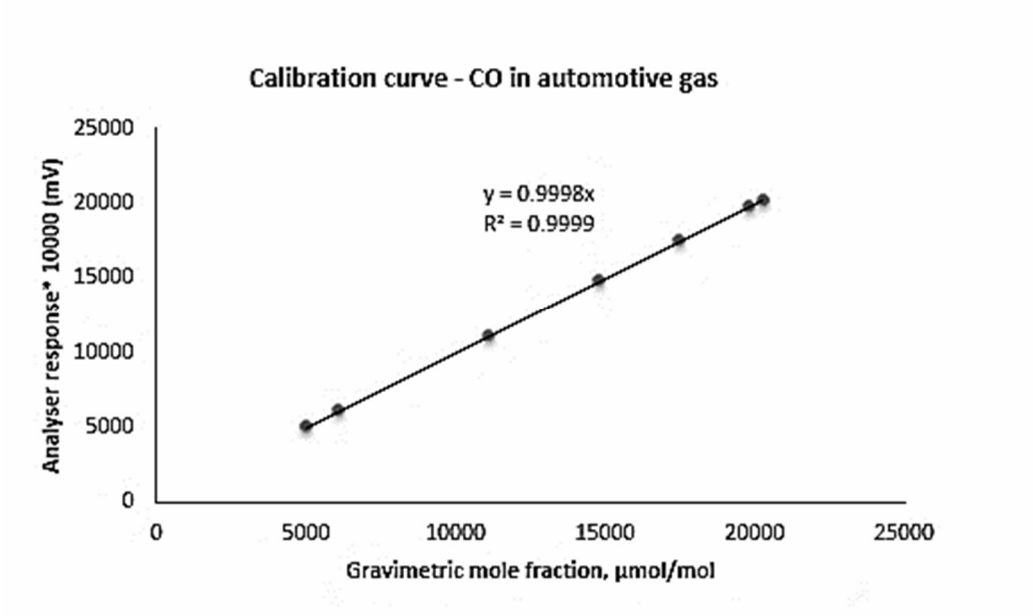


Figure 7.4: Calibration curve for the analysis of CO in automotive mixtures by non-dispersive infrared spectroscopy and multipoint calibration.

A perfect linear calibration curve was obtained for the analyser response and gravimetric mole fractions of carbon monoxide in the different mixtures. A correlation coefficient of 0.9999 was obtained. Therefore, a linear absorption of carbon monoxide in automotive gas can be assumed. The results indicate that cross interferences in the measurement of carbon monoxide, in the presence of carbon dioxide, propane and oxygen is not a problem. There is no evidence of cross interference. Note however that the design of the experiment assumed that non-dispersive infrared spectroscopy is non-linear. The results prove the converse for carbon monoxide.

At this stage, however, it is not possible to suggest that the absorbance of gas for all four components is linear. However, we can conclude and assume that the carbon monoxide gas in that specific matrix does not deviate from the Beer-lambert law, and perhaps is not affected by the matrix effect phenomenon.

The stability of carbon monoxide was evaluated by use of the stability graph and checking the behaviour of the gas.

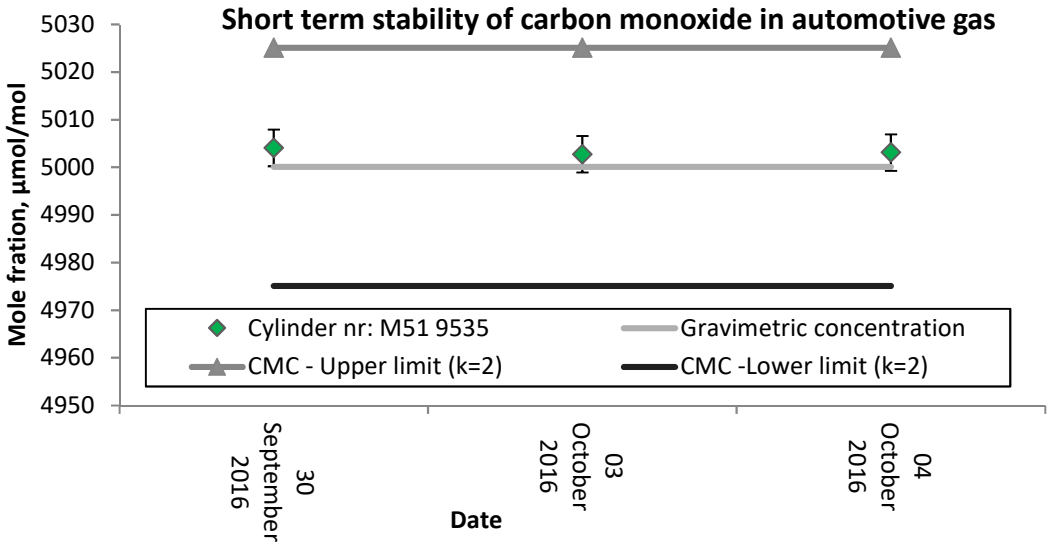


Figure 7.5: Short-term stability of carbon monoxide in an automotive mixture for M51 9535. Multipoint calibration.

Note how the stability of carbon monoxide was poor by using single point calibration method and gas chromatography for analysis. This negative effect may have resulted from the use of different standard gas mixtures. However, when the automotive samples were analysed on the non-dispersive infrared analyser, the concentration of carbon monoxide was very stable. Therefore, we can recommend the use of this instrument for analysing carbon monoxide in automotive gas.

Another multipoint calibration technique experiment was performed using gas chromatography. In the design of the analysis too, no linearity was assumed. The seven gas mixtures of different concentrations were analysed randomly but at the same position on the sampler box. This aims to provide the comparison between the two modes of analysis using the same analytical conditions. The repeatability of oxygen is ≤0.3 %RSD for three experiments and ≤0.4 %RSD for carbon monoxide excluding the results of M52 8121 (first measurement) where a higher repeatability of 0.72 %RSD was obtained. The repeatability of carbon dioxide and propane was determined at ≤0.2 %RSD. The repeatability however, was very poor at the beginning of the measurements and improved with a consequent analysis.

The longer the analytical experiment continues the better the overall repeatability of the measurements for carbon monoxide, carbon dioxide, propane and oxygen. The obtained results show a very precise method that can be used to analyse the four components by GC TCD and FID. The results of the %RSD for the repeatability assessment are shown on the raw data.

The reproducibility of the method was not satisfactory. The reproducibility of oxygen is ≤6.7 %RSD for six mixtures and almost 36 %RSD for M51 9535. For CO, the reproducibility was measured at ≤5.2 %RSD. For CO_2, a ≤3.0 %RSD was achieved and ≤1.2 %RSD for C_3H_8. In general, the C_3H_8 measurements were more reproducible followed by CO_2. The repeatability of the method is presented from **Tables 7.13** to **7.16**.

Table 7.11: Reproducibility of the multipoint calibration method for analysis of automotive samples

M51	8156				8158				8121			
Component	**O_2**	**CO**	**CO_2**	**C_3H_8**	**O_2**	**CO**	**CO_2**	**C_3H_8**	**O_2**	**CO**	**CO_2**	**C_3H_8**
% RSD	2.3	5.2	0.59	1.2	1.3	2.5	1.6	1.2	6.7	3.0	2.2	0.6

Table 7.12: Reproducibility of the multipoint calibration method for analysis of automotive samples

M51	9535				8269				8193				9517			
Component	**O_2**	**CO**	**CO_2**	**C_3H_8**	**O_2**	**CO**	**CO_2**	**C_3H_8**	**O_2**	**CO**	**CO_2**	**C_3H_8**	**O_2**	**CO**	**CO_2**	**C_3H_8**
% RSD	35.2	2.9	2.1	0.31	0.48	2.9	2.2	0.7	0.63	3.4	1.1	1.5	0.63	2.6	0.90	1.2

Table 7.13: Repeatability of oxygen measurements (multipoint)

	%RSD		
Mixture	**Measurement 1**	**Measurement 2**	**Measurement 3**
M51 8156	0.05	0.23	0.02
M51 8193	0.07	0.04	0.04
M51 8158	0.11	0.03	0.01
M51 9517	0.20	**0.37**	0.08
M51 9535	0.32	0.13	0.20
M51 8121	0.25	0.05	0.01
M51 8269	0.16	0.03	0.02

The repeatability however was very good. **Table 7.13** shows the repeatability of the oxygen measurement. The repeatability of the single point and multipoint calibration methods was comparable. The lowest % repeatability was 0.4%RSD and the highest achievable precision at 0.01% RSD.

Table 7.14: Repeatability of carbon monoxide results (multipoint)

	%RSD		
Component	**Measurement 1**	**Measurement 2**	**Measurement 3**
M51 8156	0.03	0.19	0.04
M51 8193	0.11	0.22	0.06
M51 8158	0.15	0.26	0.06
M51 9517	0.27	0.15	0.24
M51 9535	0.41	0.25	0.41
M51 8121	0.72	0.11	0.29
M51 8269	0.15	0.05	0.03

In general, the repeatability of carbon monoxide was poor compared to the other three components as shown by **Table 7.14**. The lowest precision was determined at 0.7 %RSD. However, at least 0.03 %RSD was achieved.

Table 7.15: Repeatability of carbon dioxide results (multipoint)

	%RSD		
Component	**Measurement 1**	**Measurement 2**	**Measurement 3**
M51 8156	0.09	0.02	0.01
M51 8193	0.02	0.06	0.11
M51 8158	0.06	0.05	0.02
M51 9517	0.09	0.15	0.02
M51 9535	0.15	0.04	0.05
M51 8121	-	0.01	0.07
M51 8269	0.24	0.07	0.05

The repeatability of carbon dioxide in automotive gas results very good compared to both oxygen and carbon monoxide. The highest precision observed was at 0.01 %RSD and the lowest at 0.2 %RSD.

