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QUANTITATIVE ANALYSIS OF HIGH ACCURACY GREENHOUSE GAS STANDARDS FOR AMBIENT AND EMISSION LEVELS, IN SUPPORT OF AIR QUALITY MONITORING IN SOUTH AFRICA



By

Silindile Lucia Lushozi

A thesis submitted to the faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy

October 2019

DECLARATION

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

Silindile Lucia Lushozi

This 25th day of October 2019 in Johannesburg

Supervisor Name: Prof Luke Chimuka

Co-Supervisor: Dr James Tshilongo

PUBLICATIONS AND MANUSCRIPTS

This thesis is based on the following list of papers:

I. **Preparation and verification of primary standard gas mixtures for carbon dioxide measurement in natural air samples at background level in South Africa**

   Silindile Lushozi, James Tshilongo, Napo Ntsasa, Mudalo Jozela, Nompumelelo Lesabane, David Mogale, Tshepiso Mphamo, Goitsemang Lekoto, Prelly Marebane, Gumani Mphaphuli and Luke Chimuka (Manuscript)

II. **Validation of methane gas mixture in nitrogen balance by gas chromatography with flame ionization detector**

   Silindile Lushozi, James Tshilongo, Luke Chimuka (Manuscript)

III. **Verification of nitrous oxide primary standard gas mixtures by Gas Chromatography and Cavity Ring-Down Spectroscopy for ambient measurements in South Africa.**

   Silindile Lushozi, James Tshilongo, Luke Chimuka

   Article published under the Journal of Accreditation and Quality Assurance: doi.org/10.1007/s00769-019-01375-x

IV. **Post international key comparison CCQMK-51 of carbon monoxide: Stability and uncertainty evaluation of gas mixtures.**

   Silindile Lushozi, James Tshilongo, Angelique Botha, Mellisa Janse van Rensburg, Napo Ntsasa, Nompumelelo Lushabane and Luke Chimuka (Manuscript)

V. **Development of carbon monoxide reference gas mixtures at ambient level by gravimetric method.**

Silindile Lushozi, James Tshilongo, and Luke Chimuka (Manuscript)

Other publications

VI. **Propanal and ethanol work with CSIR nano-group title and published work to be confirmed**

David Moutaung, Ioannis Kortidis, James Tshilongo, Silindile Lushozi, Nompumeleo Leshabane and Napo Ntsasa

(Manuscript. Accepted for publication under Journal: Ceramics International).

ABSTRACT

The measurement of greenhouse gases (CO_2, CH_4, N_2O and reactive gas CO) emitted in the environment is popular worldwide as these gas compounds influence global warming which poses risk in the society. The observed rise in the global temperature has been linked to the increase in the amount of greenhouse gases in the atmosphere. Therefore, the accurate measurement of atmospheric greenhouse gases is needed to understand the climate and various human activities. There is a greater demand for stable and internationally traceable gas standards with low uncertainty for accurate and comparable measurements of greenhouse gases worldwide. The need to accurately measure these gaseous pollutants is required to ensure quality air pollution monitoring. In this thesis, the development of greenhouse gas primary standard gas mixtures with amount fractions reflected in the atmosphere was carried out by static gravimetric method. The gas mixtures were prepared in different matrix such as N_2 and artificial air (Ar + O_2 + N_2). Because it was the first time the greenhouse gas mixtures were prepared in artificial air at trace level, the gas mixtures were first prepared in N_2 balance first to develop the method and accurately identify the peak of interest. The gas mixtures in artificial air were then prepared after the analysis of the gas mixtures in N_2 balance.

The development of these gaseous pollutants is tricky as the accuracy of these gas mixtures is affected by the impurities and matrix effect. Purity analysis of the starting materials or highly pure gas (N_2, Ar, O_2, CO_2, CH_4, N_2O, and CO) was carried out to obtain accurate composition of the final gas mixture. Various analytical technique such as gas chromatography with pulse discharge helium detector, flame ionization detector, cavity ring-down and non - dispersive infrared spectroscopy was used. The N_2 impurity in CO_2, CH_4, N_2O and CO was quantified as 823.4 ± 82.3 µmol.mol^{-1}, 237 ± 11.85 µmol.mol^{-1},16.5 ± 0.85 µmol.mol^{-1} and 1.05 ± 0.10 µmol.mol^{-1} respectively. A full purity table of each starting material, where the impurities in each starting material was quantified, is obtained under each paper discussed in this thesis.

The methodology used in the development of the gas mixtures included several dilutions steps from the raw material to the trace amount fraction. In the final preparation step, the gas mixtures were then prepared in different matrix for accurate quantification. The greenhouse gas mixtures prepared for this study, were gravimetrically prepared at a nominal amount fraction of 380 ± 0.11 μmol.mol^{-1}, 480 ± 0.13 μmol.mol^{-1}, 800 ± 0.11 μmol.mol^{-1} for CO_2, 2 ± 0.007 μmol. mol^{-1} for CH_4, 330 ± 0.032 nmol.mol^{-1} for N_2O, 5 ± 0.0030 μmol.mol^{-1} and 0.350 ± 0.0050 μmol.mol^{-1} where the standard uncertainty lies at k=1 coverage factor.

After gravimetric preparation, the metrological characterization of the primary standards was conducted to verify the gravimetric values of greenhouse gas mixtures. The gas chromatography, cavity ring-down and non-dispersive infrared spectroscopy were the methods used to verify the amount fraction of the gas mixtures. This was confirmed by comparison method where the gas mixture with similar amount fraction were compared against each other following a single point calibration method. A linear calibration curve of the gas chromatography and the two-spectroscopic technique used was also checked. Based on the analytical response of the instrument, the measurement criteria were set to meet the metrological targets of less than 1% of the instrumental drift. For the gas chromatography analysis, the parameters such as precision, sensitivity, instrumental drifts, relative deviation between the analytical and gravimetric values were checked. Meanwhile, for the spectroscopic methods linearity, reproducibility and precision of the analytical instrument were evaluated. The prepared standards in artificial air were then applied to check the amount of CO_2, CH_4, and N_2O in the background air samples. Only N_2O standard was also used to check the amount of N_2O in the filter air samples. The amount of CO in the background air samples was not checked as CO content is less than the prepared value of 0.350 μmol.mol^{-1}. The CO_2 contents in the background air samples was quantified as (299.06, 419.91, 403.02 and 425.02) μmol.mol^{-1}. The analyzed background air samples is reportedly within the gravimetric values of the CH_4 in artificial

air standards. The value of N_2O quantified in the background air samples ranged from 329 to 330 nmol.mol^{-1}. The N_2O content in the filtered air was obtained as 135 nmol.mol^{-1}. A good accuracy of less than 1.2% was obtained between the gravimetric and the analytical results for each gas standards. The greenhouse gas standards were certified with a final amount fraction of 380 ± 2.00, 480 ± 1.61, 800 ± 1.03 µmol.mol^{-1} for CO_2, 2.00 ± 0.042 for CH_4, 330 ± 0.066 nmol.mol^{-1} for N_2O and 0.350 ± 4.00 µmol.mol^{-1} for CO where the combined uncertainty was estimated as expanded uncertainty (2δ) at 95% confident level.

In this study, the greenhouse gas primary standards were successfully developed and used to identify and quantify the greenhouse gases present in the background and filtered air samples.

***Keywords**:* background air samples, filtered air samples, gravimetric method, analytical method, primary standard gas mixtures, uncertainty.

DEDICATION

This humble work is dedicated to my husband, Mthunzi and my children Thingolethu and Mmangaliso Lushozi for their loving support throughout my doctoral studies. Always remember, where there's a will, there's a way.

A sincere thank you to my aunt Duduzile and brother Thula Ngema for their encouraging words during my postgraduate studies.

To my late mother Jabulisiwe Ngema, your courage, teachings and love will always remain with me.

And above all,

To the Almighty God!

The Lord is my Shepherd, I lack nothing. [Psalms 23:1]

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I would also like to thank the National Research Foundation of South Africa (NRF) for the financial assist. I will forever be thankful for the opportunity granted.

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To my second mum, Duduzile Ngema. Ngiyabonga kakhulu futhi ngiyakuthanda.

CONFERENCE AND PRESENTATIONS

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2. Lushozi, S., Tshilongo, J., Chimuka, L., Ntsasa, N. Development of high accurate greenhouse gases standards in South Africa, Oral presentation at The 9th Gas Analysis Symposium 2017 held at Rotterdam, Netherlands from 13 - 15 June (2017).
3. Lushozi, S., Tshilongo, J., Chimuka, L. and Ntsasa, N Preliminary results on the development of methane standards in nitrogen. Oral presentation at Test and Measurements Conference held at Saint George Conference Centre from 31 July – 1 August (2017).
4. Lushozi, S., Tshilongo, J. and Chimuka, L. Poster presentation at National Metrology Institute of South Africa 70/10 Celebrations held at Council for Scientific and Industrial Research Conventional Centre from the 2 – 4 Aug (2017)
5. Lushozi, S., Tshilongo, J., Chimuka, L., Ntsasa, N., Lekoto, G. and Gorst-Allman, P. Application of the mass measurement technique in the preparation of greenhouse gas in air primary reference gas mixtures. Oral presentation at National Association of Clean Air Conference held at Cedarwoods of Sandton, 4 - 6 October (2017).
6. Lushozi, S., Tshilongo, J. and Chimuka, L. Analysis of carbon dioxide and methane primary reference gas mixtures using cavity ring down spectroscopy. Oral presentation at The South African Spectroscopic Society's Young Spectroscopist's Symposium held at PerkinElmer offices in Midrand, 22 November 2018.
7. Lushozi, S., Tshilongo, J and Chimuka, L. Development and validation of accurate primary gas standards for the quantification of nitrous oxide in nitrogen at low nanomole per mole levels for ambient measurements in

South Africa. Oral Presentation at National Association of Clean Air Conference held Riverside Sun in Vanderbijlpark, 30 – 1 November 2018.

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NOMENCLATURE

BIP	Built-in purifier
NMISA	National Metrology Institute of South Africa
NPL	National Physical Laboratory
NIST	National Institute Standards and Technology
KRISS	Korean Research Institute of Standards and Science
UBA	Umweltbundesamt (Federal Environment Agency), Lagen Germany
NMIJ	National Metrology Institute of Japan, Tuskuba, Japan
VSL	Van Swiden Laboratorium B V, Delft, the Netherlands
CERI	Chemicals Evaluation and Research Institute, Saitama, Japan
CENAM	Centro Nacional de Metrologia, Queretaro, Mexico
VNIIM	DI Mendeleyev Institute for Metrology, St, Petersburg, Russia
IPQ	Institute Portuguê da Qualidade, Caparis, Portugal
LNE	Laboratorie National d'Essais, Paris, France
JRC-ERLAP	European Commission, Joint Research Centre, Institute for Environment and Sustainability, Ispra, Italy
FMI	Finish Meteorological Institute, Helsinki, Finland
UBA(A)	Umweltbundesamt GmbH, Department Air Quality Control & Energy, Vienna, Austria
METAS	Swiss Federal Office of Metrology, Bern-Wabern, Switzerland
NMIA	National Metrology Institute of Australia, Lindfield, Australia
CEM	Centro Espanol de Metrologia, Madrid, Spain
SMU	Slovak Institute of Metrology, Bratislava, Slovak Republic
GUM	Central Office of Measures (Glowny Urzad Miar), Warsaw, Poland
NIM	Institute of Metrology, Beijing, Peoples Republic of China
NIMT	National Institute of Metrology (Thailand), Klong Luang, Pathumthani, Thailand
NPL(India)	National Physical Laboratory, New Delhi, India
BAM	Bundesanstalt fűr Materialforschung und – prűfung, Berlin, Germany

SI	International System of units
SAAQIS	South African Air Quality Information System
GAW	Global Atmospheric Watch
NRL	National Reference Laboratory
CCL	Central Calibration Laboratory
CMC	Calibration and measurement capabilities
SAWS	South African Weather Service

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CHAPTER I: INTRODUCTION AND BACKGROUND

The introductory chapter gives a general background to the project. The problem statement and motivation of the study outlines the importance of monitoring greenhouse gases in South Africa. It also highlights the importance of using primary standard gas mixtures during the measurement of greenhouse gas emissions. The chapter ends with giving the outline on how the work is presented in the thesis.

1. Introduction

1.1 Background

Air pollution is being identified as a global challenge since it's linked to climate change and has contributed to the disturbance of the Earth's chemical cycle (Kiehl et al.,1997; Forster et al., 2007; Montzka et al., 2011). Both natural and anthropogenic sources of air pollution continue to contaminate the atmosphere, thus deteriorating the air quality. Greenhouse gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), and trace gas carbon dioxide (CO) in the atmosphere are another type of air pollutant that is associated with climate change.

Despite all the knowledge around greenhouse gas emission, there are still some gaps (Paustian, 2013). Getting to know the Earth's chemical cycle (chemistry and physics) together with its mechanisms that control the levels of greenhouse gases with the radiative forcing is vital to tackle climate change, and a key global concern (IPCC, 2014; ACC-MIP, 2017; Boer and Yu, 2003). Solomon et., al (2010) researched on the persistence of climate change due to greenhouse gases and the behaviour of the climate system that has affected the environment, plant and human health. Therefore, long-term observations and accurate measurement of greenhouse gases using stable and highly accurate primary standards or reference standards are urgently required. The development of such standards and the analytical methods will implement the needs for national and international legislation related to air pollution of greenhouse gases. Contemporary researches have urged on the important use of primary standards that are traceable, accurate and stable for accurate determination of CO_2, CH_4, N_2O, and CO in the atmosphere.

Under the World Meteorological Organization (WMO), there are independent primary standard scales prepared in the air such as, CH_4 (X2004A), CO_2 (X2007), CO (X2014A) and N_2O (X2006A) that have been used to monitor greenhouse gases for a decade. However, these primary standard scales have been subjected to changes and application of drift

corrections after sometimes (Hall et al, 2007; Dlugokencky et al, 2005; Gerbig et al, 1999; Zhao and Tans 2006). Under the National Metrology Institutes, there are other metrological primary standards that are stable and traceable to the International System of Units, SI unit of mass, to ensure global measurement comparability and compatibility. Several international studies such as the Consultative Committee for Amount of Substance (CCQM) CCQM-K51 (2010); CCQM-K52, (2008); CCQM-K84, (2017); CCQM-K68 (2011); CCQM-K120 (2019); CCQM-P41 (2007), have been conducted to measure the degree of equivalence between the gravimetric and the analytical values between the participants. The final reported values from each study were then compared with what was achieved during this study (Botha et al, 2010; Wessel et al, 2008; Lee et al, 2017; Lee et al, 2011; Flores et al, 2019; van der Veen et al, 2007).

The use of metrologically traceable primary standard gas mixtures provides an unbroken chain hierarchy of quantity measurement, values in the greenhouse standard gas standards that donate to the measurement uncertainty (Brewer et al, 2018). There is numerous literature that details the use of primary gas standards using various analytical methods for the evaluation of greenhouse gas amount fraction in the atmosphere. Lim et al (2013) and Lim et al (2017) developed gravimetric primary standard gas mixtures for SF_6 monitoring. Kelley et al (2014) and Matsumoto et al (2016) developed certified reference materials for N_2O measurements in the atmosphere. Hu (2015) prepared CO-in-synthetic air balance for trace measurements at an ambient level. The measurement of the CH_4 amount fraction in the atmosphere was reported by Rhoderick et al (2016), when he developed continental primary standard gas mixtures at atmospheric level. In 2017, Lim et al and Rolle et al verified CO_2 primary standard gas mixtures for ambient measurements. These primary standards gas mixtures were verified using different measurement methods such as gas chromatography with electron capture detector (GC-μECD), thermal conductivity detector (GC-TCD), flame ionization detector with methanator

(GC-FID-meth), nondispersive infrared photometry (NDIR), wavelength-scanned cavity ring-down analyser (WS-CRDS). These techniques are further explained in Chapter two.

South Africa (SA) is obligated to report on its greenhouse gas emissions from various sources to international and local climate change organizations such as the United Nations Framework Convention on Climate Change (UNFCCC) and the Departments of Environmental Affairs that focus on mitigating the effects of climate change. Due to the lack of metrologically treatable greenhouse gas standards in South Africa, the National Metrology Institute of South Africa has committed to start developing the standards at trace level. This will support existing calibration laboratories and air monitoring scientist will enable them to report on accurate measurement results that will support the National Environmental Management: Act 39 of 2004. As a contribution to creating clear information on the progress of mitigation actions and their implementation, the air monitoring scientist involved in monitoring and measuring greenhouse gas emissions in SA use various analytical instruments. These include gas analyzers, gas monitors, chromatography and thermal mass flow meters to quantify and monitor the amount of greenhouse gas being emitted. Therefore, these analytical instruments need stable and SI traceable primary standard gas mixtures or reference gas mixtures with low uncertainties (comparable to other NMIs and WMO) for calibration to produce accurate and precise measurement results.

South Africa, therefore, needs internationally comparable greenhouse gas standards and measurement capabilities to accurately identify and quantify the greenhouse gas emitted in the atmosphere (Department of Environmental Affairs and Tourism 2009). To obtain accurate measurement results, SI traceable standards with small uncertainties are imported by different companies to calibrate their equipment used in the laboratory and on fields. Due to cost implications of importing the standards, efforts have been made to develop internationally traceable gas standards to measure

greenhouse gas emissions. Through this project, a national standard for accurate measurement of greenhouse gas emissions was successfully developed at ambient and emission levels. The gravimetric technique was used to develop CO_2, CH_4, N_2O, and CO primary standard gas mixtures. These primary standards are stable, SI traceable and are internationally comparable to other national metrology institutes found around the globe (**paper I, II, III, IV and V**).

1.2 Summary of the thesis

The summary of this thesis is presented as follows:

Chapter I: A summarised introduction and background to air pollution in the form of gaseous particles is specified. This chapter also highlights the motivation of this study.

Chapter II: A concise review of the five model pollutants: carbon monoxide, methane, nitrous oxide, carbon dioxide, and one trace gases: carbon monoxide is given. Thereafter, the standard preparation and verification methods, uncertainty calculations and sampling procedure for urban and background air is reviewed.

Chapter III: The aims and research objectives are elaborated under this chapter.

Chapter IV: In this chapter, the lists of manuscripts (**paper I-V**) are presented for the PhD examination.

Chapter V: General conclusions and future work based on experimental findings are discussed in this section.

CHAPTER II: LITERATURE REVIEW

Chapter two focuses on the history of greenhouse gas emitted, the details on the type of gaseous pollutants investigated in this study. This chapter also details on the different preparation methods for primary standard gas mixtures, and the basic principles of techniques used to verify greenhouse gas mixtures. Metrological uncertainty and traceability are also explained. The sampling method for background and urban air samples is also described.

2.1 History of greenhouse gases, including other air pollutant and their abundances in the atmosphere

The discovery of gas molecules that could trap heat in the earth's atmosphere was first reported in 1896 by Svante Arrhenius. Svante Arrhenius appealed that fossil fuel combustion may result in enhanced global warming by proposing a relationship between carbon dioxide in the atmosphere and temperature (Anderson et al, 2016). His findings proved that global warming exists which were only verified in the late 19th century (Hodhe et al., 1997). Svante Arrhenius argued that the Earth's average surface temperature was 15° C due to the infrared absorption size of water vapour and carbon dioxide (Hodhe et al., 1997). It was believed that the presence of carbon dioxide in the atmosphere has lead to a 5℃ temperature growth annually due to anthropogenic activities rather than natural forces (Hodhe et al., 1997). The natural forces included solar activities and the ocean circulations. At the time, the ocean was associated as a carbon sink that cancelled out air pollution. Charles David Keeling work was also linked to the rise of temperature levels due to a steady increase in carbon dioxide in the atmosphere beyond its natural existing (Hodhe et al., 1997). His famous findings known as the Keeling Curve were reported in 1960 (Harris, 2010).

Since the industrial era, the amount of greenhouse gases emitted in the atmosphere has increased rapidly (**Figure 2.1**). **Figure 2.1** illustrates the mean mole fraction of carbon dioxide, methane and nitrous oxide measured from 1985 till 2015 taken from global air monitoring stations (WMO Greenhouse gas bulletin, 2017). This has been a disadvantage to the climate because anthropogenic emissions have contributed to the increase in the radiative forcing of 2.82 Wm^{-2} by 0.2 Wm^{-2} since 2005, which has influenced global warming (Tomizuka, 2015). Literature from the International Panel on Climate Change (IPCC) shows that a large contribution to the radiative forcing is from carbon dioxide estimated as 1.8 Wm^{-2}, whilst the small contribution is from methane (0.48 Wm^{-2}) and

nitrous oxide (0.17 Wm^{-2}) as shown in **Table 2.1** (IPCC, 2014; Tomizuka, 2015). Measurement of the radiative forcing contributed by greenhouse gases is important because the information obtained is used to derive the Global Warming Potential (GWP), and the Global Temperature change Potential (GTP). The GWP integrates the radiative forcing of each greenhouse gas over time relative to carbon dioxide whilst the GTP is used to measure the change in the global surface temperature at a time from different greenhouse gas components relative to carbon dioxide. With a lifetime of literature survey and information on GWP and GTP, policymakers draw up climate policy on the regulation of greenhouse gas emissions. Since 1988 to 2017, many gas pollutants have been listed as environmental toxins in the national air quality act under the greenhouse gas emission reporting regulations (Seymore et al, 2014; Scholes and Van der Merwe, 1996).

Carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, sulphur hexafluoride, sulphur dioxide, nitrogen dioxide and nitric acids are an important hazardous environmental pollutant that poses a threat to the public's health. Greenhouse gases recorded by the Intergovernmental Panel on Climate Change (IPCC) documents contain 18 pollutants compounds with different heat trapping capabilities. The release of these pollutants, including greenhouse gases in the atmosphere has a greater impact on the vulnerable population. Children and the elderly suffer more from asthma and cardiovascular-related diseases (Brunekreef and Holgate, 2002). The environmental consequences of having abnormal levels of greenhouse gas cause for the instant rising of sea level and temperature and increase in precipitation (Marino et al., 2016). The high rise of sea water to nearby land can leach into under groundwater, contaminating drinking water supplies affecting numerous populations that rely on it (Marino et al., 2016). Temperature increase results in heat waves that could lead to hundreds of heat-related deaths. This has influences droughts, wildfires and a decrease in crop yield. (Marino et al., 2016). For these reasons, greenhouse gas regulation policies were put in place globally,

nationally and locally to report on environmental measurements. When warmer temperatures were experienced in 1998, IPCC was founded by the United Nations Environmental Program and the World Meteorological Organization. This panel is responsible for predicting the impact of the greenhouse gas effect using current data and climate models. It is believed that environmental measurements, including greenhouse gases, often influence decisions by responsible government departments.

Greenhouse gases are molecules that absorbs and emits infrared radiation. Since the increase in greenhouse radiative forcing the molecules are usually associated with heat, as they can absorb more than 90 percent of the Earth's energy. But the amount of energy absorbed, the wavelength and how long the molecules remain in the atmosphere depends on the gas type. The composition of atmospheric air is made up of the greater value of N_2, O_2 and naturally occurring greenhouse gases as illustrated in **Table 2.1**

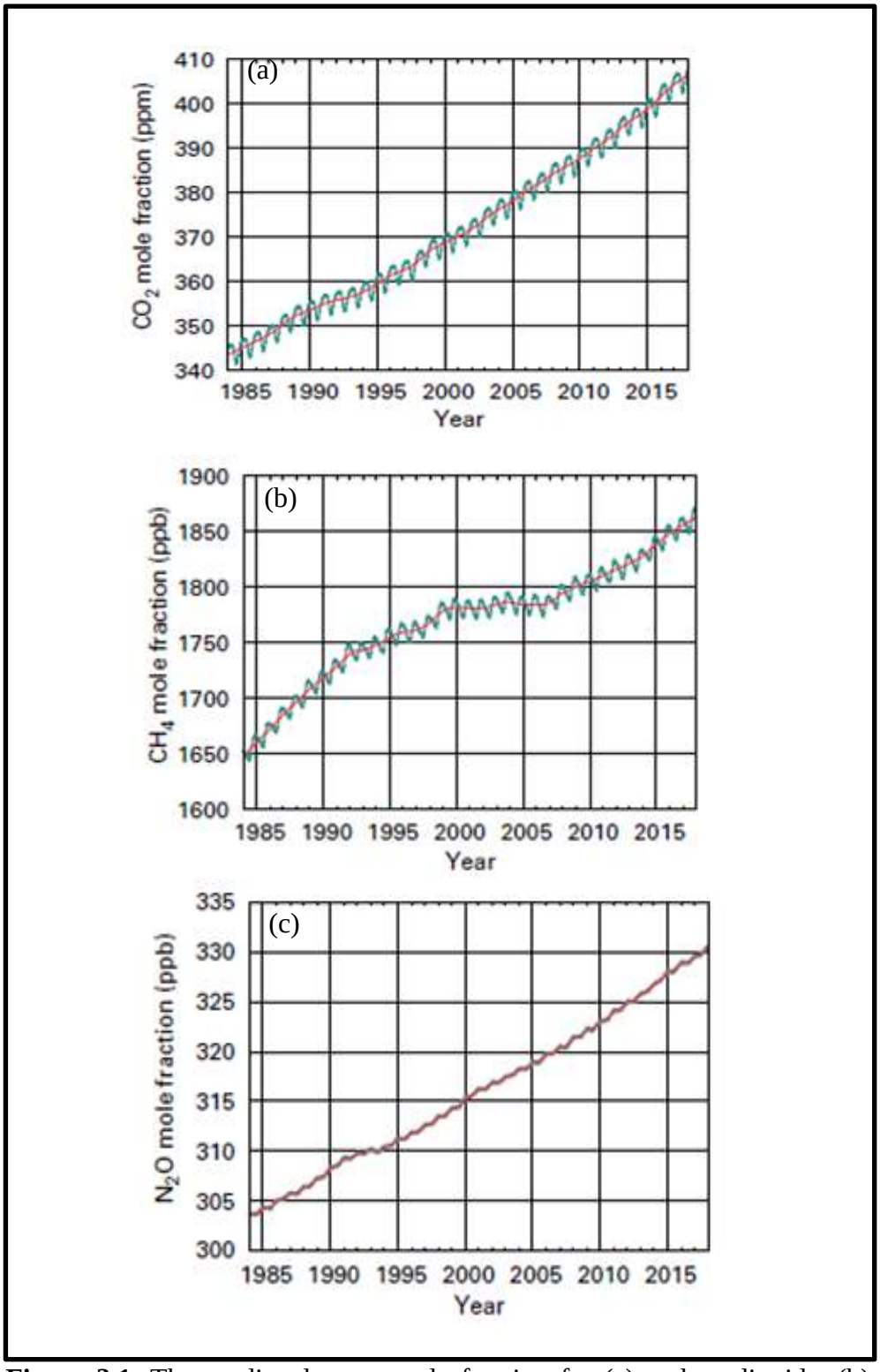


Figure 2.1. The predicted mean mole fraction for (a) carbon dioxide, (b) methane and (c) nitrous oxide worldwide. The straight line represents the monthly mean excluding the seasonal variation and the dots around the straight line shows the monthly average values (WMO Greenhouse gas bulletin, 2018).

Table 2.1 Atmospheric air composition and the estimated GWP of the main greenhouse gas contributor (Velychko and Gordiyenko, 2011; IPCC, 2014).

Gas molecules	**Natural value ($\mu mol.mol^{-1}$)**	**Natural value (%)**	**Global Warming Potential**
Carbon dioxide (CO_2)	390.00	0.039	1
Methane (CH_4)	1.79	0.000179	28
Nitrous oxide (N_2O)	0.30	0.000030	265
Carbon monoxide (CO)	0.10	0.000010	
Nitrogen (N_2)	78084	78.08	
Nitrogen dioxide (NO_2)	0.02	0.0000020	

2.2 Impact of greenhouse gas emission on global warming

Global warming has been linked to the human health deterioration, droughts, extreme temperature and sea-level rise experience worldwide due to the long existences and increase of anthropogenic greenhouse gas emission in the atmosphere for the past centuries. Though latest technologies and different carbon policies have been implemented by developed countries, research survey still shows that the world experienced its third hottest year in 2016 which resulted in more fatality, loss of food and water supply (Greenfieldboyce, 2016; NASA Goddard Institute for

Space (GISS)). The rise in the global sea levels has been measured to approximately 3.5mm annually since 1870 (Wyett, 2013). With the low global rainfalls reported in 2015, literature has been found were extreme drought occurred in the different part of the world (Müller et al., 2011). This has harmed the growth of plant-based food and water supply.

South Africa as a developing country is more vulnerable to global warming due to the lack of technical and financial support need to mitigate anthropogenic greenhouse gas emissions. The South African government has been very active in providing greenhouse gas emissions mitigation strategies and making awareness on the impact of global warming. The National Climate Change Adaptation Strategy (2019), have reported that the landscape and ecosystem has since degraded because of the wildfire outbreak and extreme weather patterns such as severe heatwave conditions and intense rainfalls. In Durban, several areas were affected by heavy rainfalls (approximately 200 millimetres rainfall) and have left the livelihood home and food less (Head, 2019 and William, 2019). Whilst, the South African beaches and commercial business along the coast have been affected by the rise in the sea tides (Mather et al., 2011; Mather and Stretch, 2012; Hughes, 1992). In the City of Cape Town Climate Change Policy document, literature shows that the wildfire outbreaks in the forest and veld of Cape Town was reported as a hazard to the nearby property and lives (City of Cape Town Climate Change Policy, 2017). The impacts of greenhouse gases to global warming has also caused high level of poverty and respiratory diseases where children are mostly affected in the community due to food price inflation and air pollution (Matooane et al., 2014; The National Climate Change Response White Paper, 2011; UNICEF, and the South African Report, 2011).

2.3 Some details of Greenhouse gases

2.3.1 Carbon dioxide

Carbon dioxide (CO_2) occurs naturally in a small amount (**Table 2.1**) and is a colourless, non-flammable gas. It is an odourless slight liquefied gas that is released into the environment as a by-product of carbon-containing processes by many industries in the petrochemical sector. It's abundantly present in the atmosphere and can stay in the Earth's atmosphere for thousands of years. Researchers believe that only a third of anthropogenic CO_2 is absorbed by the oceans. This is a soluble gas that is heavier than water and has the largest radiative effect (85%) followed by CH_4, N_2O, chlorofluorocarbons (CFC's) and sulphur hexafluoride (SF_6) When present in abundance, CO_2 imposes health threats to human life and may contribute to asthma and cardiovascular diseases (Marino et al., 2016). About 60% of CO_2 contributes to the greenhouse gas effect while the other 40% is due to other gases. South Africa's Cape Point station has reported on some historical measurements of CO_2, which has revealed a graduate increase. The CO_2 increase is from 355.6 µmol.mol^{-1} in 1983 to 383 µmol.mol^{-1} in 2008 (Brunke et al., 2009) and approximately 387 µmol.mol^{-1} in 2012 (Velychko and Gordiyenko, 2011).

2.3.2 Methane

Methane (CH_4), is also known as methyl hydride, is a colourless, and odourless gas that is extremely flammable when mixed with air. It is naturally present in the atmosphere at trace levels. This gas is emitted into the atmosphere by anthropogenic activities such as the burning of coal, gasoline, and processes in wastewater plants (Ganesan et al, 2013). It can also be emitted from the digestive processes of cattle, goats, and sheep, including agricultural feeding operations. It is also formed when fertilizer is deposited on crop fields or pastures form. One can be exposed to methane at low levels by breathing outdoor air, especially when near a coal mine, farm, oil or gas field and harvest of rice paddies. Exposure of methane at

high levels may displace the amount of oxygen needed for breathing causing suffocation, loss of consciousness, headache and dizziness. (WHO, 2000; Marino et al., 2016).

2.3.3 Nitrous oxide

Nitrous oxide (N_2O), also known as laughing gas is one of the main greenhouse gases after CO_2 and CH_4, that is monitored by various organizations (Kelley et al., 2014; Hall et al., 2007). It is a colourless, non-flammable, sweet odour substance that irritates the airways of the human body when inhaled at high concentrations. This compound occurs naturally in the atmosphere as part of the Earth's N_2 cycle and is the main cause of ozone-depleting NOx. Its natural abundance has risen by 20% since 1860 and contributes 6.24% to the overall global radiative forcing (Ciais et al 2013; IPPC, 2013). Research has shown that this gas is released naturally from soils and water exchange as part of the microbial procedure of nitrification and de-nitrification (Foster et al., 2007). It is introduced into the environment through an anthropogenic emission from vehicle exhausts, synthetic fertilizers, biomass burning and release as by-products in certain chemical processes. The impact of man-made emissions of N_2O has contributed to about 6% towards the greenhouse gas global warming potential (GWP) measured over 100 years hence significant control is required. The exposure of nitrous oxide above the set limit in an enclosed space may result in dizziness and nausea as it displaces oxygen. In general, anaesthesia, repeated exposure of this gas may contribute to later adverse neurodevelopmental outcomes in children (Fluegge, 2016).

2.3.4 Other air pollutant: Carbon monoxide

Carbon monoxide (CO), is a toxic, odourless and colourless air pollutant that is formed when carbon-containing fuels are incompletely burnt. Its amount fraction in the atmosphere is short lived, but through natural processes, CO oxidizes to form CO_2. This gas is not a greenhouse gas, but a

reactive gas that indirect elevates the levels of CH_4 and tropospheric ozone through chemical reactions with other atmospheric components (e.g. Hydroxyl radical) (Velychko and Gordiyenko, 2011). As a poisonous gas, it results in death and asphyxiation when exposed to high concentration (Weaver et al., 2000; WMO, 2010). Its main source is from industrial processes and any carbon contained materials such as domestic use of biofuels, biomass burning. Biofuel as a significant source of energy in South Africa, CO is also generated when using them. The concentration of CO is high in areas with heavy traffic. In urban areas, CO emissions come from motor vehicle exhaust (U.S. EPA, 2008).

2.4 Air pollution monitoring around the world

2.4.1 World Meteorological Organization

The Global Atmospheric Watch (GAW) is a program of the World Meteorological Organization (WMO) which was established in 1989 by merging Global Ozone Observing System (GO_3 OS) and Background Air Pollution Monitoring Network (BAPMoN) (WMO, 2008). WMO a framework that gives credible long-term scientific information about the atmosphere's chemical composition. Prior to the formation of GAW, WMO had been predicting data by measuring only moisture and temperature (WMO, 2007). The evidence showed that the atmospheric conditions are affected by chemical activities (WMO, 2007). Hence the main objectives of GAW are to provide scientific data to understand the behaviour and Earth's atmosphere and its relations to the biosphere and the ocean. GAW focus on global monitoring networks for greenhouse gas, ozone, UV, aerosols, selected reactive gases, and precipitation chemistry. Greenhouse gases which are produced by anthropogenic activities include CH_4, N_2O, SF_6, H_2 and CO_2 (GAW Report No. 197).

Cape Point station is one of the 27 WMO/GAW station around the world which monitors the atmospheric environment in South Africa and reports to the central calibration laboratories. The Cape Point WMO/GAW station is

the key station in the Southern Hemisphere for the WMO/GAW program which measures and monitors CO_2, CH_4 and N_2O, and the high-cost gas standards that they use to calibrate their instrument are sourced from the National Oceanic and Atmospheric Administration (NOAA). The data collected by WMO/GAW predict that CO_2 is the long-lived gas and has been listed with the largest radioactive effect followed by CH_4, N_2O, chlorofluorocarbons CFC's and SF_6. A reactive gas with the second largest radiative effect is CH_4. When the amount fraction of CH_4 increases, it is said to cause a rise in both ozone and the amount fraction of water vapour in the atmosphere. Nitrous oxide occurs naturally in the atmosphere as part of the Earth's nitrogen cycle and is the dominant source of ozone-depleting nitrogen oxides in the stratosphere. Chlorofluorocarbons occur in very low amount fractions and emissions but have the strongest enhancement of the greenhouse effect since CFC's produce chlorine radicals that react and destroy the ozone. Sulphur hexafluoride has the maximum global warming potential, a long atmospheric lifetime that once in the atmosphere can become essentially permanent (WMO, 2007). Due to a steady rise in the amount fraction of atmospheric CO_2 over the years, air pollution researchers from various countries must report data that are traceability one or a set of standard scale. (Kahele, 2007; Keeling, 1986). This means measured CO_2 data can be understood worldwide since similar uncertainties can be reported by different researcher's using various measurement techniques. This is also applicable to other greenhouse gas compounds and reactive CO.

It has, therefore, become ideal for NMISA gas analysis laboratory to provide the air monitoring community, including SAWS Cape Point Station with the newly developed greenhouse gas standards. Most of the air monitoring organizations do not have the scope for developing and disseminating of traceable primary standards. Through this project, the provision of the developed measurement method to the air monitoring community will be considered. This is one of the projects that NMISA gas analysis section is looking to partake in. Through participation in the

Consultative Committee for Amount of Substance Consultative Committee for Amount of Substance-Working Group on Gas Analysis (CCQM-GAWG), NMISA can disseminate measurement traceability of greenhouse gas measurements in South African trade and industry.

2.4.2 National Metrology Institutes and the World Meteorological Organization

It is noted in the government gazette under the Act No.18, 2006 that the function of the National Metrology Institutes of South Africa (NMI) is to provide national measurement standards. Consultative Committee for Amount of Substance-Working Group on Gas Analysis. The NMISA institution is also tasked to manage the national measurement system that is granting the calibration laboratories, and initiate comparison studies with other organizations with the same interest. (Varenna: Italian Physical Society, 2000). Through the International Committee for Weights and Measures' Mutual Recognition Agreement (CIPM-MRA), the role of NMISA is also to participate in comparisons with other National Metrology Institutes (NMIs) which also includes the some WMO calibration laboratories (CIPM-MRA, Thomas: Rapport BIPM-05/06). All results obtained affirms the Calibration and Measurement Capabilities (CMCs) on the gravimetric preparation and verification of the gas mixtures for each participant and the results obtained are documented under the International Bureau of Weights and Measures (BIPM) database (www.bipm.org). All measurements performed by the NMIs are traceable to the SI unit, while measurement data reported by the WMO calibration laboratories are traceable to the scale. Brewer et al (2018) explained a scale as a collection of gas mixtures based on a decided reference value or reference method. It is understood that standard scales are prepared by gravimetric or manometric methods. But the amount fraction of the standard scale is measured by a technique that provides traceability (Brewer et al, 2018). With a definite calibration curve obtained from a range of scales, a stable reference of scale at that time is defined. This is explained by the

application of 13 standards ranging from 261-371 nmol mol^{-1} that were used to define the N_2O scale, WMO-N2O_X2006A (Hall, 2007). Hence, all N_2O analytical measurements made in WMO calibration laboratories become traceable to a single source, WMO-N2O_X2006A (Hall, 2007).

Non-metrology laboratories within the GAW program currently participate in the BIPM coordinated comparison studies since an agreement between the WMO and BIPM was instituted in 2010 (Lim *et al*., 2013). Henceforth, several international key comparisons for greenhouse gas measurements have been coordinated by the BIPM between NMIs and the WMO. This initiative has helped to regulate the accuracy and compatibility of the measurement. The first key comparison was conducted in 2003 where the gravimetric scale was compared with the WMO scale (CCQM-P41) (Kim, 2012). The results between the NMI's and the WMO laboratories showed that the WMO scale had large uncertainties and was not comparable to the reference value (CCQM-P41) (Kim, 2012).

Factors like purity analysis or assessment of the raw material, the molecular weight, gravimetric value, analytical results or verification analysis and the stability of the gas in cylinder could have contributed to the large uncertainties. The WMO/GAW Central Calibration Laboratories (CCL) for greenhouse gases and other trace gases is one of the important components in the WMO/GAW programme lead to sustaining global compatibility observations from various laboratories (WMO/GAW Reports No. 172 and 197). Through the key comparisons, NMIs such as the National Institute of Standards and Technology (NIST), the National Physical Laboratory (NPL) and Korea Research Institute of Standard and Science (KRISS) has been identified as CCL for WMO/GAW. These three NMI's provide high accurate primary gas standards to the GAW stations and have achieved the WMO compatibility. Recently, Brewer et al., (2014), prepared primary standards in synthetic air for atmospheric measurements of CO_2 and CH_4. The amount fractions reported were comparable with the WMO data.

WMO/GAW standard scales are only traceable to one WMO scale that is subjected to change and need updates (Hall B, 2007). The standard scales are prepared with very small uncertainties (e.g. 0.025 µmol. mol^{-1}) which have been a challenge to achieve. The scale is disseminated amongst GAW stations under the WMO organisation (Brewer *et al* 2014). Traceability, stability and uncertainty are therefore some of the measurement challenges faced by the global observation systems for climate change. To address some of these challenges, it became important for the WMO to partake in the CCQM studies coordinated by the different NMIs.

2.4.3 Air pollution monitoring in South Africa

Air pollution has had a negative impact in the health and economy of the country (Matooane et al., 2004). It is documented under the NEM: AQA, 2004 (Act No.39 of 2004) that every human being has the right to air quality that is safe, not harmful to the health and well-being. Though this is currently not the case. As a continuous improvement, there are numerous monitoring movements around the country pioneered, under the act, that uses different monitoring methodologies to report air pollution. In South Africa, there are over 100 government-owned air monitoring networks responsible for data reporting on the South African Air Quality Information System (SAAQIS). Gwaze and Mashele (2018), outlines that there are only half of the stations that are complying (**Figure 2.2**). This remains a concern because there are still numerous amounts of air pollutants being emitted and remain unaccounted for. An alternative approach could be for the NMISA gas analysis laboratory to assists or adopt some of the non-reporting government-owned networks. This could improve the accuracy of the measurement results reported in the South African Air Quality Information System (SAAQIS) as accurate standards will be used to calibrate the measurement instruments. and will be beneficial for South Africa.

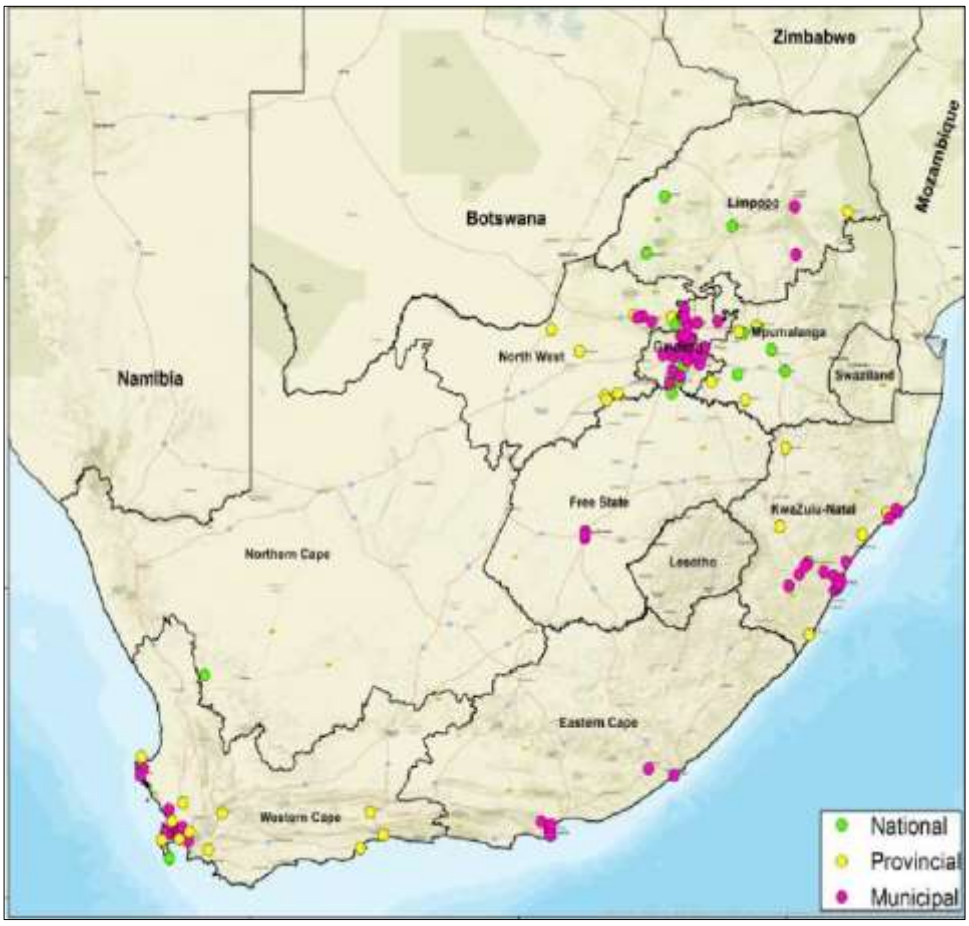


Figure 2.2. Overall government-owned air monitoring networks (DEA, 2011a, Gwaze and Mashele, 2018)**.**

2.5 Metrological Traceability

The International Vocabulary of Metrology defines metrological traceability as "a *property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty*" (VIM, 2008).