Table 7.16: Repeatability of propane results (multipoint)

	%RSD		
Component	**Measurement 1**	**Measurement 2**	**Measurement 3**
M51 8156	0.11	0.09	0.14
M51 8193	0.10	0.15	0.10
M51 8158	0.10	0.03	0.15
M51 9517	0.07	0.09	0.05
M51 9535	0.05	0.14	0.05
M51 8121	0.07	0.08	0.14
M51 8269	0.05	0.12	0.09

The repeatability of propane in automotive gas measurements was also very good. The lowest precision was determined to be 0.1% RSD. The linearity of the method was evaluated by use of calibration curves.

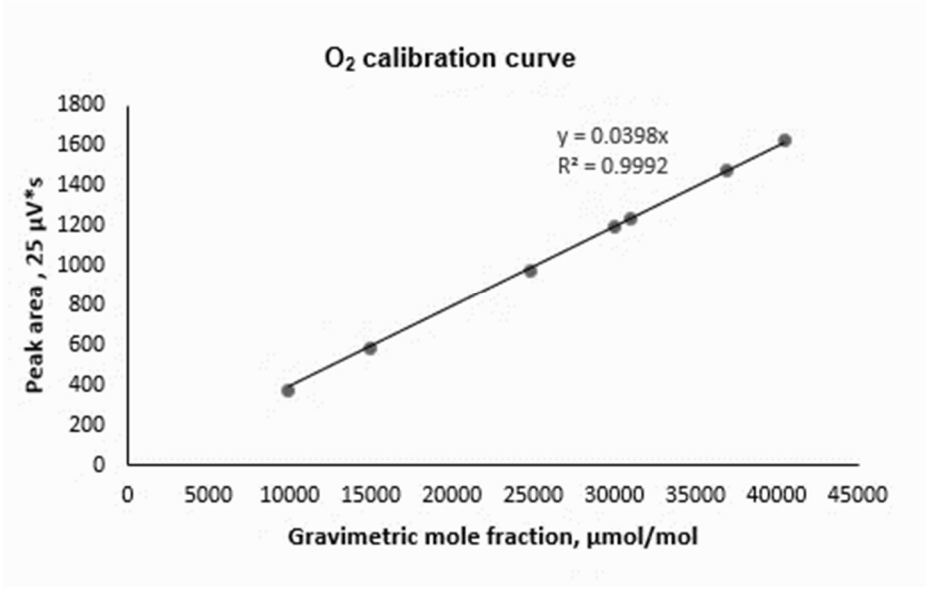


Figure 7.6a: Multipoint calibration curve of oxygen for automotive mixtures in the range 1-4 %mol/mol

The measurement of oxygen by gas chromatography was determined to be linear. The correlation coefficient was 0.9992. The calibration curve is shown on **Figure 7.6a.**

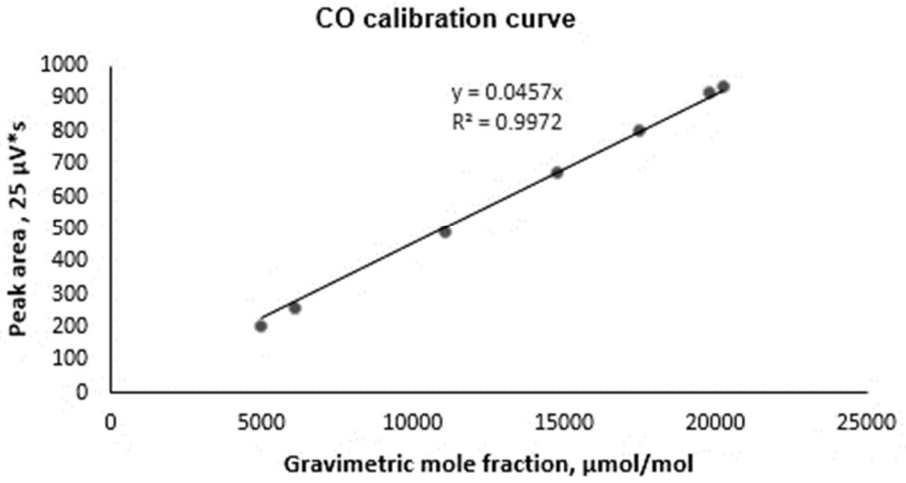


Figure 7.6b: Multipoint calibration curve of carbon monoxide for automotive mixtures in the range 0.5-2 %mol/mol

The measurement of carbon monoxide showed good linearity as shown on **Figure 7.6b**. Linear regression models can be used to calculate the concentration of unknown samples.

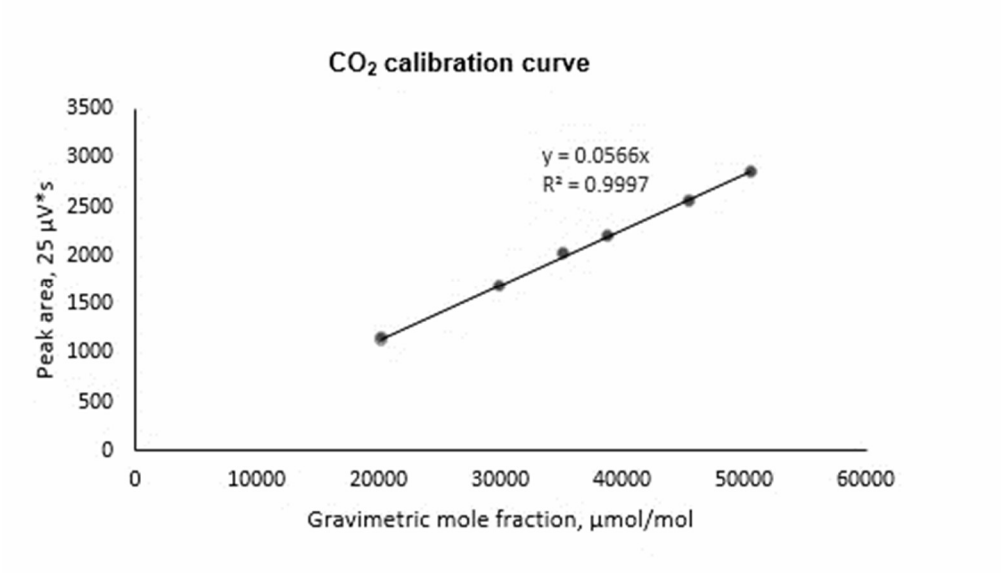


Figure 7.6c: Multipoint calibration curve of carbon dioxide for automotive mixtures in the range 2-5 %mol/mol

The measurement of carbon dioxide was determined to be linear. The correlation coefficient was 0.9997. The calibration curve is shown on **Figure 7.6c**.

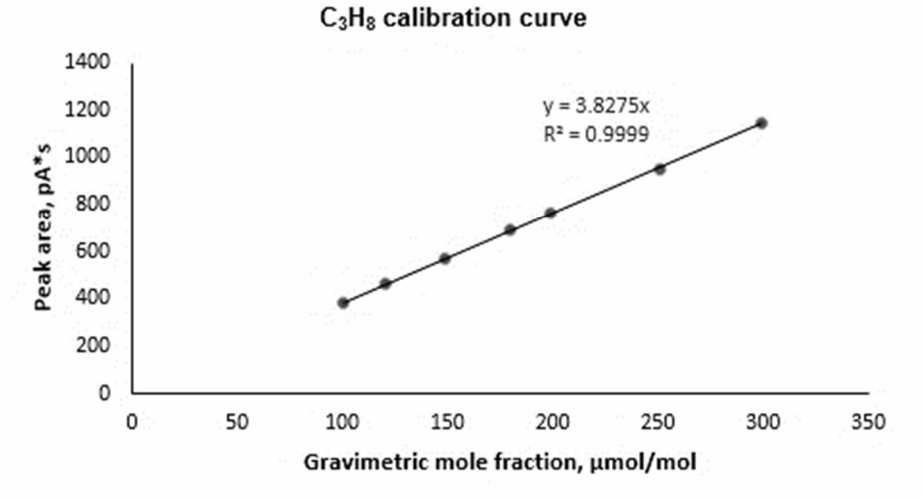


Figure 7.6d: Multipoint calibration curve of propane for automotive mixtures in the range 100-300 µmol/mol

The measurement of propane was determined to be linear. The correlation coefficient was 0.9999. The FID appeared to be more linear than TCD. In general, the gas chromatography instrument with two thermal conductivity detectors and flame ionization detector is linear in the nominal range of the proposed key comparison for the components.

7.7 Supplement gas chromatography work

Supplement work was performed to evaluate the differences of using a thermal conductivity or flame ionization detector for the analysis of carbon monoxide and carbon dioxide in automotive gas. The gas chromatography instrument was a Varian 3800 similar to one shown in **3.1**. In general, the results of carbon dioxide (tables 9.8a-d) indicate that the accuracy of the thermal conductivity detector experiment and flame ionization detector is comparable. The precision/repeatability of this experiment was also very high in comparison with the analysis performed on the thermal conductivity gas chromatography instrument (Agilent 7890). The % relative standard deviations for carbon dioxide in automotive gas measurements were 0.3 % and less. The % relative standard deviations for carbon monoxide were 0.3 % and less if the first measurements of M51 8183 as reference is rejected. The % relative was 1.1%, higher than the 0.3%. To get accurate results however, the flame ionization method requires longer periods of analysis. At the beginning individual experiments the results were not satisfactory. There was more drift than the thermal conductivity detection method. However, the Varian 3800 was not being used for some time before the automotive gas analysis. This may have attributed negatively to the drift problems. Therefore, both techniques can be used for the measurement of carbon monoxide and carbon dioxide in automotive gas. See results in **Annexure F.**

7.8 Proficiency testing scheme results

In this section of **Chapter 7**, the results of a different type of automotive gas proficiency testing scheme samples are presented. Special emphasis is placed on the accuracy and repeatability of the analytical method used. Repeatability is important for smaller deviations and consequently smaller uncertainties.

7.8.1 Results and discussion

The mole fractions were 60 µmol/mol CO, 12 %mol/mol CO_2 and 10 %mol/mol O_2 respectively.

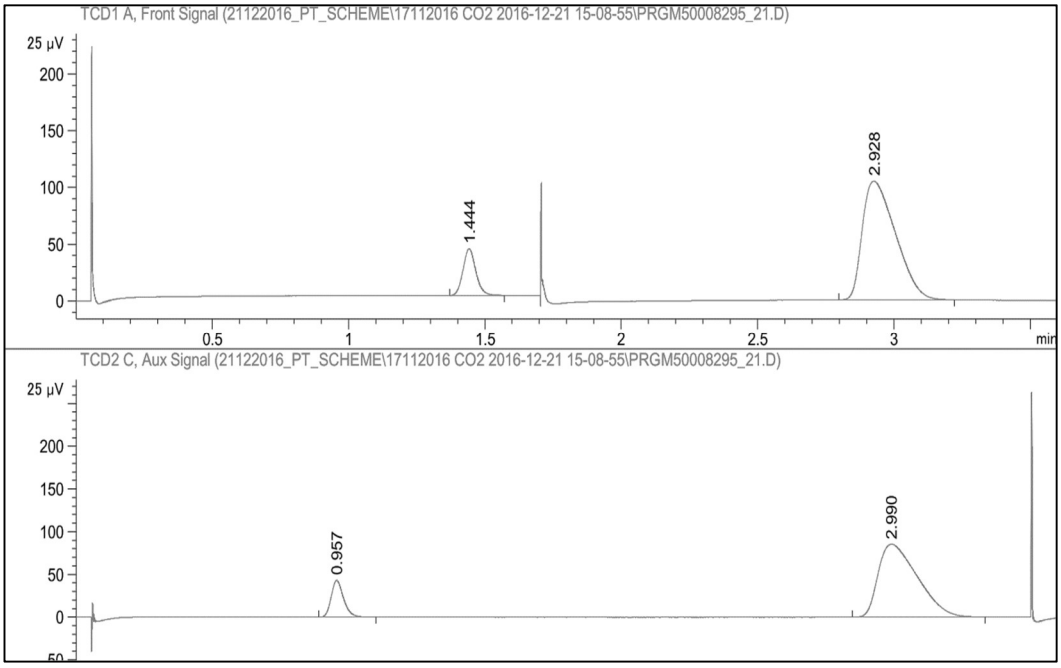


Figure 7.7: Thermal conductivity detector chromatogram for oxygen and carbon dioxide

Figure 7.7 shows the obtained for the chromatograph. Complete symmetry and peak narrowness and sharpening was not achieved. The initial and final temperatures could be increased to improve these factors and improve the overall peak retention time repeatability and method repeatability. The oxygen was detected at 1.4 and 1.0 minutes by the front and auxiliary TCDs respectively. The carbon dioxide was detected after 2.9 and 3.0 minutes respectively.

Table 7.19: Auxiliary TCD results for O_2 and CO_2 for the proficiency testing scheme's samples

Agilent 7890 Gas chromatograph – Aux **TCD results**				
D95 8295	As standard		As sample	
	O_2 (%)	CO_2 (%)	O_2 (%)	CO_2 (%)
Repeatability(precision)	0.28	0.23	0.15	0.10
Drift control (highest)	0.28	0.23	-	-
% relative deviation	-	-	0.7	0.7

*Aux Auxiliary

In this work, the two TCD's of the RGA were used and set up to detect the eluents simultaneously in this method. This was done to evaluate the performance of one to another. The RGA was also used for O_2 and CO_2 only because the configuration was set up for typically high concentrations. In **Table 7.19**, the results are shown. The accuracy of the method was within a 1% relative deviation. The repeatability was very good at less than 0.3%. The results of the front TCD are shown next.

Table 7.20: Front TCD results for O_2 and CO_2 for the proficiency testing scheme's samples

Agilent 7890 Gas chromatograph – Front **TCD results**				
D95 8295	As standard		As sample	
	O_2 (%)	CO_2 (%)	O_2 (%)	CO_2 (%)
Repeatability(precision)	0.85	0.60	0.46	0.26
Drift control (highest)	8.0	1.8	-	-
% relative deviation	-	-	0.86	0.28

Table 7.20 shows an associated decline in accuracy when the front TCD was used. The detector drifted more than the auxiliary one. Therefore, resulting in an

undesirable effect of decreasing the accuracy of the measurement method. The %relative deviation, however, is still within the 1% limit.

The carbon monoxide measurement was performed by a different chromatograph. The measurement was done using a 7890B Agilent gas chromatograph with micro electron-capture (EC-) and flame-ionisation detection systems coupled with a methaniser.

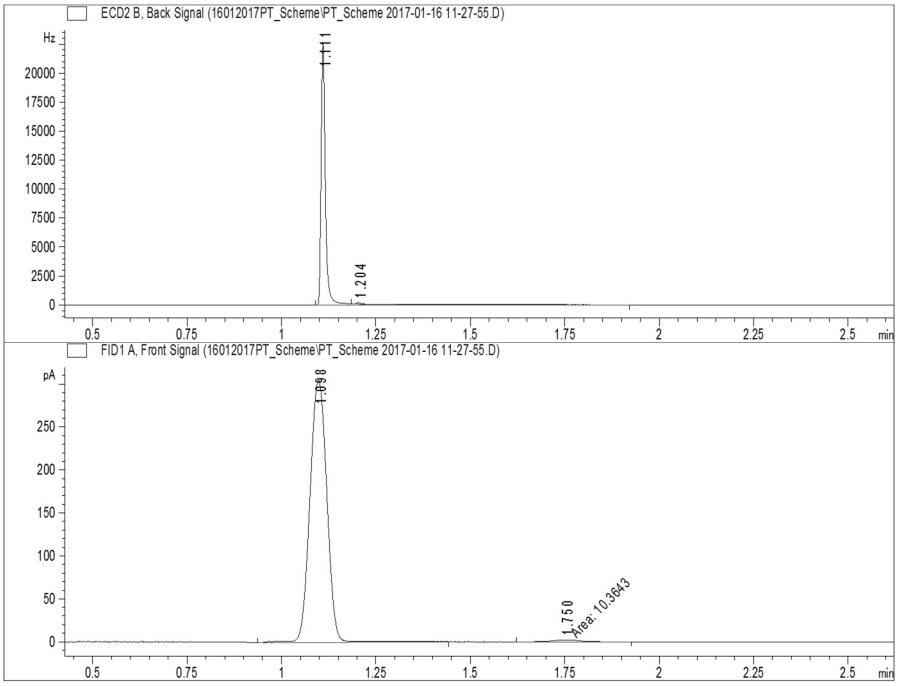


Figure 7.8: FID and ECD detectors' chromatograph of CO in the proficiency test sample.

The FID was used to detect to measure the CO content of the gas mixture. The results follow next. Here the sample was never used as a standard therefore, results of two mixtures are shown.

Table 7.21: FID results for CO of the proficiency testing scheme's samples

Agilent 7890 Gas chromatograph – CO **TCD results**		
	Standard (M55 5672)	Sample (D95 8295)
	O_2 (%)	O_2 (%)
Repeatability(precision)	0.59	0.54
Drift control (highest)	0.41	-
% relative deviation	-	0.94

The % relative deviation was less than 1% as shown by **Table 7.21**. However, a 0.94% it is not desirable as it sits on the limits of the method. In general, the three measurements were successful in providing a better measurement solution to NDIR and the use of single component reference gas mixtures by replacing it with a more accurate GC and matrix matched standard gas mixtures' method. There poor accuracy associated with carbon monoxide and carbon dioxide measurements was improved significantly. However, more still needs to be done to improve this method and thus, the measurement capability of the type multicomponent gas mixture. The effects of drift of a gas chromatograph also must be re-affirmed. It was observed that these instruments drift over time and this results in a negative effect in the accuracy. This drift can be attributed to environmental temperature and atmospheric pressure changes. Pressure and temperature must be controlled vigorously in gas-phase chromatography.

The results of the measurements by the stakeholders for this proficiency scheme were not submitted back to the laboratory. Therefore, these are not included in this chapter. However, this scheme is very important for comparison of measurement capabilities and its pursuit is very critical. This scheme will be completed shortly.

CHAPTER EIGHT - CONCLUSIONS AND RECOMMENDATIONS

8.1 Conclusions

Continuous emission monitoring is important to evaluate compliance to minimum emission standards and contributions to deteriorating air quality. In the event of implementation of the more accurate Tier 3 level approach of the 2006 IPCC guidelines as mandatory, the availability of emission primary reference gas mixtures will be central to the success of the South African monitoring programme. Therefore, effort is continuously put into development of emission reference materials including methods for stack and automotive gas components' qualitative and quantitative determination to ensure quality of measurements. This work aimed to improve the provision and measurement capability of stack and automotive reference gas mixtures by using different methods to study these and its objectives were successful.