This means it is only the measurement result attained that is metrologically traceable rather than the instrument used. According to Lecuna (2017), international measurement standards are recognized by signatories of international arrangement and are envisioned to be applied worldwide, while national standards are used for calibration in the country.

During the study, metrological traceability was applied through estimating the internal consistency of the prepared gas mixtures. This was done to

establish accuracy of the gas mixtures, and that of the measurement data and calibrate the analytical equipment's. The developed gas mixtures were verified under control measurement conditions and their uncertainties were defined. Some of the primary standards gas mixtures prepared for this study were calibrate with other national metrological institute laboratories including WMO CCLs during comparisons studies (Brewer et al,2018). It became a necessity for the prepared gas mixtures to pass the set measurement criteria of reproducibility, repeatability, percent difference, instrumental drift and stability defined for calibration of the analytical methods for quantification of air pollutant (ISO 6141, 2015 and Lushozi et al, 2019). The primary standard gas mixtures are used to certify existing standards without reference to any other measurement standard while the primary reference gas mixture is the standard sold to the customer after certification with existing standard gas mixtures. Both types of primary standard gas mixtures lie on top of the hierarchy of standard to distribute traceable standards (**Figure 2.3**) (Cox and Harris, 2006). **Figure 2.3** shows a pyramid with the SI traceability originating from the kg artefact which is used to certify NMISA mass pieces that calibrate the balance (top loaders and mass comparators). The balances are then used during the preparation of primary standard gas mixtures. These gas mixtures are then used to certify secondary standard gas mixtures from different customers. In this study, reliable measurement results of CO_2, CH_4, N_2O, and CO was assured by using suitable gas mixtures and following ISO 6142-1, (2015) and ISO 6143, (2001). The use of these parameters has made a basis for reliable quantification of CO_2, CH_4, and N_2O in different types of air samples.

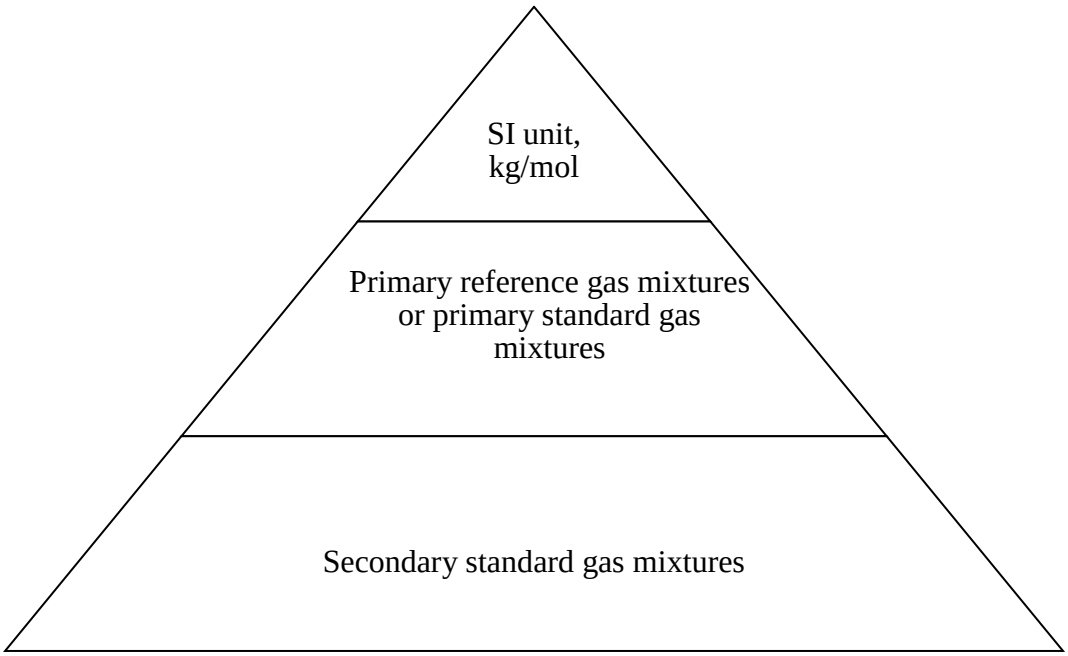


Figure 2.3 Traceability chain of gas mixtures (Brewer et al, 2018; Budiman et al, 2018).

2.6 Metrological procedures for preparation of primary standard gas materials

The procedure for preparation of gas mixtures entails the dilution of a pure component of interest into pure nitrogen or inert gas. There are two methods that permit the preparation of primary standard namely static and dynamic. To meet the targets of each application both methods were developed to advance the accuracy in the estimation of the final value and stability of the gas mixtures for calibration purposes.

2.6.1 Static gravimetric preparation

Static gravimetric preparation is the most popular method used for the manufacturing of stable gas standards to obtain small uncertainties from a pure gas (%) to low diluted (nmol.mol) amount fraction range. An international standard document, ISO 6142-1, (2015) describes this method for binary and multi-constituent gas mixtures introduced into a cylinder at different state (gas or liquid). Its principle is based on introducing a weighed gas mixture (approximately 20 g) with a known amount fraction in

a gas cylinder with a known volume (approximately 15 kg) (ISO 6142-1, 2015). Through a series of consecutive dilution steps (from % $mol.mol^{-1}$, $\mu mol.mol^{-1}$, $nmol.mol^{-1}$ then $pmol.mol^{-1}$), the obtained amount fraction is considered to have small preparative uncertainties (ideally, less than 20 mg or less) (Lim et al, 2018; Milton et al, 2011). Its application is limited to amount not lower than 10^{-4} to 10^{-5} % because, at lower target values of individual components, the stability of gas mixture decreases due to sorption effects, and, in certain cases, losses can reach up to 50 % (Platonov et al., 2018).

Literature review shows different international key comparisons studies between national metrology institutes and other international laboratories for greenhouse gas standards has been conducted such as CCQM-K51, (2010); CCQM-K52, (2008); CCQM-K84, (2017); CCQM-K68, CCQM-K120 (2019); CCQMK- P41, (2007) (Botha et al, 2010; Wessel et al, 2008; Lee et al, 2017; Lee et al, 2011; Flores et al, 2019; van der Veen et al, 2007). A static gravimetric method is one of the techniques used to dilute the gas mixtures to picomole per mole level. The comparison studies are planned to compare the capabilities for the preparation and value assignment of primary gas standards for CO, CO_2, CH_4, and N_2O maintained by participated laboratories at the set amount fractions. Verifying the stability, adsorption, and desorption of the reference gas mixtures is some of the international comparison criteria needed to be proved by participants. Usually, gas mixtures in cylinders are preferred over dynamically prepared because it is cost effective and can be carried on and off the laboratory to the field with ease.

Recent literature explains that greenhouse gas constituents behave well in the 10^{-4} to 10^{-5} % amount fraction range with short-term stability of two years. CO, CO_2, CH_4, and N_2O reference gas mixtures at high accuracy are commercially available to calibrate equipment's used to monitor emission at ambient and emission level. In metrology, measurements are positioned inside the calibration chain, therefore, gas mixtures calibrated against NMIs standard become traceable to the respected standards. For accurate and

precise measurement result, it is a necessity to calibrate equipment that measures greenhouse gases with a metrologically traceable gas standard. Previous literature has demonstrated a few drawbacks including loss of CO_2 to the internal surface of the cylinder and manifold system (a filling system made up of stainless steel) due to adsorption and chemisorption (Leuenberger et al.,2014; Miller et al., 2015; Brewer et al., 2018). These inaccuracies are noticed when the gas pressure in the cylinder is close to zero. In most studies, a known mass of the target gas component was introduced in an aluminium cylinder and stored at 12 MPa. The use of static method adds an advantage of cost-effective and easy handling of gas cylinders over dynamic methods. The static method is a primary method that provides great accuracy where the known target mass is determined by weighing on a high capacity and sensitivity balance. The weighing process is a high degree of accuracy but the effect of adsorption and desorption of gases on the cylinder interior walls and purity variation is not possible to account for during this process. Therefore, necessary corrections of buoyancy effect that might occur due to temperature, pressure and relative humidity variation are required to be determined. Other types of static methods include volumetric and partial pressure or manometric methods. Providing high metrological primary standard gas mixtures at low amount fractions (nmol.mol^{-1} and pmol. mol^{-1}) with good quality, and fewer challenges encountered during preparation is the goal because the gas mixtures would be used for different applications such as environmental, industrial and medical fields (Slomińska et al.,2014).

2.6.2 Dynamic method

Dynamic methods are used to introduce reactive standards in a flow of dilution gas in a closed system. These methods can manufacture fresh organic and inorganic primary standards in the gaseous or vapour phase because there are almost no limitations by nature and amount fraction of the target components in a closed system (Lecuna, 2017). The closed system is a continuous flow of fresh mixture that is manufactured in large volumes

with low loss of the mixture to the inner surface of the tubes or membrane because of the equilibrium between the walls of the system and flowing gas (ISO 6145-1, 2003). Its principle is based on a continuous flow of fresh laboratory air or inert gas (e.g. N_2) in a closed system to dilute pure or a premix sample following very minimal dilution step. The prepared sample can be used for various air quality applications to achieve low amount fractions ($pmol.mol^{-1}$) sample and extremely small uncertainties. The dynamic method has an advantage over the static method as reactive standards such as volatile organic compounds (VOCs) are accurately produced without interacting with the permeation tubes or membrane inner walls. The disadvantage of using dynamic methods includes the need to have continuous gas source and flow rate of the gas, therefore adsorption of the analyte on the tube or membrane walls is elimination (Platonov et al., 2018). Many VOCs are characterized as reactive and have odour natures, therefore preparation by static methods can be a big challenge as the samples react with the inner walls of the cylinders causing instability (Słominska et.al., 2014). Other dynamic methods include diffusion, permeation, injection, gas stream mixing, evaporation, an electrolytic and chemical reaction (Barratt, 1981).

Dynamic methods can be categorized into nonequilibrium and equilibrium methods (Platonov et al., 2018). Nonequilibrium method is based on a continuous diffusion of a target component at a constant rate into a dilution gas flow through a membrane or capillary. It is important to maintain the volume rate of the dilution gas flow to eliminate preparation errors when using this type of dynamic method. Equilibrium methods are based on the saturation of an inert gas flow with target components on its contact when generating a solution with certain amount fractions. When an interphase equilibrium is reached, the estimated amount fraction of the reference gas mixture is independent of the volume flow rate of the carrier gas. The principle of the two types of dynamic techniques is based on controlling the diffusion and permeation of the anticipated component into a stream of the diluting gas. Dynamic standards are only prepared when a reference gas

mixture prepared by the static method is unstable. Most greenhouse gas standard is regarded as stable in, aluminium alloy, cylinders when prepared by static methods. Hence for the purpose of this project, the static gravimetric method was used for the preparation of gas mixtures.

2.7 Preparation of greenhouse gas primary standard gas mixtures

A primary standard gas mixture is a measurement standard gas manufactured following a primary method without referring to another measurement standard. The primary standard is required to meet the repeatability, reproducibility and established shelf lives for the application intended. When the primary standard gas mixtures are used to calibrate other gas mixtures (from a customer or in-house), the result obtained becomes the secondary standard. Based on the verification result, the behaviour of the primary method is concluded. The predicted amount fraction of the gas mixture becomes traceable to the kilogram SI unit (Alink et al, 2000). The realization of the amount fraction with its uncertainty is then achieved by purity, weighing measurement and molar masses a component using ISO 6142-1, (2015). The calibrated mixture in gaseous or vaporized form is disseminated in high pressurized cylinders (Lee et al, 2017). Literature survey proves that NMIs around the world have used this method of developing greenhouse gas standards for various air measurement communities (from the background, emission and lower levels). In this study, the greenhouse gas primary standards were prepared as a binary and a multi-gas mixture.

The NMISA gas section is involved with the chemical measurement of gaseous and liquid samples at government level. This has been achieved by keeping the consistency and equivalence with the international gas measurements through comparison with other National Metrology Institutes. It is mandated to develop, maintain and disseminate national primary standards, sets up precise reference methods for gas analysis, verify gas instruments (such as ozone calibrators, air monitors etc) and gives technical advisory services in South Africa. The analysis and measurement

of gas components have been used in environmental monitoring, medical and clinical sectors, coal, petrochemicals, electronics, space and instrumental manufacturing industries. In the safety assurance sector, the use of gas components is very important to public health and economic development. The demand for gas measurements that are accurate with long-term data profile, stable, and uniform become a concern to the international treaties, air monitoring communities and government. This made gas measurements very important in chemical metrology and the world of science.

Since the beginning of metrology in 1946 to date, South African as a country has developed and researched on gas measurement. The gas laboratory of NMISA has produced primary reference gas mixtures, primary standard gas mixtures and certified many binary and multicomponent gas mixtures from high pure (%) to diluted micromole per mole ($\mu mol.mol^{-1}$) from different stakeholders. This includes organic and inorganic gas mixtures such as ethanol, benzene, toluene, ethylbenzene and xylene (BTEX), carbon dioxide (CO_2), sulphur dioxide (SO_2) etc. The laboratory continues with the development and measurement of primary standard gas mixtures which create a national gas measurement chain. Through proficiency testing and participating in international key comparability under the Consultative Committee for Amount of Substance (CCQM), the feasibility study for the formed traceability system of gas constituent measurement on a global scale is achieved. The success of NMISA during CCQM program has given a stand base from which international comparability is extended. Before preparation, impurity analysis of the starting material is first to step conducted. It then becomes the customer's responsibility to quantify the exact amount of impurity present.

2.8 Manufacturing steps of greenhouse gas primary standards by the gravimetric procedure.

Before gravimetric preparation, purity analysis or assessment of the pure gases or starting material is conducted. Purity analysis is a procedure done with the aim of checking the impurities in the highly pure gases. It is a very critical step since the impurities in the highly pure gases are often the most uncertainty contributor to the gravimetric amount fraction. The uncertainty contributions depend on the number of impurities existing in the raw material and how accurately the impurities were measured. In this study, the impurities of interest have been quantified and included in the determined uncertainty of the final gravimetric value of the gas mixtures. The manufacturing steps carried out in this study is explained below as:

2.8.1 Step 1. Cylinder type

Aluminium alloy 5 and 10 L inner volume gas cylinders are used to prepare the primary standard gas mixtures. This type of material is used because the internal surface does not react with most gases (**Figure 2.4**). Before use, the cylinder is taken for internal treatment by passivation with a deposit of a layer of oxide on its surface. **Figure 2.4** an example of the inner walls of the aluminium cylinder used in this study is shown below.



Figure 2.4. Demonstration of the inner components of a cylinder valve, the smooth inner walls of an aluminium gas cylinder.

2.8.2 Step 2. Cylinder cleaning

After passivation, the cylinder is cleaned externally by removing any foreign materials and dust particles that may contribute to an increase in the uncertainties measurements result.

2.8.3 Step 3. Evacuation of cylinders

During this process, the cylinder is first evacuated using the Pfeiffer turbomolecular vacuum pump station. The ideal vacuum reading for the degassing of cylinders for the gravimetric preparation of gas mixtures is less than $2x10^{-7}$ mbar (atmospheric pressure). This is an overnight process.

2.8.4 Step 5. Weighing of the cylinder on mass comparator balance

After the evacuation, the evacuated (empty) cylinder is weighted first on the high accurate mass comparator balance (**Figure 2.5)**. This cylinder is weighed several times against the reference cylinder to eliminate buoyancy effects. **Figure 2.5** illustrates the type of mass comparator balance that is explained in the paper section.



Figure 2.5. (a) Single-pan balance with 5 L cylinder suspended below, (b) Automated weighing system with a cylinder circular turntable plate by KRISS (Park et al, 2004).

2.8.5 Step 6. Flushing and filling of the cylinder

The weighed cylinder is placed on the centre of the top loader balance and connected to the filling station. The gas line is then flashed eight times with the parent gas (e.g. CO) before it is filled with the determine amount of parent gas. During filling of the cylinder, the target balance and pressure in the filling system was monitored during the addition of the gas to ensure the correct amount of gas is added in the cylinder.

The cylinder is weighed on the mass comparator balance after the addition of each component. Once the addition of the gas component is complete, the cylinder is filled with the balance gas (nitrogen or air). The cylinder is left for 2 hours to reach thermal equilibrium before the final weighing.

2.8.6 Step 7. Homogenize the gas mixture

After the final weighing, the cylinder is rolling on the electric roller bench for a minimum of 2 hours to homogenize the gas mixture.

2.8.7 Step 8. Verification of mixtures

Once the gas mixtures were prepared, each gravimetric value is verified by using a comparative measurement system such as non-dispersive infrared spectroscopy, cavity ring-down spectroscopy, gas chromatography coupled micro electron detector, flame ionization detector with methanator and thermal detector. In gas metrology, the amount fraction or ($mol.mol^{-1}$) is the preferred way to express the quantity of the gas composition or constituent. It is determined by the model equation as (ISO 6142-1, 2015):

$$X_r = \frac{n_r}{n_r + \sum n_j} = \frac{n_r}{n_j} \quad (2.1)$$

where X_r is the amount fraction of constituent r, n_r is the amount of substance r, n_j is the amount of substance j, p is the total number of constituents.

The mole is used since it has the advantage of providing the amount of substance of the gas constituent.

By converting equation 2.1 into equation 2.2, the procedure to realize the amount fraction by gravimetric preparation method is given as (ISO 6142-1, 2015):

$$x_i = \frac{\frac{m_i}{M_i}}{\frac{m_j}{M_j} + \sum \frac{mi}{M_i}} \quad (2.2)$$

where m_i is the mass of constituent i in grams, m_j is the mass of constituent j in grams, M_I and M_j represents the relative molar mass of constituent

i and j in grams per mole. Equation (2.2) is used to calculate the amount fraction of each gas component achieved when weighing an evacuated and clean aluminium cylinder before and after each introduction of the gas component. The use of gravimetric method makes the value traceable to the mole SI unit because atomic mass can be determined precisely. The gravimetric preparation by substitution method is only applicable to gaseous constituents that do not react with each other and the inner walls of the cylinder. Multiple dilution steps are often used in the gravimetric procedure of a gas mixture because of the advantage of obtaining acceptable and low uncertainty.

The amount fraction for the final mixture is defined by the mass of the gas added and its uncertainty detailed as an expanded i.e. the combined standard uncertainty multiplied by a 2-coverage factor (at 95 % confidence level).

The final uncertainty of the primary standard gas mixture is estimated from purity analysis, weighing stability assessment and verification (Lee et al, 2017).

2.9 Adsorption and desorption effect of the gaseous species on the aluminium compressed gas cylinders

Aluminium cylinders have an advantage over stainless steel cylinders because aluminium is not a heavy material as stainless-steel material and is resistant to oxidization, including other forms of weathering (Syed, 2006) (**Figure 2.3**). However, previous studies have discussed that greenhouse gas (carbon dioxide) and VOCs (formaldehyde and dimethyl sulphide) have shown an adsorption and desorption effect on gas cylinder inner surfaces (Miller et al., 2014, Lee et al.,2018). **Figure 2.6** shows how the adsorption test was carried out for **paper 1II**.



Figure 2.6. Illustration of adsorption and desorption test.

2.10 Uncertainty of measurement for gas constituents

To evaluate the quality of the measurement results, the uncertainty from purity assessment, the uncertainty from the weighing of the masses from the gas added, uncertainty from the molecular masses, verification and stability will be considered for each gas mixture prepared. These parameters are determined according to the metrological principle of Guide of Uncertainty of Measurements (BIPM/ISO GUM, 2008). Uncertainty is a parameter associated with the measurement result that characterises the dispersion of data that could attribute to the measurand (ISO GUM, 1995). The parameter may be recognized as, a standard deviation or standard uncertainty. The measurand is identified as the amount fraction of an analyte during chemical analysis. Amount fraction highlighting mass concentration, amount concentration, number or volume concentration.

Uncertainty of measurement comprises of various components that may be estimated by the statistical distribution of the results from a succession of measurements data characterised. Other components are evaluated from assumed probability distribution based on expensive or other information

such as Type A and Type B estimation. Knowledge of the uncertainty of the measurement increases confident in the results obtained.

The overall uncertainty is estimated when each identified source of uncertainty is treated independently to identify the known contribution from that source (ISO GUM, 1995).

To estimate the standard uncertainty associated with the results for this study, the following contributions were considered:

Type A uncertainty - estimated from statistical analysis of a series of repeated observations.

Type B uncertainty – estimated based on scientific judgment fusing all available information on the possible variability of an input quantity that has not been obtained from repeated observations. The uncertainty of the prepared standard is illustrated in **Figure 2.7**.

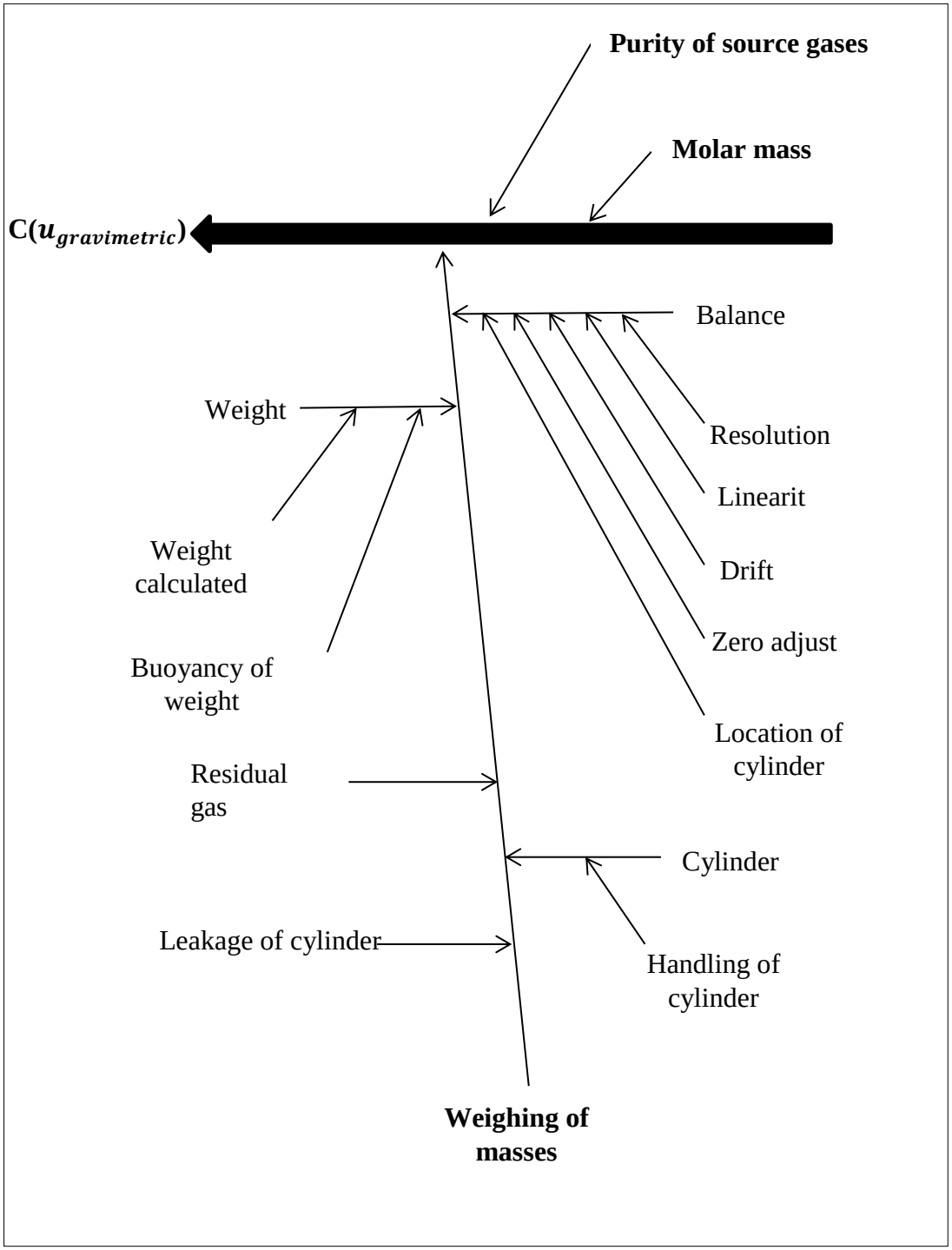


Figure 2.7. Ishikawa diagram showing the source of uncertainty for gravimetric dilution of gas mixtures.

2.11 Verification system used.

2.11.1 Gas Chromatography

In 1941, Martine and Synge were the first to develop the gas chromatography technique using a gas-liquid partitioning. This was achieved after they separated and quantitatively determining constituents of C_1-C_{12} fatty acid mixture. In Gas Chromatography (GC), a gas mobile phase and a solid or immobilised polymeric liquid are used. Analytes are separated when the difference in the stationary phase affinity and relative vapour pressure have reached an optimum (Sook, Holler and Nieman, 1998). The injected sample is transported by an inert mobile phase through a column where analytes are then separated based on their distribution between two immiscible phases. After separation, the analytes from the column effluent are then monitored with a detector.

When used this technique can produce quick analyses due to the highly efficient nature of separation achieved. It is excellent for quantitative analysis. The technique used established with the extensive literature on application. It is a rugged and reliable technique. However, this technique is restricted to samples that are volatile and is not recommended for samples that degrade at higher temperatures. In the gas analysis, different separation mechanism is used to allow the use of standard equipment at normal temperature. In this study, gas chromatography coupled with various detectors flame ionization detector, micro electron capture (GC- μECD) and pulse discharge helium ionisation detector (GC-PDHID) were used to analyse the prepared and sampled standards. The verification of the primary standard gas mixture is conducted by GC for this study.

2.11.2 Type of detectors used

2.11.2.1 Flame ionization detector

A flame ionisation detector (FID) is the most popular detector used in gas chromatography. Its principle is based on the chemi-ionisation of the gas effluent from the column which mixes with hydrogen and air (Dressler,

1986). A flame is formed when hydrogen, air and carrier gas are burnt. The flame destroys the effluents forming ions that are detected by a plate collector forming a signal. It is regarded as a linear detector which was used to detect CH_4, CO and CO_2 in the presence of a nickel catalyst in this study.

2.11.2.2 Micro electron capture detector

The micro-electron capture detector commonly used to detect electro absorbing electrons. The analytes from the column effluent capture electrons generated from ionising the carrier gas in a chamber that consists of β-emitter (Dressler, 1986). This effect causes a decrease in the current strength of the detector which in turn generates a signal. In this study, the detector was used to measure N_2O. The μECD is very sensitive at trace levels though it is regarded as a non-linear detector.

2.11.2.3 Thermal conductivity detector

A thermal conductivity detector (TCD) is among the commonly used detector. Its principle is based on measuring the change in the thermal conductivity of a gas stream flowing over the thermistor causing a change in the amount fraction of the analytes to be detected (Sook, Holler and Nieman, 1998). In this study, the detector was used during the measurement of CO_2 gas mixtures.

2.11.3 Cavity ring-down spectroscopy

In 1998, O'Keefe and Deacon introduced the Cavity ring-down spectroscopy (CRDS) technique. It is now a popular spectroscopic technique due to its high detection sensitivity than conventional direct absorption techniques such as Fourier Transform Infrared and Non-Dispersive Infrared Spectroscopy. Its principle is based on measuring the decay rate of light intensity glancing out of a high finesse cavity over time instead of absorbance. CRDS can be performed by pulse or continuous wave light source by, a continuous wave has recently become a popular

application. Consequently, CRDS measurements are not affected by laser noise as the laser is shut off during measurements and offers very long interaction path length between the sample and the optical cavity (**Figure 2.8**). Nevertheless, the CRDS technique independently selects the species of interest with high accuracy which isolates from interfering species. It has been researched to generates a highly accurate, precise and linear response of the analyser. The CRDS has the capability to measure a single spectroscopic line of the isolated species of interest which confirms that the peak area is linearly proportional to the amount fraction of the species. This proves that CRDS analyser has an advantage over conventional spectroscopic techniques. Other advantages include (i) field measurements of atmospheric species emitted from various source which requires at least two standards for linear calibrate, (ii) CRDS requires low flow of gas but still produces a signal with low drift, (iii) can analyse CO, CH_4, CO_2 and H_2O (G2401) and CO, N_2O and H_2O simultaneously and (iv) the warm- up time of the CRDS depend on the temperature and pressure of ambient air is less than the time needed for the chromatographic analysis. Since the CRDS is a new and improved technique, the discovery of the true value for an unknown sample and/or primary standard gas mixture is expected to be associated with lower uncertainties.

The CRDS used during this study consist of a continuous-wave laser (G2401), a quantum cascade laser for G5310 and a high finesse optical cavity containing three reflective mirrors. **Figure 2.8** illustrates a diagram of the CRDS components. The decay curve is calculated for each laser wavelength over decay time and an absorption spectrum is acquired. Knowing the partial pressure of the absorbing gas species inside the cavity is important for attaining absorption cross – sections information (Wheeler et al., 1998). In this study, G2401 and G5310 Picarro instruments were used for the detection of CO, CO_2, CH_4, H_2O, N_2O in primary standards, known and unknown gas mixtures.

2.11.4 Non-dispersive infrared (NDIR) measurement system

The measurement principle of the NDIR is based on the capability of gas molecules to specifically absorb infrared (IR) radiation to measure its amount fraction. The amount of IR radiation absorbed is regarded as proportional to the amount fraction of the gas molecule. The measurement technique of this instrument is based on the Beer-Lambert law, which is based on the linear relationship between absorbance and concentration of absorbing species (Sook, Holler and Nieman, 1998). In this study, a Uras NDIR supplied by ABB was used to measure the content of CO_2 in the primary standards and background air samples.

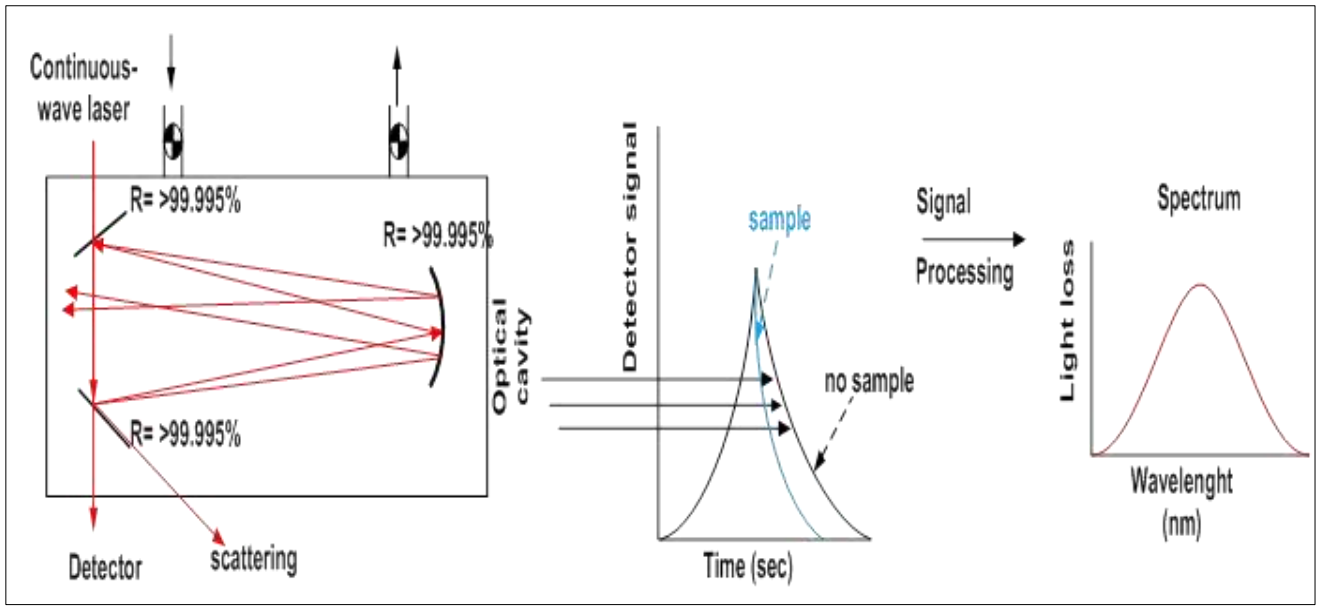


Figure 2.8. Schematic diagram of the basic principle of the CRDS (https://www.picarro.com/company/technology/crds, Accessed: March 2017)

2.12 Quality assurance of measurement results

The quality assurance of the results is of critical importance and some parameters that are a measure of it are given below.

2.12.1 Uncertainty of measurement

To ensure the quality of the results, the uncertainty of purity assessment, gravimetric preparation, verification and stability were determined for each gas mixture prepared. This parameter was determined according to the metrological principle of Guide of Uncertainty of Measurements (ISO GUM, 1995).

2.12.2 Repeatability

Repeatability is defined as the closeness of the agreement between the results of consecutive measurement of the same measurand carried out in the same conditions. (EURACHEM, 2016) Repeatability is expressed as the smallest anticipated precision. It gives an idea of the variability to expect when a method is performed by the same analyst on the same analytical instrument over a short time, Repeatability is expressed as:

$$\%RSD = \frac{standard\ deviation}{mean}. \qquad (2.3)$$

2.12.3 Reproducibility

Reproducibility is defined as the closeness of the agreement between the measurement results of the same measurand carried out under changed conditions or parameters (EURACHEM, 2016). When a sample is analysed by several laboratories for comparative purposes, reproducibility is used as precision.

2.12.4 Accuracy (Bias or Trueness study)

Bias is defined as the difference between the expected measurement value and the accepted reference value. It can also be expressed as the analytical recovery determined when the obtained results divided by the expected results.

2.12.5 Data conversion after verification

After acquiring the average of the analytical instrument response, two software are used to evaluate the measurement amount fraction and the related uncertainty of the unknown samples and or gas mixtures.

GUM Workbench Pro Version 2.3.6.141 Win 32 software was used to evaluate the measurement uncertainty. A formulated model equation which incorporates the peak area of the unknown sample and the known standard gas mixture is added under the new budget window where the model analysis and computations follow other uncertainty evaluation documents, especially the rule of the ISO Guide to the Expression of Uncertainty in Measurement (Metrodata GmbH, 2011). For this project, the model equation that was used during gas chromatography measurements is explained under the papers in each study.

XGENLINEV1_1 version 1.0 is a software that is incorporated in a Microsoft spreadsheet developed by the National Physical Laboratory (NPL) to carry out general least-squares polynomial evaluations according to ISO 6143, 2001 (XLGENLINE Version 1.0 Software Document, 2007). In this study, the software was used and a calibration curve from a range of standard gas mixtures for CRDS and NDIR response was drawn along with the analytical uncertainties of the unknown were calculated.

Once the gravimetric and analytical values with their related uncertainties have been predicted, a stability graph is drawn. This assist with establishing the shelve life of gas composition in the aluminium cylinder over a period

of measurement within the desired calibration and measurement capabilities (CMC). By combining the analytical uncertainty with the gravimetric uncertainty, a final uncertainty is predicted for the gravimetric amount fraction treated as the true value of the gas mixture. This is further explained in the results section of the papers.

2.12.6 Validity of the developed greenhouse gas mixture

After the validity of the developed or manufactured greenhouse gas primary standard gas mixtures by verifying its constituent as determined by gravimetric preparation with the analytical value, a positive condition demonstrated in the model equation 2.9 is checked (ISO 6142-1, 2015).

$$\left|x_{grav} - x_{anal}\right| \leq 2\sqrt{u_{grav}^2 + u_{anal}^2} \tag{2.4}$$

where x_{grav}, is gravimetric of preparation amount fraction, x_{anal}, is the analytical or verification value determined, 2, is a coverage factor for a normal distribution at 95 % confidence level, (2σ), u_{grav}^2 is the preparative or gravimetric uncertainty and u_{anal}^2 is the uncertainty obtained from the verification procedure of the gas mixtures

For this study, once the described criteria (Equation 2.9) is met, the gas mixtures were accepted and rejected when the criteria is not met.

2.13 International key comparison

The international key comparison is the testing of a laboratory preparative or analytical capability to establish the equivalence of the measurement between the national metrology institute's and other global laboratories. In this study, the right application of the SI treatability method for primary standard gas mixtures is checked by comparison with other standards with similar hierarchy (metrological chain). It is a statistical process whereby

data is collected, statistically analysed and the degree of equivalence between the participated laboratories is estimated. During the statistical analysis, a summary of NMI's measurement and assessment of the corresponding uncertainty is important. The basic principles of key comparison are internationally accepted. It is significant because

i. it gives supporting evidence of measurement capability claims by the participating laboratory,
ii. compares e.g. NMISA preparative and analytical value - assignment of primary reference materials or primary standard gas mixtures, and
iii. demonstrates international equivalence of South Africa to support our country's trade and industry.

After the study, measurement results attained become internationally comparable at the reported uncertainty for each the participated. Therefore, the benefit of participating in key comparisons is that the country can claim the calibration and measurement capabilities (CMCs) which are registered on the BIPM key comparison database.

CHAPTER III: RESEARCH AIM, OBJECTIVES AND APPROACH

This chapter focuses on the aim, objectives and approach of the study highlighting the general and specific objectives. The motivation of the study and the hypothesis is also presented.

3.1 Aim of the study

The aim of the research is to develop primary standard gas mixtures in nitrogen and synthetic air at ambient (2; 350; 340) µmol.mol^{-1}, background (380; 400) µmol.mol^{-1} and emission (above 400 µmol.mol^{-1}) level that are traceable to the SI unit for analysis of greenhouse gas emissions/level in the background and urban air samples for air pollution monitoring in South Africa.

3.2 General objective

The main objective is to develop primary standard gas mixtures in micromole per mole and nanomole per mole levels for measurement of greenhouse gas emitted at ambient and emission levels in South Africa.

3.2.2 Specific objectives of the study are:

(i). To conduct purity analysis of all high pure CO_2, CH_4, N_2O, CO, N_2 BIP^{TM}, Ar and O_2 using various techniques to quantify the exact amount fraction of impurities present for each gas before preparation of the mixtures according to ISO 6142-1, (2015).

(ii). To prepare highly accurate primary gas standards for CO_2, CH_4, N_2O, and CO in nitrogen and in air traceable to the SI and may be compatible/comply with the WMO scale following 'Borda' substitution gravimetric method.

(iii). To develop the analytical method used to quantify the newly prepared reference gas standards on the Gas Chromatography with micro Electron Capture Detectors (GC-µECD), Gas Chromatography with Flame Ionisation Detector (GC-FID), and Gas Chromatography with Thermal Conductivity Detector (GC-TCD).

(iv). To verify the gravimetrically prepared primary gas standards by Cavity ring-down Spectroscopy (CRDS) and the non-dispersive infrared (NDIR) spectroscopy.

(v). To quantify and compare the amount fraction of greenhouse gases found in the air samples from different locations (around Cape Point and CSIR campus) using the newly developed greenhouse gas primary standard gas mixtures in South Africa.

(vi). To study the short and long - term stability of the primary standard gas mixtures by checking the internal consistency of the gas in the aluminium cylinder at different times after preparation.

(vii). To establish the international equivalence of the newly developed gas standards through participation in international key comparisons organised by CCQM.

(viii). To develop accurate analytical measurement methods used to verify the new primary standard gas mixtures for future support of the air monitoring community, especially in South Africa.

3.3 Research Question and Hypotheses

3.3.1 Research Questions

The sought to answer the following question:

(i) the methods traceable to the SI unit used to produce greenhouse gas mixtures comparable to other international laboratories?

3.3.2 Hypotheses

When pure starting materials containing low amount fractions of impurities, (hydrogen, argon, nitrogen, carbon dioxide, methane, carbon monoxide, nitrous oxide, sulphur hexafluoride and oxygen) is used, can the final uncertainty of less than 1 $\mu mol.mol^{-1}$ be achieved?

3.4 Novelty

The development of greenhouse gas mixtures traceable to SI unit has not been fully done in South Africa before. The goal for the developing the national greenhouse gas primary standard gas mixtures is to provide the

South African industry (health, safety and environmental) and air monitoring community with accurate and stable reference gas mixtures with the lowest uncertainty with metrological traceability to contribute to the monitoring and mitigation technology of greenhouse gas emission in the country.

3.5 Research Process

In this study, numerous greenhouse gas standard mixtures were developed and applied on the background air samples for CO_2, N_2O and CH_4 determination.

The research process includes:

(i) Selection of the desired greenhouse gas CO_2, CH_4, N_2O, and reactive gas CO as outlined in the methodology section of the papers.

(ii) Impurity check of the pure starting material guided by manufacturer's specification and literature survey.

(iii) Gravimetric preparation of the reference or primary standard gas mixture procedure by a primary method.

(iv) Verification of the amount fraction by various measurement techniques.

(v) Application of the standard gas mixtures to the real air samples by monitoring the repeatability of the peak area, averaged mean, % RSD, sensitivity or response factor, percentage difference, and drift of the instrument.

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CHAPTER IV: LIST OF PUBLICATIONS

This section outlines the PhD work in publication format. Where the publication has been accepted or published, it is indicated.

Paper I

Lushozi S, Ntsasa N, Jozela M, Leshabane N, Mogale D, Mphamo T, Lekoto G, Marebane P, Mphaphuli G, Tshilongo J and Chimuka L. Preparation and verification of primary standard gas mixtures for carbon dioxide measurement in natural air samples at background level in South Africa

Manuscript.