Objective one of the research project was concerned with gravimetric preparation and analysis of the components of the prepared mixtures. Stack gas mixtures of CO, CO_2, NO, SO_2 and C_3H_8 in a balance of N_2 were successfully prepared gravimetrically following the international standard of ISO 6142-1:2015. These were analysed by using non-dispersive spectroscopy and gas chromatography techniques. For calibration purposes, multipoint calibration was used and standard gas mixtures of different matrices were used for NDIR. The use of matrix and non-matrix reference gas mixtures was done for comparing results and to investigate the significance of matrix differences in stack gas. The results obtained showed that the use of binary standard gas mixtures often resulted in synergistic effects especially for nitric oxide and carbon monoxide. This prodigy was not observed on sulphur dioxide and carbon dioxide. The use of sulphur dioxide in nitrogen standard gas mixtures for the determination of the molar fraction of sulphur dioxide in stack mixtures was a more accurate method than use of stack standard gas mixtures. The discrepancy needs to be investigated and explained scientifically. The determination of carbon dioxide at percent level mole fractions was

independent of matrix effects. The analysis of larger concentrations is often less challenging than lower levels in simple binary mixtures. Therefore, we can assume that these (large concentrations) are also independent of matrix gas. However, for stack mixtures, this can be confirmed only for carbon dioxide with confidence. The use of binary standard gas mixtures and those similar in matrix to the samples resulted in comparable accuracies. The relative expanded uncertainty for carbon dioxide was from 0.4% to 0.8% and 0.4% to 1.3% depending on the matrix of the standard gas mixtures used, 0.5% to 1% for propane excluding the measurements of M51 8268, 2% to 6% for carbon monoxide, and 0.3% to 2.3% for sulphur dioxide.

Generally, the measurements of CO_2, NO and C_3H_8 were better compared to SO_2 and CO. SO_2 and CO are reactive gases, some difficulty was expected. Problems such as adsorption which were not studied or quantified, would need to be extensively researched to understand the stack mixture system. It is important in the measurement of stack gas, to understand the behaviour of all component gases. The relative accuracy of CO_2, NO and C_3H_8 measurements compared to the results of CCQM K71 were improved. More work however, still needs to be done to improve NO and CO measurements. The reduction of associated uncertainties for all five components of stack mixtures needs improvement as well.

The use of gas chromatography with thermal conductivity detection to analyse carbon dioxide in stack gas was exploited for a stack primary reference gas mixture. However, this was not done for carbon monoxide since the detector is less sensitive to ppm levels. The carbon dioxide was analysed simultaneously with propane (flame ionisation detection). This method was very precise and accurate for the intended purposes. In general, the NDIR and gas chromatography techniques complement each other very well for the analysis of carbon dioxide using either type of reference gas mixtures. While the use of gas chromatograph with flame ionisation detection was available to the laboratory, the contents of stack gas made it impractical to analyse carbon monoxide and carbon dioxide with the detector. Nitric oxide and sulphur dioxide are known to deactivate the catalyst. For the primary reference gas mixture, the mole fractions of the reactive gases were higher than the CCQM K71 mole fraction ranges. Therefore, the results were

expected to be better. In this determination, a different type of calibration method was used. The concentrations of the sample and standard gas mixtures were matched and single point calibration used. This resulted in better accuracy. Therefore, we can assume that matching mole fractions and single point may solve prior challenges.

Objective two of this work was concerned with purity analysis. Purity of select gases was performed successfully by use of various methods and rectangular and normal distributions for uncertainty calculations. Improvements needs to be made however, for the analysis of moisture in source gases.

Objective three was concerned with the development of new national measurement standards for automotive gas. These mixtures of carbon monoxide, carbon dioxide oxygen and propane in nitrogen were prepared for a key comparison CCQM.K3-2018 (tentative). A method was developed that achieved separation of oxygen and nitrogen; however, the separation of oxygen and argon was not achieved. Only matrix matched standards were used in this part of the project since they proved to be a more correct way of analysing multicomponent samples. The use of a single point calibration is also recommended more than multipoint calibration to calculate unknown concentrations. The repeatability of the method is very good; however, its reproducibility is very poor. The % relative standard deviation was used as a measure of repeatability (precision). The precision of oxygen measurement was ≤0.2%, ≤0.1% for carbon monoxide, ≤0.5% for carbon dioxide and ≤0.3% for propane. The relative uncertainties at which these components were measured were 0.4% for oxygen, 0.8% for carbon monoxide and carbon dioxide and 0.5% for propane. A proficiency testing scheme was done for automotive emission. This scheme unfortunately was not concluded since the results from the stakeholders were not submitted back to the laboratory. However, this will be concluded soon. This scheme will be pursued since it is critical for emission monitoring and the capabilities of the monitoring framework.

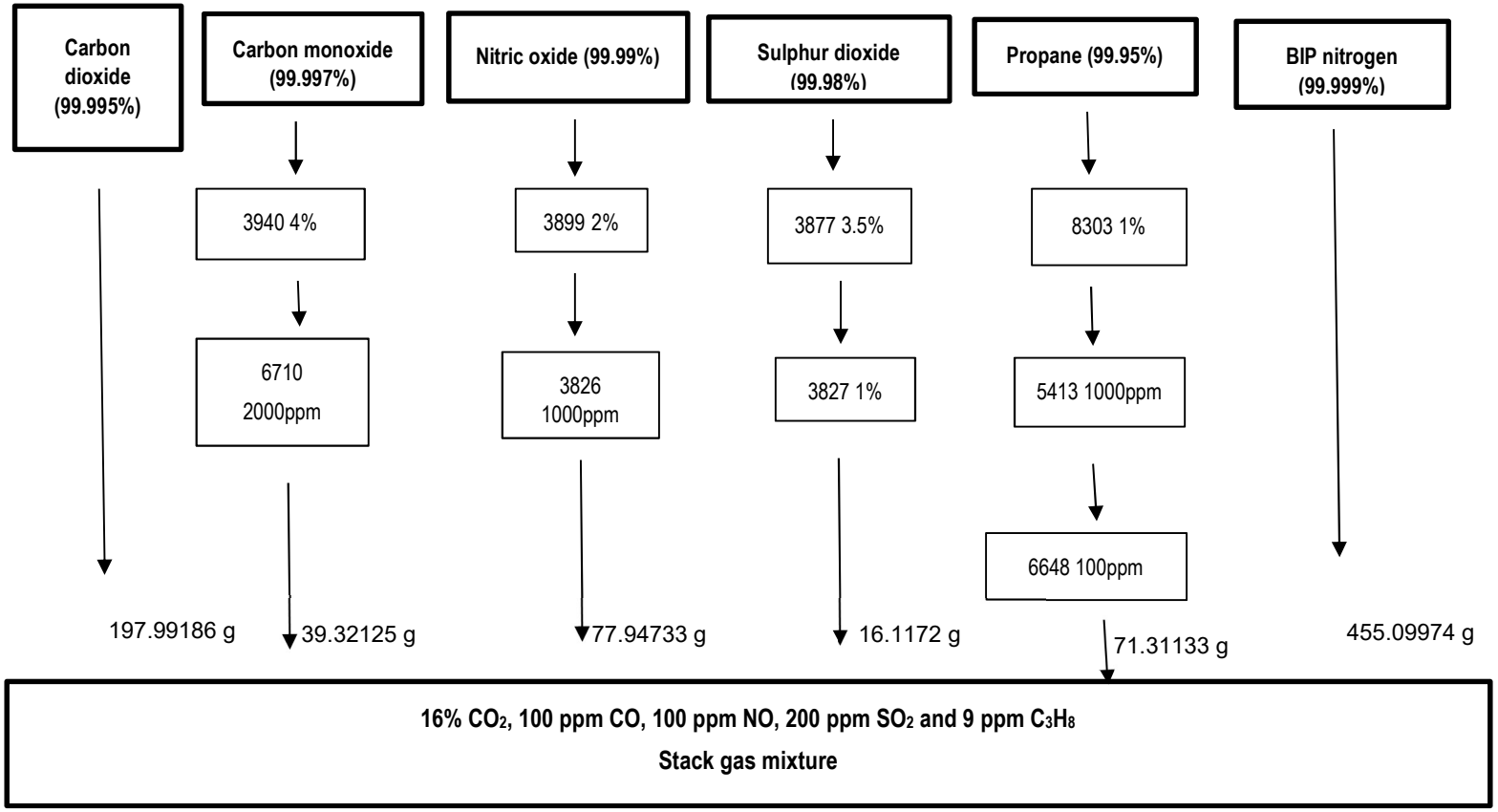
The final objective was stability testing. Overall, the best stability observed was associated with the carbon dioxide measurement. The stabilities of the other component gas for stack mixtures was not very satisfactory. However, the statistical D test revealed that there was no significant instability for most of these

when individual measurement results were compared. It was propane that has significant instability associated with the final homogeneous mixture. However, this can be attributed to instrument drift. There was poor stability observed for the components of automotive mixtures. During measurement, different standard gas mixtures were alternated and this may have caused some instability. The gas mixtures will be continuously analysed using the same standards to observe any improvements.

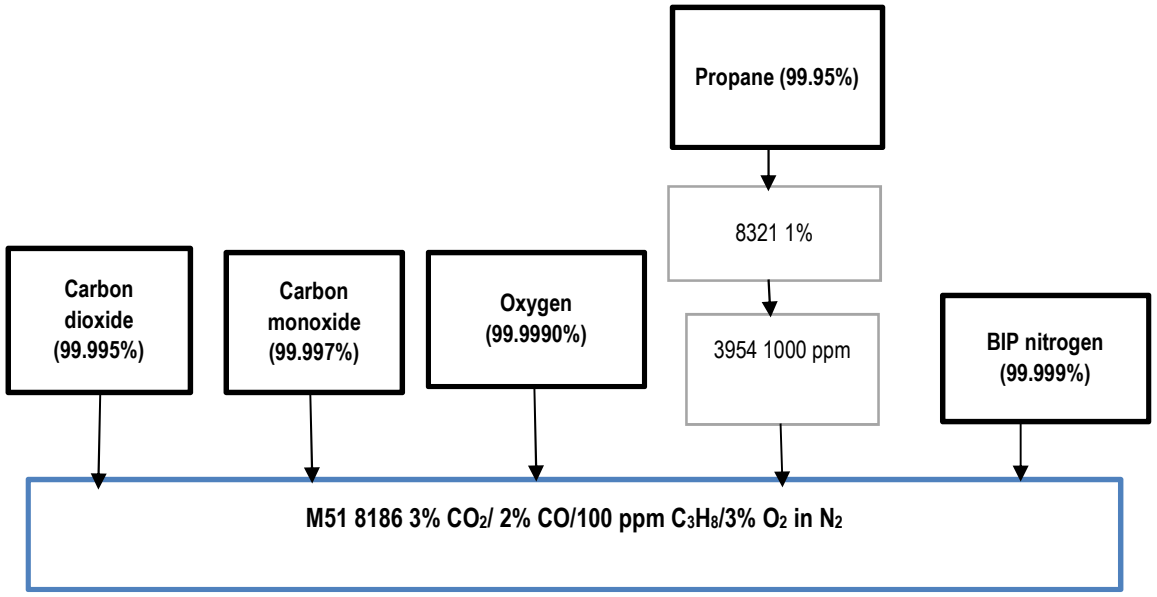
8.2 Recommendations

This project was successful in meeting its objectives. However, one of the key factors it identified but did not evaluate is the chemical behaviour (properties) of gases in a stack mixture that often result in cross-interferences. A recommendation is made that quantification or modelling of these interferences is critical to real-time mathematical corrections. The stack and automotive emission monitoring network may liase and engage with the gas metrology laboratory to provide them with these reference gas mixtures and the laboratory will continuously work to improve their measurement of these complex mixtures owing to its huge social impact.

ANNEXURE A: Typical production diagram of a stack gas mixture from high pure source gases



ANNEXURE B: Typical production diagram of automotive samples



Annexure C: Weighing formula of a stack gas mixture

Weighing of the empty cylinder – Vacuum pressure 4.7 x 10^{-7} mbar

Cylinder number: M51 8268 Mixture description: 14% carbon dioxide, 80 ppm carbon monoxide, 80 ppm nitric oxide, 150 ppm sulphur dioxide and 4 ppm propane in nitrogen					
Weighing cycle	Mass (g)	Standard deviation (g)	Temperature (°C)	Pressure (mbar)	Relative humidity (%r.h)
Reference + sensitivity	7911.06800	0.00146	21.6	871.03	47.6
Reference	7910.06673	0.00139	21.6	871.02	47.6
Sample cylinder	7910.65130	0.00079	21.6	871.00	48.2
Reference	7910.06597	0.00156	21.6	870.97	48.2
Sample cylinder	7910.65650	0.00057	21.6	870.98	48.2
Reference	7910.06780	0.00100	21.6	870.91	48.2
Sample cylinder	7910.65717	0.00109	2`.6	870.96	48.2
Reference	7910.07323	0.00086	21.7	870.77	48.5
Reference + sensitivity	7911.07027	0.00101	21.7	870.71	48.5
		Sensitivity = 1.0074 g	Weighing difference = 20.58668 g	Uncertainty = 0.00444 g	

Weighing of first component

Nitric oxide pre-mixture M51 8184 Target mass = 37.0 g, actual mass = 37.12445 g					
Weighing cycle	Mass (g)	Standard deviation (g)	Temperature (°C)	Pressure (mbar)	Relative humidity (%r.h)
Reference + sensitivity	7948.16010	0.00158	20.7	865.31	51.3
Reference	7947.16040	0.00077	20.7	865.45	51.3
Sample cylinder	7947.87397	0.00096	20.7	865.48	51.3
Reference	7947.16423	0.00082	20.7	865.46	51.6
Sample cylinder	7947.87593	0.00094	20.7	865.43	51.6
Reference	7947.16630	0.00099	20.7	865.43	51.6
Sample cylinder	7947.87877	0.00068	20.7	865.47	51.6
Reference	7947.16633	0.00171	20.7	865.56	51.6
Reference + sensitivity	7947.16633	0.00048	20.7	865.	51.6
		Sensitivity = 1.00004 g	Weighing difference = 57.71113 g	Uncertainty = 0.00375 g	

Weighing of second component

Sulphur dioxide pre-mixture 6711 Target mass = 51.7 g, actual mass = 51.93255 g					
Weighing cycle	Mass (g)	Standard deviation (g)	Temperature (°C)	Pressure (mbar)	Relative humidity (%r.h)
Reference + sensitivity	8000.21577	0.00073	23.9	862.83	42.6
Reference	7999.21360	0.00067	23.9	862.84	42.6
Sample cylinder	7999.85797	0.00049	23.9	862.99	42.6
Reference	7999.21230	0.00060	23.9	863.07	42.6
Sample cylinder	7999.85653	0.00051	23.9	863.19	42.6
Reference	7999.21063	0.00103	24.0	863.23	43.4
Sample cylinder	7999.85593	0.00078	24.0	863.16	43.4
Reference	7999.21107	0.00037	24.0	863.08	43.4
Reference + sensitivity	8000.20963	0.00110	23.9	863.20	43.2
		Sensitivity = 0.99952 g	Weighing difference = 109.64367 g	Uncertainty = 0.00275 g	

Weighing of third component

Carbon monoxide pre-mixture M51 8076 Target mass = 37.0 g, actual mass = 36.94841 g					
Weighing cycle	Mass (g)	Standard deviation (g)	Temperature (°C)	Pressure (mbar)	Relative humidity (%r.h)
Reference + sensitivity	8037.21007	0.00134	23.9	864.34	49.1
Reference	8036.21020	0.00071	23.9	864.34	49.1
Sample cylinder	8036.79963	0.00116	23.9	864.40	49.1
Reference	8036.20513	0.00051	23.8	864.75	49.2
Sample cylinder	8036.79740	0.00086	23.8	864.88	49.2
Reference	8036.20393	0.00094	23.8	864.93	49.2
Sample cylinder	8036.79433	0.00048	23.8	865.10	49.2
Reference	8036.19967	0.00092	23.8	865.24	49.2
Reference + sensitivity	8037.19520	0.00135	23.8	865.66	49.5
		Sensitivity = 1.00169 g	Weighing difference = 146.59209 g	Uncertainty = 0.00411 g	

Weighing of the fourth component

propane pre-mixture 6648 Target mass = 12.0 g, actual mass = 11.94389 g					
Weighing cycle	Mass (g)	Standard deviation (g)	Temperature (°C)	Pressure (mbar)	Relative humidity (%r.h)
Reference + sensitivity	8049.18747	0.00051	25.3	864.56	47.5
Reference	8048.18833	0.00137	25.3	864.47	47.5
Sample cylinder	8048.72620	0.00081	25.3	864.47	47.5
Reference	8048.18917	0.00059	25.3	864.40	47.5
Sample cylinder	8048.72617	0.00059	25.3	864.34	47.5
Reference	8048.18933	0.00076	25.4	864.29	48.1
Sample cylinder	8048.72480	0.00092	25.4	864.25	48.1
Reference	8048.18913	0.00068	25.4	864.22	48.1
Reference + sensitivity	8049.18707	0.00025	25.4	864.23	48.1
		Sensitivity = 1.00136 g	Weighing difference = 158.53598 g	Uncertainty = 0.00242 g	

Weighing fifth component

High pure carbon dioxide (99.995%) Target mass = 60.9 g, actual mass = 60.69419 g					
Weighing cycle	Mass (g)	Standard deviation (g)	Temperature (°C)	Pressure (mbar)	Relative humidity (%r.h)
Reference + sensitivity	8110.17163	0.00177	22.6	869.38	52.4
Reference	8109.17633	0.00127	22.6	869.30	52.4
Sample cylinder	8109.40663	0.00140	22.6	869.27	52.4
Reference	8109.18113	0.00051	22.7	869.28	52.9
Sample cylinder	8109.41057	0.00138	22.7	869.29	52.9
Reference	8109.17717	0.00190	22.7	869.35	52.9
Sample cylinder	8109.40990	0.00132	22.7	869.35	52.9
Reference	8109.17990	0.00194	22.7	869.37	52.9
Reference + sensitivity	8110.17863	0.0113	22.8	869.39	53.8
		Sensitivity = 1.00288 g	Weighing difference = 219.23017 g	Uncertainty = 0.00473 g	

Weighing of balance gas

High pure nitrogen (99.9990%) Target mass = 100 g, actual mass = 97.10692 g					
Weighing cycle	Mass (g)	Standard deviation (g)	Temperature (°C)	Pressure (mbar)	Relative humidity (%r.h)
Reference + sensitivity	8207.26963	0.00076	24.6	868.72	55.9
Reference	8206.26737	0.00049	24.6	868.74	55.9
Sample cylinder	8206.60630	0.00065	24.7	868.75	56.1
Reference	8206.26817	0.00079	24.7	868.78	56.1
Sample cylinder	8206.60593	0.00052	24.7	868.82	56.1
Reference	8206.26817	0.00095	24.7	868.83	56.1
Sample cylinder	8206.60980	0.00081	24.7	868.84	56.1
Reference	8206.27080	0.00092	24.7	868.83	56.1
Reference + sensitivity	8207.26960	0.00107	24.7	868.86	56.8
		Sensitivity = 0.99936 g	Weighing difference = 316.33709 g	Uncertainty = 0.00288 g	