Lushozi, Ntsasa, Jozela, Leshabane, Mogale, Mphamo, Lekoto Marebane and Mphaphuli – 30 % (conducted the research)

Lushozi – 40 % (wrote the manuscript)

Chimuka – 15 % (supervisor, reviewed the manuscript)

Tshilongo – 15 % (co-supervisor, reviewed manuscript)

Preparation and verification of primary standard gas mixtures for carbon dioxide measurement in natural air samples at background level in South Africa

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Abstract

Carbon dioxide plays a central role in the atmosphere and climate change. Ambient carbon dioxide is monitored at the global scale and has been reported at micromole per mole (µmol.mol^{-1}) level. Developing accurate carbon dioxide standards in ambient levels is important for tracking the long-term trends and understand the chemical role of carbon dioxide in the atmosphere. Metrologically traceable primary standards prepared gravimetrically in aluminium cylinders are mostly used for calibrating analytical equipment. Therefore, an accurate and stable primary standard gas mixture at 380 µmol.mol^{-1} nominal amount fraction is required for traceable carbon dioxide ambient measurement at the background and urban areas. A mass comparator with an automated circular turntable cylinder exchanger, gas filling station, Wave-Scanned Cavity Ring-Down Spectroscopy, Non-dispersive infrared spectroscopy (NDIR) and Gas chromatography coupled with a Flame ionization detector (GC-FID) has been used during the manufacturing and verification of the gas mixtures. The primary standard gas mixtures were certified as 379.76 ± 1.00, 379.89 ± 1.00; 479.044 ± 0.80, 479.13 ± 0.80; 798.04 ± 0.51, 798.20 ± 0.51 µmol.mol^{-1} expanded uncertainty after comparison with other international standards. The standards were then used to calibrate the instrument that was used to measure the amount of CO_2

in the background air sample. The CO_2 content in the background air sample correlated with the reported values of the standards with a maximum deviation ranging from 0.90% to 0.03% obtained during the NDIR and GC-FID measurements. The WS-CRDS proved to be a more precise method than the NDIR and GC-FID have small uncertainties of less than 0.10 % relative to the measured value was obtained. The background air samples were evaluated as 299.06 ± 0.01, 419.91± 0.01, 403.02 ± 0.01 and 425.02 ± 0.02 on the WS-CRDS measurements. For this study, the preparation, verification and application of the primary standard gas mixtures for ambient and emission levels in South Africa will be explained.

Keywords: automatic weighing system, primary standard gas mixtures, gravimetric preparation, background air samples

1.Introduction

There has been an accelerating global interest in measurements of carbon dioxide amount fraction in the atmosphere because it gives additional information in the role of carbon dioxide (CO_2) plays in the natural existing carbon cycle. For example, changes in the amount fraction of atmospheric CO_2 can be used to predict anthropogenic activities such as deforestation and burning fossil of fuels have and will in the future contribute to the global climate changes, such as temperature, altered balance between terrestrial and oceanic carbon reservoirs. Recently, the contribution of the CO_2 radiative forcing has been predicted as 82% (WMO Bulletin, 2018). The impact of global climate change can pose challenges in the current and future generations (Barker et al., 2003). Since the industrial era, CO_2 amount fraction in the atmosphere has risen from 280 μmol.mol^{-1} to 400 μmol.mol^{-1} level (IPCC, 2001; Flores et al., 2017). The value of CO_2 in the atmosphere has been scrutinized using non-dispersive infrared gas analyser (NDIR), Wave scanned cavity ring -down spectroscopy (CRDS), Fourier transform infrared spectroscopy (FTIR) and a few researchers have used

gas chromatography coupled with flame ionisation detector (Brown and Keeling, 1956; Pales and Keeling, 1965; Flores et al., 2018; Crosson, 2008; Brewer, et al.,2014; Lim et al., 2017; van der Laan et al., 2009). High accurate and metrological traceable primary standards or primary standard gas mixtures in pressurized aluminium cylinders are essential for the calibration of these instruments. To understand the distribution of CO_2 emitted from various source and to coordinate terrestrial carbon cycle measurements made by different laboratories, a study was conducted. In 2016 to 2017 the international key comparison of CO_2 in scrubbed real air or synthetic air was demonstrated under the support of the Consultative Committee for the Amount of Substance (CCQM). Several laboratories participated in this study were prepared gas mixture from the participants were submitted to the International Bureau of Weights and Measures pilot laboratory for simultaneous comparison. The measurement instruments used was calibrated with CO_2 in air standard gas mixtures to confirm the amount fraction of each gas mixtures received. The compatibility of the national metrology institute (NMIs) and the National Oceanic and Atmospheric Administration (NOAA) preparative capabilities at (380-480) $\mu mol.mol^{-1}$ and (480-800) $\mu mol.mol^{-1}$ amount fraction was checked respectively (Flores et al, 2019). The results showed an excellent agreement between the different laboratories.

To support the South African air quality legislation since CO_2 is regarded a priority greenhouse gas, an ensemble of primary standard gas mixtures (PSGMs) of CO_2 in synthetic air were gravimetrically prepared and verified on the gas chromatography (GC-FID, GC-TCD) and wavelength-scanned cavity ring-down spectroscopy (WS-CRDS). After a comparison study under repeatable conditions, four cylinders per amount fraction (380, 480, 800) $\mu mol.mol^{-1}$ was carried out and the primary standard gas mixtures were certified as 380 ± 2.0 $\mu mol.\ mol^{-1}$(MC1-A), 480 ± 1.6 $\mu mol.mol^{-1}$ (MC2-B), 800 ± 1.0 $\mu mol.mol^{-1}$ (MC4-C) at 95 % confidence level. The results in the CCQM-K120 (2019) report shows that the PSGMs were certified as: 379.74 ± 2.00, (MC1-A); 479.04 ± 1.61 (MC2-B); 798.19 ±

1.03 (MC4-C) on the FTIR technique (Flores et al, 2019). These values lie within the key comparison reference value (KCRV) and were accepted (CCQM Guidance note, 2013).

Four background air samples at background level were then measured using the NDIR, WS-CRDS and GC-FID. The background air samples were evaluated as 299.06 ± 0.01, 419.91± 0.01, 403.02 ± 0.01 and 425.02 ± 0.02 on the WS-CRDS. The standard uncertainty, $u_{c,co2}$ represent the standard deviation of the data set at one sigma where k=1 coverage factor. These results show a good significant reproducibility required by the WMO and were accepted.

In this study, the development of CO_2 gas mixtures in synthetic air matrix and the quantification of background air samples is discussed.

2. Experimental

2.1 Materials

2.1.1 High purity gases

The source materials used to prepare the standard gas mixtures were high purity gases CH_4 (99.995%), CO_2 (99.995%), Built-in Purifier technology (BIP^{TM}) N_2 (99.9997%), O_2 (99,9995%) and BIP Ar (99.9999%) Air Products South Africa supplied all starting materials.

2.2 Equipment

2.2.1 Automatic weighing system with a mass comparator balance

A highly automated weighing system (AWS) used in this work consist of a mass comparator balance (Mettler Toledo XPE26003LC, Switzerland, maximum capacity 26.1 kg; minimum readability; 1 mg), single circular turntable plate, enclosed in a transparent chamber with built-in pressure (Vaisala PTB3300(500-1100)), temperature and humidity (Vaisala, HMT331) sensors and a computer readout (Yang et al, 2017). The mass comparator balance was placed on a granite top table to minimize vibrations

that might contribute to the balance drift. The single circular turntable plate is designed with four position holders (A, B, C, and D) capable of load a maximum of four identical cylinders to minimise uncertainties during long weighing cycles. It rotates to a selected position to apply weight on the mass comparator by down then up movement monitored by position sensor with the computer - controlled program.

2.2.2 Gas transfer system

The transfer of gas mixtures from high to the low pressurized cylinder was achieved using an Air and Vacuum Technologies DCU 110 filling station (with a turbomolecular vacuum pump, rotary vane for a pump, electro polish stainless steel tubing, pressure indicator, and needle valves). The sample cylinders with the regulator were placed on a top loader balance (Mettler Toledo SB12001) to connect to a 1/8 inch (3.14mm) stainless steel transfer line (Swagelok, South Africa) on the filling station. The gas transfer apparatus was designed to withstand 1,5 times its maximum operating pressure by a pressure-relief valve which is installed to discharge outside of the preparation area (ISO 6142-1, 2015). The apparatus was leak tested at this pressure using appropriate means.

2.2.3 Gas cylinders for preparation of CO_2 primary standard gas mixtures

Aluminium cylinders (Luxfer, UK) with 5 L fine polished internal volume and stainless-steel valve (Rotarex, Luxembourg) were used to evaluate the uncertainty of the system. Once received from Luxfer, the cylinders are taken to Air Product South Africa for devalving to check the internal surface of the cylinder then leak check by adding 5 - 8 MPa He (99.999% mol/mol, high pure, Air Product, SA) after valving. All cylinders were transported to Pelchem (Pty) Ltd, SA for fluorination. Prior to use, the cylinders were cleaned outside to remove any dust particles present and evacuated to 2 x 10-7 Pa using a turbomolecular pump system plus a scroll pump to remove water and other components from the internal cylinder

surface. Following the evacuation, the cylinders were pressurized with a BIP^{TM} N_2 (99.999% mol/mol, high pure, Air Product Company, SA) up to 0.1 MPa.

2.3 Methods

2.3.1 Purity Assessment

The purity assessment of the starting material was determined by the quantification of impurities such as N_2, Ar, O_2, CO_2 by gas chromatography with different detectors such as flame ionization detector with methanator (GC-meth-FID), pulse discharge helium detector (GC-PDHID), and thermal conductivity detector (GC-TCD). Undetected impurities by a method were included in the final amount fraction of the pure by dividing the manufactures specification value by 2. The amount fraction of the pure starting material was calculated by deducting the sum of impurities from 1.

2.3.2 Preparation of carbon dioxide primary standard gas mixtures.

Primary standard gas mixtures (PSGMs) were prepared following the gravimetric procedure according to ISO 6142-1 (2015) respectively. The gravimetric method comprises of adding a pre-calculated mass of pure CO_2 and N_2 (Air Product, SA) gases in a standard cylinder to obtain a CO_2/N_2 pre-mixture through weighing the aluminium cylinder before and after filling. Pure O_2, pre-mixture of Ar (20%) and BIP^{TM} N_2 were added to the gas mixture to obtain the synthetic matrix of air. After a minimum of two hours, the cylinders were weighed on a calibrated mass comparator balance and rolled to obtain optimal homogeneity (Lim et al, 2017). Usually, the tare cylinder used in the weighing procedure is not evacuated as its main purpose is to reduce the correction necessity in the weighing results of the sample cylinder (Alink and van der Veen, 2000). The limits of the gas matrix and balance gas composition of the PSGMS was taken from Consultative Committee on Quality of Material (CCQM) CCQM-K52 for CO_2 in air protocol (Wessel et al., 2008). The CO_2 cylinders were prepared

at nominal amount fraction ranging from 376.28 to 380.20, 478.09 to 480.00 and 799.09 to 799.81 µmol.mol^{-1} CO_2 in synthetic air following a three-step dilution (**Figure 1**). The final CO_2 value in the standard gas mixtures underlined in listed **Table 1** denoted as MC1-A to MC4-A, MC1-B to MC4-B and MC1-C to MC4-C. After preparation, the CO_2 content was analysed using different measurement techniques for validation purpose. The amount fraction of the final PSGM was defined by the following model equation:

$$x_l = \frac{\sum_{Q}^{R}=1 \left(\frac{x_{l,B} . m_B}{\sum_{l}^{n}=1 x_{l,B} \cdot M_l} \right)}{\sum_{Q}^{R}=1 \left(\frac{m_B}{\sum_{l}^{n}=1 x_{l,B} \cdot M_l} \right)} \quad (3)$$

where x_l is the amount fraction of the gas constituent l in the final mixture, R is the total number of parent gases, n is the total number of gas constituent in the final mixture, m_B is the measured weight of the parent gas B determined by weighing, M_l is the molar mass of gas constituent l, $x_{l,B}$ is the amount fraction of gas constituent l in the parent gas B.

The combined uncertainty, $u_{preparaetion}$ of the final primary standard gas mixture will include the uncertainty sources from the 1) weight of each component, 2). the purity of pure materials, 3). the relative molar masses of the components, and 4). buoyancy. Because an automatic weighing system with a single pan and a cylinder exchanger capable of holding four, buoyancy is neglected as an uncertainty. The $u_{preparation}$ is calculated by multiplying the preparation amount fraction, $x_{CO2,prep}$, with the square root of the sum of squares for all the preparation constituents:

$$u_{preparaetion} = x_{CO2,prep} * \sqrt{1^2 + 2^2 + 3^2 + 4^2} \quad (4)$$

Table 1. Amount fraction of PSGMs prepared by the gravimetric method.

	Cylinder number	Cylinder symbol	Gravimetric amount fraction			
			CO_2 ($\mu mol.mol^{-1}$)	N_2 (%)	O_2 (%)	Ar ($\mu mol.mol^{-1}$)
Set 1	**M518232**	**MC1-A**	380,20 (0.06%)*	78.07	20.96	9380.16
	M518084	**MC2-A**	385,42 (0.10%)	78.08	20.96	9126.40
	M518071	**MC3-A**	379,39 (0.04%)	78.10	20.94	9136.16
	M518166	**MC4-A**	376,29 (0.07%)	78.31	20.72	9323.73
Set 2	**M518171**	**MC1-B**	478.09 (0.06%)	78.06	20.95	9441.45
	M518167	**MC2-B**	479.46 (0.06%)	78.09	20.96	8978.03
	M518262	**MC3-B**	479.43 (0.04%)	78.07	20.93	9518.72
	M519531	**MC4-B**	480.00 (0.04%)	78.09	20.95	9185.76
Set 3	**M519511**	**MC1-C**	799.42 (0.03%)	77.98	20.99	9506.52
	M518075	**MC2-C**	799.81(0.06%)	77.82	21.00	9400.86
	M518195	**MC3-C**	799.36 (0.03%)	77.98	21.01	9267.37
	M518244	**MC4-C**	799.09 (0.03%)	77.93	21.06	9285.76

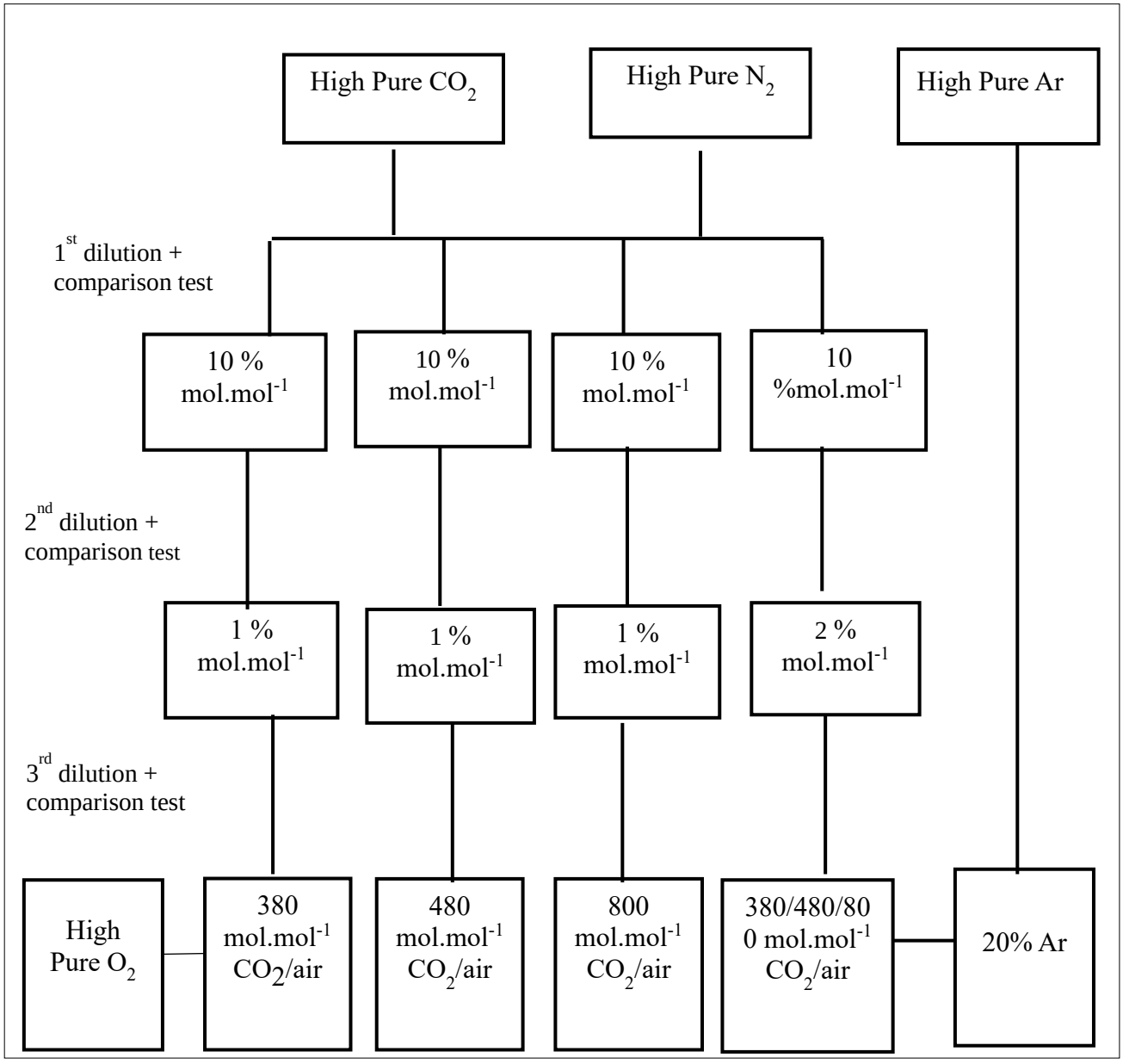


Figure 1. Production illustration of the carbon dioxide in synthetic air.

2.3.3. Collection of background air samples

The background air sample at the background level was collected from the South African Weather Service (SAWS) Cape Point station operated as one of the WMO/ Global Atmosphere Watch monitoring baseline sites. The SAWS station is in the southern tip of the Cape Peninsula within the Cape Point National Park, South Africa (latitude:34º21'N, longitude: 18º29'E,

and elevation:230m). Its location is surrounded by pristine environment free from the influence of urban pollution sources. Background air or modified background air samples was verified against NOAA reference standards scales prepared by the manometric system. Four clean and evacuated aluminium cylinders (Luxfer, England) with 10 L internal volume were used as sample holders. The samples were collected in June 2018 at a pressure of ±10 MPa. The air was drawn from the atmosphere through a sampling tube connected to a 30-meter sampling tower directed in the laboratory. An oil-free type air compressor (SA–3E series, RIX Industries) was used to draw the air sample. During sampling, moisture content was removed by using magnesium perchlorate (Mg $(ClO_4)_2$; Sigma – Aldrich Co. LLC., USA) and analysed using various techniques. The sampled air was conditioned and dried to meet the high-quality precision set by the WMO/GAW organization (GAW Report No 186). Trends and seasonal variations of greenhouses gas composition such as CO, CO_2, N_2O and CH_4, are continuously monitored using analytical instruments such as the gas chromatography with electron capture detector (GC-μECD) and flame ionisation detector (GC-FID) and, Non-dispersive infrared spectroscopy (NDIR) and Wavelength-scanned cavity ring-down spectroscopy (WS-CRDS) (Brunke et al.,1990, Rhoderick et al., 2012). After the analysis, all pressurized cylinders were returned to NMISA for verification and certification with the gravimetrically prepared CO_2 primary standard gas mixtures.

2.3.4 Wavelength-scanned cavity ring-down spectroscopy sample measurement

A WS-CRDS analyser (model G2401 Picarro, Santa Clara, California, USA) was used to verify the CO_2 amount fraction in the standards and background air samples. The analyser simultaneously measured carbon dioxide, carbon monoxide, methane, and water vapour but for this study, the focus was on the CO_2 values. The WS-CRDS analyser was calibrated

with MC1-A cylinder at an assigned value of 379.89 μmol.mol^{-1} in synthetic air. Gas molecules were introduced into the modified analyser at a constant flow rate regulated with a mass flow controller (MFC) (M17203188F Bronkhorst, Holland) calibrated by the manufacturer against N_2 at 1000ml.min^{-1}. A 1/8 inch' stainless steel line connected to the pressure reducer of the nitrogen gas with a built-in purifier, PSGM /air sample cylinder and MFC through a 3-way valve was purged with nitrogen gas with a built-in purifier set at a 200mL min^{-1} optimum flow rate. After every 30 minutes, the PSGM and/or background air sample was introduced in the cavity through a 1/16 inch' stainless steel line connected from the exhaust of the MFC to the analyser. A coiled bypass outline was connected to keep a steady flow and a constant pressure of the gas (Lim et.al., 2017). After analysis, the measurement results were collected, and the analyser response value was stable within 15min. For good measurement repeatability, the regulator connected to the cylinder and sample line was purged for approximately 30min before introductory of gas samples.

2.3.5 Non-dispersive infrared analyser sample measurements

Gas molecules from reference and sample cylinder flow through conditioned pressure reducer to a 16-port streamer selection valve via 1/8" O.D plastic tubing (**Figure 3**). The absorbance of CO_2 is measured by the NDIR analyser is related to the partial pressure in the sample cell (Ling Jun et.al, 2016). The gas molecule is fed through an MFC set at 200 mL/min leading to the analyser. Background air (unknown) is compared to a set of five primary standard gas mixture spanning the amount fraction range of the unknown. A 180 second purge period for each cylinder in a 90-second data acquisition period was set. The gas mixtures were introduced in random order of CO_2 amount fraction. The generated raw digital measurement value corresponds to the difference in amount fraction between the standard or sample gas and reference gas stored in two independent cells. Amplified signal and the differential voltage are processed, recorded by the acquisition system as data then transported to the computer.

The value of the sample was predicted using the generalized least squares regression analysis where the preparation and analytical uncertainties in the x and y-axis were considered (Lee et al, 2006).

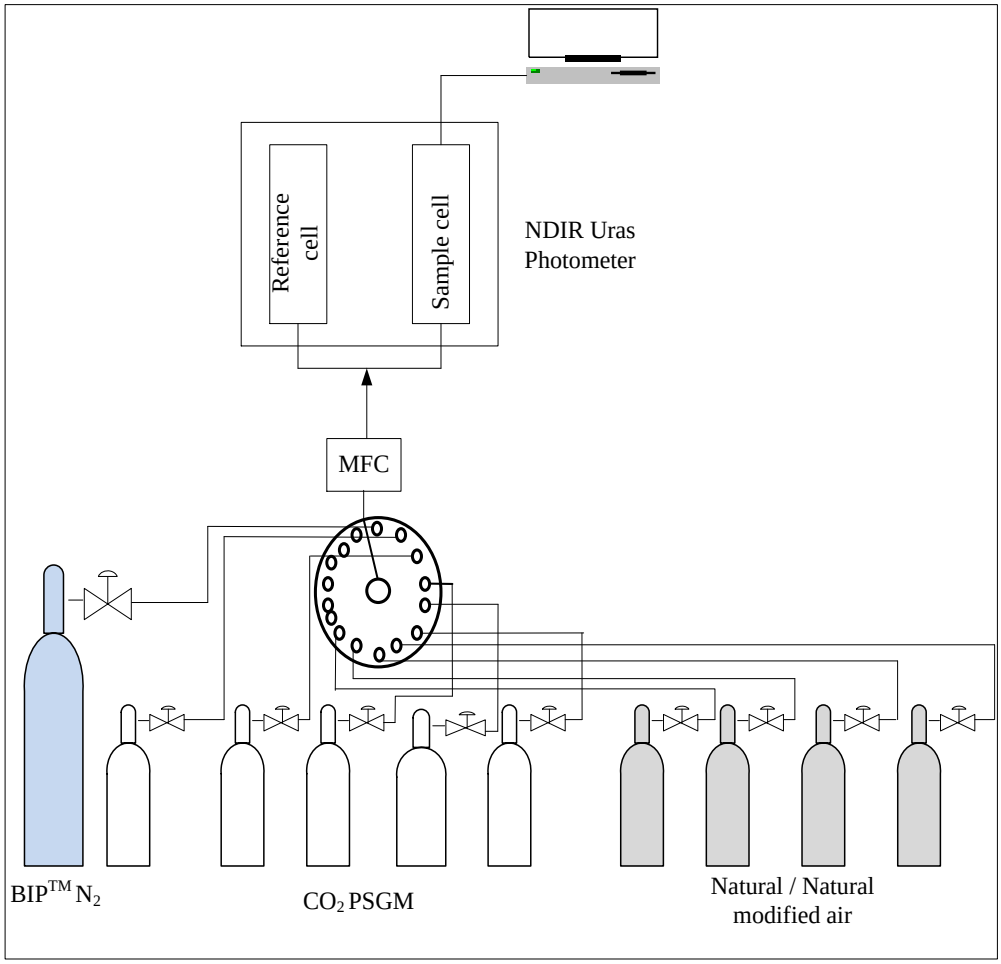


Figure 3. Schematic diagram of the analysis of CO_2 by NDIR spectrometer. (Lee et al, 2006).

2.3.6 Verification of the standard gas mixtures by gas chromatography technique

Twelve cylinders at 380, 480 and 800 µmol.mol^{-1} nominal values were divided into three sets and verified by comparison under repeated conditions. The content of CO_2 in the gas cylinder was determined using Agilent 7890 B Refinery Gas Analyser (RGA) with GC-TCD, GC-meth-FID and the WS-CRDS analysers. The sample line and the regulator of each

cylinder were purged several times before the analysis. During the analysis, one of the standard gas mixtures among the four samples in a set was chosen as a reference cylinder to measure the instrumental drift and determine the measurement ratio. The primary standards were analysed for several days following a sequence Reference – Sample – Reference method. **Table 2, 3 and 4** shows the conditions used to verify CO_2 in synthetic air amount fraction using GC-meth-FID, GC-TCD, and WS-CRDS. After verification one cylinder from each set was shipped to the central calibration laboratory, BIPM with 14 MPA (MC1-A), 12 MPA (MC2-B) and 10 MPA (MC4-C) pressure certified with the final values of 380, 480 and 800 µmol.mol $^{-1}$ respectively.

Table 2: Analytical conditions for GC-methanathor-FID

Analytical Parameters	***Conditions***
Column oven temperature	100 °C
Column	ShinCarbon, 2m, 80/100, Restek
Carrier gas flow (N_2)	84 mℓ/min
Detector temperature	300 °C, H_2 -55 mℓ/min, Air-400 mℓ/min
Methaniser temperature	375 °C
Sample flow	35 mℓ/min
Sample loop	1 mℓ

Table 3: Analytical conditions for GC-TCD

Analytical Parameters	*Conditions*
Column oven temperature	65 °C
Column	ShinCarbon, 1m, 80/100, Restek
Column flow	6 mℓ/min
Column pressure	133 kPa
Carrier gas flow (H_2)	5 mℓ/min
Detector temperature	250 °C
Sample flow	30 mℓ/min
Sample loop	1 mℓ - 480 µmol.mol^{-1} and 500 µL for 800 µmol.mol^{-1}

Table 4: Optimum parameters for WS-CRDS

Parameter	*Setting*
Sample flow	450 mL.min^{-1}
Warm Box temperature	45 °C
Cavity temperature	45 °C ± 0.005
Cavity pressure	140 ± 0.02Torr

3. Results and discussion

3.1 Purity assessment

Table 5 projects the obtained amount of impurities in the pure starting materials with its associated uncertainties. The aim of purity assessment was to check the number of impurities such as CO_2, N_2, O_2, and Ar present in each pure gas since it might have an impact on the uncertainty associated with the final amount fraction of the standard. The impurities content was verified using various techniques and the measurement results obtained are tabulated below. The amount of CO_2 impurity was determined as 0,011, 0.11 and 0.010 µmol.mol^{-1} in N_2, O_2 and Ar starting material. Nitrogen impurity in carbon dioxide was quantified as 823.4 µmol.mol^{-1} which is the largest impurity respectively. Newly born research by Lim et al, 2017 reported fewer values (0.002, 0.195, and <0.002 µmol mol) of CO_2impurity

in pure N_2, O_2, and Ar. Their nitrogen impurity was reported as 12.8 $\mu mol.mol^{-1}$ and was the highest value obtained.

All the determined values in the analysis procedure were combined in the reported gravimetric amount fraction of the standards.

Table 5. Purity table of highly pure gases with the amount fraction of the impurities with its associated uncertainties.

Impurity	***Highly pure gases (μmol.mol^{-1}) k=2***				
	CO_2	**O_2**	**Ar**	**N_2**	**Technique used**
CO_2	-	0.11 ±0.032	0.0098 ± 0.011	0.011 ± 0.013	GC-FID
N_2	823.4 ± 82.30	2.00 ± 2.31	0.0070 ± 0.0020	-	GC-PDHID
Ar	0.22 ± 0.02	2.50 ± 2.89	-	54.99 ± 5.50	GC-PDHID
CH_4	4.27 ± 1.28	0.006 ± 0.007	0.0058 ± 0.0070	0.0047 ± 0.0050	GC-FID
H_2O	0.026 ± 0.03	0.001 ± 0.001	0.010 ± 0.012	0.010 ± 0.012	*
H_2	0.040 ± 0.004	-		0.0090 ± 0.00090	*
CO	0.022 ± 0.026	0.26 ± 0.078	0.021 ± 0.024	0.00674 ± 0.0080	GC-FID
C_2H_6	0.006 ± 0.007	0.006 ± 0.007	0.0061 ± 0.0070	0.0071 ± 0.0080	GC-FID
O_2			0.0050 ± 0.0060	0.0012 ± 0.0010	*
Purity % mol.mol^{-1}	**999218 ± 80**	**999995 ±4.0**	**999999 ± 0.0324**	**999944 ±5.0**	

*The abstract refers to the manufacturer's specification.

3.2 Calibration of the primary standard gas mixtures

Gas mixtures in set 1, 2, and 3 were verified by comparing the detection sensitivity of carbon dioxide. In checking the gravimetric procedure explained, MC2-A, MC3-B, and MC2-C were selected as reference cylinders to verify CO_2 amount fraction prepared in the cylinders while the remaining cylinders were used as samples. A single point calibration method was used where the chosen reference (R) bracketed the sample cylinder (S) under repeated conditions listed in **Table.2 and 3**. Standard gas mixtures in set 1 and 2 were verified in both GC-FID and GC-TCD analyser whilst set 3 was verified by GC-TCD. Deviations of CO_2 value determined by GC-FID and GC-TCD and values from gravimetric value were obtained as less than 0.01%, 0.02 % and 0.06 % for set 1 to 3 which is less than $2\sqrt{u_{CO2\,prep}{}^2 + u_{assigned}{}^2}$. This comparison shows that there is no bias found in the preparation procedure used and CO_2 in synthetic air was internally consistent within the cylinder walls. An instrumental drift of less than 0.3 % was calculated several times and prove that the selected methods worked accordingly. A good precision was obtained and a drift between the cylinders was comparable to their repeatability uncertainty. The WS-CRDS results confirmed the assigned values obtained during chromatography measurements for set 1 and 2 (**Table 6**). The gas mixtures were verified for 30min and only the average response in the last 15 min was considered. The standard uncertainty was considered as the standard deviation of the average analyser response. Cylinder MC1-A, MC2-B, and MC4-C were shipped to participate in the international key comparison study.

After verification of several cylinders from international laboratories on the FTIR and GC – FID at the BIPM laboratory, the CO_2 amount fraction in our cylinders was reported as (379.74 ± 2.00, 379.87 ± 1.00) µmol.mol^{-1}; (479.04 ± 1.61, 479.14 ± 1.61) µmol.mol^{-1}; (798.19 ± 1.03, 798.20 ± 1.02) µmol.mol^{-1} respectively. **Figure 4a-c** shows the graphs taken from the CCQM-K120 (2019) report where a comparison between the degree of equivalence (y-axis) to the reference value of the participants (x-axis) is shown. A deviated of (0.46, 0.33; 0.46, 0.36; and 0.91, 0.91) µmol.mol^{-1}

was reported after measuring the CO_2 cylinders on the FTIR and GC-FID techniques at BIPM laboratory. These differences are accepted as the amount fraction of the mixtures were within 10 µmol.mol^{-1} as per protocol request (Flores et al, 2019).

After the key comparison study, the cylinders were returned to the gas analysis laboratory for reanalysis and stability check. The final values of the gas mixtures were reported as 380 µmol.mol^{-1} ± 2.00, 480 µmol.mol^{-1} ± 1.60 and 800 µmol.mol^{-1} ± 1.00 relative expanded uncertainty. The combined uncertainty was calculated as:

$$u(combined) = \sqrt{u^2_{(prep)} + u^2_{(analy)} + u^2_{(stab)}} \quad (5)$$

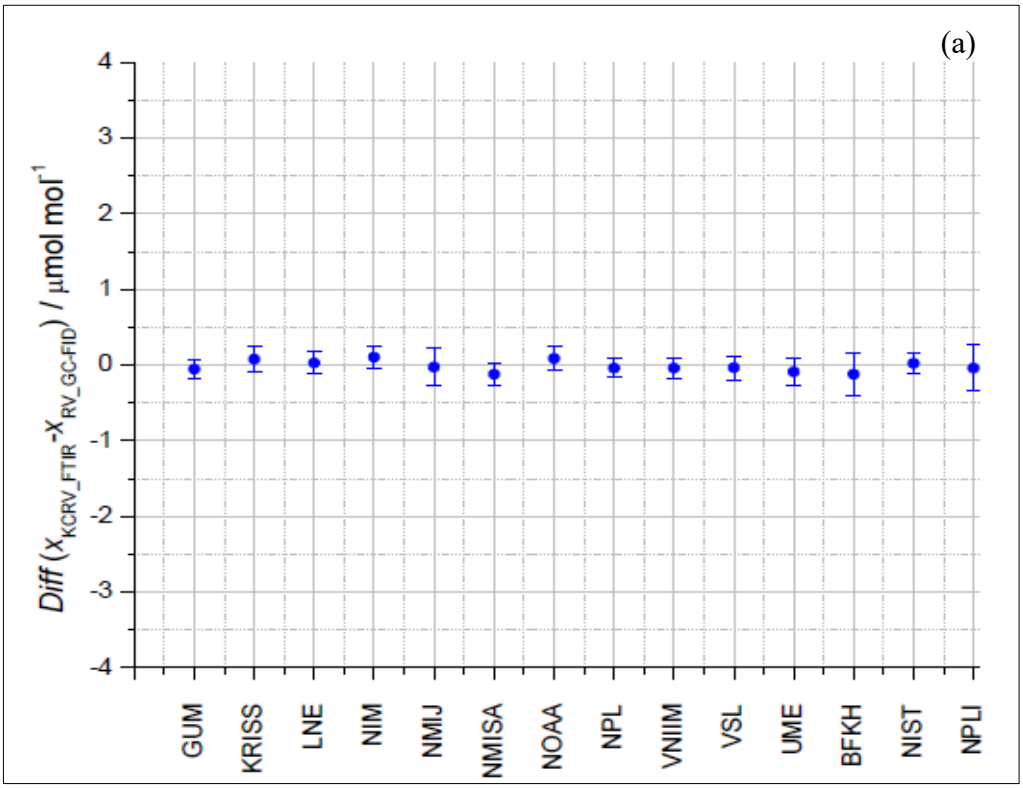
(where $u^2_{(prep)}$, is the uncertainty from the gravimetric value, $u^2_{(analy)}$, is the uncertainty from the analytical value and $u^2_{(stab)}$, represent the uncertainty from the time the cylinder was verified before and after shipment.

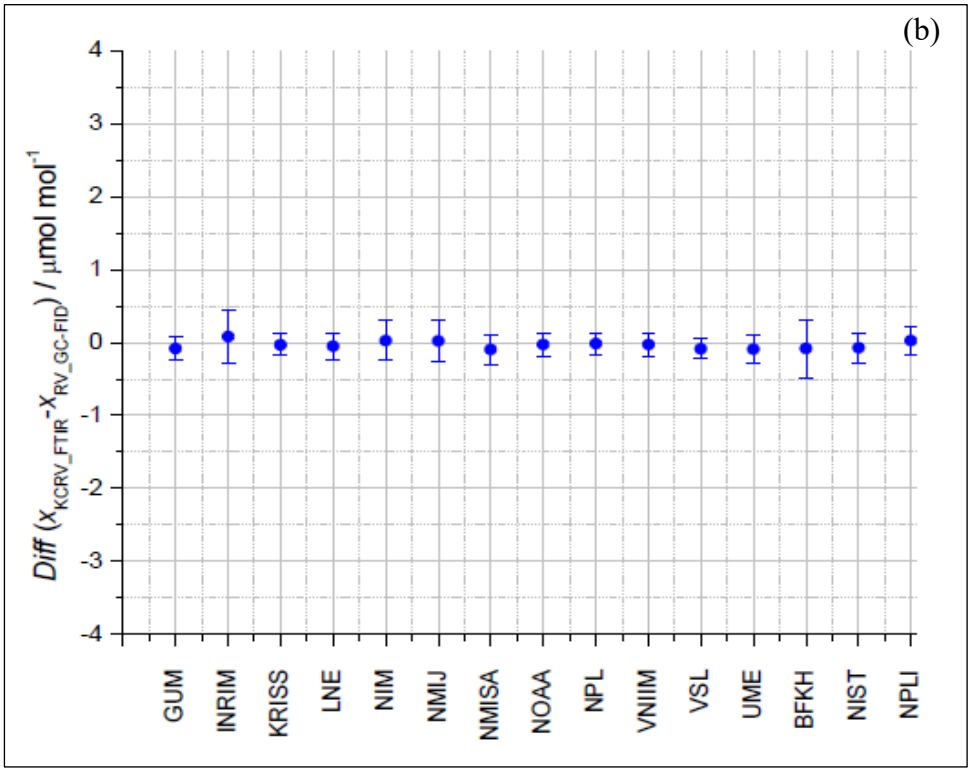
The previous study, CCQM-K52 of CO_2 at 360 µmol.mol^{-1} in synthetic air (N_2 and O_2), NMISA gas laboratory received a cylinder from the pilot laboratory where the amount of CO_2 was calculated as 364.9 ± 3.883 µmol.mol^{-1} (2δ).The expanded uncertainty value has decreased from 3.88 µmol.mol^{-1} to 2.00 µmol.mol^{-1}in the similar amount fraction range. Based on the results, NMISA uncertainties have improved since 2006 till 2017.

The conclusion drawn from the previous study was that this value together with values reported by the other NMIs was found to within 0.3 % relative to the reference value.

Table 6. Measurement results of CO_2 PSGMs.

PSGM number	*GC Results*	*WS-CRDS Results*
MC1-A	380.30 (0.69)	380.21 (0.0032)
MC2-A	385.34 (1.00)	385.40 (0.0079)
MC3-A	379.28 (1.04)	379.56(0.0044)
MC4-A	376.38 (1.14)	376.64 (0.0067)
MC1-B	478.13 (0.14)	478.12 (0.0076)
MC2-B	479.47 (0.10)	479.37 (0.0069)
MC3-B	479.35 (0.14)	479.66 (0.0079)
MC4-B	479.36 (0.32)	479.95 (0.0088)
MC1-C	799.58 (0.35)	
MC2-C	799.40 (0.72)	
MC3-C	799.81 (0.17)	
MC4-C	799.72 (0.13)	





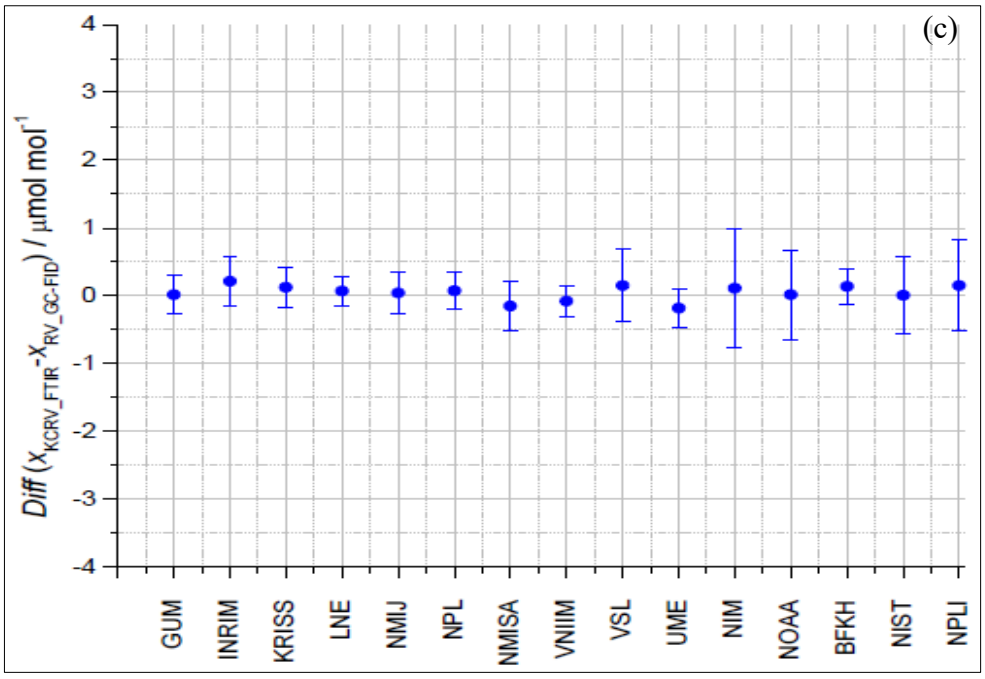


Figure 4 a-c. The difference (blue dot) between the two reference values obtained from the FTIR and GC techniques for (a) 380 µmol.mol^{-1}, (b) 480 µmol.mol^{-1} and (c) 800 µmol.mol^{-1} CO_2 nominal value. The error bars represent the expanded uncertainty at 95% confidence level (Flores et al, 2019).

3.2 Calibration of the background air sample by various techniques

After collection of four background air samples from the SAWS Cape Point station, the amount fraction of CO_2 in the cylinders was verified on the WS-CRDS analyser prior to shipment to our laboratory. **Table 7** shows the reported amount of CO_2 in the background air samples at background level. After shipment of the cylinders to our laboratory, the amount of carbon dioxide in the air samples was verified in different days using three different techniques.

From adopting the assigned values of carbon dioxide from BIPM, the standards were used to draw the NDIR calibrated curve as shown in **Figure 5**. Five consistent standards ranging from 379.89 to 798.20 µmol.mol^{-1} were sampled and the average of the four measurements in a single run was used to calculate the uncertainty of the measured value. The analyser was purged with BIP^{TM} N_2 before measurement of a cylinder to prevent sample carrier over. The amount of carbon dioxide in the verified background air samples, y_{CO2}, were predicted from the obtained calibration curve as listed in Table 8. Although sample NT-1 was not fitted into the calibration curve because its value lied outside the PSGM range, its value was calculated as 301.64 ± 0.10 µmol.mol^{-1}. A good correlation coefficient r^2 = 0.99999 was obtained indicating a good linear curve as the PSGMs used corresponds to the generalized least squares regression analysis in the second order polynomial. This shows that the standards used were internally consistent in the cylinder walls as the deviation of the data from the calibration curve is very small and unbiased (Lee et al, 2006). A goodness-of-fit less than 2 was obtained which correlate with what the requirements of ISO 6143 (2001) standard. Recent researcher, Rolle et al, 2017 obtained similar values of CO_2 after verification of gas mixtures in synthetic air by NDIR.

During the analysis on the calibrated WS-CRDS, the amount of CO_2 in the background air samples was verified as listed in **Table 9**. The uncertainty of the measurement values was taken from the standard deviation of the mean. The standard uncertainty of 0.005 % obtained corresponds to the WMO data objectives or precision set for the southern hemisphere. The analytical

value of CO_2 obtained by this technique was accepted as the deviation between the reported and the measured value differed by 0.10 % (Table 10). Small uncertainties were obtained when the WS-CRDS was used. The obtained results correspond with de Lima Fioravante et al, (2018) who also reported small measurement uncertainties of CO_2 when he compared his results with other measurement techniques.

During the verification of the background air samples on the GC-FID with a methanathor, the amount of CO_2 and uncertainty were computed by the GUM software as 298.92 ± 0.32, 420.90 ± 1.55, 402.92 ± 0.35 and 424.82 ± 0.29 (1σ). The new value of MC1-A, 379.74 µmol.mol^{-1} was employed as a reference cylinder in three measurement cycles (**Figure 8 and 9**). The CO_2 peak area of the reference cylinder (MC1-A)was compared with a CO_2 peak area of the background air sample (**Figure 9**). **Figure 9** shows a chromatogram obtained for the background air sample which represents the first measurement cycle. In the last column of **Table 10**, the difference between the analytical value from the reported value is shown when the background air samples were bracketed with the reference cylinder. Though large analytical uncertainties were obtained during the measurements, the GC-FID yield smaller deviations between the amount fractions. The data shows that the effect of a large amount of O_2 in the synthetic air standard and background air sample did not have an impact on the detector during this measurement even though it automatically switched off then on again.

In 2008 Rhoderick argued that the presences of oxygen in synthetic air standards influenced the FID detector. He further explains how the O_2 gas molecule could bleed off the column then impacting on the intensity of the FID. It was not the case for this experiment. The elution order of a shincarbon column is CO, CH_4 and CO_2 (Ueta, 2014). In this study, a large CO_2 peak and trace CO and CH_4 peaks were observed. Though the flame switched off and on again during the injection the elution of the main peak was not interrupted. (**Figure 9**). **Figure 9** shows the consecutive injections of CO_2 for the air sample. The method was then optimized and only when the baseline was stable, the CO_2 peak eluted from the column at the same

retention time over repeated measurements. Although the relative standard uncertainty related to the background air was evaluated as 0.011 %, the amount fractions agreed with the reported value at less than 0.049 %. In **Figure 6**, a comparison between the reported and the assigned amount fraction using three-technique is illustrated.

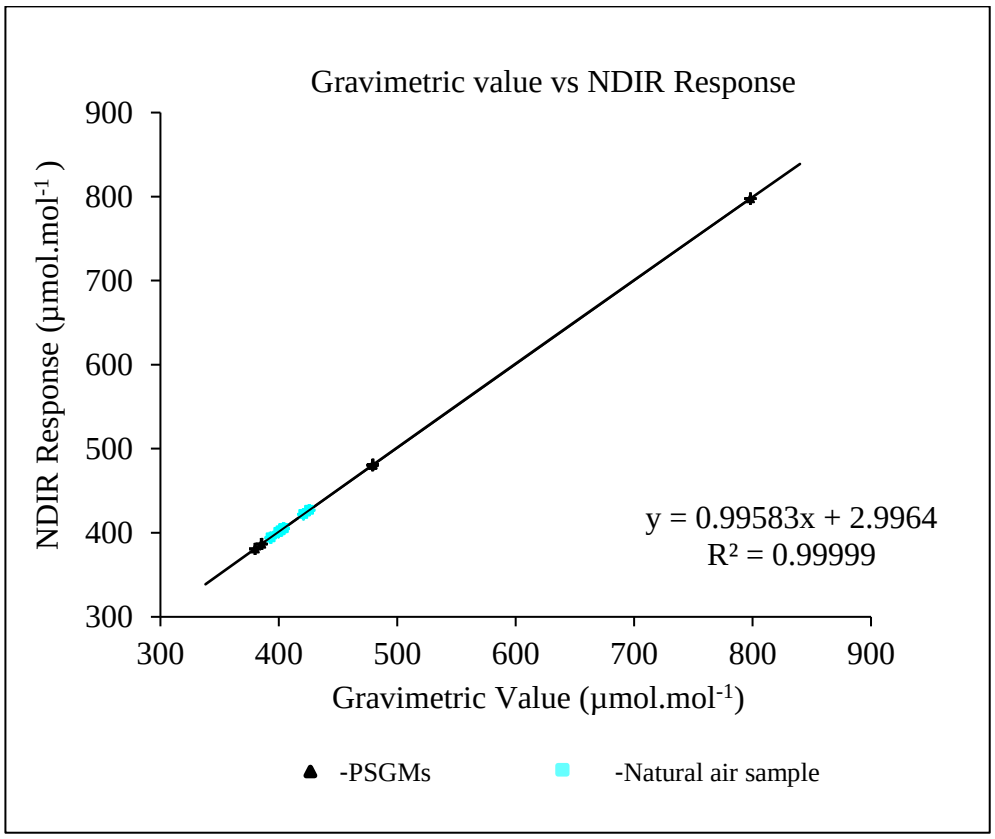


Figure 5. Calibration line of showing a plot of background air samples. The error bar is associated with the gravimetric, $u_{x(preparation)}$, and the assigned, $u_{x(anal)}$ values.

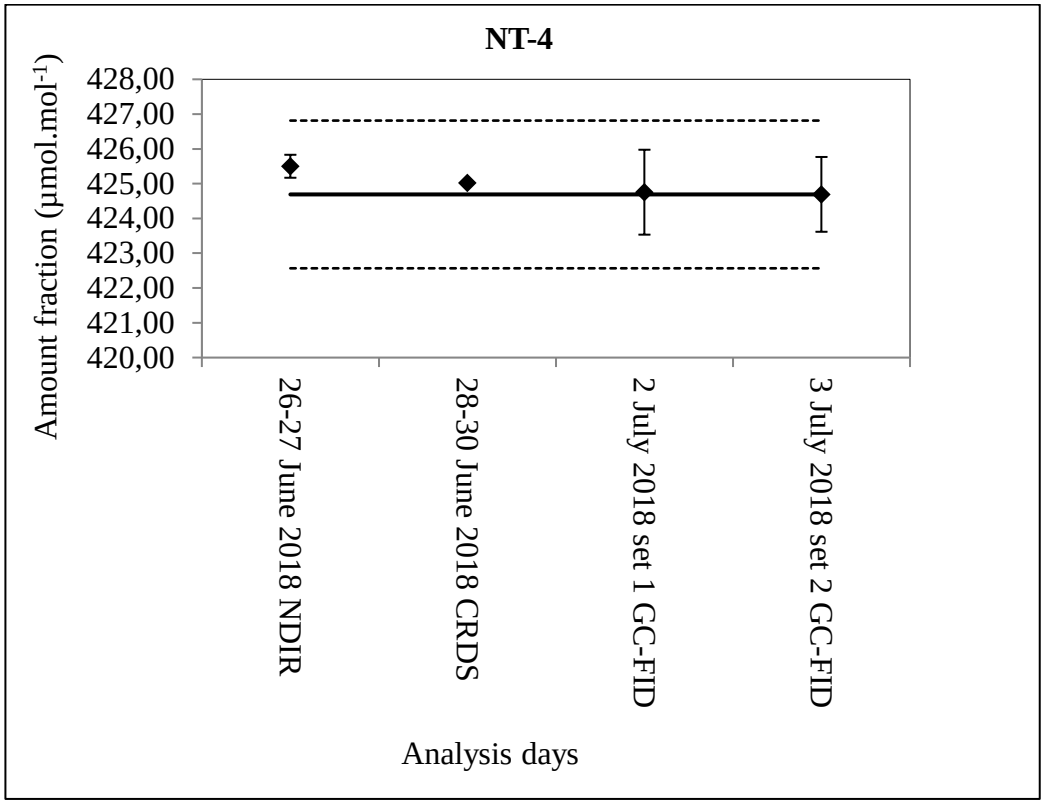


Figure 6. A comparison of background air CO_2 analysis data from the reported data. Three different techniques verified the gas mixture. The solid line represents the true value and the dotted lines represents the upper and lower limits.

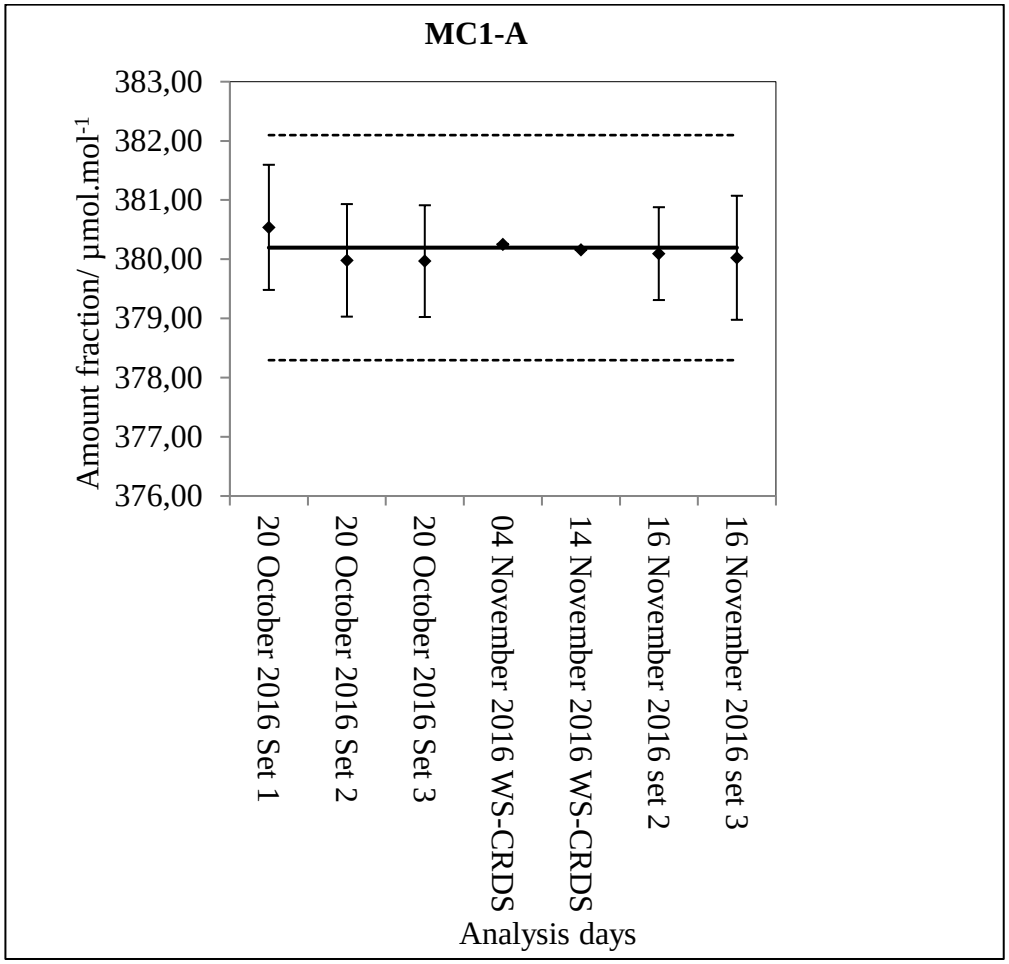


Figure 7: Short-term stability of cylinder MC1-A cylinder verified on GC-TCD, WS-CRDS and GC-FID prior shipment to a calibration laboratory. The solid line represents the true value and the dotted lines represents the upper and lower limits.

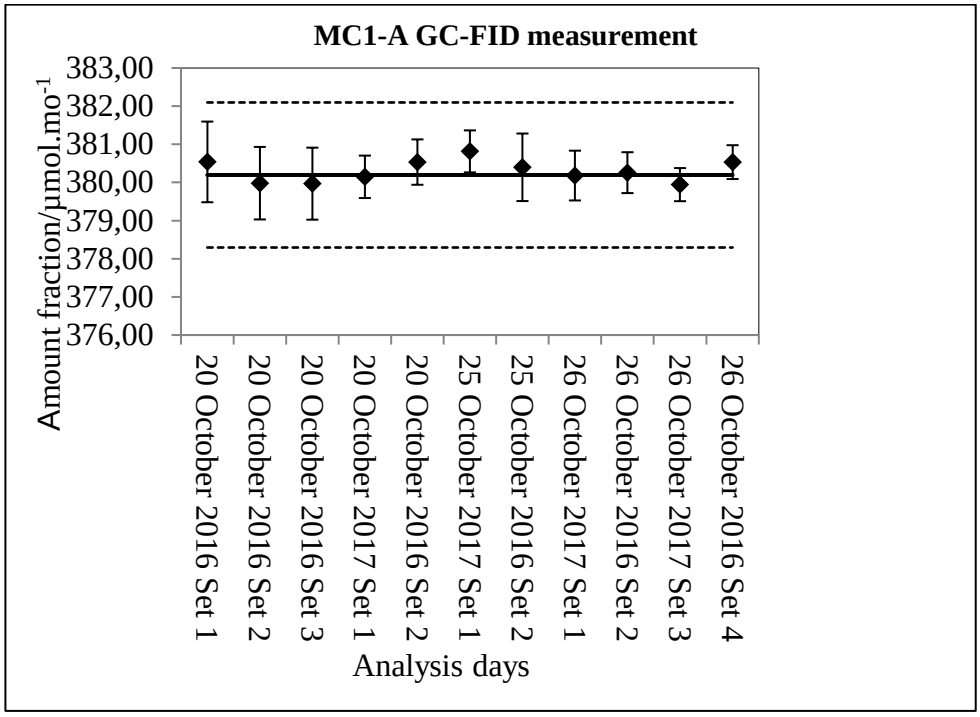


Figure 8: Long-term stability of MC1-A cylinder after 1 year of preparation verified with the GC-FID. The cylinder was verified before shipment and after the international study. The solid line represents the true value and the dotted lines represents the upper and lower limits.

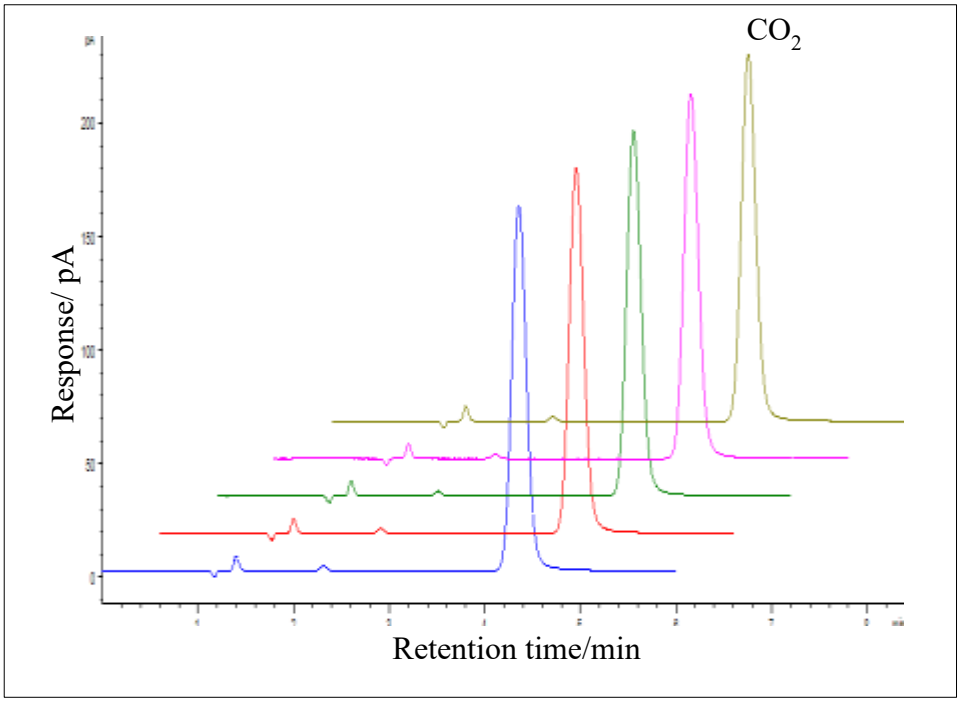


Figure 9: GC-FID chromatogram for background air sample

Table 7. Reported results of background air samples.

CO_2 WS-CRDS Reported values µmol.mol^{-1}			
NT-1	NT-2	NT-3	NT-4
299.02 (0.04)*	419.62 (0.04)	402.77 (0.04)	424.69 (0.04)

*The values in the parenthesis represents the uncertainties estimated at 68% confidence level.

Table 8: Amount fraction of background air samples from NDIR analyser.

NDIR VALUES $x_{CO2}, NDIR$ *(µmol.mol^{-1})*				
Runs	**NT-1**	**NT-2**	**NT-3**	**NT-4**
1	301.82 (0.11)*	420.59 (0.21)	403.74 (0.25)	425.51 (0.30)
2	301.29 (0.10)	420.52 (0.17)	404.18 (0.22)	425.33 (0.41)
3	301.80 (0.089)	420.77 (0.20)	403.81 (0.21)	425.67 (0.28)
Average	301.64 (0.10)	420.40 (0.19)	403.91 (0.23)	425.50 (0.33)

*The values in the parenthesis represents the uncertainties estimated at 68% confidence level.

Table 9: WS-CRDS results of background air samples

Runs	***WS-CRDS Response*** $x_{CO2}, WS-CRDS$ ***(µmol.mol^{-1})***							
	Value	u_{CO2}	**Value**	u_{CO2}	**Value**	u_{CO2}	**Value**	u_{CO2}
	NT-1		**NT-2**		**NY-3**		**NT-4**	
1	299.05	0.020	419.90	0.030	403.00	0.020	425.00	0.02
2	299.06	0.010	419.92	0.010	403.02	0.010	425.03	0.010
3	299.07	0.010	419.92	0.020	403.03	0.020	425.04	0.010
Average	**299.06**	**0.010**	**419.91**	**0.010**	**403.02**	**0.010**	**425.02**	**0.02**

* The standard uncertainty related to the standards deviation of the average mean.

Table 10: Deviation between the CO_2 values obtained by different methods.

Sample	WS-CRDS and NDIR	WS-CRDS and SAWS-Cape Point station WS-CRDS	NDIR and SAWS-Cape Point station WS-CRDS	GC-meth-FID and SAWS-Cape Point station
NT-1	-0.88	0.010	0.88	0.034
NT-2	-0.12	-0.070	0.11	0.047
NT-3	-0.22	0.060	0.28	0.037
NT-4	-0.11	0.060	0.19	0.0078

4. Conclusion

The carbon dioxide value for cylinder MC1-A, MC2-B, and MC3-C calculated from the three measurement techniques agree with each other with the obtained uncertainties. A 1 µmol.mol^{-1} difference between NMISA gravimetric value and the BIPM assigned was obtained. This means necessary improvements are needed in the purity assessment of pure starting materials.

The amount fraction of carbon dioxide in the background atmosphere samples was verified with four background air sample cylinders collected from the SAWS Cape Point Station in 2018. NDIR, WS-CRDS, GC-FID

and gravimetrically prepared standard gas mixture in synthetic air were used during the measurement. Though the CO_2 isotopic ratio variation between the cylinders in background air and synthetic air were not studied at NMISA, the deviations between NMISA and the reference value were can be estimated as less than 1%. The amount fraction of CO_2 in the background air samples was evaluated as (299.06 ± 0.010, 419.91± 0.01, 403.02 ± 0.010 and 425.02 ± 0.020) µmol.mol^{-1} by WS-CRDS. The combined uncertainty was set at 68 % confidence level where k=1. These values meet the precision of 0.025 µmol.mol^{-1} (1δ) set by the WMO and are therefore accepted. The developed gas mixtures can be used to support various regional air monitoring companies and laboratories.

5. Recommendations

We recommend that the study of δ^{13} C and δ^{18} O isotope ratio in the different air cylinder be conducted in the future as the variation in these values could cause bias in spectroscopic techniques.

6. Acknowledgements

This work was supported by the National Metrology Institute of South Africa under the NMISA cross-cutting project clean air under green economy for measurement technology. The National Research Foundation of South Africa for their grant provision during the Ph.D. studies. The SAWS Cape Point Station staff for the sampling of the background air samples.

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Paper II

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Chimuka – 25 % (supervisor, reviewed the manuscript)

Tshilongo – 25 % (co-supervisor, reviewed the manuscript)

Validation of Methane gas mixture in nitrogen balance by gas chromatography with flame ionization detector

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Abstract

The development of highly accurate and precise methane primary standard gas mixtures in nitrogen and artificial air has been achieved with the aim of supporting air quality monitoring community for accurate background measurement results. Four CH_4 in N_2 and CH_4 in Air gas mixtures were gravimetrically prepared in 5 L high-pressure aluminium cylinders in accordance with ISO 6142-1(2015) method. The standard uncertainty was less than 1.5%. High pure CH_4 was analysed to determine the purity of the starting material. Gas Chromatography with a flame ionization detector (GC-FID) was used to analyse the content of methane in the PSGMs. GUM version 2.3 Software program was used to determine the amount fraction and uncertainties of CH_4 in the gas mixtures.

In this paper, CH_4 in nitrogen with the concentration level of 2.00 $\mu mol.mol^{-1}$ was prepared by a primary method and the standard uncertainty obtained was less than 0.35 %. By using gas chromatography coupled to FID/methanator the standard deviation of the peak area was less than 0.4 % through the optimization of gas chromatographic conditions. After preparation and verification, the gas mixtures were certified at 2.00 ± 0.021 $\mu mol.mol^{-1}$ standard uncertainty.

Keywords: preparation; CH_4, high accuracy, uncertainty, GC-FID.

1.Introduction

South Africa (SA) is one of the global industrialized countries in the African continent that contributes to the global increase of greenhouse gas emissions, hence has committed to reduce and restrict anthropogenic emissions of such atmospheric pollutants (Ziervogel, et al 2014; Seymore et al, 2014; The Department of Trade and Industry 2014). Since the advent of the Industrial Revolution and an explosion of human growth, a huge amount of greenhouse gases being emitted into the atmosphere, contributing to an ever-accelerating greenhouse effect, which in turn causes global warming and climate change which should be monitored (Short et al, 2017).

Methane has the second largest radiative effect and since it's a reactive trace gas, when its amount fraction increases, it causes a rise in the amount fraction of both ozone and water vapour in the atmosphere (Van Amstel, 2012). It contributes to 18.1 % radiative forcing and had the abundance of 0.700 µmol.mol-1 in the year 1750 (pre-industrial level) to 1.803 µmol.mol^{-1} in 2009 (Velychko and Gordiyenko, 2011). One of the anthropogenic sources for CH_4 is the combustion of fossil fuel (Ganesan et al., 2013). To mitigate anthropogenic emissions of such greenhouse gas, it is necessary to measure and monitor CH_4 emissions using calibrated instruments with highly accurate and precise methane standard traceable to the SI, the kg. In order to measure CH_4 and other greenhouse gases in the atmosphere precisely, long term methane observations in SA and other chemical composition of the Earth's atmosphere are measured and monitored by the South African Weather Service under the World Meteorological Organization Global Atmospheric Watch Cape Point station at background level (GAW Report No. 186). Many industries, on the field and laboratories, now make routine measurements of CH_4 and other greenhouse gas emissions to determine the amount, trend and sources. In order to

accurately determine the exact amount fraction, stable, accurate and precise CH_4 gas mixtures are required.

The gas analysis laboratory of National Metrology Institute of South Africa (NMISA) places its priority on establishing and disseminating national measurement standards that have traceability to the International Standard of units, the kilogram (kg), through gravimetric preparation. In this article, the development of CH_4 in nitrogen and artificial air primary standard gas mixtures (PSGMs) at 2.00 µmol.mol^{-1} using a gravimetric method will be described. (ISO 6142-1, 2015, Milton and Brown 2011). The CH_4 in Air gas mixtures will be used to verify the amount fraction in the background air samples.

2.Experimental

2.1 Materials

2.1.1 Pure Starting Gases

The source materials used to prepare the standard gas mixtures were high pure gases of methane (CH_4) (99.995%), Nitrogen with built–in Purifier technology) (BIP^{TM} N_2 (99.9997%), O_2 (99,9995%). All these raw materials were supplied by Air Product PTY (Ltd) in South Africa.

2.2 Equipment

Various equipment and materials were employed to execute the purpose of this project. This includes Pfeiffer-Hi cube 400 evacuation station, Air and Vacuum Technologies DCU 110 filling Station (with turbomolecular vacuum pump, rotary vane fore pump, electro polish stainless steel tubing, pressure indicator and needle valves), roller bench for homogeneous mixing, Gas chromatography with flame ionization detector, Cavity ring-down spectroscopy (CRDS), Luxfer aluminum Cylinders with water

capacity volume of 5 L, certified mass pieces for calibration of the mass comparators.

2.3 Methods

2.3.1 Purity analysis of the starting material

In metrology, mixtures prepared by gravimetric methods are of high quality since the calculated amount fraction is directly traceable to the SI unit, the kilogram. Before gravimetric preparation of the mixtures, the purity analysis of high purity gases (CH_4, Ar, O_2 and BIP^{TM} N_2) was performed to quantify the impurities of starting material. Impurities of interest such as hydrocarbons, N_2, O_2, Ar, CO, CO_2 and CH_4 were determined at trace level on each starting material. This is a highly critical step since the impurities often contribute the most uncertainty to the gravimetric amount fraction. Gas Chromatography coupled with different detectors such as pulse discharge helium ionization detector (PDHID), thermal conductivity detector (TCD) and flame ionization detector with mechaniser (FID) was used to determine the amount fraction of each impurity of interest and the accuracy with which the impurities were measured was considered since it also contributes to the gravimetric uncertainty. When the analysis showed that the component was not detected, the detection limit was divided by the square root of 3. The impurities of the component are included in the calculation of the uncertainty of the final gas mixture. After quantification, the final impurity of the highest purity gas is determined following the model equation described below:

$$x_{pure} = 1 - \sum_{i=1}^{N} x_i \qquad (1)$$

where x_i: the amount fraction of impurity $_i$, determined by analysis, N: the number of impurities likely to be present in the final mixture, x_{pure}: the amount fraction “purity” of the “pure” parent gas.

Table 1. Purity table with uncertainties for the nominally highly pure gases.

Component	Distribution	Amount fraction ($\mu mol.mol^{-1}$)	Expanded Uncertainty (k=2)	Analysis Technique
(a) CH_4		999712.0	33.41	
Ar	Normal	2.89	0.29	GC-PDHID
CnHn excl C_2H_6	Rectangular	25.00	28.87	*
CO_2	Normal	1.12	0.11	GC-FID
N_2	Normal	237	11.85	GC-PDHID
C_2H_6	Normal	0.613	0.061	GC-FID
O_2	Normal	9.00	0.90	GC-PDHID
H_2O	Rectangular	2.50	2.89	*
H_2	Rectangular	10.00	11.55	*
(b) N_2 BIP™		999.95	6.0	
Ar	Normal	52.89	5.23	GC-PDHID
CO	Rectangular	0.0070	0.0081	GC-FID
CO_2	Rectangular	0.0115	0.013	GC-FID
CH_4	Rectangular	0.0043	0.0050	GC-FID
C_2H_6	Rectangular	0.0070	0.0081	GC-FID
O_2	Rectangular	0.0050	0.0058	*
H_2O	Rectangular	0.010	0.012	*
H_2	Rectangular	0.0090	0.010	*
(c)Argon BIP		999999.90	0.032	
N_2	Rectangular	0.0070	0.0020	GC-PDHID
CO	Rectangular	0.021	0.0243	GC-FID
CO_2	Rectangular	0.0098	0.011	GC-FID
CH_4	Rectangular	0.0058	0.0070	GC-FID
O_2	Rectangular	0.0050	0.0060	*
C_2H_6	Rectangular	0.0061	0.0070	GC-FID
H_2O	Rectangular	0.0100	0.012	*
N_2	Rectangular	0.0070	0.002	GC-PDHID
(d) O_2		999995.12	3.70	
N_2	Normal	2.00	2.31	*
CO	Normal	0.26	0.079	GC-FID
CO_2	Normal	0.11	0.032	GC-FID

CH_4	Rectangular	0.0060	0.0069	GC-FID
C_2H_6	Rectangular	0.0060	0.0069	GC-FID
H_2O	Rectangular	0.0010	0.0012	*

2.3.2 Preparation of primary standard gas mixtures by gravimetric procedure

Before preparation, a 5 L aluminium Luxfer cylinder used was pre-treated to ensure no adsorption effects or side reactions take place on the inner surface occurs. The pre-treatment includes hydrostatic, fluorination and eddy testing, which is conducted at Air Product SA (Pty) Ltd and NECSA. The preparation was done by evacuating a clean cylinder (cleaned externally to remove dust particle which might contribute to uncertainty) to 10^{-7} Pa of pressure using a Pfeiffer vacuum system. The cylinder was then weighed on the highly accurate mass comparator balance (Mettler Toledo PR10003; capacity 10 kg; readability; 1 mg) to obtain the vacuum mass. Using the Borda- substitution method, the vacuum cylinder is weighed against a reference cylinder to eliminate the buoyancy effect. The vacuum and reference cylinder have different masses which are compensated for by adding or removing the certified mass pieces to the cylinder that reads less. The vacuum cylinder is placed on a top loader balance (Mettler Toledo SB12001) and then connected to a stainless steel line to the filling station where a pre-calculated mass of the gas component (e.g. CH_4) is transferred into the cylinder via the Pfeiffer filling station. The cylinder with the first component and the reference is weighed again to add the balance gas (N_2). When a multicomponent gas mixture is prepared, more than one gas component is added into the cylinder before the balance gas following the above procedure. When all gas components are added, the final gas mixture is weighed after leaving the cylinder to equilibrate to environmental conditions and is rolled on a bench for a minimum of 2 hours to reach homogeneity. The main objective of preparing primary standard gas mixtures (PSGMs) is to support SAWS Cape Point Station, various

industries and the air monitoring community that measure CH_4 in the atmosphere.

A group of four gas mixtures at a nominal amount fraction of 2.00 μmol.mol^{-1} CH_4 in the artificial air were also developed for atmospheric measurements. A pre-calculated mass of 64 g CH_4 in artificial air was added into the evacuated cylinder and weighed against the reference cylinder. Diluted Ar (20% mol.mol^{-1}) and high pure O_2 were also transferred as gas component 2 and 3 via filling station into the mixture cylinder followed by weighing. The gas component 2 and 3 were filled and weighed separately. The mixture cylinder was then filled with N_2 balance as a final component to achieve the desired CH_4 amount fraction. Following the ideal gas law, the final CH_4 amount fraction was calculated on a mol. mol^{-1} bases from the masses of the gas components added into the cylinder and their appropriate molar masses (MM). The gas mixture was left for a minimum of 2 hours to equilibrate to room temperature, then weighed and rolled for a minimum of 2 hrs. The preparation began with a dilution of high pure CH_4 into four cylinders to result in approximately 6% mol.mol^{-1} in nitrogen gas mixtures. The gas mixtures in each step were prepared from the previous parent and diluted into nitrogen. The primary standards in level 4 were prepared in N_2 and artificial air at a nominal amount fraction of 2.00 μmol.mol^{-1}. **Figure 1** illustrates the production scheme of CH_4 in both matrices and **Table 2** illustrates the gravimetric amount fraction and the standard uncertainty at a coverage factor k=1. The gas mixtures were analysed on the GC-FID for their validation purpose.

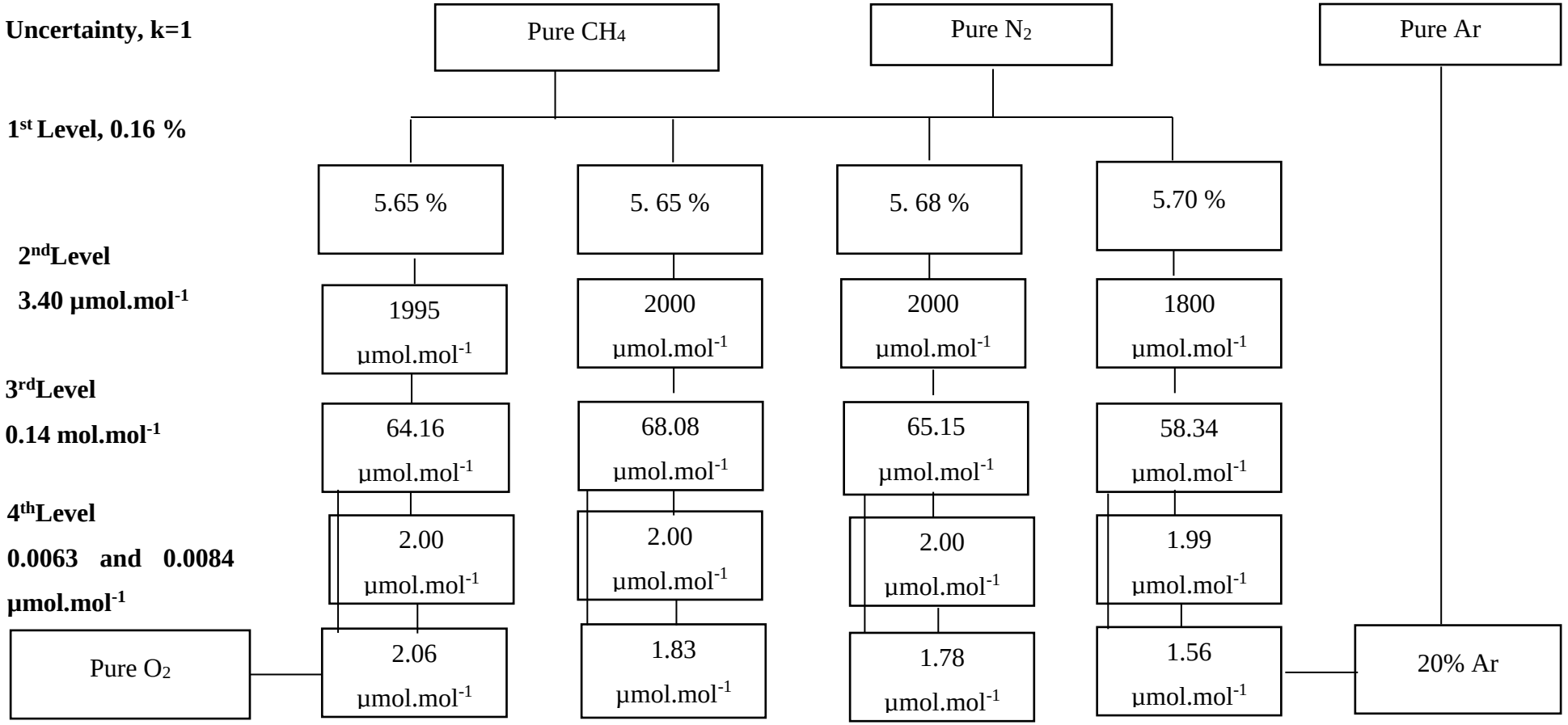


Figure 1. Production scheme of the gravimetric dilution of 2µmol.mol^{-1} CH_4 in nitrogen and artificial air from pure to trace level.

Table 2. Gravimetric amount fraction and the standard uncertainty of the primary standard gas mixtures.

Cylinder Number	Cylinder Symbol	Gravimetric fraction of CH_4 ($x_{CH_4,prep}$)	Amount
M518245	**M1**	2.06±0.0053	Artificial Air
M555723	**M2**	1.83±0.0042	
M518176	**M3**	1.78±0.0049	
M555728	**M4**	1.56±0.0037	
M518182	**CHN-1**	2.00±0.0062	
M518187	**CHN-2**	2.00±0.0062	
M518234	**CHN-3**	2.00±0.0063	
M518190	**CHN-4**	1.99±0.0061	

2.3.3 Dried air sample collected from the SAWS Cape Point station

Four evacuated cylinders (Luxfer, UK) (cylinder number: M93976, M93972, M93847, M93800 identified as CA-1, CA-2, CA-3, CA-4) from the laboratory were shipped to the SAWS Cape Point station where background air was transferred. The sample air was drawn from the 30-meter sampling tower into the lab where it was pumped with an oil-free air compressor (SA–3E series, RIX Industries) into the cylinder. Before introducing into the cylinder, the sampled air was conditioned and dried using magnesium perchlorate to remove moisture. After sampling, dry air was analysed to determine various components such as CO, CO_2, CH_4, and N_2O using various techniques such as GC-FID, GC-μECD, NDIR and CRDS calibrated with their own standards (from NOAA) were quantified prior shipment. Cylinders were returned to the laboratory for analysis against the gravimetrically prepared primary standard gas mixtures in artificial air.

2.3.4 Measurement of the newly prepared methane gas mixtures in artificial air and nitrogen by gas chromatography.

The CH_4 contents in eight aluminium cylinders were verified using gas chromatography equipped with using a flame ionization detector (FID). For verification of the gas standards in artificial air, an Agilent 7890B gas chromatography equipped with an FID was used. Prior to any connection of a primary standard gas mixture to the GC system, the sample lines and regulator connected to each cylinder were purged several times to ensure good repeatability of measurement results. A 2m stainless steel column packed with ShinCarbon ST (80/100 mesh) is used at a temperature of 40ºC. Nitrogen column carrier gas purged through a heated gas purifier at an optimum flow rate of 70 mL min^{-1}. The FID (250 ºC) is supplied with 550 mL min^{-1} synthetic air and 65 mL min^{-1} hydrogen. A 6-port stainless steel gas sampling /injection valve introduced the CH_4 in artificial air samples into the column. The sample was carried by a 2mL stainless steel sample loop prior introduction into the column. The measurement took 3 minutes to take a chromatogram as illustrated in **Figure 3** where the peaks represent CO and CH_4. It is assumed that CO peak is a residual from the other gases since the elution order for a ShinCarbon column is CO then CH_4 (Ueta and Saito, 2014). During the verification of the primary standard gas mixtures of CH_4 in N_2, a Varian CP3800 GC model equipped with FID was used. The CH_4 analytes from each cylinder was transported by a stainless-steel line to the solenoid valve then the Mass Flow Controller (MFC). The sample flow was controlled at a constant flow rate of 100 mL.min^{-1}. The gas lines were purged several times prior to eliminate dead volume and environmental contamination. The CH_4 analytes from the MFC were then transferred through a 1mL sample loop before reaction the column. Helium gas passed through a heated gas purifier to carry the gas molecules at a flow rate of 30mL.min^{-1} from the sample loop to the column for separation. The CH_4 analytes were separated by a molecular sieve 13X packed with (45-60 mesh) column at an optimum oven temperature set at 65°C isotherm. The

FID was supplied with 300 mL.min^{-1} of synthetic air and 20 ml.min^{-1} of hydrogen.

After setting the optimum parameters on both GC equipment's, one gas standard out of the four cylinders in each set (CH_4 in Air and CH_4 in N_2) was chosen as a control (C_1 and C_2) cylinder to bracket the other cylinders as the unknown samples. A measurement cycle was yield when a sequence: C_1, unknown sample$_1$, C_1, unknown sample$_2$, C_1, unknown sample$_3$, C_1, and sequence C_2, unknown sample$_1$, C_2, unknown sample$_2$, C_2, unknown sample$_3$, C_2 one measurement cycle was followed during verification. Using the single point calibration method, the amount fraction of the unknown sample (PSGM or background air) was predicted using the GUM Software 2.3.6141 software following the model equation as:

$$C_{unknown\ sample} = \left(\frac{A_{unknown\ sample}}{A_{control}}\right) \times C_{C_j} \quad (1)$$

where C_{C_j} is the amount fraction of CH_4 in the control cylinder j, C_j represents C_1 or C_2, A is the average peak area of the unknown sample and control.

Three measurement cycles were made and a minimum of 3 out of 7 injections per unknown sample or C_j determined the average peak area and the standard uncertainty. The control cylinder was also used to correct the instruments drift and calculate the sensitivity ratios of the unknown samples. The sensitivity ratios of the unknown samples were calculated as:

$$\text{Sensitivity value} = \frac{sensitivity_{C_{j1}}}{Average(C_{j1}+C_{j2})} \quad (2)$$

where sensitivity is obtained by dividing the gravimetric amount fraction of the average peak area of C_j, control cylinder. Corrected sensitivity was

calculated by the average of the sensitivity of the control before, C_{j1}, and after, C_{j2}, bracketing the unknown sample. This method tracks the changes in the sensitivity of the detector to monitor the short and or long-term drift of the instrument throughout the analysis. The final level four gas mixtures were developed in the artificial air to support atmospheric CH_4 measurements at ambient level. Therefore, after verification and data manipulation, one gas mixture in the artificial air verified the amount fraction of CH_4 in the background air samples.

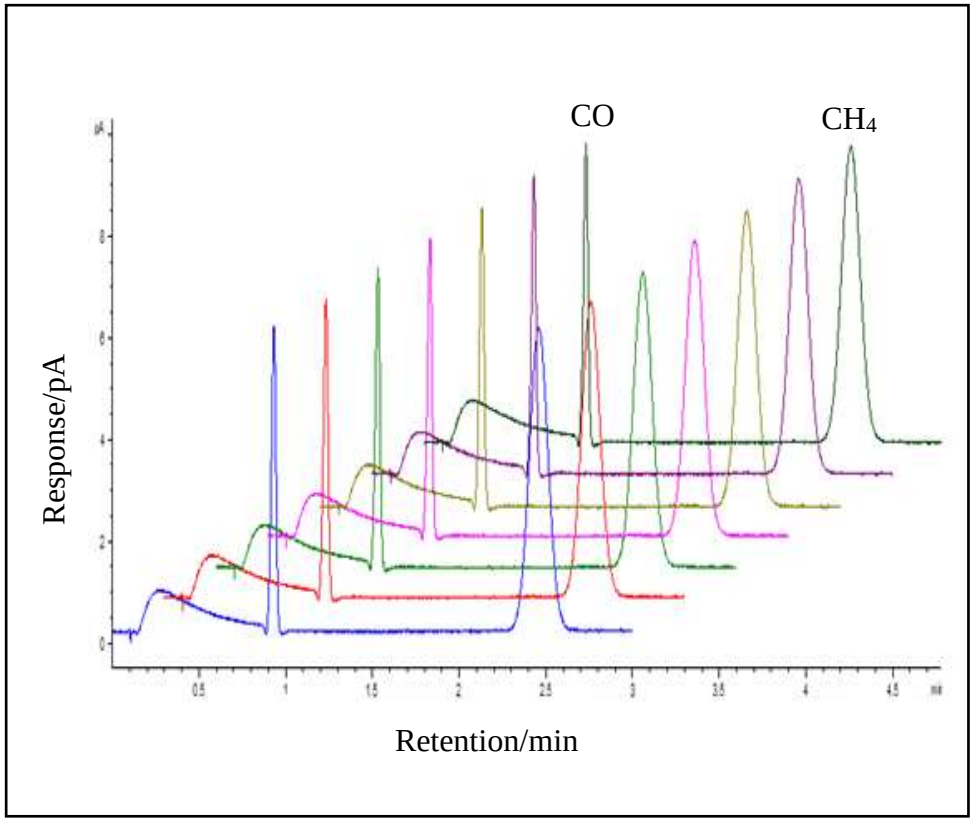


Figure 3. Chromatogram of the CH_4 in the artificial air after the analysis on the Agilent 7890B GC-FID system.

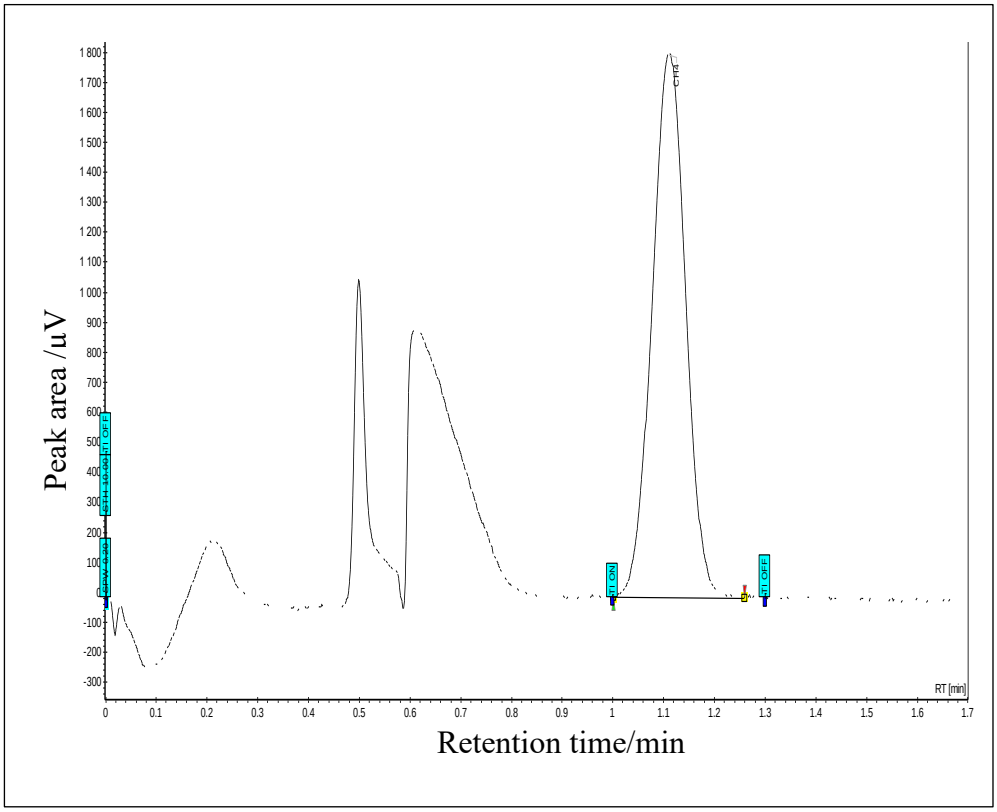


Figure 4. Chromatogram of CH_4 in N_2 gas mixture after analysis on the Varian CP3800 GC-FID system.