Annexure D: Gravimetry summary results for stack gas mixtures in 5 litre aluminum cylinders

Mixture	Vacuum pressure (mbar)	Mass (g)					
		Carbon dioxide	Carbon monoxide	Nitric oxide	Sulphur dioxide	Propane	Nitrogen
6633	5.0×10^{-7}	197.99186	39.32125	77.94733	16.1172	71.31133	455.09974
6634	4.6×10^{-7}	153.68956	51.54281	76.39293	69.80993	37.88838	411.01922
M9 3885	4.0×10^{-7}	112.41862	78.7687	77.24515	78.34258	64.02019	400.00321
M9 3878	2.2×10^{-7}	238.68191	62.46231	84.24382	70.54999	59.23989	411.85913
M9 3970	3.0×10^{-7}	135.97546	72.55258	77.06431	77.41484	44.93631	410.96053
M51 8268	4.7×10^{-7}	60.69419	36.94841	37.12445	51.93255	11.94389	97.10692
M51 8141	1.2×10^{-7}	106.75302	38.18344	19.07177	18.96928	12.47855	409.57779

Annexure E: % relative deviation graphs of carbon monoxide, carbon dioxide, propane, sulphur dioxide and nitric oxide from CCQM-K71

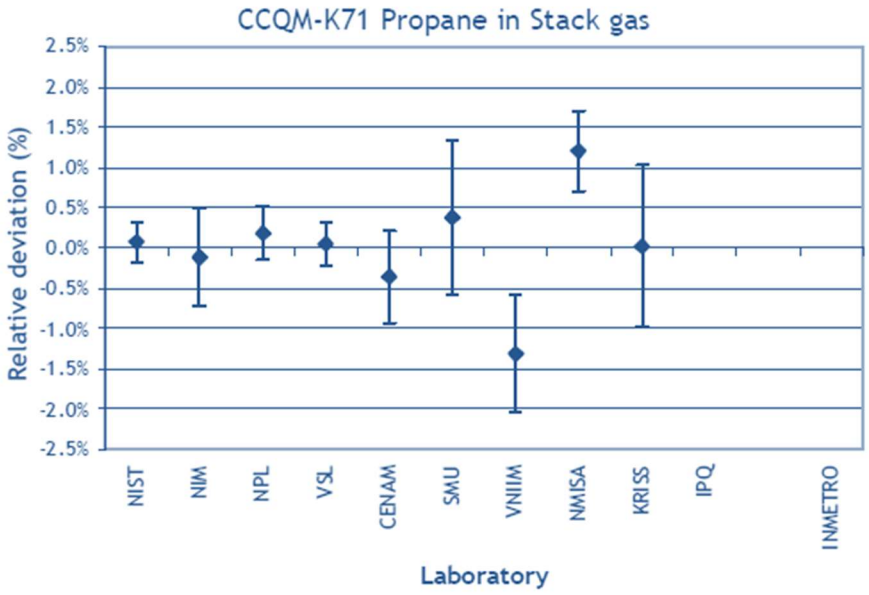


Figure E1: Propane in stack gas measurement equivalence

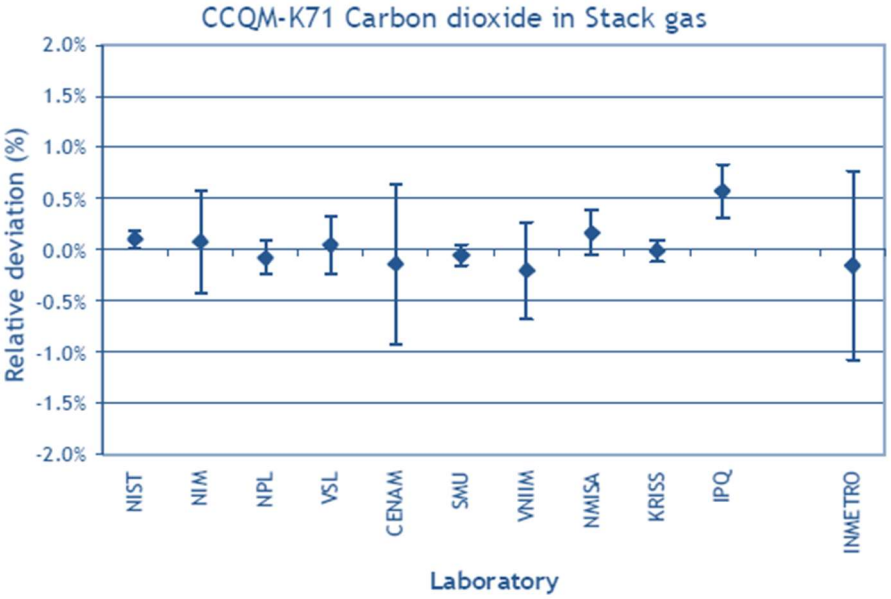


Figure E2: Carbon dioxide in stack gas measurement equivalence

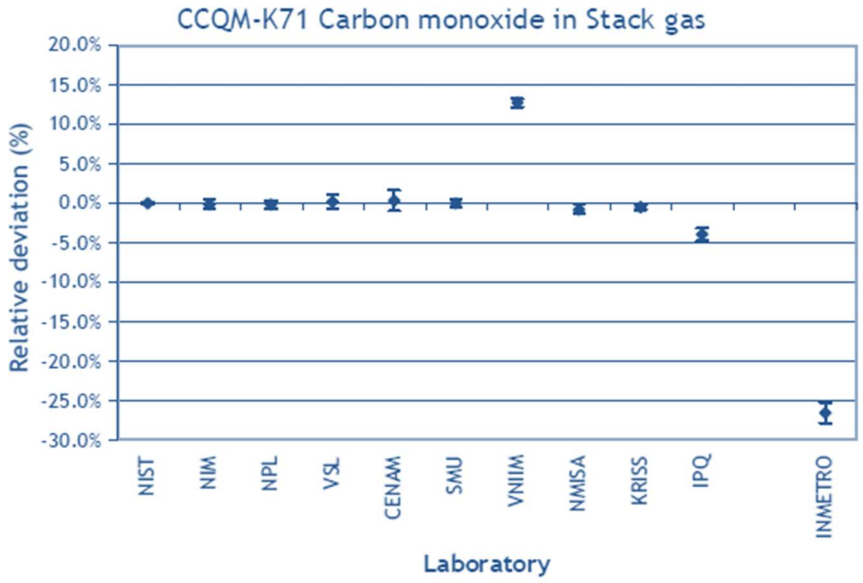


Figure E3: Carbon monoxide in stack gas measurement equivalence

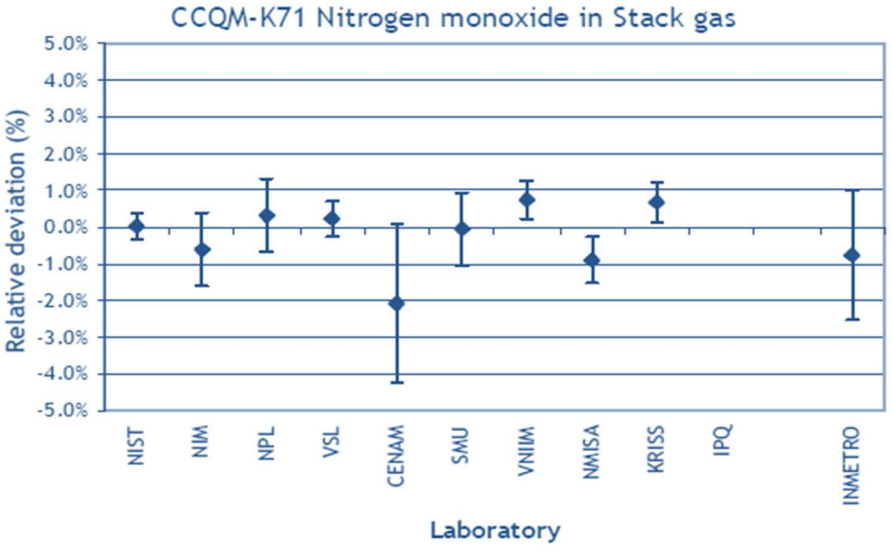


Figure E4: Nitric oxide in stack gas measurement equivalence

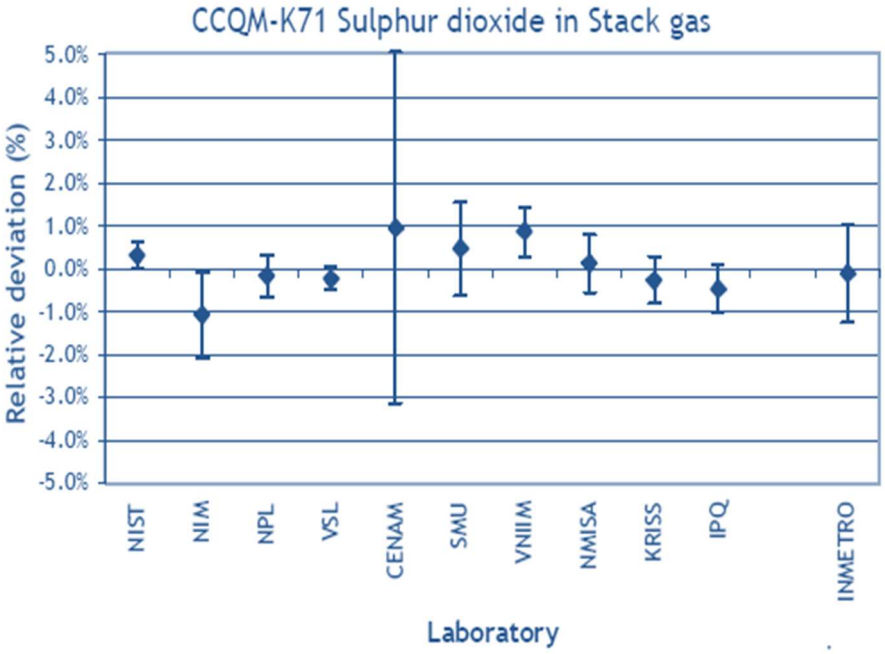


Figure E5: Sulphur dioxide in stack gas measurement equivalence

Table E1: CCQM K71 results for CO_2

Lab	Cylinder	X_{prep} (mmol/mol)	U_{prep} (mmol/mol)	U_{ver} (mmol/mol)	U_{KCRV} (mmol/mol)	X_{lab} (mmol/mol)	U_{lab} (mmol/mol)	D (µmol/mol)	D/x	U(D)	U(D)x
NIST	a	119.800	0.012	0.11960	0.12040	119.93	0.11	0.130	0.11%	0.265	0.22
NIM	b	120.100	0.012	0.12010	0.12070	120.20	0.60	0.100	0.06%	0.647	0.54
NPL	c	119.790	0.012	0.11979	0.12039	119.20	0.20	0.090	0.06%	0.313	0.26
VSL	d	120.010	0.012	0.12001	0.12061	120.07	0.34	0.060	0.05%	0.417	0.35
CENAM	e	120.330	0.012	0.12033	0.12093	120.17	0.94	0.160	0.13%	0.971	0.81
SMU	f	120.040	0.012	0.12004	0.12064	119.98	0.12	0.060	0.05%	0.269	0.22
VNIIM	g	120.240	0.012	0.12024	0.12084	120.00	0.57	0.240	0.20%	0.619	0.51
NMISA	**M937424**	**119.970**	**0.012**	**0.11997**	**0.12057**	**120.17**	**0.26**	**0.200**	**0.17%**	**0.355**	**0.30**
KRISS	h	119.890	0.012	0.11989	0.12049	119.88	0.12	0.010	0.01%	0.269	0.22
IPQ	i	119.920	0.012	0.11992	0.12052	120.61	0.32	0.690	0.58%	0.401	0.33

Table E2: CCQM K71 results for C_3H_8

Lab	Cylinder	X_{prep} (mmol/mol)	U_{prep} (mmol/mol)	U_{ver} (mmol/mol)	U_{KCRV} (mmol/mol)	X_{lab} (mmol/mol)	U_{lab} (mmol/mol)	D (µmol/mol)	D/x	U(D)	U(D)x
NIST	a	5.9745	0.0037	0.00597	0.00703	5.979	0.015	0.0045	0.06%	0.0206	0.34%
NIM	b	5.9758	0.0037	0.00596	0.00703	5.969	0.036	0.0068	0.11%	0.0386	0.65%
NPL	c	5.9692	0.0037	0.00597	.00702	5.960	0.020	0.0108	0.16%	0.0244	0.41%
VSL	d	5.9770	0.0037	0.00596	0.00703	5.960	0.017	0.0030	0.05%	0.0221	0.37%
CENAM	e	5.9550	0.0037	0.00596	0.00701	5.934	0.034	0.0210	0.35%	0.0368	0.62%
SMU	f	5.9812	0.0037	0.00596	0.00703	6.004	0.068	0.0228	0.38%	0.0597	1.00%
VNIIM	g	5.9793	0.0037	0.00596	0.00703	5.901	0.0043	0.0783	1.31%	0.0452	0.76%