2.3.5 Measurement of the background air samples by Cavity ring-down spectroscopy

The CRDS analyser model G2401 Picarro Inc., USA can simultaneously measure CO_2, CH_4, H_2O and CO down to part-per-trillion. During this study, the CRDS analysis was used to determine CH_4 amount fraction and monitor water vapour in the dried samples. With the strongest absorption bands in the infrared region, the gaseous sample is introduced into a $35cm^3$ volume CRDS optical cavity controlled by 45ºC temperature and 140 Torr pressure. The cavity consists of three highly reflective small mirrors. A laser coupled with the CRDS passes light inside the cavity which is reflected by the mirror back and forth. With each light reflected, a small amount of light exits the cavity and the decay of the light is then measured. Light is scanned at a wavelength around 1.651µm for CO_2 and H_2O and 1.603 µm for CH_4 of the gas sample molecule which is measured by the

photodetector to give a spectrum of each (Winderlich et al., 2010). The CRDS analyser was calibrated cylinder M1 to M4. Gaseous molecules were introduced into the modified analyser at a constant flow rate regulated by a mass flow controller (M17203188F Bronkhorst, Holland) calibrated by the manufacturer against N_2 at 1000ml/min. The MFC connected to 1/8-inch stainless steel tube was set at 200ml min^{-1} flow rate and after measurement of each cylinder, only the last 7min average CRDS response was collected. For good measurement repeatability, the regulator connected to the cylinder line was purged for 5 min before measurement.

3. Results and discussion

3.1 Purity analysis

It became essential to conduct, purity analysis of the starting materials prior to preparation of the gas mixtures because the amount of CH_4 main impurity in the highly pure Ar, O_2 and N_2 can cause bias to the amount fraction, $x_{CH_4,prep,}$ of the gas mixture. **Table 1** shows the trace amount of CH_4 found in pure gases Ar, O_2 and N_2 BIP^{TM} as 0.0058, 0.11, 0.0043 µmol.mol^{-1}. These values are less than 0.20 µmol.mol^{-1} and were accepted. The amount of Ar, O_2 and N_2 in the highly pure CH_4 was obtained as 2.89, 9.00 and 237 µmol.mol^{-1}. However, these values led to a bias of 0.289, 0.90 and 11.85 but were combined in the final uncertainty of the gravimetric values. All the values were added in the final amount fraction of the gas mixtures.

3.2 Verification of the newly prepared gas mixtures in artificial air and nitrogen matrices.

For each level in the production scheme, a GC-FID was used to confirm the gravimetric reproducibility of the primary standard gas mixture by comparing the detector sensitivity of the unknown samples to the control (Prinn et al., 2000). The comparison was achieved by measuring the deviation between the analytical and the gravimetric values in each step following equation 3. The results obtained are shown in **Table 3**. During

the verification of the gas mixtures in level 3, a deviation, $|y_{\mathrm{CH_4},prep} - y_{\mathrm{CH_4},ver}|$, about 0.65 % was obtained. The verification amount fractions, $y_{\mathrm{CH_4},ver}$, were calculated as 63.83, 64.59 and 58.20 µmol.mol^{-1}. The relative standard deviation of 0.10 % and instrumental drift of < 0.3% confirmed the precision of the instrument being less subjected to any environmental changes. After obtaining these values, level 4 primary standard gas mixtures were prepared. Since the FID is a linear detector, the detector sensitivity of all unknown samples was verified by comparison to also check the internal consistency of the gas mixtures. Since the gas mixtures were prepared with almost similar amount fractions in the last level for both matrices (2.00 µmol.mol^{-1} CH_4 in N_2, CHN-1 to CHN-4 and approximately 2.00 µmol.mol^{-1} CH_4 in Air M1 to M4), similar detector sensitivity values were expected. **Table 3** also shows the internal consistency of the gas mixtures as similar detector sensitivity values were obtained throughout the analysis. The comparison criteria used is explained in ISO 6143 (2001) as:

$$|y_{\mathrm{CH_4},prep,j} - y_{\mathrm{CH_4},ver,j}| \leq 2\sqrt{u^2(y_{\mathrm{CH_4},prep,j}) + u^2(y_{\mathrm{CH_4},ver,j})} \qquad (3)$$

where $y_{\mathrm{CH_4},prep,j}$ is the gravimetric preparation value predicted during preparation, $y_{\mathrm{CH_4},ver,j}$ is the analytical amount fraction determined by comparing the peak area all the unknown samples against the control cylinder and j represents the gas mixture in artificial air or N_2 matrix.

The combined standard uncertainties of CH_4 in both matrices were calculated according to ISO 6142-1, (2015) as:

$$u_c(y_{CH_4}) = \frac{1}{2}\sqrt{u^2(y_{N_20,prep,j}) + u^2(y_{N_20,ver,j}) + (y_{N_20,prep,j} - y_{N_20,ver,j})^2} \qquad (4)$$

The model equation (4) includes both uncertainties from preparation and verification. The combined standard uncertainty, $u_c\left(y_{CH_4}\right)$, of CH_4 is 0.030 and 0.010 μmol.mol^{-1} in both artificial air and nitrogen balance. These values are larger than the WMO precision goals, but the standards represent a good agreement between independent gas mixtures. Rhoderick et al (2016) also reported a larger deviation value (-2.7 ±0. 6) that did not meet the WMO precision goal, but that of other calibration scale. It is rather difficult to meet the required precision goals as uncertainty from various sources (purity, preparation and verification) must be considered. In this case, the large uncertainty contribution arises from the analysis. The gravimetric values for all the gas mixtures were considered as the certified value at approximately 2.00 ± 0.050 μmol.mol^{-1} CH_4 in Air and 2.00 ± 0.020 μmol.mol^{-1} CH_4 in N_2.

Table 3. Results of the internal consistency test of primary standard gas mixtures.

Cylinder Symbol	***Amount fraction of CH_4*** [a] ***(μmol.mol^{-1})*** $(y_{CH_4,ver})$	***Sensitivity Value*** [b]	
M1	2.05±0.070	28.27±0.21	Artificial Air
M2	1.82±0.090	28.12±0.30	
M3	1.78±0.047	28.22±0.39	
M4	1.55±0.12	28.29±0.47	
CHN-1	1.99±0.010	69.58±0.17	
CHN-2	2.02±0.0091	69.44±0.24	
CHN-3	2.016±0.0066	69.53±0.33	
CHN-4	1.99±0.0075	69.84±0.13	

[a]Expanded uncertainty where k=2. [b]Standard deviation (%) where the number of measurements was 4.

3.3 Verification of the background air samples by Gas chromatography method.

To achieve the objective of this study, the certified gas standard in artificial air was used to quantify the amount of CH_4 in the background air samples. From the four samples collected at SAWS Cape Point Station in 2016, the amount fraction of CH_4 in the background air was directly measured by GC-FID. After the verification of the gas mixtures, one CH_4 in artificial air gas standard certified at 2.061 ± 0.30 μmol.mol^{-1} final amount fraction was employed as a control gas mixture. The peak area of the background air sample was compared with the peak area of the control gas mixture under repeated measurement. Following the same verification sequence and method the amount of CH_4 in the background air sample was calculated as 1.79 ± 0.033 μmol.mol^{-1}, 1.80 ± 0.034 μmol.mol^{-1}, 1.78 ± 0.034 μmol.mol^{-1}, 1.78 ± 0.32 μmol.mol^{-1} where uncertainty is standard with a coverage factor k=1. The reported values are for cylinder CA1, CA2, CA3 and CA4 with a deviation from the reported values ranging from 0.32 to 0.88 % (**Table 4**). **Table 4** shows a comparison in the calculated and reported amount fraction of CH_4 determined by GC and CRDS.

3.4 Verification of background air samples by Cavity ring-down spectroscopy method.

The CRDS analyzer was used to quantify the amount fraction of the dried air sample. The CRDS analyzer was calibrated with existing CH_4 primary standard gas mixture (2.12 ± 0.011, 1.81 ± 0.011 and 1.78 ± 0.011) μmol.mol^{-1} in the artificial air prior to analysis that yielded accurate and reproducible results. A calibration curve was produced after a plot of the standard gas average CRDS response against its gravimetric value. After calibration, the background air samples were measured and assigned values. Comparison of the CRDS analysis with the gravimetric values indicates good linearity with a value of $r^2 = 1$ as shown in **Figure 4**. During the measurement, one sample line and one regulator was used at a time and the average CRDS response over three replicates are reported in **Table 4**. The

NMISA CRDS response of the background air sample is in good agreement with the SAWS Cape Point station reported results showing an overall deviation ranging from 0.00030 to than 0.06 % from the CH_4 amount fractions. Though the final reported amount fractions of the analyzed background air sample from both NMISA and SAWS Cape Point station are lower than the globally reported values (1.845 μmol.mol^{-1} CH_4) (WMO Greenhouse Gas Bulletin 2016), due to the northern global gradient difference that propagates to the Southern Hemisphere, the measurement results however are comparable. The experiment demonstrated good accuracy and precision with a relative standard deviation of <0.1% respectively.

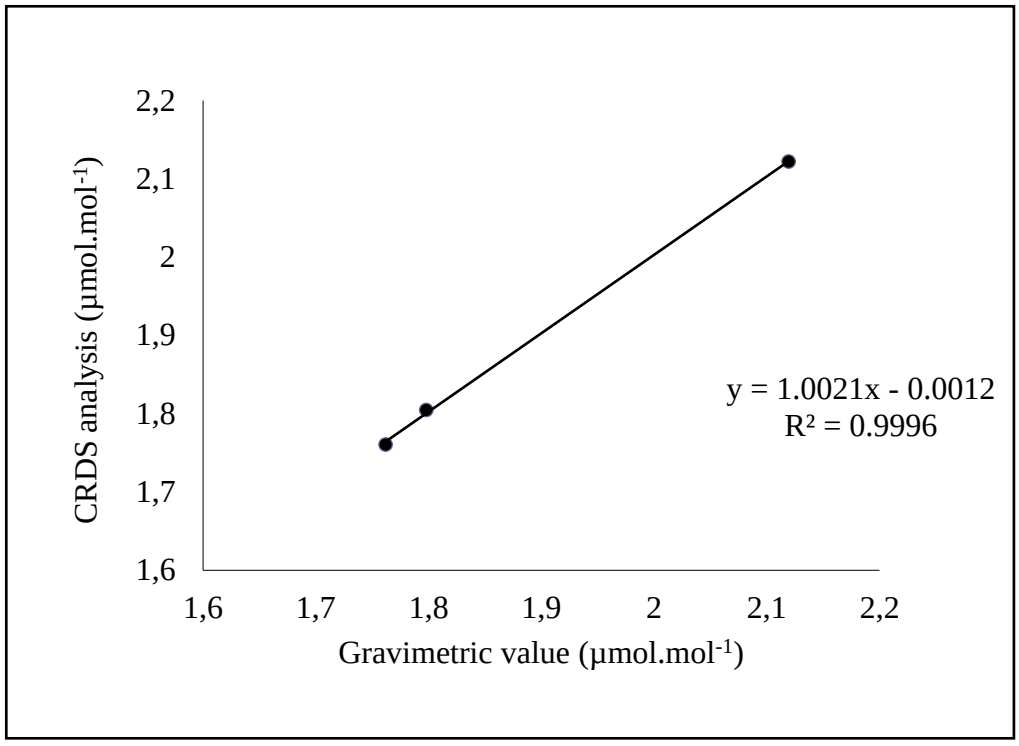


Figure 4. Linearity graph of CH_4 Gravimetric value vs CRDS analysis value.

Table 4. Comparison of CRDS results measured by different laboratories.

Background air sample	***NMISA GC µmol.mol^{-1}***	***NMISA CRDS µmol.mol^{-1}***	***SAWS Cape Point Station µmol.mol^{-1}***	***GC % DIFF***	***CRDS % DIFF[c]***
CA1	1.7950	1.7863	1.7862	0.50	0.0077
CA2	1.7779	1.7946	1.7936	0.88	0.053
CA3	1.8012	1.7959	1.7959	0.32	0.00030
CA4	1.7758	1.7812	1.7824	037	0.023

[c]CRDS % DIFF = (SAWS CAPE POINT STATION – NMISA)/ NMISA*100

4. Conclusion

There is a great demand to use the gravimetrically prepared primary standard gas mixtures for the quantification of greenhouse gases for traceability of results to the SI unit. During purity analysis of the BIP^{TM} N_2, the Ar amount fraction differed by 50 to 90 µmol/mol. The deviation impacted on the amount fraction of the PSGMs as different balance gases (BIP^{TM} N2) was used during the preparation of the gas mixtures. When the standards were verified on the GC-FID system precision of less than 0.65% was obtained because the response of the analytical system did not change throughout the analysis. The deviation between the calculated amount fraction and the reported values are larger on the GC than CRDS. The CRDS measurements proved to be more precise and sensitivity as little to no instrumental drifts on CH_4 measurements was obtained. The stability of the PSGMs and background air samples will be monitored over time and more studies will be done to achieve better precision. Future CH_4 work may require results that agree with the set precision goals. The maybe achieved by improving purity, buying starting materials with extremely low amount fraction of the main impurity. Or buying sampled from areas with less air pollution emitted. The developed gas mixtures can be used to support various regional air monitoring companies and laboratories.

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Paper III

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Tshilongo – 25 % (co-supervisor, reviewed the manuscript)

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GENERAL PAPER

Verification of nitrous oxide primary standard gas mixtures by gas chromatography and cavity ring-down spectroscopy for ambient measurements in South Africa

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Abstract
Nitrous oxide (N_2O) is an important greenhouse gas and is the third-largest contributor to global warming with a global warming potential (GWP) higher than that of carbon dioxide. Ambient N_2O is monitored globally and described at nanomole per mole (nmol mol^{-1}) levels. Metrologically traceable and highly accurate N_2O gas standards are required to understand the behaviour of the greenhouse gases in the atmosphere and GWP. A group of primary standard gas mixtures (PSGMs) in aluminium cylinder material has been prepared in synthetic air for the calibration of analytical instruments for measurement of N_2O at an ambient level. An automatic weighing system with a mass comparator and a fully automated circular rotary plate, as well as a gas filling station, was used in the preparation of the gas mixtures. Analytical methods such as gas chromatography coupled with micro-electron capture detector and cavity ring-down spectroscopy were adopted in the verification process. Four PSGMs in the final preparation step were used to analyse unknown background and filtered air samples at the ambient level. An expanded uncertainty relative to the gravimetric amount fraction was found to be 0.02 %. Results show that the background air samples lie within the calibration range with 329 to 330 nmol mol^{-1} obtained and 135 nmol mol^{-1} obtained for filtered air sample.

Keywords Primary standard gas mixtures · Gas chromatography coupled with a micro-electron detector · Cavity ring-down spectroscopy · Background · Filtered air samples

Introduction and background

Nitrous oxide (N_2O) naturally occurs in the Earth's atmosphere in the nitrogen cycle and is the dominant source of ozone-depleting nitrogen oxides in the stratosphere. It contributes 6.24 % to the overall global radiative forcing, and its global warming potential (GWP) is 300 times above CO_2 [1]. Its anthropogenic major source is emission from vehicle exhausts with constituting to about 40 % of all emissions [2, 3]. The stability of N_2O at 154–356 nmol mol^{-1} in highly pressurized gas cylinders was prepared by National Oceanic and Atmospheric Administration (NOAA) [4]. The amount fraction of N_2O emitted in the atmosphere and contained in the vehicle exhausts has been measured with gas analysers based on mid-infrared spectroscopy [5]. These analysers cannot measure the complete absolute amount fraction of N_2O. For reliable data, gas standards with values traceable to the primary standard gas mixtures (PSGMs) are required. Such gas mixtures are manufactured by National Metrology Institutes (NMIs). An international key comparison on N_2O in the artificial air at 320 nmol mol^{-1} gravimetric value was performed for the demonstration of equivalence on PSGMs. Several NMIs and NOAA prepared cylinders which were compared against each other. The uncertainty of the ambient level N_2O in the artificial air was reported by the participants [6, 7]. The study was conducted to set harmonized tropospheric measurements made by the different laboratories that wanted to understand the distribution and behaviour of N_2O emitted from different sources. It is rather challenging

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to use various data sets by many laboratories due to the lack of harmonized calibration scales with low uncertainties [8].

In South Africa, the air quality legislation in the form of the National Environmental Management: Air Quality Act (No. 39 of 2004) has also declared greenhouse gases including N_2O as priority air pollutants since 2017 [9]. Therefore, it becomes important for the National Metrology Institute of South Africa (NMISA) to embark on the preparation of N_2O in nitrogen and artificial air matrix at the low amount fraction for the calibration of monitoring instruments used to check anthropogenic N_2O emitted into the atmosphere. The harmonized data obtained can be used to come up with mitigation solutions for different sources.

This study describes the preparation and verification process of nitrous oxide in the synthetic air at 330 nmol mol^{-1} based on the static gravimetric method, the analysis of international standard, background and filtered air sample.

Experimental

Starting materials

Highly pure source gas

The starting materials used for preparation were argon BIP (Ar < 99.99 %), oxygen (O_2 < 99.9995 %) and nitrogen with built-in purifier technology (BIP^{TM} N_2 < 99.9999 %) (Air Product, South Africa), and nitrous oxide (N_2O < 99.999 %) (Air Liquide, South Africa) gas was used as source material. Purity analysis is a procedure done to confirm the highest metrological values with a high level of confidence before the preparation of primary standard gas mixtures (PSGMs).

Equipment

Cylinders

Aluminium gas cylinders (Luxfer, UK) were used in the preparation of the N_2O gas standards. The cylinders were fitted with stainless steel valve (Rotarex, Southern Africa (Pty) Ltd) followed by passivation and cylinder pre-treatment called fluorination process. In order to test the leaks on the valve, the cylinders were pressurized with helium gas. A continuous quality assurance system developed in our gas analysis group has been put in place to demonstrate the stability of the gas mixtures over the last 10 years.

Mass comparator balance

A precise mass comparator balance (Mettler Toledo XPE26003LC, Switzerland, a maximum capacity of 26.1 kg; minimum readability; 1 mg) were used and placed in a well-controlled room. The weighing process were performed in the balance room where the temperature and relative humidity were controlled at (22 ± 1) °C and (50 ± 10) % RH, respectively. The mass comparator is enclosed in a transparent chamber with a built-in pressure (Vaisala PTB 3300 (500-1100)), temperature and humidity (Vaisala, HMT 331) sensors, and an automated single circular rotary plate capable of loading three cylinders and a mass artefact.

Analytical techniques used during the analysis

Gas chromatography with micro-electron capture detector (μECD) and cavity ring-down spectroscopy (CRDS) was the equipment's used during the analysis. The CRDS analyser model G5310 was purchased from Picarro Inc., USA, for the quantification of N_2O in air samples up to part-per-billion level, while the μECD (7890B Agilent, USA) quantified the N_2O in the sample and standard gas mixtures.

High-pressure oil-free air and gas compressor for the collection of filtered air

A RIX Microboost high-pressure oil-free air and gas electric compressor (Microboost—BD-230 model, Ecochem Pumps, South Africa) are used to fill filtered air into the cylinder. The compressor holds high- (H015039 series 45 model) and low-air-pressure filters and a dryer (activated alumina). The low-pressure filters have 10-μm pre-filter on the regulator with the different filter elements (1.0, 0.01 and 0.001 μm). The dryer has activated alumina packing for drying large water vapour/or oil particles that may be present in the sample.

Methods

Purity analysis of source gaseous materials

Different detectors coupled to a gas chromatography (GC) were used to quantify the impurity profile of the pure starting material. These detectors include a micro-electron capture detector (μECD), flame ionization detector (FID) and pulse discharge helium ionization detector (PDHID) which recorded the chromatograms. In this study, the spectroscopic techniques used are the CRDS and non-dispersive ultraviolet (NDUV) for impurity quantification in the highly pure gases. The amount fraction of the impurities in N_2O, Ar, O_2 and N_2 determined by the analytical methods was conventionally calculated from Eq. (1).

$$x_{\text{pure}} = 1 - \sum_{t=1}^{N} x_t \tag{1}$$

where x_t is the amount fraction of impurity t, found during analysis, N is the number of impurities found in the final standard gas mixture and x_{pure} stands for the amount fraction of the highly pure source material. The results of purity analysis are illustrated in Table 4. The amount fraction of the non-detectable impurity in the pure source material by the analytical technique was set to half of the limit of detection $\frac{LOD}{2}$, and the associated standard uncertainty was defined as the amount fraction divided by $\sqrt{3}$ (e.g. $\frac{LOD}{(2*\sqrt{3})}$) based on the rectangular distribution between 0 and the LOD value of the analytical technique [10]. The standard uncertainty of each impurity is expressed as expanded uncertainty (U) and is calculated according to Eq. (2);

$$U = u \times k \tag{2}$$

where k is the coverage factor of 2 at 95 % confidence level.

Gravimetric method: preparation of the primary standard gas mixtures

Primary standard gas mixtures of nitrous oxide in nitrogen and artificial air matrix at 330 nmol mol^{-1} nominal value were prepared using the gravimetric method based on ISO 6142-1, 2015 [10]. The preparation procedure was carried out by adding a pre-calculated mass of the analysed pure N_2O (99.999 %, Air Liquide, SA) and N_2 (99.999 %, Air Product, SA) into a 10-litre gas cylinder to form a pre-mixture. Each pressurized gas cylinder was weighed before and after the addition of a component gas. The pre-mixture was diluted further to trace level 330 nmol mol^{-1} as shown in Fig. 1. Pure oxygen (99.999 %, Air Product, SA) and a 20 % argon in nitrogen pre-mixture were added into the cylinder only in the final step to get air composition. To ensure accurate mass measurements, the highly precise mass comparator was calibrated with mass artefacts that were certified against a national kilogram standard. An automatic weighing system (AWS) patent by the Korean Research Institute of Standard and Science (KRISS) was used to manage the loading of the cylinders in the exact area of the mass comparator pan. Its automated circular rotary plate supported the sample and tare cylinders. Buoyancy effect applied on the cylinders and the drift of the mass comparator likely to occur got cancelled when the following sequence was used: sample A cylinder–tare B cylinder–sample C cylinder [11]. Four cylinders were prepared in each step after mixing the gas mixture for less than 2 h, and the final gravimetric value of

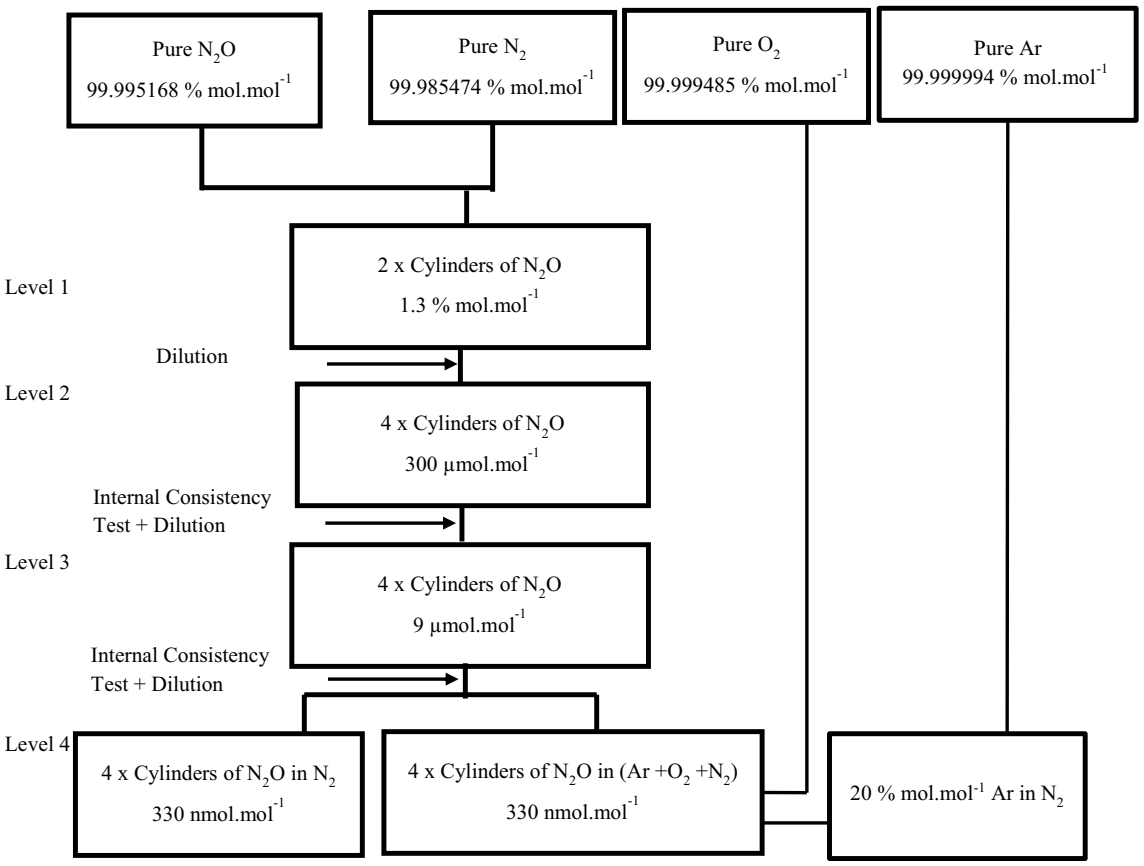


Fig. 1 Production plan of the preparation of nitrous oxide primary standard gas mixtures (PSGMs) at trace level

the standard gas mixture was calculated using the following model equation:

$$x_t = \frac{\sum_{C=1}^{S}\left(\frac{x_{t,C}.m_C}{\sum_{t=1}^{n} x_{t,C}.M_t}\right)}{\sum_{C=1}^{S}\left(\frac{m_C}{\sum_{t=1}^{n} x_{i,C}.M_t}\right)} \quad (3)$$

where x_t is the amount fraction of the gas composition t in the gas mixture, $t = 1, \ldots, n$, S is the overall number of parent gases, n is the overall total number of gas components in the final gas mixture,m_C is the measured mass of the parent gas C determined by weighing, M_t is the molar mass of component t,$t = 1, \ldots .n$, and $x_{t,C}$ is the amount fraction of gas component t in the parent gas C [12].

The amount fractions with the relative expanded uncertainties in the final step are shown in Table 1, and SL1, SL2, SL3 and SL4 denote the gravimetrically prepared cylinders of the nominal composition of the primary standard gas mixtures (PSGMs). The metrological traceability of the PSGMs to the quantity of the amount fraction is established by traceability of the masses to the international standards of mass, the International Union of Pure and Applied Chemistry (IUPAC) definition atomic/molecular masses of the gas components and the purity of the gas components. The major uncertainty is from purity analysis [13]. The amount fractions of the PSGMs in the first step were quantified by verification of the standard gas mixtures against each other by GC-μECD to check the internal consistency of the N_2O before further dilution. The gas composition of the standard gas mixture was determined by individual analysis of the amount fraction of each analyte thereafter. The composition was certified by comparison methods using a set of mixtures with predetermined assigned values (Table 1).

Preparation of background and filtered air samples

Four clean and evacuated aluminium cylinders (Luxfer, UK) with 10 L internal volume were shipped from NMISA to South African Weather Service–GAW Station in Cape Point for the sampling of background air in South Africa. At the station, atmospheric air is drawn from outside through a sampling tube connected to a 30-metre sampling tower, into the laboratory. An oil-free air compressor (SA–3E series, RIX Industries) is used to draw the atmospheric air into the laboratory where the air is conditioned and dried using magnesium perchlorate to remove moisture before introducing into the cylinders and the analytical instruments for measurements. Gas components such as CO, CO_2, CH_4 and N_2O are continuously measured using analytical instruments such as the gas chromatograph coupled with flame ionization and micro-electron capture detector (GC-FID/methanator, μECD) and CRDS [14–16]. After the analysis, all pressurized cylinders were returned to NMISA for the analysis against the gravimetrical PSGMs. The filtered air around NMISA (D1) campus was sampled into a cylinder at 5 MPa for approximately 2 h. after connecting on the valve. The RIX Microboost high-pressure air compressor was assembled outside our facilities on a level surface and filtered air was sampled as follows: the air was sucked into the compressor through the low- and high-pressure filters to remove different particles (water, oil, fumes, dust, etc.), then dried and compressed to 0.8 MPa. A 10-L cylinder was connected to a stainless steel cylinder regulator attached to the system. The regulator contains a low-pressure filter with activated alumina packing to dry the air sample prior the introduction into the cylinder. A tube between the cylinder and pump was pressurized before filling valve on the compressor unit, and the filtered air was introduced slowly into the cylinder. The cylinder was left in the laboratory to equilibrate to room temperature before analysis (Fig. 2).

Verification of primary standard gas mixtures

Gas chromatography system coupled with a μECD system Measurements of the gravimetrically prepared standards were conducted on the Agilent 7890B GC-μECD. The estimated amount fraction was verified by determining the detector sensitivities (GC response over the gas mixture value) of the four standard gas mixtures in each step except the first step. The measurements procedure for analysing the group of N_2O in artificial air gas standards is based on the analysis of one N_2O in artificial air gas mixture nominated as the reference standard (SL1), and rest of the gas mixtures were treated as samples. To keep a constant detector

Table 1 Gravimetric amount fraction of component gases in the standard gas mixture

PSGM	Gas composition			
	N_2O (nmol mol^{-1})	Ar (mol mol^{-1})	O_2 (mol mol^{-1})	N_2 (mol mol^{-1})
SL1	346.4 (0.04)[a]	0.009353	0.2112	0.7794
SL2	337.9 (0.05)	0.009451	0.2073	0.7833
SL3	321.4 (0.05)	0.009396	0.2095	0.7811
SL4	243.8 (0.06)	0.009094	0.2100	0.7809

[a]The values in the parentheses represent the relative expanded uncertainty where $k = 2$

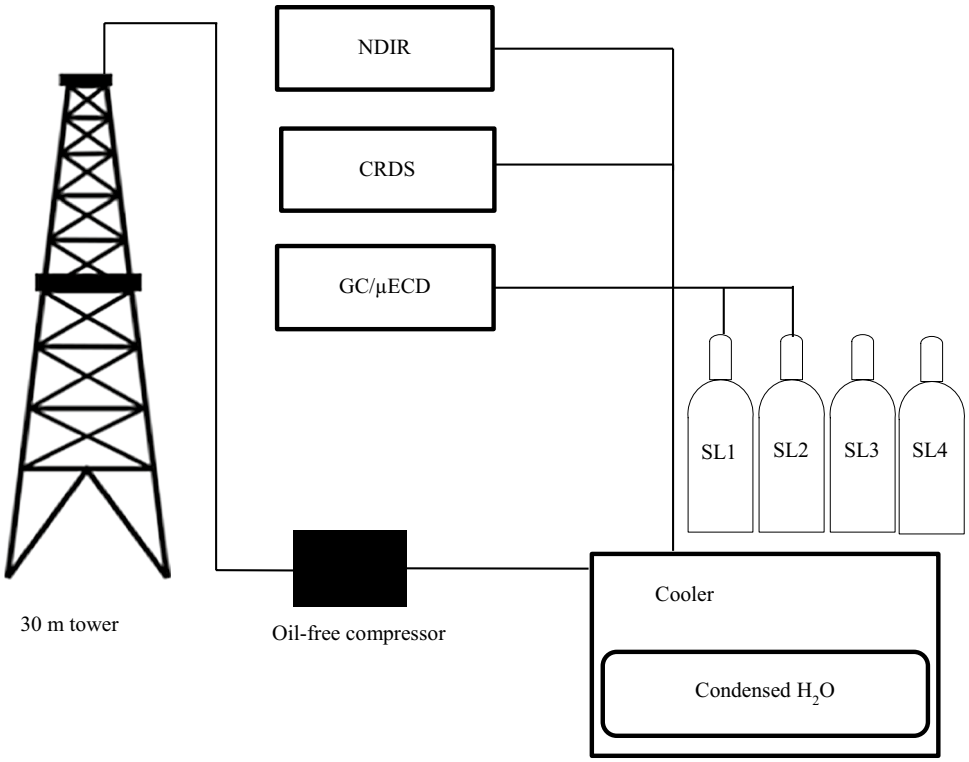


Fig. 2 Schematic diagram for background air sampling and continuous measurements processes

Table 2 Analytical parameters used to analyse the gas mixtures on the GC-µECD

Parameters	Conditions
Column type	Activated alumina 80/100 mesh 12-ft stainless steel
Oven temperature	55 °C
Detector	µECD
Detector temperature	350 °C
Carrier gas	P5 (5 % mol mol^{-1} CH_4 in Ar)
Carrier gas flow	220 kPa
Sample flow	100 ml/min
Sample loop	1 ml
Total runtime	7.5 min

pressure and sample loop by creating a damping effect, two flow restrictors (Valco Instruments Co. Inc., USA) were installed at the end of sample and detector vent lines [7]. To compensate for any instrumental drifts during the analysis and check the internal consistency of the gas composition within the cylinder, an analysis sequence SL1 (Ref)–sample SL2–SL1(Ref)–sample SL3–SL1(Ref) was followed. Prior to any connection of the sample cylinder to the GC system, each analysis began by purging a 1.58 mm electropolished stainless steel sample line and pressure regulator, connected to each cylinder, several times to ensure good repeatability of measurement results at optimum analytical conditions (Table 2). Under the laboratory conditions of 20 ± 2 °C and 50 ± 10 %RH, the sequence was repeated three times and the ratios to the reference cylinder were calculated. A reference cylinder randomly chosen amongst the four cylinders in each step confirmed the amount fraction of the sample cylinders in a single calibration method. A single calibration method allowed for each analytical mean of the reference cylinder to be compared by A-B-A-B-A procedure to correct for instrumental drift. The ChemStation software installed in the analytical instrument integrated the chromatographic peaks after separation. The response factor (RF), defined as the mean analytical response divided by the gravimetric value, between standards of N_2O gas mixtures verified the gravimetric values of the calibration standards which were similar in each dilution step [11].

Cavity ring-down spectroscopy The CRDS analyser (model G5310 Picarro, Santa Clara, California, USA) was used. The instrument simultaneously measures carbon monoxide and nitrous oxide down to 100 part-per-trillion sensitivities at 10 s and water vapour at parts per million [17]. During the study, the CRDS analyser was used as an alternative to check the amount fraction of N_2O in the PSGMs and air sample collected GAW station (latitude 34º21′N, longitude 18º29′E and elevation 230 m) and NMISA campus (latitude 25.7468°S and longitude 28.2770°E). The CRDS analyser was calibrated with four gravimetrically prepared N_2O PSGMs ranging from 243 to of 346 nmol mol^{-1} nominal

value in Ar, O_2 and N_2 ratios close to that in the atmosphere before use. A linear absorbance curve proportional to the amount fraction with $R^2 = 0.9999$ is shown in Fig. 5 and Table 3. Gas molecules were introduced into the analyser at a constant flow rate regulated with a mass flow controller (MFC) (M17203188F Bronkhorst, Holland) calibrated by the manufacturer against N_2 at 500 ml min^{-1}. A 1/16-inch' electropolished stainless steel line was connected to the pressure reducer of the PSGM then MFC through a 16-port multi-position valve. The line was purged with the gas mixture at 200 ml min^{-1} flow rate. After every 15 min, the air samples were also introduced in the cavity through a 1/16-inch' stainless steel line connected from the exhaust of the MFC to the analyser (Fig. 3). A coiled bypass outline was installed to keep a steady flow, a constant pressure of the gas and minimize backpressure diffusion [11]. After analysis, the data were collected, and the analyser response value was stable within 10 min. For good measurement repeatability, the regulator connected to the cylinder and sample line was purged for 3 min before introducing the gas mixture. The regression analysis was performed with XLGenline, version 1.1, a computer program developed by National Physical Laboratory which implements this methodology by considering the uncertainties in both the x- and y-axes [18].

Table 3 Results of CRDS calibrated by highly precise gravimetric prepared mixtures

Cylinder ID	Gravimetric value (nmol mol^{-1})	CRDS response (nmol mol^{-1})	% Difference (nmol mol^{-1})
SL1	346.42	346.33	−0.32 (−0.03)
SL2	337.65	337.87	0.22 (0.02)
SL3	321.42	321.31	−0.11 (−0.03)
SL4	243.80	243.68	−0.12 (−0.19)

Adsorption test determined by cylinder-to-cylinder division

Gas mixtures prepared by the gravimetric method at nmol mol^{-1} level can be affected by direct adsorption of gas components on the interior surface of the cylinder. To test the adsorption of nitrous oxide at nmol mol^{-1} levels on the interior surface of the cylinder, equal division method was used [6, 7, 19]. A cylinder used to verify the PSGMs

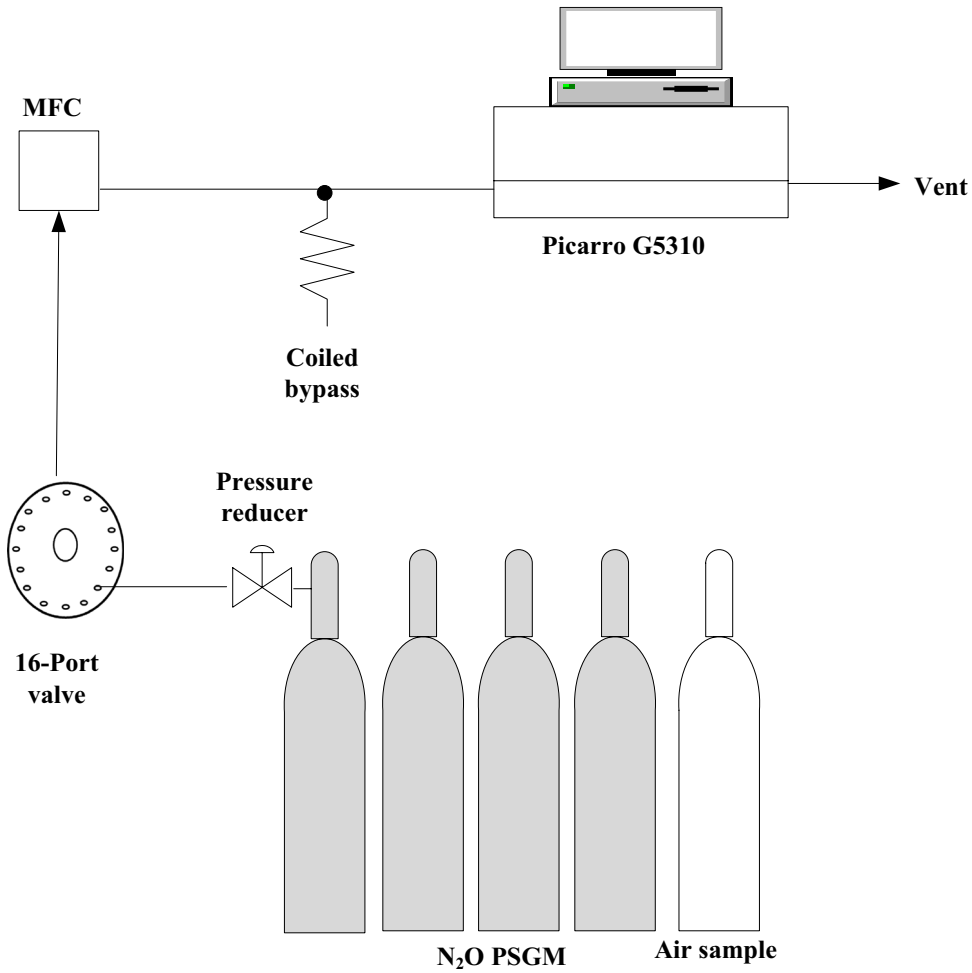


Fig. 3 Schematic diagram of the flow of gas samples to the cavity ring-down spectroscopy

(reference cylinder) was chosen as the optimum standard to determine any adsorption over the short term and monitor the stability. Previous studies reported that nitrous oxide standard gas mixture in air matrix (containing O_2 and N_2) prepared by gravimetric method is stable in aluminium cylinders [7, 8]. Two clean empty cylinders were evacuated (~ 8.6×10^{-8} MPa) while being heated overnight at 60 °C. The cylinders were left to equalize to room temperature prior to the transfer. The gas mixture prepared in the fourth step at approximately 330 nmol mol^{-1} was used as the mother (M) cylinder to transfer to the two evacuated daughter (D_1 and D_2) cylinders. A T-shaped 1/8-inch' stainless steel tube was used to connect M, D_1 and D_2 cylinders. The tube was purged several times with the gas mixture contained in cylinder M to remove possible contamination and condition the tube before gas transfer. The gas mixture was transferred into D_1 and D_2 cylinder by slowly opening the cylinder valves to equalize the gas pressure [13]. The cylinders were kept standing for ± 2 h before closing the valves to ensure equal pressures and cylinder temperature were reached. After the adsorption test, all three cylinders had the same pressure at 3.71 MPa. The gas mixtures were analysed on the CRDS and GC-μECD the following day. The analyser response to the amount fraction was used to evaluate the adsorption loss on the cylinders.

Results and discussion

Purity analysis

It is crucial to accurately quantify the exact amount of the main impurities (N_2O) in pure Ar, O_2 and N_2 pure gases respective since the weighed amount of the main impurity present in the mixture can cause bias in the gravimetrically prepared N_2O standard gas mixture. Table 4a–d shows the impurity profile of pure N_2O, O_2, Ar and N_2 gases and outlines the impurity amount fraction associated with the uncertainties devoted by different detectors. The amount of N_2O in pure Ar, O_2 and N_2 was quantified as less than 0.02 μmol mol^{-1}. This value did not affect the final gas mixtures of N_2O at 330 nmol mol^{-1}. However, the amount of N_2 in high pure N_2O source material led to a measurement bias of 1.70 μmol mol^{-1} and is combined in the uncertainty of the final amount fraction of the reference gas mixture. These values were considered during in the gravimetric preparation of the gas mixtures.

Verification of prepared primary standard gas mixtures by gravimetric method

In all the gravimetric preparation steps, a GC-μECD was used for the analysis of the four nitrous oxide in artificial air primary standard gas mixtures by checking the detector sensitivity through comparison of all the standard [7, 20]. The results obtained by separation chromatography are shown in Table 5. The linearity of the μECD was tested by plotting the detector response y_{axis} (31695.9, 31870.0 and 31948.8) arbitrary unit corresponding to the gravimetric amount fraction of the gas mixture x_{axis} (8.96, 9.08 and 8.99) μmol mol^{-1} [21]. The detector response in the third step, PL2, PL3 and PL4, was linear over the amount fraction range from 8.96 to 8.99 μmol mol^{-1} (Fig. 4). Comparison criteria set is expressed in Eq. 3 in accordance with ISO 6143:

$$|y_{N_20,\text{prep}} - y_{N_20,\text{ver}}| \leq 2\sqrt{u^2(y_{N_2O,prep}) + u^2\left(y_{N_2O,ver}\right)} \quad (4)$$

where $y_{N_20,\text{prep}}$ is the gravimetric preparation value estimated during preparation and $y_{N_2O,\text{ver}}$ is the assigned amount fraction determined by comparing the RF of PL2, PL3 and PL4 standard cylinders against PL1 reference cylinder. Because the precision of the measurement system of < 0.3 % (1 σ) and the preparation uncertainty of 0.02 % (2 σ) were obtained, the approval criteria were satisfied on the left side $|y_{N_20,\text{prep}} - y_{N_20,\text{ver}}|$ [12]. The deviation of the RF in the second and third dilution steps was calculated as 0.9 % and 0.6 %. The gas standards met the set criteria at each step, and further dilutions were made till nmol mol^{-1} level. Only in the final step, more preparations were made as some of the standards did not pass verification. It is not easy to confirm the value of the gas mixtures prepared by the static gravimetric procedure because there is no other absolute method to use. For this reason, several primary standard gas mixtures with almost equal or similar amount fractions were made and verified on the GC-μECD. These standards also passed the internal consistency test set at 1 %. In the last step, 330 nmol mol^{-1} N_2O in nitrogen (QL1, QL2, QL3 and QL4) and artificial (SL, SL2, SL3 and SL4) standard gas mixtures were prepared to cover the tropospheric range (260 to 370) nmol mol^{-1} [8]. These PSGMs were verified using Eq. 3 with the same measurement criteria adopted. The verification precision obtained was < 0.5 and 0.4 % (1 σ), and gravimetric uncertainty was obtained 0.05 % and 0.06 % (2 σ), respectively. The maximum deviation obtained amongst the estimated and assigned amount fractions of the PSGMs in nitrogen and the artificial air was 0.6 % for both cylinders in the difference matrix (QL2; SL2). The approach used verifies that the prepared amount fractions of the reference cylinders in each step were correct. The combined standard uncertainties of N_2O gas mixtures in both matrices were calculated according to [12] as:

$$u_c\left(y_{N_20}\right) = \frac{1}{2}\sqrt{u^2\left(y_{N_20,\text{prep}}\right) + u^2\left(y_{N_20,\text{ver}}\right) + \left(y_{N_20,\text{prep}} - y_{N_20,\text{ver}}\right)^2} \quad (5)$$

Table 4 (a–d) Impurity analyses and standard uncertainties of source material

Component	Distribution	Amount fraction (μmol mol^{-1})	Standard uncertainty (μmol mol^{-1}) at k = 1	Analysis techniques
(a) N_2O		999951.7	2.0	
CO_2	Normal	1.28	0.192	GC-FID
N_2	Normal	16.5	0.850	GC-PDHID
Ar	Rectangular	0.25	0.144	*
CH_4	Rectangular	0.27	0.156	GC-FID
H_2O	Rectangular	0.5	0.289	*
NH_3	Rectangular	2.5	1.443	*
CO	Rectangular	0.04	0.020	GC-FID
NO_2	Rectangular	0.5	0.289	*
O_2	Rectangular	0.25	0.144	*
NO	Normal	26.24	0.105	NDUV
(b) Ar BIP		999999.94	0.02	
N_2	Rectangular	0.01	0.007	PDHID
CO	Rectangular	0.02	0.012	FID
CO_2	Rectangular	0.01	0.006	FID
CH_4	Rectangular	0.001	0.003	FID
O_2	Rectangular	0.005	0.003	PDHID
C_2H_6	Rectangular	0.006	0.004	FID
H_2O	Rectangular	0.01	0.006	
N_2O	Rectangular	0.0002	0.0008	CRDS
(c) O_2		999994.9	2.0	
Ar	Rectangular	2.5	1.443	*
N_2	Rectangular	2	1.155	*
CO	Normal	0.28	0.042	FID
CO_2	Normal	0.35	0.052	FID
CH_4	Rectangular	0.006	0.003	FID
C_2H_6	Rectangular	0.006	0.003	FID
H_2O	Rectangular	0.001	0.006	FID
N_2O	Rectangular	0.0002	0.0008	CRDS
(d) N_2 BIP™		999854.7	8.4	
Ar	Normal	144.6	8.35	PDHID
CO	Rectangular	0.029	0.016	FID
CO_2	Rectangular	0.244	0.141	FID
CH_4	Rectangular	0.003	0.002	FID
O_2	Rectangular	0.005	0.003	PDHID
C_2H_6	Rectangular	0.013	0.007	FID
H_2O	Rectangular	0.01	0.006	*
H_2	Rectangular	0.5	0.288	*
N_2O	Rectangular	0.0005	0.003	CRDS

*The asterisk stands for the manufacture specification

Table 5 illustrates the combined uncertainties calculated in this work. The standard uncertainty as combined of N_2O amount fraction $u_c\left(y_{N_2O}\right)$ is approximately 0.3 % (1 σ) which is higher than 0.007 % relative standard uncertainty of the WMO target goal set at 330 ± 0.025 nmol mol^{-1} (1 σ). For this study, N_2O measurements at ambient level can be taken within some measurement uncertainties of 0.002 nmol mol^{-1} (1 σ) at 330 nmol mol^{-1} which includes the value obtained during calibration of the standards, $\sqrt{0.3^2 + 0.5^2} = 0.6$ % (1 σ), assuming the relative standard deviation is not high than 0.5 %.

The gravimetric value was adopted as the certified value of the PSGMs. Due to the large uncertainties obtained on the PSGMs, the gas mixtures in the artificial air were further analysed on the CRDS. Table 6 shows the results obtained

Table 5 Results of the consistency test of primary standard preparation

Cylinder ID	Amount fraction (μmol mol^{-1})	Response factor (RF)	Remarks
OL1	299.22 ± 0.030[a]	3225 ± 0.20[b]	Second step
OL2	298.29 ± 0.040	3225 ± 0.20	
OL3	299.07 ± 0.040	3232 ± 0.10	
OL4	297.42 ± 0.040	3233 ± 0.20	
PL1	8.99 ± 0.0010	3535 ± 0.10	Third step
PL2	8.99 ± 0.0010	3543 ± 0.20	
PL3	8.98 ± 0.0010	3537 ± 0.40	
PL4	8.96 ± 0.0010	3528 ± 0.10	
	(nmol mol^{-1})		
QL1	330.17 ± 0.10	6482 ± 0.10	Fourth step
QL2	325.72 ± 0.10	6500 ± 0.20	
QL3	328.22 ± 0.10	6474 ± 0.30	
QL4	325.72 ± 0.10	6451 ± 0.30	
SL1	346.43 ± 0.20	6995 ± 0.21	Artificial air
SL2	337.83 ± 0.20	7714 ± 0.21	
SL3	321.39 ± 0.20	7022 ± .0.30	
SL4	243.68 ± 0.20	7724 ± 0.10	

[a]Expanded uncertainty where $k = 2$. [b]Relative standard deviation where the number of measurements was 5

from two measurement techniques. A maximum percentage difference of 0.4 % was obtained when the cylinders were analysed by GC-μECD. A percentage difference of less than 0.1 % between the analysed and the prepared value was obtained on the CRDS analyser. The CRDS proves to be a more precise method than the GC-μECD because low standard uncertainty (0.02 nmol mol^{-1}) and percentage drift (0.05 %) were obtained. The long acquisition time taken to attain a chromatography has impacted negatively on the separation method influencing the instruments precision and measurement results. The amount fractions of the calibration standards were determined as the average of the mean observed over a period of the last 5 min after approximately 3-min intervals for sample stabilization before measurements.

Adsorption test determined by cylinder-to-cylinder division

Nitrous oxide has been reported to have dissociative adsorb on aluminium metals surfaces by desorbing nitrogen and depositing oxygen atoms on the metal surface [22]. The RF of the original and divided cylinders was compared. Though the cylinder-to-cylinder test was only executed in the final preparation step, it had been investigated that the adsorption effect on the amount fraction increases at low levels [19]. The adsorption loss model equation was estimated following the equation explained in [23] as:

$$x'_p = x'_{p-1}\frac{f_n r'_p}{r' + f_n r'_p - r'_{pd}} \tag{6}$$

where x'_j and x'_{pd} are the amount fraction of D_1 and D_2 cylinders divided in the last step similar to M cylinder (x_0) gravimetric amount fraction, r'_p and r'_{pd} are the averaged instrument response, $f_n = \frac{n_{A(p=1)}}{n_{Ap}}$, $n_{A(p=1)}$ and n_{Ap} are the total amount fraction in $(p-1)$th and pth division cylinder.

According to [23], the loss due to adsorption of N_2O onto the inner walls of the cylinder is expressed as:

$$\left(\Delta x = x_0 - x'_0\right) \tag{7}$$

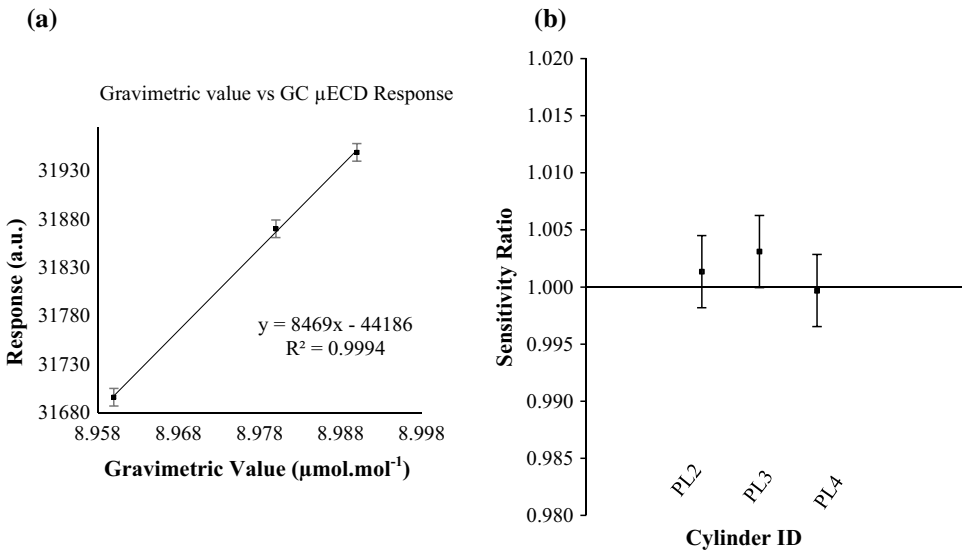


Fig. 4 Verification results for the third preparation step. **a** Linearity curve related to the gravimetric amount fraction and the detector response with its associated expanded uncertainty giving $R^2 = 0.9994$. **b** Sensitivity ratio of the verified gas mixtures against the reference cylinder proving the consistency of the gas mixtures. The error bars agree to the expanded uncertainties of the sensitivity ratio

Table 6 Amount fraction obtained based on CRDS and GC-μECD analysis

Cylinder ID	CRDS (nmol mol^{-1})		GC-μECD (nmol mol^{-1})	
	CRDS Value	Standard uncertainty[c] ($k=1$)	Assigned value	Standard uncertainty[d] ($k=1$)
SL1	346.43	0.010	345.79	0.60
SL2	337.65	0.010	337.83	0.30
SL3	321.42	0.020	321.39	0.10
SL4	243.68	0.010	243.16	0.60

[c]Standard uncertainty derived from the standard deviation of the CRDS response value obtained in 15 min. [d]Combined standard uncertainty of the days of measurements based on the estimated standard deviation of four measurements

where Δx is defined by the difference between the gravimetric amount fractions x_0 and x_0'.

The origin and divided cylinders were compared on the CRDS and GC-μECD method. The adsorption values obtained for D_1 and D_2 cylinders after analysis against M cylinder were 346.06 and 346.28 nmol mol^{-1} on chromatography analysis, and 346.01 and 346.05 nmol mol^{-1} on the CRDS analyser. The instrumental drift on GC-μECD method was compensated for when the original cylinder was measured between the two divided cylinders over three consecutive sequences per cylinder. The adsorption loss (Eq. 7) was calculated as 0.023 at a 3.7 MPa pressure for 346.43 nmol mol^{-1}. The standard adsorption loss uncertainty was found as $0.013 < 0.08$. With these findings $u\Delta x < ux_0$, we assume that there are no adsorption losses experienced during cylinder-to-cylinder test and the standards passed the short-term stability.

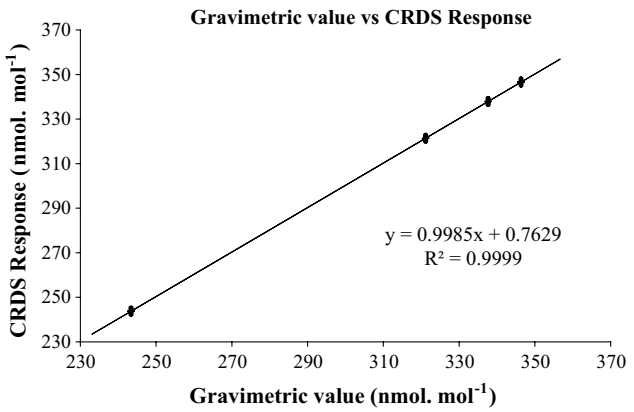


Fig. 5 Analyser response plot as a function of the gravimetric amount fraction for assigning the international air standards, background and filtered air samples. The error bars agree to the expanded uncertainties of the analyser response

Quantification of background and filtered air sample by CRDS

Before the analysis of background air samples on the CRDS, the analyser was calibrated with the existing PSGMs at a nominal value range from 243 to 346 nmol mol^{-1} [24]. Due to a small deviation between the real gravimetric value and the measured CRDS value, a good consistency of 0.998 (close to 1) (sensitivity ratio) was obtained with a precision of < 0.02 %. This shows that the PSGMs are mixed well and are stable within the inner walls of the cylinder. After calibration, the purchased standard, background and filtered air samples were measured and assigned values using the response equation with an $R^2 = 0.9999$ coefficient indicating good linearity as illustrated in Fig. 5. During the measurement, a sequence and two pressure regulators were used, while the average analyser response over three replicates is reported in Table 7. The analyser response of the purchased standards is in good agreement with the PSGMs in the artificial air as the results show an overall deviation of less than 0.05 %. The response curve was estimated by the least-square second-order polynomial fit of the data yield an agreement of $R^2 = 0.99981$. Residuals are listed in Table 7, and all the background air samples certified values (330–329 ± 0.010) nmol mol^{-1}) lie within the linear calibration curve except for filtered air cylinder values (135.36 ± 0.010) nmol mol^{-1}). The low amount fraction results from N_2O and CO_2 being adsorbed on activated alumina packing [25]. Because

Table 7 Amount fraction of N_2O obtained by CRDS for the standard N_2O gas mixtures

N_2O (nmol mol^{-1})	
Cylinder No.	Reported value Standard uncertainty[e] (k = 1)
International air standard	
S1	350.10 (0.20)
S2	331.34 (0.10)
S3	285.35 (0.30)
Background air sample	
CPT1	329.07 (0.010)
CPT2	329.16 (0.010)
CPT3	329.77 (0.010)
CPT4	329.95 (0.010)
Filtered air sample	
D1	135.36

[e]Standard uncertainty derived from the standard deviation of the CRDS response value obtained in 15 min

of this assumption, filtered air sample shows the lower N_2O amount fraction than that of background air. The reported values were adopted as the certified values with a standard uncertainty related to the standard deviation of the CRDS measurements.

Conclusion

The development of a group of primary gas standards having N_2O in the artificial air was produced using a primary method. Verification was made by using CRDS and GC-μECD. The lowest range of the group of the PSGMs covers the ambient amount fraction range of 243–346 nmol mol^{-1}. The final expanded uncertainty (2δ) of the certified gas mixtures is reported as 1.80 nmol mol^{-1} within the measurement capability of 1 %. The uncertainty obtained is small enough to support the ambient air measurements set at 1 nmol mol^{-1} standard uncertainty ($k=1$) acceptable level. This the lowest uncertainties in primary standards achieved at NMISA to date. The consistency of the gas mixtures was within the set criteria of 1 % ratio. The analysis of three purchased standard shows a correlation between nitrous oxide primary standard gas mixtures. To improve on the precision of the GC-μECD, the set measurement time will be perfected to less than 5 min by improving the set analytical parameters in the future. Further studies will include studying the pressure broadening issues between the PSGMs and the purchased air standard and the long-term stability of N_2O PSGMs in Ar, O_2 and N_2 matrix.

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Supporting document

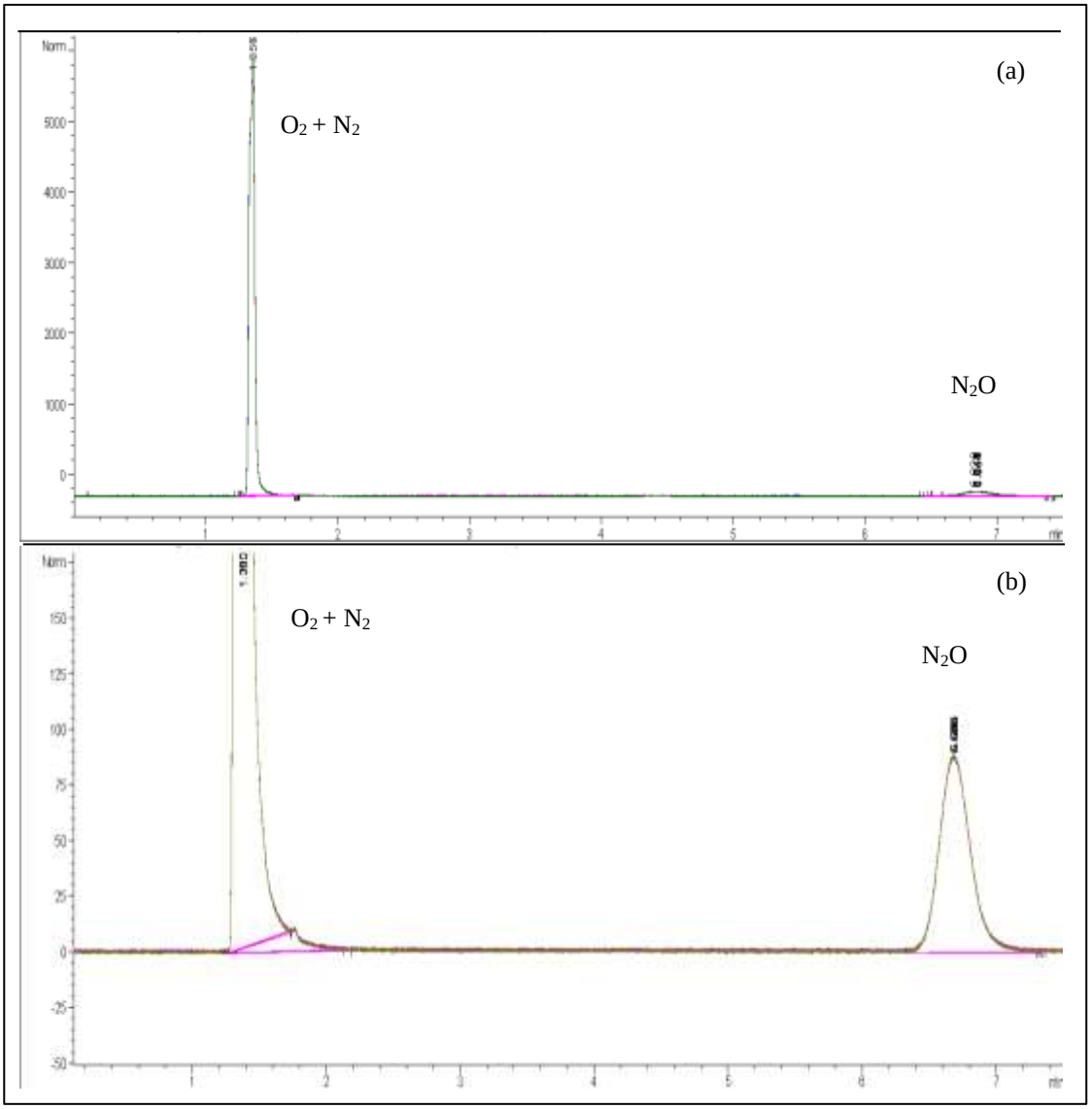


Figure S1 a to b: (a) A chromatogram for the PSGM obtained from the GC-μECD. **(b)** A magnified version of chromatogram.

Paper IV

Lushozi S, Tshilongo J, Angelique B, Mellisa J, Napo N, Ipeleng L, Nompumelelo M and Chimuka L. Post international key comparison CCQMK-51 of Carbon monoxide: Stability and uncertainty evaluation of gas mixtures. *Manuscript.*

Lushozi – 50 % (performed the experiments and wrote the manuscript);

Chimuka – 25 % (supervisor, reviewed the manuscript)

Tshilongo – 25 % (co-supervisor, reviewed the manuscript)

Post international key comparison CCQMK-51 of Carbon Monoxide: Stability and uncertainty evaluation of gas mixtures.

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Abstract

The evaluation of carbon monoxide primary standard gas mixtures prepared at the National Metrology Institute of South Africa for CCQM K51 in 2006 was performed at emission level. A group of CO gas mixtures at a nominal value of 5 µmol.mol^{-1} were verified at the coordinating laboratory. The content of CO gas mixtures was evaluation over a range of old in-house primary standard gas mixture prior shipment to the participating laboratory. For this study, a new set of 5 µmol.mol^{-1} in N_2 was gravimetrically prepared in 2015 and 2018 to monitor the long-term study of CO since 11 years of preparation. After evaluating the consistency of the newly prepared gas mixtures, the amount fraction and stability of the contents of CO in the old 5 µmol.mol^{-1} was estimated by non-dispersive infrared and gas chromatography. The results obtained shows an agreement between the measurement values obtained from both instruments. The uncertainties associated with the measurement value was estimated at 0.05 and 0.01 µmol.mol^{-1} for both NDIR and GC-FID. The values were accepted since the expanded uncertainty of the old 5 µmol.mol^{-1} gas mixture, prepared in 2006 and re-analysed in 2018, was certified at 0.5 % standard uncertainty relative to the gravimetric value. In this study, the old cylinder was certified with the final value of 5.01 ± 0.05 µmol.mol^{-1}.

Keywords: Carbon monoxide, primary standard gas mixtures, long-term stability

1. Introduction

Carbon monoxide (CO), is a strong reactive gas that plays a key role in Earth's chemistry (Logan et al., 1981). The global warming potential of CO is small but can lead to indirect global radiative effects. CO is not a greenhouse gas but its reaction with hydroxyl radicals (OH) can lead to the production of stratospheric ozone (O_3) in the presence of NOx int the atmosphere (van der Laan et al, 2009). The emission of CO from biomass and fossil fuel burning enhances the production of CO_2, CH_4 and H_2O, which increases their long lifetime (Prather, 1996; Turball et al., 2011; Miller,et al,2012, Levin and Karstens, 2007). The amount fraction of CO contained at emission level have been measured with non-dispersive infrared (NDIR), vacuum ultra-violet resonance fluorescence (VUF) (Gerbig et al, 1999), turntable diode laser spectroscopy (TDLS) (Fried et al., 1991), gas analysers and most recently commercially available analytical instruments. These analytical includes closed – path Fourier Transform Infrared (FTIR), Cavity – enhanced off-axis Integrative Cavity Output Spectroscopy (ICOS) and Cavity ring-down spectroscopy (Zellweger, 2012). However, these instruments require accurate and stable pressurized primary standard gas mixtures for calibration provided at by national metrology institutes. The prepared primary gas standards must have small uncertainties and measurement taken from different laboratories and equipment's should be harmonise. To outline these issues, several comparison studies have been conducted by different laboratories (Ou Yang et al., 2009; Zellweger et al., 2009). In 2007 and 2008, an international comparison of CO in nitrogen at 5 $\mu mol.mol^{-1}$ nominal value was performed for the demonstration of measurement equivalence on standard gas mixtures sent to participants, and check the stability of the gas mixtures after 10 years since the first comparison study performed in 1992. Twenty-

three national metrology institutes (NMIs) and one laboratory Umweltbundesamt (Federal Environment Agency), Langen (UBA) took part in the international key comparison study under the direction of the Consultative Committee for the amount of substance (CCQM). These participants received a 5 L highly pressurized aluminium cylinder from the coordinating laboratory, NMISA. Each cylinder was prepared following the gravimetric technique on the single pan balance according to ISO 6142-1 (2015) at an approximate pressure of 12 MPa. The gas mixtures were verified before and after shipment to and from the respective laboratories. At the international coordinating laboratory, the gravimetric value for each gas mixture was used as the reference value for each participant cylinder. It was decided in the CCQM meeting that the gravimetric uncertainty of the participants cylinders be set to 0.0030 µmol.mol^{-1} (CCQM K51, 2010). Ever since the international comparison study was conducted in 2006-2007, the long-term stability of 5 µmol.mol^{-1} CO in nitrogen gas mixtures at that time have not been checked.

This study describes the gravimetric preparation and verification procedure of a new set of standard gas mixtures for the stability evaluation of CO content in aluminium cylinder after 11 years of preparation.

2. Experimental

2.1 Materials

2.1.1 Pure starting materials

Pure starting material Built-in Purifier technology (BIP^{TM}) N_2 (99.9997%), (Air Product, South Africa) and carbon monoxide CO (99.997%), (Air Liquide, South Africa) gases were used during the preparation of the CO gas mixtures. The impurities in the pure starting materials were checked before gravimetric preparation using gas chromatography coupled with different detectors such as pulse discharge helium ionization detector (PDHID), and flame ionization detector with methanator (FID) was used for the detection of Ar, N_2, CO_2, CO and CH_4. **Table 1** shows a summary of

impurities calculated according to model equation explained in ISO 6142-1,(2015).

Table 1. Purity table of the source materials used.

Component	***Distribution***	***Amount fraction (µmol.mol^{-1})***	***Expanded Uncertainty (k=2)***	***Analysis Technique***
(a) CO		999995.3	0.04	
O_2	Rectangular	2.50	2.89	*
N_2	Normal	1.05	0.10	GC-PDHID
H_2O	Rectangular	1.50	1.73	*
H_2	Rectangular	0.50	0.58	*
CH_4	Rectangular	1.00	1.15	GC-FID
Ar	Normal	0.16	0.02	GC-PDHID
CO_2	Rectangular	0.50	0.58	GC-FID
(b)N_2 BIP^{TM}		9999.5	6.0	
Ar	Normal	52.89	5.23	GC-PDHID
CO	Rectangular	0.0070	0.0081	GC-FID
CO_2	Rectangular	0.0115	0.013	GC-FID
CH_4	Rectangular	0.0043	0.0050	GC-FID
C_2H_6	Rectangular	0.0070	0.0081	GC-FID
O_2	Rectangular	0.0050	0.0058	*
H_2O	Rectangular	0.010	0.012	*
H_2	Rectangular	0.0090	0.010	*

2.2 Equipment's

2.2.1 Cylinders

In this study, CO gas mixtures were gravimetrically prepared in 5 and 10 L aluminium alloy cylinder (Luxfer, UK) with 5 and 10 L internal volume. The inner walls of the cylinders were treated by fluorination process prior to gravimetric preparation of gas mixtures.

2.2.2 Weighing apparatus

A mass comparator device with a single pan suspended below (Mettler Toledo model PR 10003, 10 kg capacity and 1 mg readability) for 5 L cylinder weighing, and a mass comparator with a single automated pan (Mettler Toledo XPE 26003LC) with a 26.1 kg capacity and 1 mg readability weighed the cylinders during gravimetric preparation of old and new gas mixtures

2.2.3 Non-dispersive infrared analyser

The CO content was analysed using a Uras 26 Non-dispersive infrared (NDIR) analyser (ABB, SA) calibrated with a group of standards of CO-in-nitrogen over the amount fraction range of 1 to 10 µmol.mol^{-1} prepared to draw a linear curve.

2.2.4 Gas Chromatography coupled with a methanator and flame ionization detector

The amount fraction of CO gas mixtures was determined by gas chromatography (Varian Chrompack CP-3800 GL) with a flame ionization detector including a methanator.

2.3 Methods

2.3.1 Production method of the Primary Standard Gas Mixtures

In this work, the primary standard gas mixtures and primary reference gas mixtures were prepared by mixing pure CO and BIP^{TM} N_2 (<99.997 %, <99.9999 %, Air Product, SA) gases to produce a scheme of CO -in-nitrogen gas mixtures. It is important to quantify for hydrocarbons, Ar, O_2, N_2, CO_2 and CO impurities in each pure cylinder using calibrated analytical instruments with certified gas mixtures prepared in-house by a gravimetric procedure. A gas chromatography with several detectors such as flame ionization detector (FID) with methanator and pulse discharge helium ionization detector was the measurement system used during impurity analysis. After impurity check, pure CO gas was calculated as 99.999 ± 0.000004 %mol.mol^{-1} and BIP^{TM} N_2 as 99.994 ± 0.000003 %mol.mol^{-1} at 95 % coverage factor where k=2. The amount fraction of each pure source material calculated by adding all the impurities then subtracting with 1. The standard uncertainty related with the estimated amount fraction of each impurity was shown by the evaluated probability distribution. **Figure 1** shows a four-step dilution production diagram of the primary standard gas mixtures (PSGMs). Four PSGMs of CO in N_2 balance gas were gravimetrically prepared in high pressurized cylinders according to ISO 6142-1, (2015). These gas mixtures were prepared in 5 L aluminium material cylinders at a nominal gravimetric value of 5 µmol.mol^{-1} (x_{PSGM}), ($x_{CO\ cert}$). Sample and tare cylinders (named as cylinder S and cylinder T) were manually weighed after placement on a single suspension pan set below the mass comparator balance before and after filling. During this process, only the sample cylinder was filled with a pre-calculated mass of CO and N_2 gas components. Weighing was achieved by a manual interchange of the cylinders on the suspension pan using an optimized sequence cylinder T + sensitivity mass piece - cylinder T- cylinder S - cylinder T- cylinder S - cylinder T – cylinder T + sensitivity mass piece. Cylinder T and S were weighed consecutively to reduce buoyancy effects due to ambient air pressure that might have an impact on the measurement

values. The weight difference between both cylinders was compensated for by loading calibrated mass pieces on the mass comparator pan. Four new 5 µmol.mol^{-1} PSGMs prepared in 2015 and two prepared in 2018 are denoted as CL1-4 and CS 1-3. Old PRGMs, x_{PSGM}, gravimetrically prepared in 2006 for a key comparison study. were re-analysed against newly prepared PSGMs, $x_{Cert\ CO}$, to evaluate the stability of CO at trace level.

After stability evaluation, the final gravimetric value for the CCQM-K51 sample was calculated following the model equation (1)

$$x_{PSGM,} = x_{veri} + \delta_{CO\ insta} + x_{grav} \quad (1)$$

where x_{veri} is the analytical value of the gas mixture after verification, $\delta_{CO\ insta}$ is the difference due to long-term instability deduced from the deviation between the analytical value and the amount fraction value attributed in CO 2007 group, x_{grav}, is the gravimetric amount fraction (Matsumoto et al, 2016). The standard uncertainty related with the final amount fraction of newly prepared gas mixture x_{PSGM}, u_{PSGM} is

$$u^2_{PSGM,new} = u^2_{veri} + u^2_{CO\ insta} + u^2_{grav} \quad (2)$$

where $u^2_{PSGM,new}$, u^2_{veri}, u^2_{grav}, and $u^2_{CO\ insta}$ are the uncertainties of $x_{veri}, \delta_{CO\ insta}, x_{grav}$ at 68 % confident level where the coverage factor k=1.

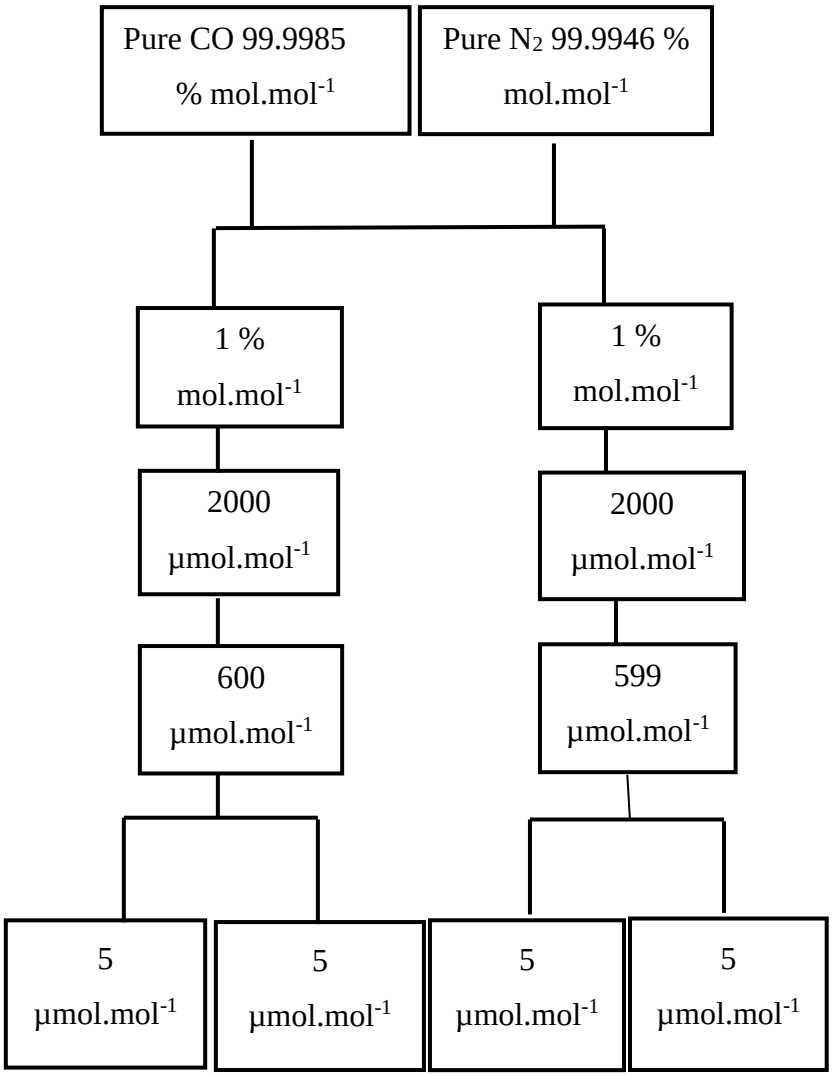


Figure 1. Schematic diagram of the production of new CO in nitrogen gas mixtures.

2.3.2. Verification of old primary standard gas mixtures by NDIR method

The NDIR analyser is a commercial instrument designed to measure the intensity of infrared light that passes through the sample cell with gas molecules of interest. The reference cell which holds the zero gas with a trace of no amount of CO analytes (Lee et al., 2006). It has high sensitivity, low detection limits and simple to use. NDIR analyser was calibrated with six PSGMs, $x_{CO\ cert}$, ranging from 1 to 10 µmol.mol^{-1} using a multi-point calibration method. Each cycle in the three-consecutive cycles included

three measurements of the sample and the PSGMs. The CO molecules from the PSGMs were introduced into the sample cell from an automatic 16-port mass flow controller (MFC). A pressure reducer connected to the cylinder and polyethylene tube connected to the MFC were flashed several times for repeatable measurements. The flow of the sample and pure BIP^{TM} N_2 gas were alternated in the cell during CO measurement. Prior to the analysis, the analyser was validated, to set optimum measurement condition to determine the absorbance of CO in the sample cell related to the existing partial pressure inside the cell. The obtained response resulting in the differences in CO amount fraction between the PSGMs, the CCQM CO sample gas and the BIP^{TM} N_2 confined in the two cells were amplified. The differential voltage was integrated and moved to the computer. The nominal value of the calibration standard gas mixtures is listed in **Table 2**. The gas standards are denoted as CF1 to CF6. The NDIR data was evaluated using XLGENLINE 1_1 software, a computer programme developed by National Physical Laboratory (NPL software). The programme implements a methodology of consideration the uncertainties in both the x and y-axes that represents the gravimetric value with its standard uncertainty, and the analyser response with its standard uncertainty. The sample response time of the analyser was set at 100 s with several pressure and sample reading set at 30, and 90 seconds. The analyser response value was determined after 3 number of runs with cylinders positioned randomly.

Table 2. Gravimetric value of CO gas mixtures used as primary standards.

Cylinder Number	*Cylinder Symbol*	*Amount fraction*[a] $x_{CO\ cert}$ / *µmol.mol*$^{-1}$
M93784	**CF1**	1.02 ± 0.020
M93904	**CF2**	2.00 ± 0.0053
D958415	**CF3**	4.00 ± 0.0060
M555695	**CF4**	5.99 ± 0.0060
M93871	**CF5**	8.01± 0.012
D555672	**CF6**	10.00 ± 0.0060

[a]Expanded uncertainty, $u\ (x_{CO\ cert})$ / µmol.mol^{-1}

2.3.3 Verification of the primary standard gas mixtures by GC-FID measurement system.

Gas Chromatography with methanator-flame ionization detector was used for the precise measurements of CO in nitrogen gas mixtures in this study (**Figure 2**). Pressure reducers without the gauge, to reduce the unexpected contribution of gases tied in the dead volume, were connected to the gas cylinders, and flushed several times to remove any contaminations. A 16-port sampler box equipped with a calibrated mass flow controller (MFC, M17203188F Bronkhorst, Holland) set at 35 mL.min^{-1} and 1.58 mm (Swagelok, SA) stainless steel line continuously flushed the 2 mL.min^{-1} sample loop and analytical column with the gas mixture. This was done to produce repeatable measurement values after the analytes were swept with purified N_2 carrier gas. A molecular sieve 5Å packed stainless steel column (80-100 mesh, 2m) separated the CO analytes from any other present gas components according to its molecular weights. The temperature oven was set at 160℃ isothermal. The detector operated at 186℃, detected the converted CO eluent as CH_4 after passing through the methanator set at 375℃. The detector flame was engine by pure gases of 20 mL.min^{-1} hydrogen and 300 mL.min^{-1} synthetic air flow. A CO chromatogram was recorded using the signal intensity of the flame ionization detector (Lim et al, 2013). A comparison method used verified the contents of the prepared

gas mixtures at trace level. In this procedure, a series of measurements performed whereby one PSGM selected as the control cylinder, alternated between the analytes of the remaining sample cylinders. This method was selected because the instrumental drift can be monitored as a ratio value. The ratio value is a product of the deviation between the average instrumental response, $\underline{Ctrl,}$ deduced from the final control (C_2) and the first control cylinder (C_1). The gas mixtures were analysed using online and sequence method (**Figure 4a-c**).

Table 3. The analytical conditions used for the GC-FID system.

Parameters	***Conditions***
Column type	Molecular sieve 5 A 80/100 mesh, 2m, 1/8
Column oven temperature	160 ºC, isothermal
Detector	FID
Detector temperature	186 ºC
Carrier gas	N_2
Carrier gas flow	50 mL/min
Sample flow	35 mL/min
Sample loop	2 mL
Methanator temperature	375 ºC
Total run time	3 min

3.Results and discussion

3.1 Purity analysis of pure BIP^{TM} N_2 and CO source materials

Table 1 list the amount of CO and N_2 detected in the pure nitrogen and carbon monoxide cylinder at trace level. A N_2 in He gas standard certified at 179 µmol.mol^{-1}. was used to identify the amount fraction of nitrogen in pure CO by comparing the retention times of the obtained N_2 peak. The CO impurity was found as 0.007 ± 0.008 µmol.mol^{-1} in pure N_2 while the nitrogen impurity was detected as 1.05 ± 0.10 µmol.mol^{-1} at 3.5 min in pure carbon monoxide gas as depicted. The impurity value values were accepted

as incorrect quantification may have an impact in the final uncertainty of the gas mixture. Each value was therefore added in the final gravimetric values of the gas mixtures.

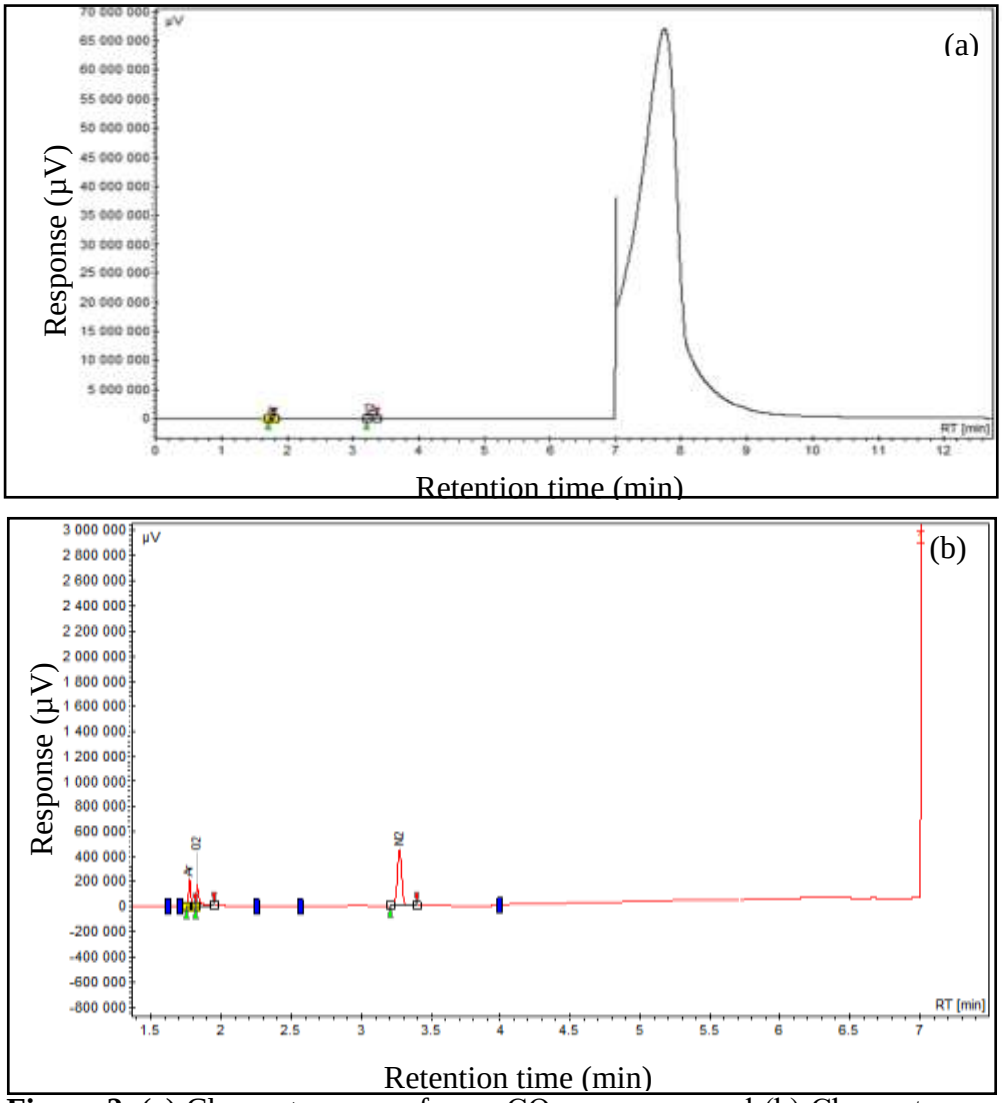


Figure 2. (a) Chromatograms of pure CO source gas and (b) Chromatograms' of impurities of Ar, O_2 and N_2 in pure CO starting material.

3.2 Internal consistency evaluation of the Primary Standard Gas Mixtures

Table 3 shows the amount fractions of the PSGMs with its associated expanded uncertainty for cylinders CL1-4 and CS1-4 prepared by the gravimetric technique.