NMISA	**M937424**	**5.9760**	**0.0037**	**0.00596**	**0.00703**	**6.048**	**0.030**	**0.0720**	**1.20%**	**0.0331**	**0.55%**
KRISS	h	5.9787	0.0037	0.00596	0.00703	5.98	0.06	0.0013	0.02%	0.0616	1.03%
IPQ	i	-	-	-	-						

Table E3: CCQM K71 results for NO.

Lab	Cylinder	X_{prep} (mmol/mol)	U_{prep} (mmol/mol)	U_{ver} (mmol/mol)	U_{KCRV} (mmol/mol)	X_{lab} (mmol/mol)	U_{lab} (mmol/mol)	D (µmol/mol)	D/x	U(D)	U(D)x
NIST	a	80.120	0.052	0.0801	0.0955	80.14	0.29	0.020	0.02%	0.347	0.43%
NIM	b	80.138	0.051	0.0802	0.0950	79.65	0.80	0.488	0.61%	0.822	1.03%
NPL	c	80.049	0.051	0.0800	0.0949	80.3	0.8	0.251	0.31%	0.822	1.03%
VSL	d	80.156	0.052	0.0802	0.0955	80.34	0.39	0.184	0.23%	0.434	0.54%
CENAM	e	79.859	0.052	0.0799	0.0953	78.20	1.70	1.659	2.08%	1.711	2.14%
SMU	f	80.210	0.052	0.0802	0.0956	80.18	0.80	0.030	0.04%	0.823	1.03%
VNIIM	g	80.185	0.052	0.0802	0.0956	80.78	0.42	0.595	0.74%	0.461	0.58%
NMISA	**M937424**	**80.142**	**0.052**	**0.00801**	**0.0955**	**79.42**	**0.51**	**0.722**	**0.90%**	**0.545**	**0.68%**
KRISS	h	80.176	0.052	0.00802	0.0956	80.72	0.45	0.544	0.68%	0.489	0.61%
IPQ	i										

Table E4: CCQM K71 results for CO

Lab	Cylinder	X_{prep} (mmol/mol)	U_{prep} (mmol/mol)	U_{ver} (mmol/mol)	U_{KCRV} (mmol/mol)	X_{lab} (mmol/mol)	U_{lab} (mmol/mol)	D (µmol/mol)	D/x	U(D)	U(D)x
NIST	a	40.083	0.034	0.06012	0.06907	40.112	0.063	0.03	0.07%	0.1518	0.38%
NIM	b	40.092	0.034	0.06014	0.06908	40.050	0.240	0.04	0.10%	0.2769	0.69%
NPL	c	40.047	0.034	0.06007	0.06903	40.000	0.200	0.05	0.12%	0.2430	0.61%
VSL	d	40.101	0.034	0.06015	0.06910	40.200	0.380	0.10	0.25%	0.4043	1.01%
CENAM	e	39.953	0.034	0.05993	0.06890	40.100	0.510	0.15	0.37%	0.5283	1.32%
SMU	f	40.128	0.034	0.06019	0.06913	40.110	0.190	0.02	0.04%	0.2350	0.59%
VNIIM	g	40.116	0.034	0.06017	0.06912	45.220	0.250	5.10	12.72%	0.2857	0.71%
NMISA	**M937424**	**40.094**	**0.034**	**0.06014**	**0.06909**	**39.800**	**0.210**	**0.29**	**0.73%**	**0.2514**	**0.63%**
KRISS	h	40.111	0.034	0.06017	0.06911	39.910	0.140	0.20	0.50%	0.1967	0.49%
IPQ	i	40.090	0.034	0.06014	0.06908	38.530	0.300	1.56	3.89%	0.3303	0.82%

Table 35: CCQM K71 results for SO_2.

Lab	Cylinder	X_{prep} (mmol/mol)	U_{prep} (mmol/mol)	U_{ver} (mmol/mol)	U_{KCRV} (mmol/mol)	X_{lab} (mmol/mol)	U_{lab} (mmol/mol)	D (µmol/mol)	D/x	U(D)	U(D)x
NIST	a	80.004	0.048	0.0800	0.0933	80.25	0.25	0.25	0.31%	0.3120	0.39%
NIM	b	80.022	0.048	0.0800	0.0933	79.16	0.79	0.86	1.08%	0.8117	1.01%
NPL	c	79.933	0.048	0.799	0.0932	79.8	0.4	0.13	0.17%	0.4413	0.55%
VSL	d	80.039	0.048	0.0800	0.0933	79.85	0.21	0.19	0.24%	0.2810	0.35%
CENAM	e	79.743	0.048	0.797	0.0931	80.5	3.3	0.76	0.95%	3.3052	4.14%
SMU	f	80.094	0.048	0.00801	0.0934	80.47	0.87	0.38	0.47%	0.8898	1.11%
VNIIM	g	80.068	0.048	0.00801	0.00934	80.77	0.47	0.70	0.88%	0.5057	0.63%
NMISA	**M937424**	**80.026**	**0.048**	**0.0800**	**0.0933**	**80.13**	**0.54**	**0.10**	**0.13%**	**0.5713**	**0.71%**
KRISS	h	80.060	0.048	0.00801	0.0933	79.84	0.44	0.22	0.27%	0.4780	0.60%
IPQ	i	80.017	0.048	0.0800	0.0933	79.64	0.44	0.38	0.47%	0.4779	0.50%

Annexure F: Supplement chromatography work by GC FID for automotive mixtures.