The target value of the gas mixtures prepared in 2007 is within the range of the PSGMs CL1 to CL4 and CS1 to CS3 cylinders. To check for mismatch in the gravimetric procedure and calibrate the GC-FID analyser with methanator, the area under the curve corresponding to $x_{CO\ Cert}$ were measured in three consecutive measurement cycles (Oh et al, 2001). Because the FID is a linear technique, a single point calibration method was the preferred method where CL4 was chosen as the control cylinder that was used to check the instrumental drifts due to atmospheric changes (Zuas and Budiman 2017, Dressler 1986). The highest drift obtained in a measurement cycle was 0.84 %. This value was acceptable because it was less than 1 %. A measurement sequence *control (CL4) – sample$_1$ (CL1) – control (CL4) – sample$_2$ (CL2) – control (CL4) – sample$_3$ (CL3) – control (CL1)* bracketed the analysed sample with CL4. A single measurement of the control had four replicate injections (Rhoderick, 2008). Ratio defined as sensitivity value (average instrumental response/gravimetric value) of the control divided by the corrected sensitivity value of the sample was first calculated.

During the analysis, there was a significant difference in the peak areas. The average peak areas varied between 230 to 235 and 1787. The variation in the peak area resulted from an unidentified peak that appeared after 1.8 min (**Figure 3 a**). When high amount fraction range of CO was analysed, the unidentified peak was not visible. This had a negative impact on the peak area, CO eluting time and measurement precision. The peak height was small compared to what was expected and the retention time (after 3 minute) of the carbon monoxide chromatogram was longer when compared to the previous data. The highest precision of 1.20 % was obtained that showed that the instrument was not precise. After modification of the

analytical instrument, the peak height increased, and the peak eluted earlier (after 2 min). The repeatability of the measurement system improved as a percentage relative standard deviation of less than 0.8 % was obtained (**Figure 3b**). **Figure 4a-b** shows a graphic illustration of 2016 PSGM ratios obtained and the error bars associated with the sensitivity ratio uncertainty at 95 % confidence level were the coverage factor k=2.

Figure 4a-c illustrates the internal consistency graphs of the gas composition within the aluminium cylinder that were compared in different days. The values on the line indicate good internal consistency the sample cylinder where the sensitivity ratio for CL4 was estimated to be equal to 1. The highest deviation between the sample and control ratio was 0.80 % for sample CL2 while the lowest was 0.06 %. **Table 4** lists the amount fraction for the two PSGM with its associated standard uncertainty calculated by the GUM Software. The software inputs included the average instrumental response of control and sample cylinder, gravimetric amount fraction and expanded uncertainty of the control cylinder to yield an estimated sample amount fraction as explained in equation 3:

$$x_{veri,PRGM} = x_{CO\ cert\ control} * \frac{Av_{CL\ j}}{\underline{Ctrl}} \quad (3)$$

where $Av_{CL\ j,}$ is the average instrumental response of the sample CL_j j = 1,2,3, $\underline{Ctrl}$, is the average instrumental response of the CL4 before and after bracketing the sample and $x_{CO\ cert\ control}$ is the gravimetric amount fraction of the CL4.

The following model equation determined the verification uncertainty of the unknown gas mixture after estimation:

$$u_{Ver,PRGM} = x_{CO\ cert\ control} * \frac{Av_{CL\ j}}{\underline{Ctrl}} * \sqrt{\frac{u\,(x_{CO\ cert\ control})^2}{x_{CO\ cert\ control}} + \frac{u(\underline{Ctrl})^2}{\underline{Ctrl}} + \frac{u(Av_{CL\ j})^2}{Av_{CL\ j}}} \quad (4)$$

where $u\,(x_{CO\ cert\ control})$ is the uncertainty from the gravimetric standard uncertainty of the PSGM, $(\underline{Ctrl})$, $u(Av_{CL\ j})$ experimental standard deviation of the mean of the standard and unknown sample (Lim et al, 2013).

The method of obtaining the CO value was carried out over three days. The analytically assigned amount fraction of CO with a relative standard uncertainty of 0.6 % was derived from the software. The $|x_{CO\ cert} - x_{Anal,PRGM}|$ values were smaller than $2\sqrt{u_{CO\ Cert}{}^2 + u_{Anal}{}^2}$ values indicating the amount fractions of CO at 5 μmol.mol^{-1} were internally consistent and preparation of the standard gas was successful (Kim et al 2018). The values passed the acceptance criteria.

Table 3. Amount fraction and expanded uncertainty of the prepared PSGMs prepared in 2015 and 2018.

Cylinder Number	*Cylinder Symbol*	*CO amount fraction* $x_{CO\ cert}$ / *μmol.mol*$^{-1}$	*Manufactured date*
M93923	**CL1**	5.02 ± 0.003	2015
M93824	**CL2**	5.00 ± 0.003	2015
M93833	**CL3**	5.00 ± 0.003	2015
M93965	**CL4**	4.99 ± 0.003	2015
D631097	**CS1**	4.97 ± 0.0057	2018
D631091	**CS2**	5.00 ± 0.0075	2018
D626416	**CS3**	5.00 ± 0.0057	2018

*The expanded uncertainty of the gas mixtures that were prepared in 2015 are the values decided after the CCQM-K51 study due to a large variation in the gravimetric uncertainty reported from participated laboratory.

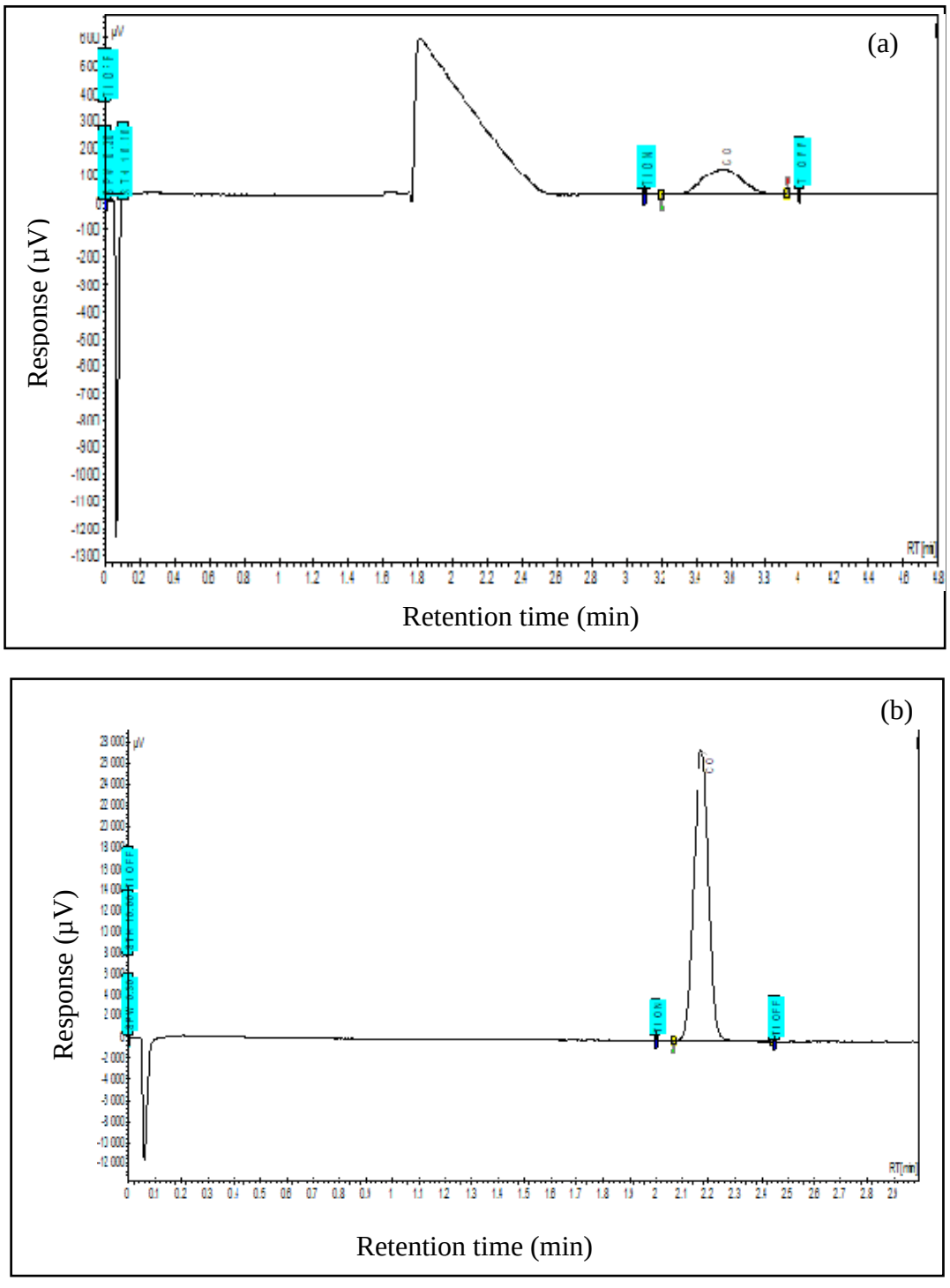
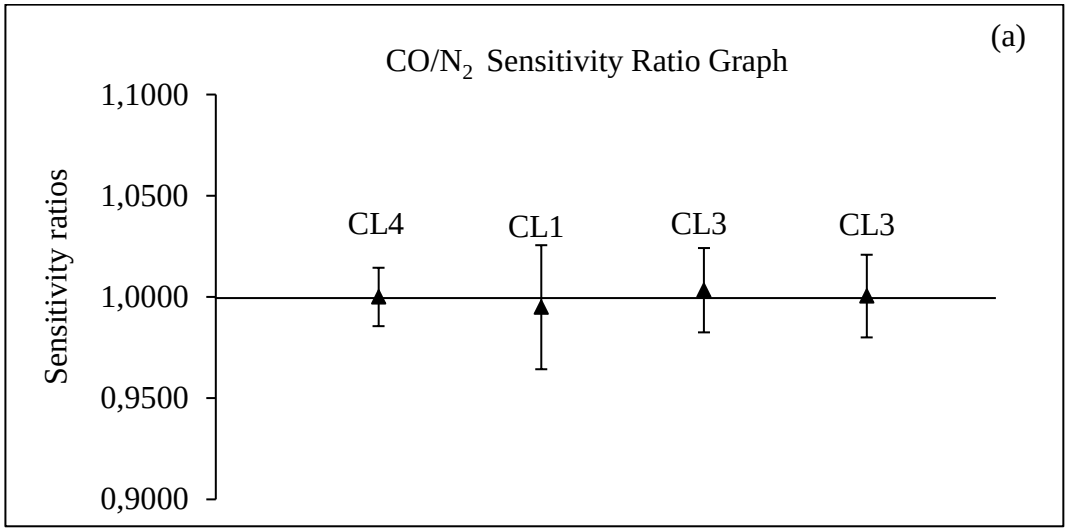
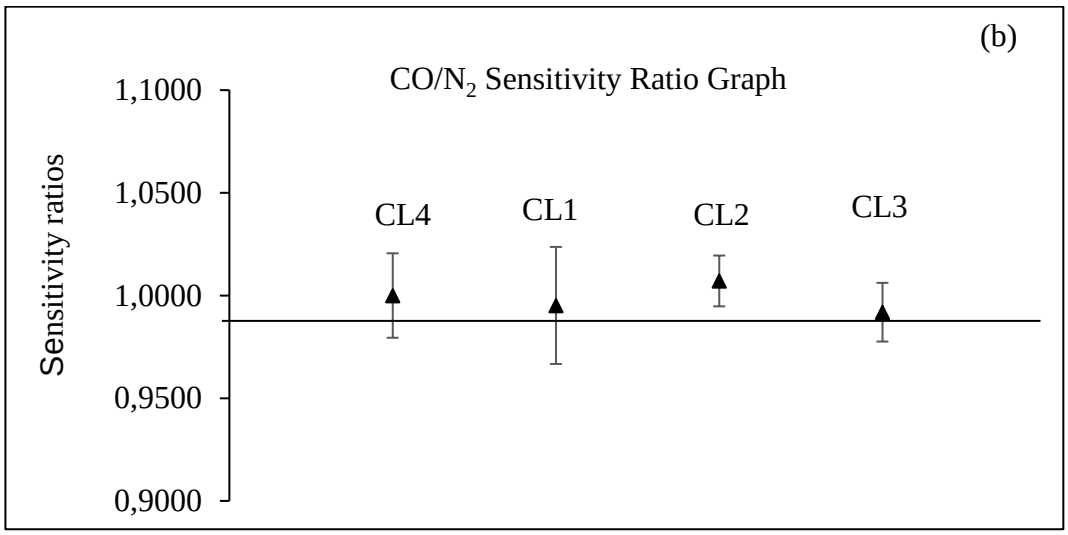


Figure 3 a-b. Chromatogram of 5 µmol.mol^{-1} CO in N_2 under different conditions.





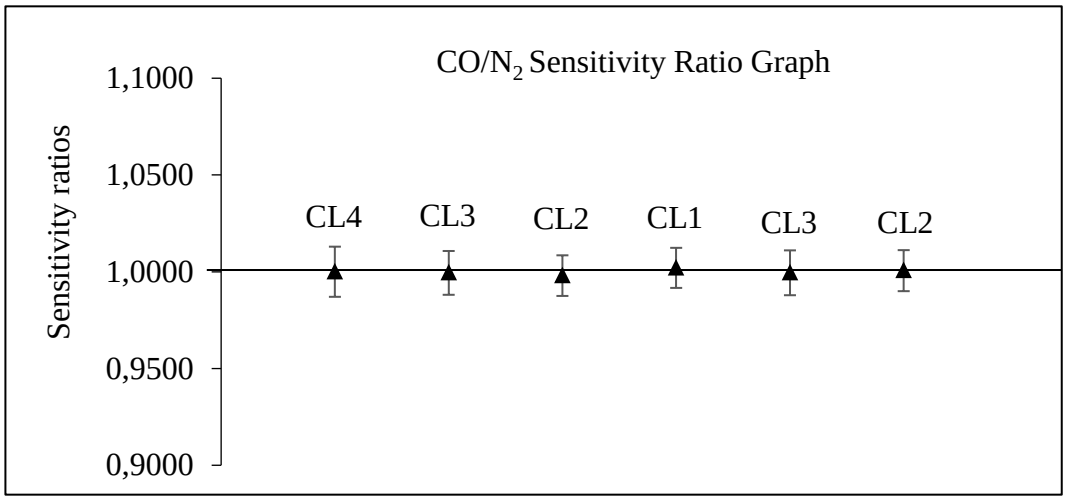


Figure 4 (a-c). Sensitivity ratios of the 2015 PSGMs.

(c)

Table 4. Estimated amount fraction of CO sample with the uncertainties.

Sample	***CO amount fraction*** $x_{CO\ anal}$ / ***μmol.mol^{-1}***	***Expanded uncertainty*** $U(x_{CO\ anal})$ / ***μmol.mol^{-1}***	***Coverage factor***	$\lvert x_{grav} - x_{Anal,PRGM} \rvert$	$2\sqrt{u_{CO\ Cert}{}^2 + u_{Anal}{}^2}$
CL1	5.01	0.10	$k = 2$	0.004	0.10
CL2	5.00	0.09	$k = 2$	0.010	0.09
CL3	5.00	0.11	$k = 2$	0.007	0.10

3.3 Verification of the primary standard gas mixtures

The content of CO inside the cylinder after years of preparation was rechecked to reconfirm its long-term stability. The standard gas mixtures had been verified in 2015 than 2018 on the NDIR and GC-FID with methanator methods. NDIR measurements in 2016 were measured by testing the relationship between the amount fraction of CO molecule ($x - axis$) and the absorption in the infrared region, ($y - axis$), based a regression analysis performed off-line by the XLGENLINE 1_1 software developed for the application of ISO 6143 (2001). Since NDIR is a non-linear technique, its instrumental drift was compensated for by a linear calibration curve from the adequate range of standard gas mixture signal obtained following the second-order polynomial fit (**Figure 5**). A correlation coefficient R^2 = 0.99999 obtained indication good linearity between x and y–axis values. The calculated amount fraction of CO samples is shown in **Table 5** proved good preparation of the CO samples.

After the procurement of the new automatic weighing system, a new set of 5 µmol.mol^{-1} CO PSGMs in 10-L volume was produced. The aim of repreparation of the standards gas mixtures was to replace the 2016 set of CO-in-nitrogen PSGMs because the internal pressure had reduced below 5 MPa. The control cylinder CL4 bracketed the new set of CO-in-nitrogen PSGMs on the GC-FID with methanator under similar measurement conditions explained in **Table 1**. **Figure 6** shows a plot of the ratios obtained from the average peak area and the sensitivity expanded uncertainty. When the old PSGM, x_{PSGM} cylinder, was reanalysed in 2018 on the GC-FID, were the analysis was calculated as standard uncertainty equal to 0.4% for both measurements respectively. **Table 5** shows the results of the old PSGM cylinders, prepared in 2006 as part of the CCQM K51, after treating as unknown cylinders. The three unknown cylinders where identified as ITC-1 to ITC-3 after confirming the CO contents by NDIR and GC technique. **Table 6** shows the uncertainty budget for CO amount fraction for one measurement cycle obtained from the GUM software after incorporating equation 3.

Table 5. Results of the old primary standard gas mixtures re-analysed in 2018.

Cylinder Symbol	*CO amount fraction* x_{PRGM} / *µmol.mol^{-1}*	*NDIR* y_{PRGM} / *µmol.mol^{-1}*	*GC-FID* y_{PRGM} / *µmol.mol^{-1}*
ITC-1	5.01	5.00	Not analysed
ITC-2	5.01	6.04	Not analysed
ITC-3	5.01	5.01	5.00

* not analysed

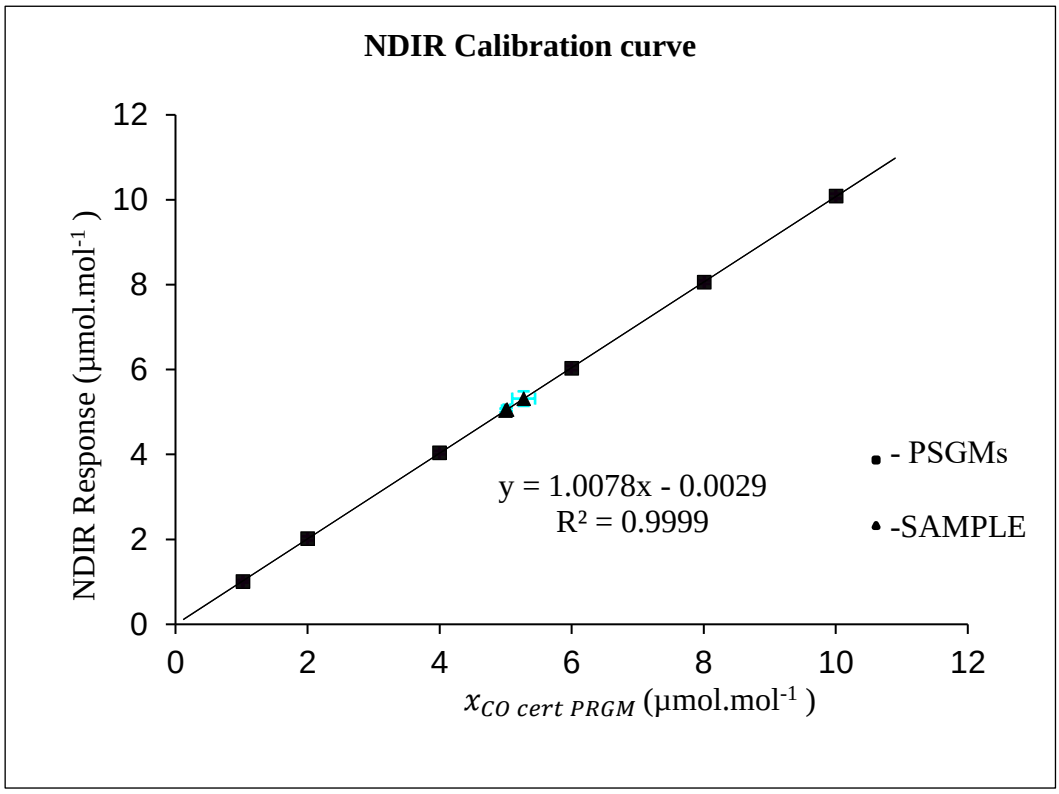


Figure 5. NDIR linear calibration curve of CO PSGMs at different range.

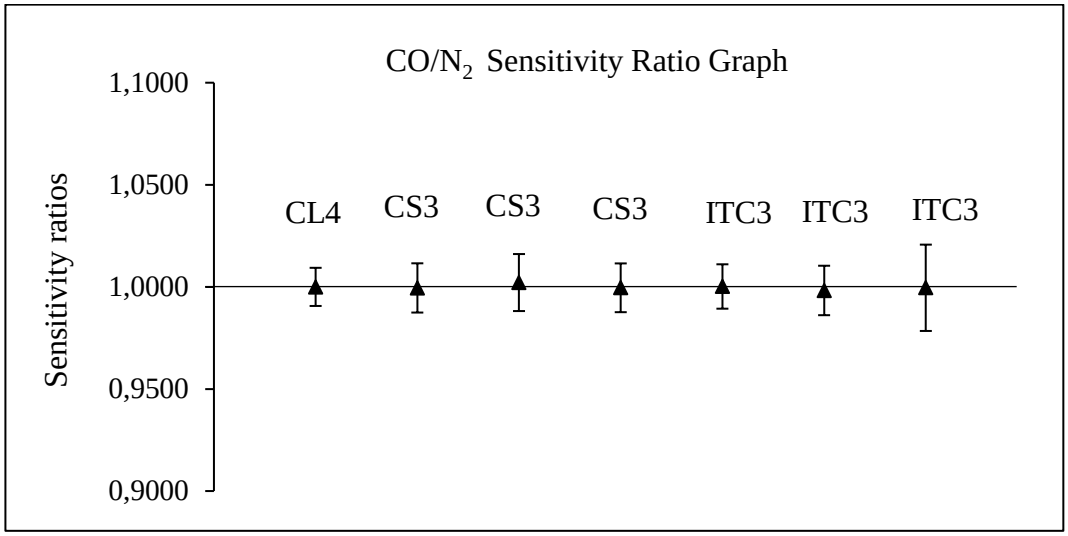


Figure 6 Sensitivity ratio of the PSGM and PRGM over three measurement cycles.

Table 6. Uncertainty budget for CO PRGM representing one cycle of analysis.

Quantity	*Estimate*	*Statistical distribution*	*Standard uncertainty (%)*	*Combined standard Uncertainty (µmol.mol^{-1})*	*Expanded uncertainty (µmol.mol^{-1})*	*% Relative Uncertainty*
$Av_{CL\,j}$	151.92	Type A	0.315			
$\underline{Ctrl}$	152.33	Type A	0.025			
$x_{CO\ cert\ control}$	5.02	Type B	0.003			
$x_{Anal,PRGM}$	5.0023		0.31	0.0155	0.032	0.631

3.4 High accurate measurement of CO PRGM after 11 years of preparation

Each participant verified the gas mixture as unknowns at their respective laboratories using their own calibration gas mixtures and analytical instruments. After assigning a value, the cylinders were returned with pressure enough to the NMISA gas laboratory for a second verification. As part of the protocol, each participant sent a measurement report that explained their verification process. The final report of CCQM K51 (2007) includes a plot of measurement results obtained during the study that compares the degree of equivalence to the gravimetric reference value between the participants (**Figure 7**). The x-axis shows the lists of participants while the y-axis shows a deviation between the reported amount fraction from a participant and the gravimetric reference value of the gas mixture certified at NMISA in percentage. The conclusion drawn from this study was that the cylinders showed agreement with the reference value of 1 % relative expanded uncertainty.

To test for the long-term stability of CO in the cylinder, a cylinder that was sent to a one of the participants during the comparison study was verified against freshly prepared standard gas mixtures using two independent measurement systems. After calibration of the gas mixture on the NDIR and GC-FID systems, the cylinder was re-assigned a value estimated from the calibration curve defined by the consistent standard gas mixtures.

Figure 8a and b show the long-term stability results of the CO amount fraction maintained after 11 years of preparation. In **Figure 8 (a)**, the assigned amount fraction obtained from 2008 to 2018 is represented by the black dots. The error bars correspond to the standard uncertainty of the assigned value. All the assigned values are within the acceptable limits derived from 1% upper and lower limits from the true value (gravimetric value). When the NDIR analyser was used to verify the gravimetric value of the old PSGM, large standard uncertainty 0.05 µmol.mol $^{-1}$ was obtained. This is represented by the July 2015 measurement results. For measurements performed on the GC-FID with methanator, small standard

uncertainties were obtained as 0.01, 0.008, 0.006, and 0.021 µmol.mol $^{-1}$ over the years of analysis. In **Figure 8b**, the x-axis represents the time of measurement in years and the y-axis is explained as:

$$\delta_{x_{veri,y}} = x_{veri,y} - x_{grav} \quad (4)$$

where $x_{veri,y}$ is the predicted amount fraction of the reference gas mixture, y is the different years of analysis and x_{grav} is the gravimetric value of the reference gas mixture. The error bars agree to the expanded uncertainty of each data. The $\delta_{x_{veri,y}}$ values obtained (0.0137, 0.003, 0.0001 and 0.000063) are close to zero. Only 2007-2008 data where the $\delta_{x_{veri,y}}$ value is slightly higher than the gravimetric standard uncertainty (0.003) of the reference gas mixture. Based on this assumption, the $\delta_{CO\ insta}$ value in Equation 1 is equal to zero and its associated uncertainty, $u^2_{CO\ insta}$, in Equation 2 is 0.01 µmol.mol $^{-1}$ based on the maximum value of $\delta_{x_{veri,y}}$. The final amount fraction of the old gas mixture prepared 11 years ago is certified at 5.01 ± 0.05 expanded uncertainty respectively. These results prove that the gas mixture is very stable in the aluminium cylinder.

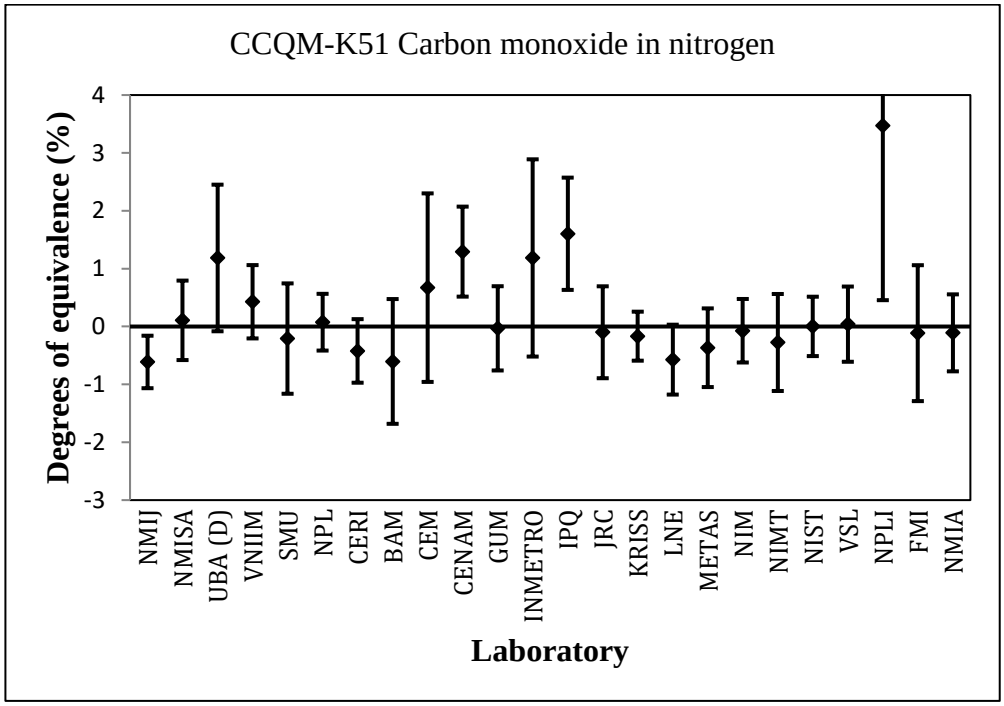
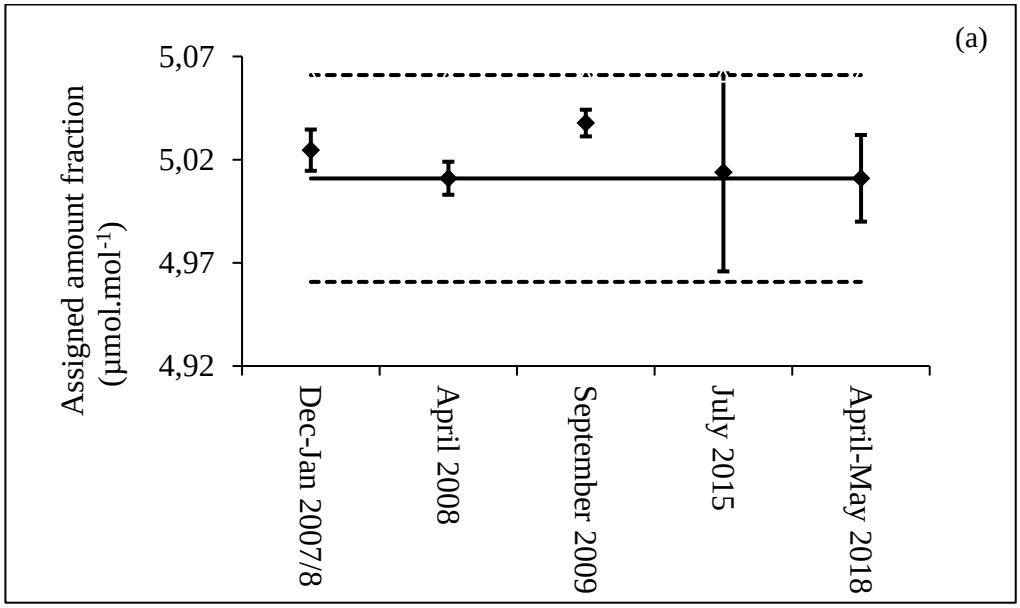


Figure 7. Results comparing the laboratories and the reference value from CCQM-K51 CO in nitrogen study. The comparison study shows that the most laboratories values lie within the reference value determined by $D = x_{laboratory\ value} - x_{reference\ value}$.



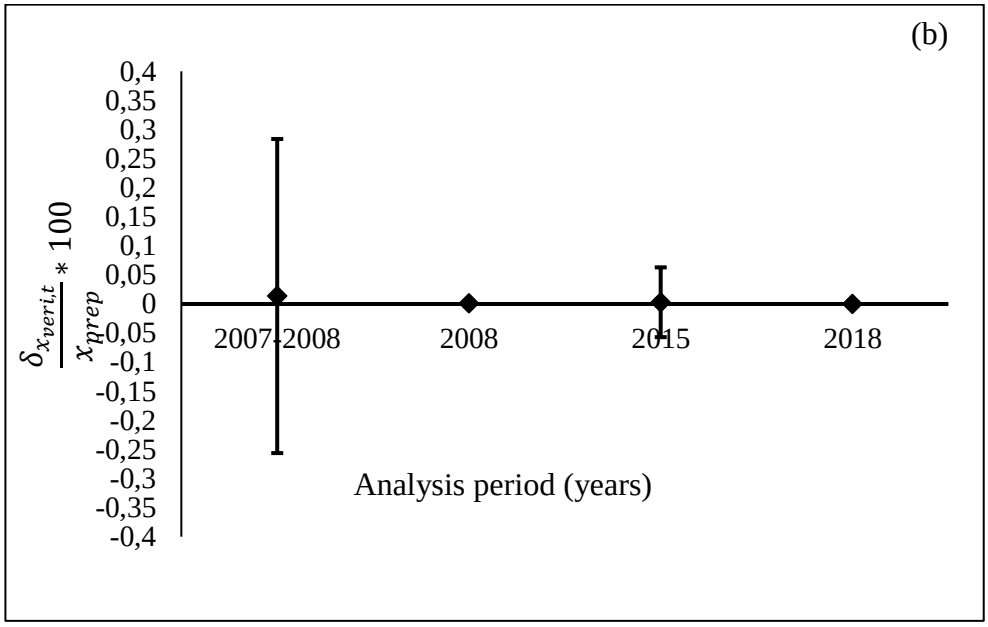


Figure 8a and b. Results of CO PSGMs long-term stability study. The solid line represents the true value. The dotted lines in graph (a) represents the upper and lower limits.

4. Conclusion

The certification of an old primary reference gas mixture against freshly prepared standard gas mixtures was successful. In this study, small uncertainties were obtained when the GC-FID with methanator was used to verify CO gas mixture as compared to NDIR method. Based on the results obtained both measurement techniques can still be used to verify the amount fraction of CO gas mixtures as similar gravimetric values. Out of 25 participants during the comparison study, more than 70% participants result showed a degree of equivalence to the gravimetric reference value. The relative expanded uncertainty (k=2) of the final value is 1% which agrees with the uncertainty value obtained in the previous study. The developed gas mixtures can be used to support various regional air monitoring companies and laboratories.

5. Acknowledgements

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Paper V

Lushozi S, Tshilongo J, and Chimuka L. Development of Carbon monoxide reference gas mixtures at ambient level by gravimetric method *Manuscript.*

Lushozi – 50 % (performed the experiments and wrote the manuscript);

Chimuka – 25 % (supervisor, reviewed the manuscript)

Tshilongo – 25 % (co-supervisor, reviewed the manuscript)

Development of carbon monoxide reference gas mixtures at ambient level by gravimetric method

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Abstract

With a short-lived lifetime in the atmosphere, carbon monoxide has an influence in enhancing the amount fraction of other greenhouse gases (CO_2, CH_4 and O_3) in the atmosphere during its reaction with OH radical groups. In this way, CO indirectly contributes to the global climate change. This reactive gas is monitored at globally at different institutions and is reported at trace micro-mole per mole nominal levels. Developing accurate, stable and traceable CO standard gas mixtures at ambient level is important for tracking the amount fraction distribution and variation of the greenhouse's gases in the atmosphere. For calibration of gas instruments used to monitor CO emissions primary standard gas mixtures prepared with internationally traceability SI unit is needed. In this study, standard gas mixtures at 0.350 µmol.mol $^{-1}$ CO in nitrogen and synthetic air were produce and verified using chromatography method with methanator and flame ionisation detector. The mixtures were prepared with a final expanded uncertainty of 0.02 µmol.mol $^{-1}$. The gas mixtures were consistent with a difference between the amount fraction of less than 0.5%. The short-term stability test shows that the composition of CO was very stable in both matrixes.

Keywords: carbon monoxide, primary standard gas mixtures, ambient measurements, stability.

1. Introduction

Carbon monoxide (CO) is formed when CO-containing fuels are burnt incompletely. Its amount fraction in the atmosphere is short-lived but through natural processes, CO oxidizes to carbon dioxide. CO has an indirective radiative forcing effect which elevates the amount fraction of CH_4 and tropospheric ozone by chemically reacting with hydroxyl radicals in the atmospheric (Velychko and Gordiyenko, 2011). The amount fraction of CO in the troposphere is influenced by anthropogenic activities namely deforestation, burning of waste, transport and fuel. For many years, the content of CO in the atmosphere has been verified using different techniques such as spectroscopic methods and chromatography with a methanator for conversion of CO to methane. (Novelli, 1999). The flame ionisation detector of the gas chromatography then detects the product methane and this technique has been used for many years to measure CO amount fractions. It has been researched that in urban areas, CO concentrations occur at micromole per mole (μmol/mol) levels due to emissions from automobile exhausts and industries. In areas far from anthropogenic activities such as background areas, the amount fraction of CO is much lower than those in urban areas. It is well documented that there is the amount fraction latitude gradient where the average CO level in the northern hemisphere is almost double that in the southern hemisphere (Zellweger et al 2009). CO levels in both hemispheres varies by seasons. In the northern hemispheres, the abundance of CO varies between 30 $nmol.mol^{-1}$ in summer and 96 $nmol.mol^{-1}$ in winter (Dentener et al 2001). While measurement in the southern latitude CO levels varies from 4530 $nmol.mol^{-1}$ during summer and an average maximum of 70 $nmol.mol^{-1}$ in the spring (Novelli et. al 1991). Measurements of such pollutant play a key role in the attempt of understanding temporal trends and regional deviations of the level of CO as these changes affect the amount of CH_4 that oxidizes with the hydroxyl radical. The overall oxidation capacity of the atmosphere will also be understood by the air monitoring community worldwide. In fulfilling the reasons above the National Oceanic & Atmospheric

Administration/Earth System Research Laboratory-Global Monitoring Division (NOAA/ESRL-GMD) as a designated Central Calibration Laboratory has played a key role of providing standards with natural air at a set uncertainty of ±2 nmol.mol^{-1}. NOAA, under the World Meteorology Organization Global Atmospheric Watch (WMO GAW) program, provides the standards to the WMO GAW networks (such as Cape Point station in the southern hemisphere) to measure the level of CO in the atmosphere. However, accurate quantification of CO at ambient level by different laboratories has been proven to be significantly different due to the nonexistence of stable standard scales with harmonised uncertainties (Tanimoto et al 2007, Novelli et al, 1998). To support the WMO-GAW activities and other CO monitoring and measurement community an international key comparison, Consultative Committee on the Quantity of Material K84, (CCQM-K84) between WMO and other National Metrology Institutes was implemented. The key comparison study was coordinated by the Korean Research Institute of Standards and Science (KRISS) where a set of approximately 350 nmol.mol^{-1} CO in air reference gas mixtures was gravimetrically prepared and disseminated to several participants. The aim of the international key comparison was to compare the assigned/ analysis value defined by KRISS against the value obtained by the participating laboratories. This process establishes a traceability chain to a single scale of CO between NMIs by harmonizing the results from different standards. The National Metrology Institute of South Africa did not participate in this key comparison therefore, this work describes the preparation and verification of a set of a primary standard gas mixture of CO in synthetic air and nitrogen balance at a nominal amount fraction of approximately 0.350 µmol.mol^{-1}.

2. Materials and methods

2.1 Materials

2.1.1 High purity gases

The source materials used to prepare the standard gas mixtures were highly purity gases CO (99.997%), CO_2 (99.995%), Built-in Purifier technology (BIP^{TM}) N_2 (99.9997%), O_2 (99,9995%). Air Products South Africa supplied all starting materials. Before gravimetric preparation of the standard gases, impurities in source materials were quantified since the impurities contribute to the uncertainty of the amount fraction. Gas chromatography coupled with different detectors such as pulse discharge helium ionization detector (PDHID), thermal conductivity detector (TCD) and flame ionization detector with methanator (FID) was used for the detection of Ar, O_2, N_2, CO_2, CO and CH_4. After quantification of the impurities, the amount fraction for the source material was established as follows:

$$x_{pure} = 1 - \sum_{s=1}^{N} x_i \quad (1)$$

where x_s is the amount fraction of impurity s, determined by analysis, N is the number of impurities likely to be present in the final mixture, and x_{pure} is the amount fraction of the source material. The amount fractions of the non-detectable impurities were determined when the limit of detection is divided in 2, and the standard uncertainty was calculated when the assigned amount fraction was divided by square root of 3 e.g., (LOD/ (2·√3)) (ISO 6142-1, 2015). The compositions of the pure gases are summarized in **Table 1** only showing the major impurities such as CO, Ar, N_2 and O_2 with the uncertainties. and. The gravimetric preparation of the standard gas mixtures is explained in the next section and the uncertainty is reported as expanded uncertainty ($U_{95\%}$) and is calculated from

$$U_{95\%} = u * k \quad (2)$$

where k is the coverage factor 2 at 95% confidence level and (u) is the standard uncertainty.

Table 1. Purity table of the source materials used.

Component	***Distribution***	***Amount fraction (µmol.mol^{-1})***	***Expanded Uncertainty (k=2)***	***Analysis Technique***
(a) CO		**999995.3**	**0.04**	
O_2	Rectangular	2.50	2.89	*
N_2	Normal	1.05	0.10	GC-PDHID
H_2O	Rectangular	1.50	1.73	*
H	Rectangular	0.50	0.58	*
CH_4	Rectangular	1.00	1.15	GC-FID
Ar	Normal	0.16	0.02	GC-PDHID
CO_2	Rectangular	0.50	0.58	GC-FID
(b) N_2 BIP^{TM}		**9999.5**	**6.0**	
Ar	Normal	52.89	5.23	GC-PDHID
CO	Rectangular	0.0070	0.0081	GC-FID
CO_2	Rectangular	0.0115	0.013	GC-FID
CH_4	Rectangular	0.0043	0.0050	GC-FID
C_2H_6	Rectangular	0.0070	0.0081	GC-FID
O_2	Rectangular	0.0050	0.0058	*
H_2O	Rectangular	0.010	0.012	*
H_2	Rectangular	0.0090	0.010	*
(c)Argon BIP		**999999.90**	**0.032**	

N_2	Rectangular	0.0070	0.0020	GC-PDHID
CO	Rectangular	0.021	0.0243	GC-FID
CO_2	Rectangular	0.0098	0.011	GC-FID
CH_4	Rectangular	0.0058	0.0070	GC-FID
O_2	Rectangular	0.0050	0.0060	*
C_2H_6	Rectangular	0.0061	0.0070	GC-FID
H_2O	Rectangular	0.0100	0.012	*
N_2	Rectangular	0.0070	0.002	GC-PDHID
(d) O_2		**999995.12**	**3.70**	
N_2	Normal	2.00	2.31	*
CO	Normal	0.26	0.079	GC-FID
CO_2	Normal	0.11	0.032	GC-FID
CH_4	Rectangular	0.0060	0.0069	GC-FID
C_2H_6	Rectangular	0.0060	0.0069	GC-FID
H_2O	Rectangular	0.0010	0.0012	*
Ar	Rectangular	2.50	2.89	*

2.2 Analytical Method

2.2.1 Gravimetric preparation of carbon monoxide primary standard gas mixtures.

Four standard gas mixtures in the synthetic balance of O_2, Ar and N_2 were developed in five-step dilutions by the gravimetric method according to ISO 6142-1 (2015). The first step involved the preparation of the standards at 1% level. Pure O_2, N_2 and diluent Ar in nitrogen balance were added into the CO/N_2 cylinders to attain ambient level in synthetic air. Carbon monoxide standard gas mixtures at a nominal amount fraction of 0.350 µmol.mol^{-1} were also prepared in nitrogen balance. **Figure 1** shows the production diagram of the standard gas mixtures. The composition of the

gas mixtures in synthetic air was selected based on the dry air composition in monitoring sites that were measured and now used for the WMO-GAW program (Park et al. 2004). The standards were prepared at nominal amount fractions of 0.350 μmol.mol^{-1} of CO. The amount fractions of CO in the final standard gas is shown in **Table 2** denoted as DM1 to DM4 and CM1 to CM4. A high accuracy mass comparator balance (Mettler Toledo PR10003; capacity 10 kg; readability; 1 mg) placed in a room where temperature and humidity at 22 ± 1 °C and 50 ± 5 % was used to fulfil the weighing process. Aluminium cylinders with a 5 L internal volume were cleaned, externally, to remove dust particles and evacuated to 1 x 10^{-7} Pa pressure at 60°C using a Pfeiffer turbomolecular pump system. Using the Borda - substitution method according to ISO 6142-1, (2015), the sample cylinders were weighed against a tare cylinder to correct for buoyance from ambient air pressure. According to Alink and van der Veen (2000), the tare cylinder is not evacuated as its purpose is to reduce the corrections required in the weighing results of the sample cylinder. The sample cylinders (D1 to D4) were placed on a top loader balance (Mettler Toledo SB12001) to connect to a stainless-steel line on the filling station. A pre-calculated mass of 5 μmol.mol^{-1} CO in N_2, 20 % Ar in nitrogen pre-mixtures, and pure O_2 were transferred into the cylinder as gas component 1,2 and 3 then weighed after filling of each gas. Pure N_2 gas was added as a balance to complete the gas mixtures in synthetic air and after a minimum of two hours the cylinders were weighed again and rolled on the roller bench to obtain optimal homogeneity. The PSGMs in nitrogen (CM1 to CM4) was prepared as binary mixtures were CO and N_2 gas were added in the cylinders. The standard gas mixtures were weighed on the single-pan mass comparator balance (Mettler Toledo PR10003; capacity 10 kg; readability; 1 mg) and during weighing of the sample and tare cylinders certified mass pieces were added to compensate for any mass difference between the two cylinders. The contents of reference cylinders were analyzed on the GC-FID-methanator for validation purpose. The amount fraction of CO in the final mixture is computed as follows:

$$x_i = \frac{\sum_{A=1}^{P}\left(\frac{x_{c,A}\,.\,m_A}{\sum_{c=1}^{n} x_{c,A}\cdot M_A}\right)}{\sum_{A=1}^{P}\left(\frac{m_A}{\sum_{c=1}^{n} x_{c,A}\cdot M_c}\right)} \qquad (3)$$

where x_c is the amount fraction of constituent c in the final mixture, P is the total number of raw materials, n is the total number of constituents in the final mixture, m_A is the measured mass of the parent gas A, M_c is the molar mass of constituent c, $x_{c,A}$ is the amount fraction of constituent c in the parent gas A.