Table F1: Gas chromatography flame ionization detector results for CO_2 in automotive gas

Automotive gas samples (M51)									
Statistic parameter	8183	8269	8183	9512	8183	8186	8183	8091	8183
Average	205652.6	202014.2	204978.8	207032.6	204824.4	201482.6	205576.6	207404.1	205493
Standard dev	227.4	324.2	110.5	101.5	157.1	449.0	225.9	115.8	90.6
%RSD	**0.11**	**0.16**	**0.05**	**0.05**	**0.08**	**0.22**	**0.11**	**0.06**	**0.04**
ESDM	101.7	145.0	49.4	45.4	70.2	200.8	101.0	51.8	40.5
Sensitivity	6.9	6.8	6.8	6.8	6.8	6.7	6.9	6.9	6.9
Corr. Sensit		6.9		6.8		6.8		6.9	
% Diff		**1.4**		**0.09**		**2.0**		**0.09**	
Conc.Grav	299601.0	29903.3	29961.0	30299.5	29961.0	29992.9	29961.0	30260.3	29961.0
Uncer.Grav (k=2)	5.0	5.4	5.0	13.0	5.0	5.5	5.0	4.4	5.0
Cal.conc		29479.2		30272.6		29418.1		30233.5	
Drift			**0.33**		**0.08**		**-0.37**		**0.04**

*Conc.Grav	Gravimetric concentration
Uncer.Grav	Gravimetric uncertainty
Cal.conc	Calculated concentration
%Diff	% difference
Corr. Sensit	Corrected sensitivity
ESDM	Estimated Standard Deviation of the Mean
%RSD	% Relative Standard Deviation
Dev	Deviation

Table F2: Gas chromatography flame ionization detector results for CO_2 in automotive gas

Automotive samples (M51)									
Statistics parameter	8186	8269	8186	8183	8186	9512	8186	8091	8186
Average	202230.4	204064.4	202751.2	205590.5	203459	207691.3	203368.6	208014	204648.3
Standard dev	467.1	102.8	524.4	328.5	525.3	151.1	659.5	133.3	289.5
%RSD	**0.23**	**0.05**	**0.26**	**0.16**	**0.26**	**0.07**	**0.32**	**0.06**	**0.14**
ESDM	208.9	46.0	234.5	146.9	234.9	67.6	294.9	59.6	129.5
Sensitivity	6.7	6.8	6.8	6.9	6.8	6.9	6.8	6.9	6.8
Corr. Sensit		6.8		6.8		6.8		6.8	
% Diff		**-1.1**		**-1.3**		**-1.1**		**-1.1**	
Conc.Grav	29992.9	29903.3	29992.9	29961.0	29992.9	30299.5	29992.9	30260.3	29992.9
Uncer.Grav (k=2)	5.5	5.4	5.5	5.0	5.5	12.9	5.5	4.4	5.5
Cal.conc		30225.9		30359.9		30623.6		30581.8	
Drift			**-0.26**		**-0.35**		**0.04**		**-0.63**

Table F3: Gas chromatography flame ionization detector results for CO_2 in automotive gas

Automotive samples (M51)									
Statistics parameter	9512	8186	9512	8269	9512	8183	9512	8091	9512
Average	207660.8	204447	207303.3	203797.6	207606.4	205582.2	207467	207388.5	207671.2
Standard dev	221.5	65.5	194.0	534.8	67.1	69.2	170.2	324.3	120.4
%RSD	**0.11**	**0.03**	**0.09**	**0.26**	**0.03**	**0.03**	**0.08**	**0.16**	**0.06**
ESDM	99.1	29.3	86.8	239.2	30.0	31.0	76.1	145.0	53.8
Sensitivity	6.9	6.8	6.8	6.8	6.9	6.9	6.8	6.9	6.9
Corr. Sensit		6.8		6.8		6.8		6.9	
% Diff		**0.46**		**0.46**		**-0.18**		**-0.04**	
Conc.Grav	30299.5	29992.9	30299.5	29903.3	30299.5	29961.0	30299.5	30260.3	30299.5
Uncer.Grav (k=2)	13.0	5.5	13.0	5.4	12.9	5.0	12.9	4.4	12.9
Cal.conc		29856.3		29765.3		30014.1		30273.1	
Drift			**0.17**		**-0.15**		**0.07**		**-0.10**

Table F4: Gas chromatography flame ionization detector results for CO_2 in automotive gas

Automotive samples (M51)									
Statistic parameter	8091	8186	8091	8269	8091	8183	8091	9512	8091
Average	207719.8	204836	207498.5	204547.2	207739.4	205984.3	208351.6	207636.8	207827.5
Standard dev	32.1	153.0	121.2	77.6	139.4	252.4	108.7163	201.5	257.6
%RSD	**0.02**	**0.07**	**0.06**	**0.04**	**0.07**	**0.12**	**0.052179**	**0.10**	**0.12**
ESDM	14.4	68.4	54.2	34.7	62.3	112.9	48.6194	90.10	115.2
Sensitivity	6.9	6.8	6.9	6.8	6.9	6.9	6.885314	6.9	6.9
Corr. Sensit		6.9		6.9		6.9		6.9	
% Diff		**0.46**		**0.30**		**0.002**		**0.16**	
Conc.Grav	30260.3	29992.9	30260.3	29903.3	30260.3	29961.0	30260.3	30299.5	30260.3
Uncer.Grav (k=2)	4.4	5.5	4.4	5.4	4.4	5.0	4.355968	12.9	4.4
Cal.conc		29856.1		29812.6		29960.5		30251.0	
Drift			**0.11**		**-0.12**		**-0.29**		**0.25**

Table F5: Gas chromatography flame ionization detector results for CO in automotive gas

Automotive samples (M51)							
Statistic parameter	8183	8269	8183	9512	8183	8186	8183
Average	107148.5	103650.1	103899.1	106600.9	104078	105632.5	104209.4
Standard dev	1517.6	278.3	203.8	176.0	83.1	114.9	272.2
%RSD	**1.4**	**0.27**	**0.20**	**0.17**	**0.08**	**0.11**	**0.26**
ESDM	678.7	124.5	91.2	78.7	37.2	51.4	121.7
Sensitivity	5.3	5.2	5.2	5.3	5.2	5.3	5.2
Corr. Sensit		5.3		5.2		5.2	
% Diff		**0.56**		**-3.0**		**-1.9**	
Conc.Grav	20069.9	19824.8	20069.9	19963.2	20069.9	19977.2	20069.9
Uncer.Grav (k=2)	8.3	8.2	8.3	20	8.3	8.5	8.3
Cal.conc		19713.5		20574.1		20356.8	
Drift			**3.1**		**-0.17**		**-0.13**

Table F6: Gas chromatography flame ionization detector results for CO in automotive gas

Automotive samples (M51)							
Statistics parameter	8186	8269	8186	8183	8186	9512	8186
Average	105554.7	102501.2	105325.9	104407.8	105425.9	105820.6	105145.9
Standard dev	33.3	339.1	74.5	464.3	133.9	63.2	62.3
%RSD	0.03	0.33	0.07	0.44	0.13	0.06	0.06
ESDM	14.9	151.6	33.3	207.6	59.9	28.3	27.8
Sensitivity	5.3	5.2	5.3	5.2	5.3	5.3	5.3
Corr. Sensit		5.3		5.3		5.3	
% Diff		2.1		1.40		-0.57	
Conc.Grav	19977.2	19824.8	19977.2	20069.9	19977.2	19963.2	19977.2
Uncer.Grav (k=2)	8.5	8.2	8.5	8.3	8.5	20.4	8.5
Cal.conc		19420.3		19793.6		20078.6	
Drift			0.22		-0.09		0.27

Table F7: Gas chromatography flame ionization detector results for CO in automotive gas

Automotive samples (M51)							
Statistic parameter	9512	8186	9512	8269	9512	8183	9512
Average	105683.1	104940	105641.5	104154	105252.3	105528.5	105263.5
Standard dev	80.7	87.6	39.2	209.5	1601.0	110.8	82.9
%RSD	**0.08**	**0.08**	**0.04**	**0.20**	**0.15**	**0.11**	**0.08**
ESDM	36.1	39.2	17.5	93.7	72.0	49.6	37.09
Sensitivity	5.3	5.3	5.3	5.3	5.3	5.3	5.3
Corr. Sensit		5.3		5.3		5.3	
% Diff		**0.76**		**0.54**		**0.28**	
Conc.Grav	19963.2	19977.2	19963.2	19824.8	19963.2	20069.9	19963.2
Uncer.Grav (k=2)	20	8.5	20	8.2	20.4	8.3	20.4
Cal.conc		19826.7		19718.4		20014.5	
Drift			**0.04**		**0.369759**		**-0.01**

Table F8: Gas chromatography flame ionization detector results for CO in automotive gas

Automotive samples (M51)							
Statistics parameter	8269	8186	8269	8183	8269	9512	8269
Average	103990.8	104182.7	104206.2	104757.3	103836.5	104700.9	103688.3
Standard dev	119.5	100.3	260.6	130.5	77.1	122.2	76.9
%RSD	**0.11**	**0.10**	**0.25**	**0.12**	**0.07**	**0.12**	**0.07**
ESDM	53.4	44.9	116.6	58.4	34.5	54.7	34.4
Sensitivity	5.2	5.2	5.3	5.2	5.2	5.2	5.2
Corr. Sensit		5.3		5.2		5.2	
% Diff		**0.7**		**0.53**		**-0.20**	
Conc.Grav	19824.8	19977.2	19824.8	20069.9	19824.8	19963.2	19824.8
Uncer.Grav (k=2)	8.2	8.5	8.2	8.3	8.2	20.4	8.2
Cal.conc		19840.8		19965.1		20004.1	
Drift			**-0.21**		**0.36**		**0.14**

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