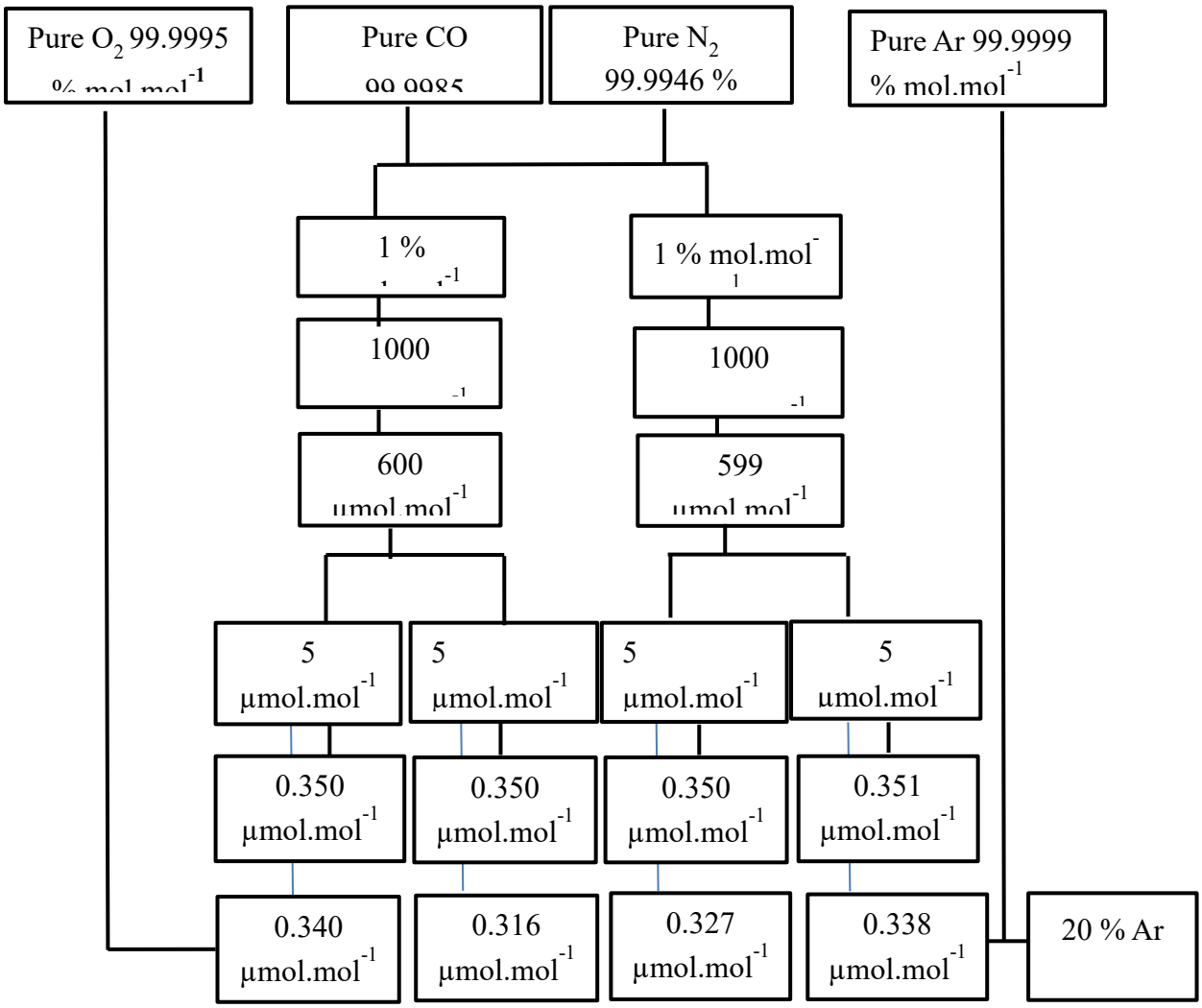


Figure 1. Production diagram of CO in synthetic air.

Table 2. Gravimetric value and expanded uncertainty in calibration standards.

Cylinder numbers	***Cylinder symbol***	*CO* *(µmol. mol^{-1})*	*Uprep* *(%)*	*Ar* *(% mol/mol)*	*O_2* *(% mol/mol)*	*N_2* *(% mol/mol)*
M93912	**CM1**	0.351	2.69			
M51804	**CM2**	0.350	2.70			
M93964	**CM3**	0.350	0.96			
M93779	**CM4**	0.351	0.96			
M93922	**DM1**	0.327	2.65	0.9466	21.03	78.03
M93881	**DM2**	0.316	2.96	0.9301	21.02	78.04
M93906	**DM3**	0.340	2.76	0.9387	21.42	77.64
M93836	**DM4**	0.338	2.80	0.9409	20.97	78.09

2.2.2 Verification of standard gas mixtures in synthetic air and nitrogen

The CO content in the four standard gas mixtures was compared using the Agilent 7890B gas chromatography methanator coupled with the flame ionisation detector (GC-meth-FID) to determine the systematic error of the gravimetric procedure described above. Prior to any connection of the sample to the GC system, each analysis began with purging the sample line and regulator of each cylinder several times to ensure good repeatability of results. A well-calibrated mass flow controller (M17203188F Bronkhorst, Holland) calibrated by the manufacturer against N_2 at 1000ml/min was used to introduce the sample at constant flow into the sample loop. To increase instrumental sensitivity and improve the stability of the instrument a flow restrictor (Valco Instruments Co. Inc., USA) was installed at the end of the sample vent line on the GC system (**Figure 2**). Relying on comparing the area response from the GC-meth-FID, CO was separated from the other reduce gases by a 2m molecular sieve 5A 80/100 mesh column. Air was injected into the column and with the presence of hydrogen, CO was oxidised to CH_4 over a nickel catalyst as follows:

$$CO + 3H_2 + Ni \ 385℃ \rightarrow \ CH_4 + H_2O \quad (4)$$

The column oven was kept at 60 °C and high pure BIP nitrogen gas was used as a carrier gas at 50 ml.min^{-1} and the detector temperature was 300 °C. CO eluted after 4min and it took 6.5min to complete the run. For the analysis of gas mixtures in nitrogen, the similar parameters were used except for the run time was set at 2 min.

The uncertainty associated with the analytical or verification value was calculated based on the drift of the analyser of the integrated peak area and repeatability (Lee et al., 2014).

Table 3. The analytical conditions used for the GC FID system.

Parameters	***Conditions***
Column type	Molecular sieve 5 A 80/100 mesh, 2m, 1/8
Column oven temperature	60ºC, isothermal
Detector	FID
Detector temperature	300 ºC
Carrier gas	N_2
Carrier gas flow	50 mL/min
Sample flow	100 mL/min
Sample loop	10mL
Methanator temperature	385 ºC
Total run time	6.5 min

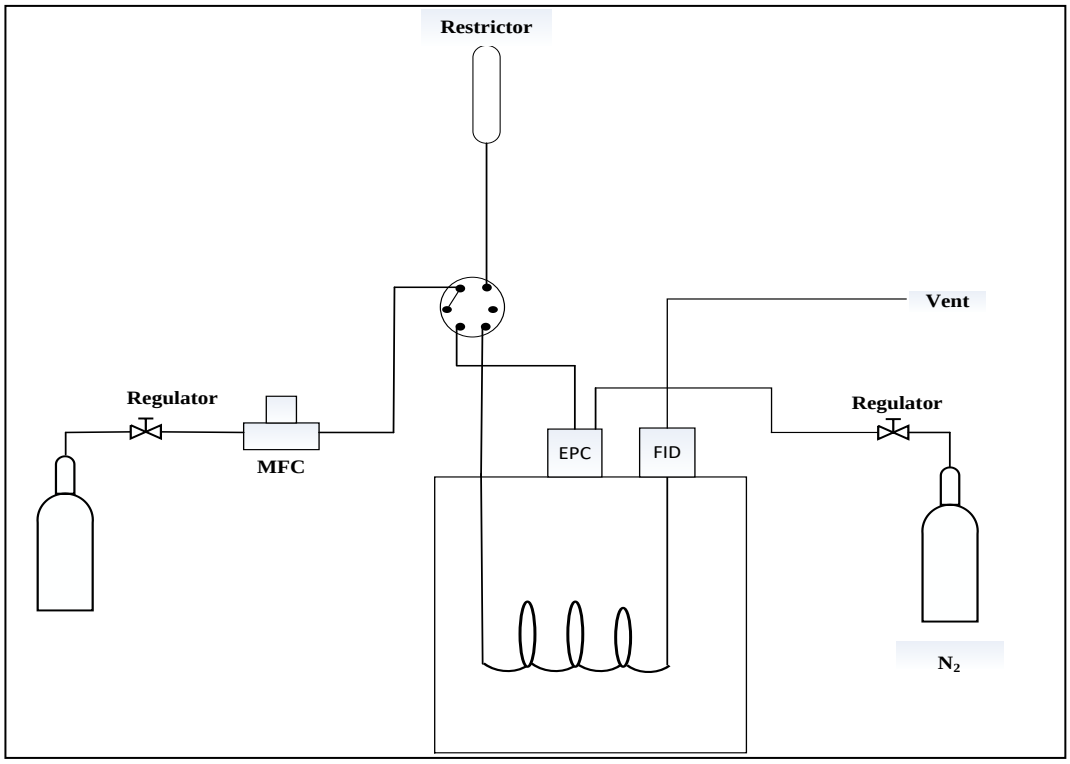


Figure 2. A schematic diagram of the GC meth-FID system for the determination of CO in synthetic air.

3. Results and Discussion

3.1 Purity assessment

After the quantification of the impurities in the pure carbon monoxide, argon, oxygen and nitrogen, a final purity amount fraction and its standard uncertainty from the sum of each source gas was assigned. **Table 1 a-e** shows the purity tables of the starting materials. In this study, it was crucial to check for were CO, O_2, Ar, and N_2 as the major impurities in each source materials because these impurities might contribute negatively to the uncertainty of the gravimetric amount fraction of the PSGMs when not considered.

3.2 Verification of standard gas mixtures in nitrogen and synthetic air

The composition of the CO gas mixture was verified to check that the composition in nitrogen and synthetic air is internally consistent with the analysis carried out. This step highlights for possible human error that might have happened during the preparation procedure. These types of errors are assumed to contribute to bias to the estimated amount fraction of the gas mixtures and, no bias was found at 5 $\mu mol.mol^{-1}$ CO/N_2 premixture used to produce gas mixtures at trace level. (Kim et al, 2018). The production of gas mixtures in different matrices at 0.350 $\mu mol.mol^{-1}$ ambient level continued. The gas mixtures at 0.350 $\mu mol.mol^{-1}$ ambient level was prepared in nitrogen and synthetic air balance (Ar, O_2 and N_2). Gas mixtures in the balance of nitrogen were used to develop the analytical method as it was the first time the laboratory had to prepare and verify carbon monoxide gas mixtures in synthetic air at this level. The verification process was conducted by comparison method was the consistency of CO composition with similar prepared nominal values were checked (ISO6143, 2001). During the verification process of the standard gas mixtures, DM4 and CM4 were randomly selected as the control cylinders (c), while the other three cylinders in each group were treated as unknown samples (s). The analysis sequence control-sample1-control-sample2-control-sample3-

control was followed where the average peak area of the unknown samples was bracketed to monitor the drift of the instrument. **Figure 3** shows a linear calibration curve was drawn to determine the value of the samples in synthetic air as these mixtures are critical. A maximum instrumental drift obtained was 0.2 % whilst the lowest drift obtained was -0.01 % throughout the analysis sequence of the PSGMs in nitrogen and synthetic air. The average peak area of the gas mixtures was used to determine the amount fraction of the unknown samples as follows:

$$C_{sample} = (\frac{A_{sample}}{A_{control}}) \times C_{control} \quad (5)$$

where C is the amount fraction of CO, A is the average area response of the unknown samples and control.

Because the FID is a linear detector, one-point calibration method was selected to calibrate the analyser by an analytical comparison of traceable gas mixtures. **Figure 3 and 4**, shows the internally consistent of the unknown samples when the verification sensitivity ratio of carbon monoxide as compared to the control cylinder value and the error bars correspond to the expanded uncertainties on the vertical axis (Kim et al 2018). These mixtures pass the preparation acceptance criteria set as:

$$|y_{CO,grav} - \ y_{CO,ver}| \leq 2\sqrt{u^2(y_{CO,grav}) + \ u^2\ (y_{CO,ver})} \quad (6)$$

where $y_{C0,grav}$ is the gravimetric preparation value projected during preparation and $y_{CO,ver}$ is the assigned amount fraction determined by comparing the average peak area of CM1, CM2, CM3, DM1, DM2, and DM3 standard cylinders against DM4 and CM4 control cylinder in each group.

After analysis, the GUM software was used to predict the analytical amount fraction of the gas mixtures with the corresponding uncertainties of the unknown samples and the values obtained are listed in **Table 4**. The resulting carbon monoxide was detected with high precision of analysis of less than 2.72 % (1 σ) for mixtures in nitrogen balance and less than 3.0 % (1 σ)for gas samples in synthetic air matrix with the sum of gravimetric uncertainty obtained as final standard uncertainty of 2.70 % and 2.96 %. The set acceptance criteria were met as the left side of $|y_{CO,grav} - y_{CO,ver}|$ spanned over only 2.10 %. Gas mixtures only pass the verification test when $|y_{CO,grav} - y_{CO,ver}|$ is less than the acceptable limit, $2\sqrt{u_{CO,grav}{}^2 + u_{CO,ver}{}^2}$. For CM2 and DM3 cylinders the gravimetric and verification standard uncertainties where obtained as (2.70, 2.71) % and (2.76, 2.81) % which an acceptance limit of 7.66 % and 7.88 %. **Table 5** shows the acceptance limits for the CO composition of the unknown sample cylinders. The findings indicate that the amount fraction of CO at low µmol.mol^{-1} was consistent and pass the verification test (**Table 6**). Only DM2 cylinder had a gravimetric uncertainty, $y_{CO,grav}$ greater than the verification uncertainty $y_{CO,ver}$ in the prepared mixtures, this does not give confidence in the verification amount fraction (ISO 6143, 2001). The deviation in the control cylinders between CO in N_2 (0.351± 0.035) µmol. mol^{-1} versus the standards in synthetic air (0.339 ± 0.035) µmol. mol^{-1} is 3.85 %. These results display that there is a substantial difference of CO analyte in nitrogen and air matrix when the gas separation with FID technique was used. Similar observations were reported by Rhoderick in 2008 when he obtained a 0.63% difference between propane in nitrogen and air matrix.

To further evaluate the DM2 cylinder, a linear calibration curve was drawn between the gravimetric value and the estimated amount fraction with the error bars corresponding to standard uncertainties. A good correlation coefficient value R^2 = 0.998 was obtained between the values except for DM2 cylinder (**Figure 5**). But because the difference between the uncertainties was smaller than the acceptance limit, the cylinder passed the

verification test. The final combined uncertainty $u_{c(CO)}$, of CO gas mixtures, was obtained as ± 4 % (2 σ) with an exception of excluding DM2 cylinder. The final CO/N_2 and CO/air gas mixtures were certified at approximately 0.350 ± 0.028 µmol.mol^{-1} expanded uncertainty which includes gravimetric, verification and the stability uncertainty. In 2015, Hu carried out an experiment on the preparation of carbon monoxide in air and reported a standard uncertainty of less than 0.3 %. This value is lower compared to the current study. The large uncertainty obtained is attributed to purity analysis, gravimetric and analytical uncertainty.

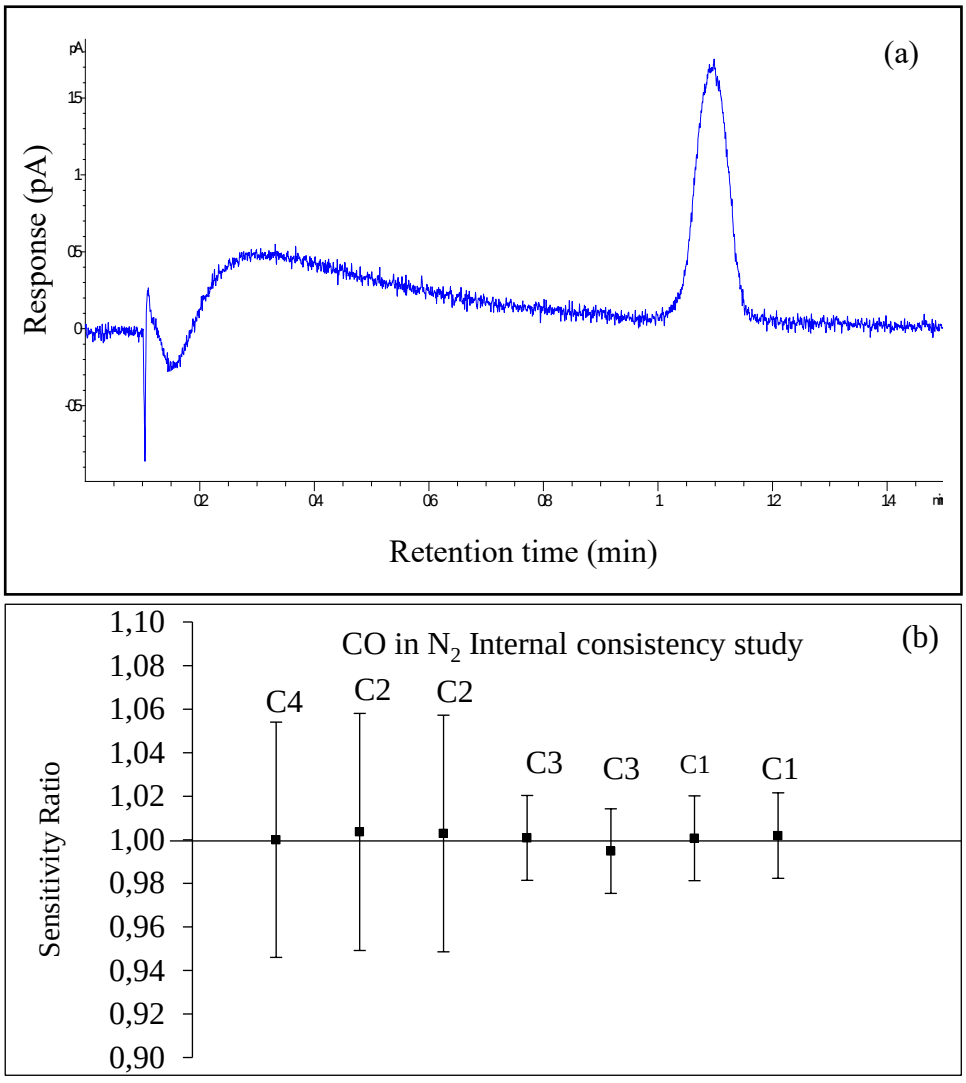


Figure 3a and b: (a) A chromatogram of CO/N_2 composition obtained from the GC-FID with methanator. (b) A plot of sensitivity ratio showing the internal consistency of the CO/N_2 gas mixture.

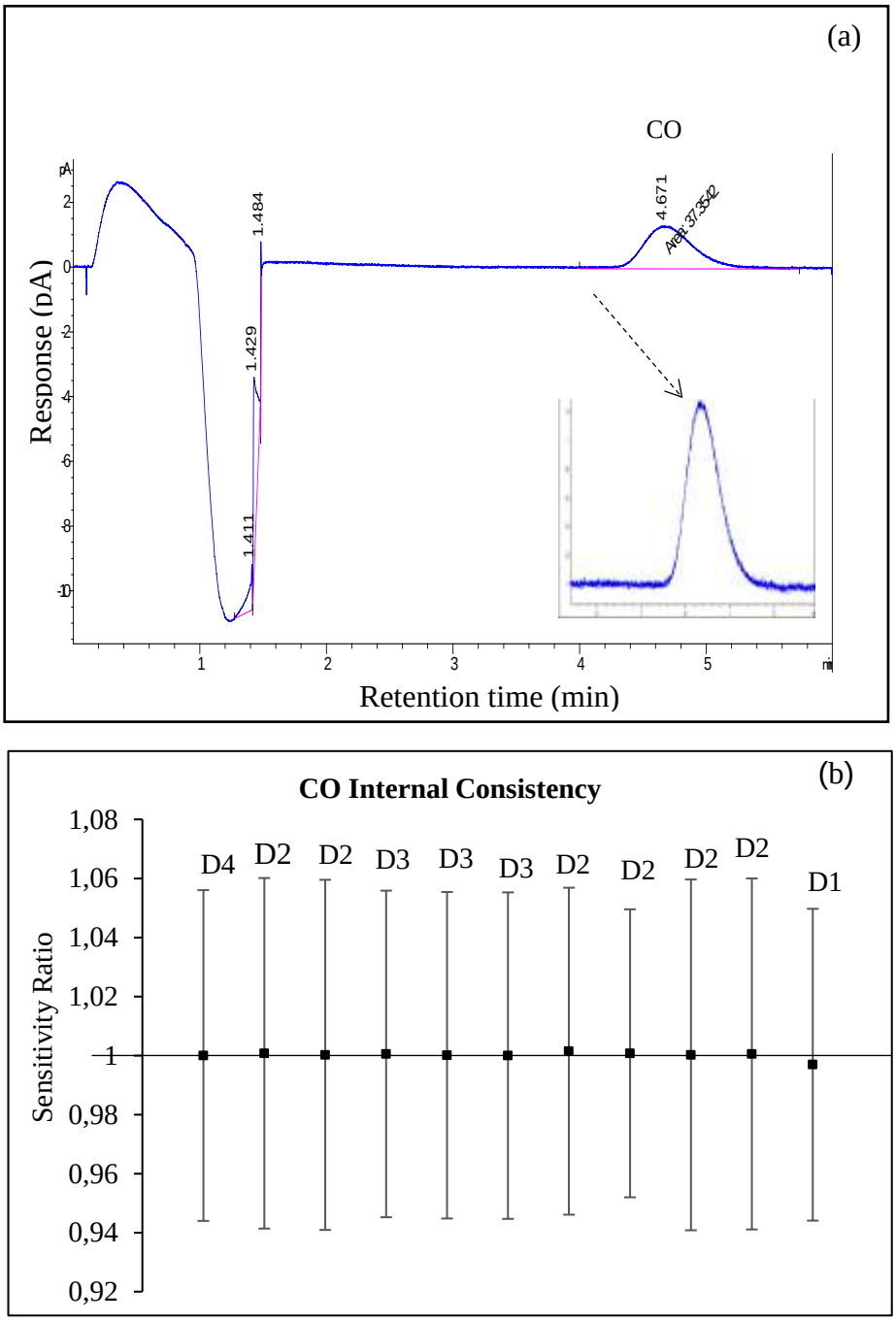


Figure 4a and b: (a) A chromatogram of CO/Air composition obtained from the GC-FID with methanator. (b) A plot of sensitivity ratio showing the internal consistency of the CO/Air gas mixture.

Table 4. Analytical amount fraction of CO with the estimated standard uncertainties

Cylinder Symbol	*CO amount fraction* x_{anal} / *µmol.mol*$^{-1}$	*Expanded uncertainty* $u(x_{CO\ anal})$ / *µmol.mol*$^{-1}$	$\lvert x_{grav} - x_{Anal,PRGM} \rvert$	$2\sqrt{u_{CO\ Cert}{}^2 + u_{Anal}{}^2}$ * (2σ)
CM1	0.351	0.0067	0.0011	0.020
CM2	0.350	0.019	0.0000085	0.027
CM3	0.351	0.0066	0.00087	0.020
DM1	0.327	0.017	0.0011	0.018
DM2	0.315	0.013	0.00080	0.026
DM3	0.339	0.013	0.0010	0.027

*2 is the coverage factor (k) at 95 % confidence level.

Table 5. Results of analytical acceptance test with the gravimetric and uncertainty values.

Cylinder Symbol	x_{grav} / *µmol. mol^{-1}*	$u(x_{CO\ grav})$ / *%*	x_{ver} / *µmol. mol^{-1}*	$u(x_{CO\ ver})$ / *%*	$\lvert x_{CO,grav} - x_{CO,ver} \rvert$ (1σ)	$2\sqrt{u_{CO,grav}{}^2 + u_{CO,ver}{}^2}$	$u_{c(CO)}{}^*$ (%)
CM1	0.351	0.95	0.350	2.71	1.76	5.75	1.44
CM2	0.350	2.70	0.350	2.71	0.01	7.66	1.92
CM3	0.351	0.95	0.350	2.72	1.76	5.75	1.69
DM1	0.327	0.27	0.326	2.81	2.54	5.64	1.90
DM2	0.315	2.96	0.316	2.91	0.12	8.31	2.08
DM3	0.339	2.76	0.339	2.81	0.042	7.88	1.97

*Relative uncertainty (1 σ) of CO amount fraction $u_{(CO)} = 0.5\sqrt{u_{CO,grav}{}^2 + u_{CO,ver}{}^2 + (x_{CO,grav} - x_{CO,ver})^2}$

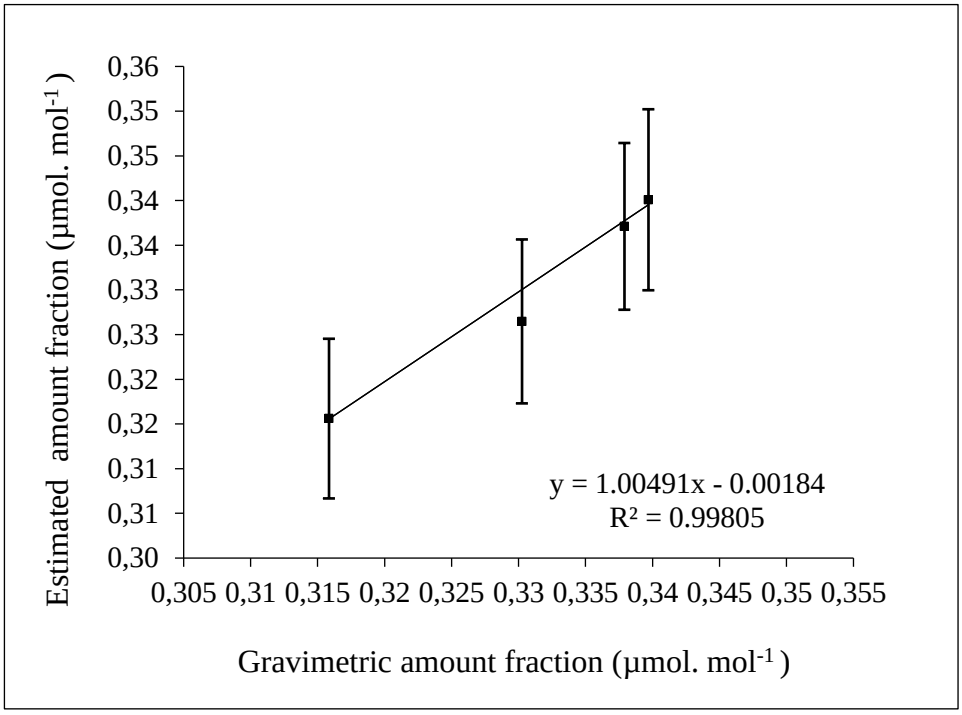


Figure 5: A linear curve plot for CO in synthetic air gas mixtures.

3.3 Stability of primary standard gas mixtures

To evaluate the short-term stability of the CO, the analysis value of the gas mixture was tracked over three days of preparation (**Figure 6**). The mixtures were first analysed over several days to determine the best cylinder to use as the control cylinder for the three-day analysis step. The centre line represents the reference value (gravimetric value) while the dash lines represents the upper and lower limits of the reference value set at 3% calibration and measurement capability (CMC). The graphs show the deviation between the reference and the estimate amount fraction is very small (less than 0.5%). The composition of CO at trace level in different balance has been known to be stable over a few years (Lee et al, 2017). Based on the Korean Research Institute of Standard and Science (KRISS), carbon monoxide composition in nitrogen cylinders is stable for four years within 0.02% (Lee et al, 2017). During the key comparison study, the coordinating laboratory conducted a stability test on the gas mixture before

and after dissemination to the participating labs. It was reported that the composition of carbon monoxide was stable on the 8th months from the first analysis month and once the cylinders were returned by the participating laboratory with a deviation of <0.1% between the gravimetric and verification value.

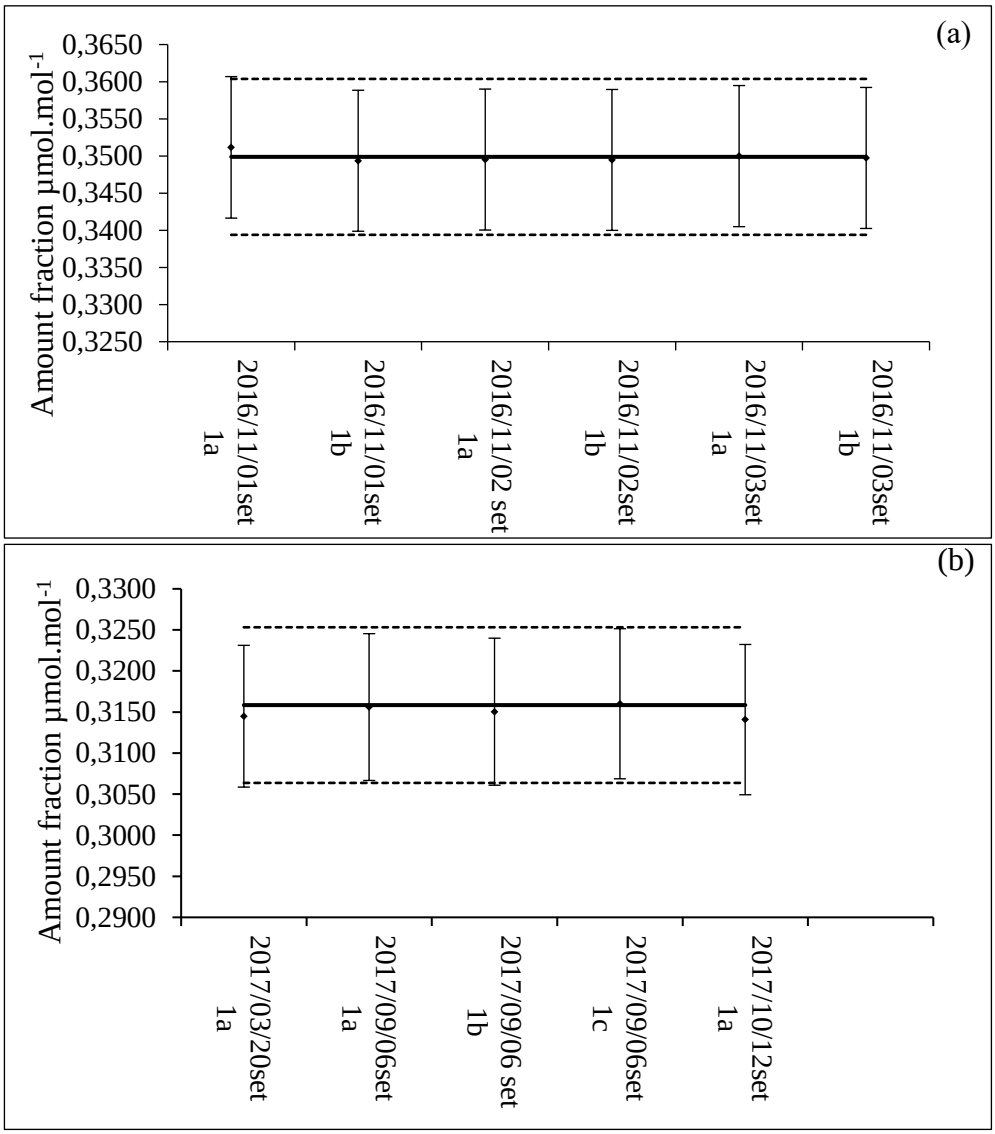


Figure 6a and b: Stability graph of CO gas mixture in (a) nitrogen balance and (b) in synthetic air balance. The solid line represents the true value and the dotted line is for the upper and lower limits.

In the previous study, CCQM-K84 CO 0.350 µmol.mol^{-1} in synthetic air (O_2 and N_2) the expanded uncertainties of the amount fraction reported by the participated laboratories ranged from 7.00 to 1.06 µmol.mol^{-1}. These values are smaller than the expanded uncertainties reported under this study. More work will be done in the future to improve this method to reduce the uncertainties.

4. Conclusion

Carbon monoxide gas mixtures in nitrogen and synthetic air balance were successfully prepared by gravimetric procedure with an associated relative standard uncertainty of 2.90 %. The short-stability results show that the gas mixtures are stable after several days of preparation. The final results obtained indicate that the gas mixtures can be used to monitor CO emissions at ambient levels with expanded uncertainty reported as 0.02 µmol.mol^{-1}. For future work, the improvements will be made on the purity analysis of the starting material. The current PSGMs will be reanalysed against freshly prepared gas mixtures to evaluate the long-term stability especially for gas mixtures in synthetic air balance. The new PSGMs will be prepared on the new automatic weighing system to improve on the gravimetric uncertainty. The verification system will be improved to such a point that the peak area of CO is enhanced and separation from O_2/N_2 peak do not interfere with the peak of interest. For gas mixtures in synthetic air, the CRDS will also be used to verify the cylinder content and improving on the verification uncertainties. The developed gas mixtures can be used to support various regional air monitoring companies and laboratories.

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CHAPTER VI: CONCLUSION AND FUTURE PROSPECTS

In this chapter, a conclusion based on the finds of the conducted experiments is explained. The work conducted in this study including the achieved objectives is also presented. The future prospects are also explained under this chapter.

5.1 Conclusions

The development of primary standard gas mixtures for the environmental monitoring of greenhouse gas emission in South Africa was successful and has been used by various air monitoring companies and laboratories locally.

The results obtained were good and confirms that the gravimetric method used to develop the gas mixtures was suitable and that these gas mixtures are accurate and reliable for calibrating the measurement instruments.

The verification of a group of primary standard gas having N_2O in artificial air was successfully achieved by using CRDS and GC-μECD. The primary method used to produce the standards showed no bias as the mixtures were proven to be internally consistent with no adsorption effect. The application of the N_2O standards in synthetic air show that the background air samples lie within the calibration range with 329 to 330 nmol.mol^{-1} results obtained, and 135 nmol.mol^{-1} results obtained for filtered air sample. The uncertainty obtained (1.80 nmol. mol^{-1}) was small enough to support the ambient air measurements set at 1 nmol.mol^{-1} standard uncertainty (k=1) acceptable level (**paper II).**

The recent certification of CO in nitrogen gas mixtures prepared in 2007 was successfully achieved. The CO content was verified by spectroscopic (NDIR) and chromatography (GC-FID) methods. The results obtained shows that CO is indeed a stable molecule as the gas mixture did not get adsorbed or desorbed in the interior surface of the aluminium cylinder. This was validated during the internally consistency test that was performed after 11 years of storage. Out of 25 participants during the comparison study, more than 70% showed a degree of equivalence to the gravimetric reference value. The relative expanded uncertainty (k=2) of the final value is 1% which agrees with the uncertainty value obtained in the previous study **(paper IV)**.

In **paper V**, the development of carbon monoxide in two matrices (N_2 and synthetic air balance) was achieved by gravimetric method. The uncertainty related to the gravimetric value was reported as 2.90%. The short-term stability test proved that the standard gas mixtures were stable after several days of preparation. These gas mixtures can be used to monitor CO emitted into the atmosphere at ambient level.

Preparation of primary standard gas mixtures in synthetic air was successfully applied for the determination of carbon dioxide in background air samples. The natural air samples were verified in three optimized measurement techniques and its results were compared with the reported results which both showed an agreement (**paper VI**).

Greenhouse gas standards in nitrogen for the determination of CH_4 at ambient level has been prepared and validated against each other. The gas mixtures were analysed from percentage (% $mol.mol^{-1}$) to micromole per mole ($mol.mol^{-1}$) levels. In the ambient range, only three standards passed the verification test and M1 calibrated the other standards by GC-FID. The results shows that the standards contains 2.00 ± 0.02 $\mu mol.mol^{-1}$ CH_4 (**paper II**).

After the development of standard gas of methane in nitrogen, standards in synthetic air were then developed for the validation of real atmospheric air. In **paper II**, CH_4 in synthetic air were certified at 1.80 to 1.82 ± 0.0018 $\mu mol.mol^{-1}$ at k=1. The amount fractions and uncertainties of the standards were comparable even though the GUM uncertainties are slightly small but higher than the gravimetric uncertainties, therefore the results were accepted. Through the collaboration with the WMO-GAW Cape Point station operated by the South African Weather Service, the results showed a deviation of 1.12%. This was not anticipated, and the background air samples were then recalibrated by freshly prepared primary standards as explained in **paper VI**.

In **paper I**, six gas mixtures with carbon dioxide and methane in synthetic were development by two weighing systems. The standards were used to calibrate the real atmospheric air by GC-FID and CRDS. The CRDS measurements proved to be more precise and sensitivity as little to no instrumental drifts on CH_4 measurements was obtained. During the analysis dried air samples were confirmed to have a amount fraction range from 376. 18 to 420.39 μmol.mol^{-1} of CO_2 and 1.78 to 1.80 μmol.mol^{-1} of CH_4. The results obtained were comparable with what was reported. These standards can be used to predict the emission of CO_2 and CH_4 in the atmosphere.

Preparation of primary standard gas mixtures in synthetic air was successfully applied for the determination of carbon dioxide in background air samples. The samples were verified in three optimized measurement techniques and its results were compared with the reported results by the SAWS Cape Point Station. The obtained results from both laboratories showed good agreement (**paper I**).

The outcome of the key comparison study for CO_2 shows that the NMISA primary standard gas mixtures are comparable with the gas standards prepared by other NMIs around the globe. However, meeting the anticipated data quality objectives set by the WMO for CO_2, CH_4 and N_2O is a challenge as the combined uncertainties of the gas standards were large. Though the final uncertainty of the gravimetrically prepared gas mixtures did not meet the recommended WMO precision, the uncertainties obtained do lie within the requirements of the NMISA stakeholders (Brewer et al, 2018). To meet the WMO precision, highly pure gases with very low impurities of the main component or that closely meet the atmospheric isotopes is required.

5.2 Future prospects

Future studies will include:

i. to improve on the purity analysis of highly pure gases or starting materials.
ii. to prepare for the upcoming international key comparison of N_2O in air matrix (CCQMK-68, 2019). This study is a repeat but the NMISA laboratory will be participate for the first time. The gas mixtures prepared during this study will be compared with gas mixtures from other international laboratories.
iii. to monitor the developed gas mixtures in synthetic air to further study the long-term stability and determine if there is any adsorption or desorption effects of N_2O, CO, CH_4 and CO_2 analytes at trace level within the aluminium cylinder after several years of preparation.
iv. to study any pressure broadening effects that might occur when gas mixture in synthetic and real atmospheric air are analysed with spectroscopic methods.
v. to monitor the stability of the background air samples and the purchased international standards scales in air.
vi. to sample air around CSIR at different times using different air filters, then quantify the levels of greenhouse gases using the developed gas mixtures.

APPENDIX

Paper VII

This manuscript “Selective Detection of Propanol Vapour at Low Operating Temperature Utilizing ZnO Nanostructures” has been accepted for publication to the *Journal of Ceramics International*. It investigates the selective detection of propanol vapour performances of the ZnO based sensor exposed to various concentrations of other interfering gases such as acetone, benzene, ethanol from 2.5 to 80 ppm at an operating temperature of 125 °C. The high response (i.e. resistance ratio), sensitivity and selectivity toward each gas is studied.

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Selective detection of propanol vapour at low operating temperature utilizing ZnO nanostructures

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ABSTRACT

We report on the propanol vapour (C_3H_8O) gas sensing characteristics of ZnO nanostructures prepared via hydrothermal assisted method. The ZnO-4h sensor showed a high response (i.e. resistance ratio), sensitivity and selectivity toward C_3H_8O gas at low operating temperature of 125 °C. A response and recovery times of approximately 190 and 200 s were recorded. The response of ZnO-4h based sensor to 40 ppm C_3H_8O was approximately 2 times higher than that of other sensing materials in dry air, while in the presence of 40% RH the response was 5 times higher. The exceptional C_3H_8O-sensing performance of ZnO-4h is related to more C_3H_8O adsorption sites provided by V_O. The ZnO-04h based sensor showed a clear repeatability towards 40 ppm C_3H_8O for four successive cycles in the presence of various RH of 40 and 60% at 125 °C. The sensor response improved in the presence of RH humidity showing that the water vapour was not competing with the C_3H_8O for the pre-adsorbed oxygen ions, thus its interfering effect in the C_3H_8O sensing was considerably minimized. The ZnO-4h based sensor was further tested for long-term stability and the sensor was very stable after 45 days. The fundamental sensing mechanism towards C_3H_8O vapour is also discussed.

1. Introduction

Lately, there has been a considerable environmental apprehension over the several toxic, flammable gases and vapors established in places such as coal mines, households, and natural gas industries that are triggering danger to human health. Therefore, gas sensors with high sensitivity, selectivity, speed of the response and long-term stability (abridged as 4S) [1] are desirable. Substantial determinations have been dedicated to the developments of gas sensing performances i.e. 4S of the nanomaterials by tuning the morphology, surface structure and the selection of metal catalyst incorporated to semiconductor metal oxide (SMO) nanomaterials [2,3]. Volatile organic compounds (VOCs) comprise alcohols, aldehydes, ketones, benzene, toluene, ethylbenzene and xylenes are the utmost shared pollutants in indoor and outdoor air with worldwide treats [4]. Currently, SMO based gas sensors are among the most popular devices for the detection and monitoring of hazardous gases and vapors [5–7]. This is because of their rapid response, low cost, and simple design. Among the n-type SMO, ZnO is considered as vital material, due to its excellent performance for detection of numerous dangerous and poisonous gases. This is because of its high sensitivity and selectivity [8,9], although its higher operating temperature needs to be addressed [8–10].

Therefore, herein, we developed a simple strategy to fabricate a low operating temperature propanol gas sensing material derived from ZnO nanostructures. The ZnO-4h shows exceptional sensing behaviour towards propanol with improved response and selectivity, among other tested VOCs such as acetone, toluene, ethanol, and benzene. The long-term stability measurements of 45 days were carried out. The plausible gas sensing mechanism related to ZnO is proposed.

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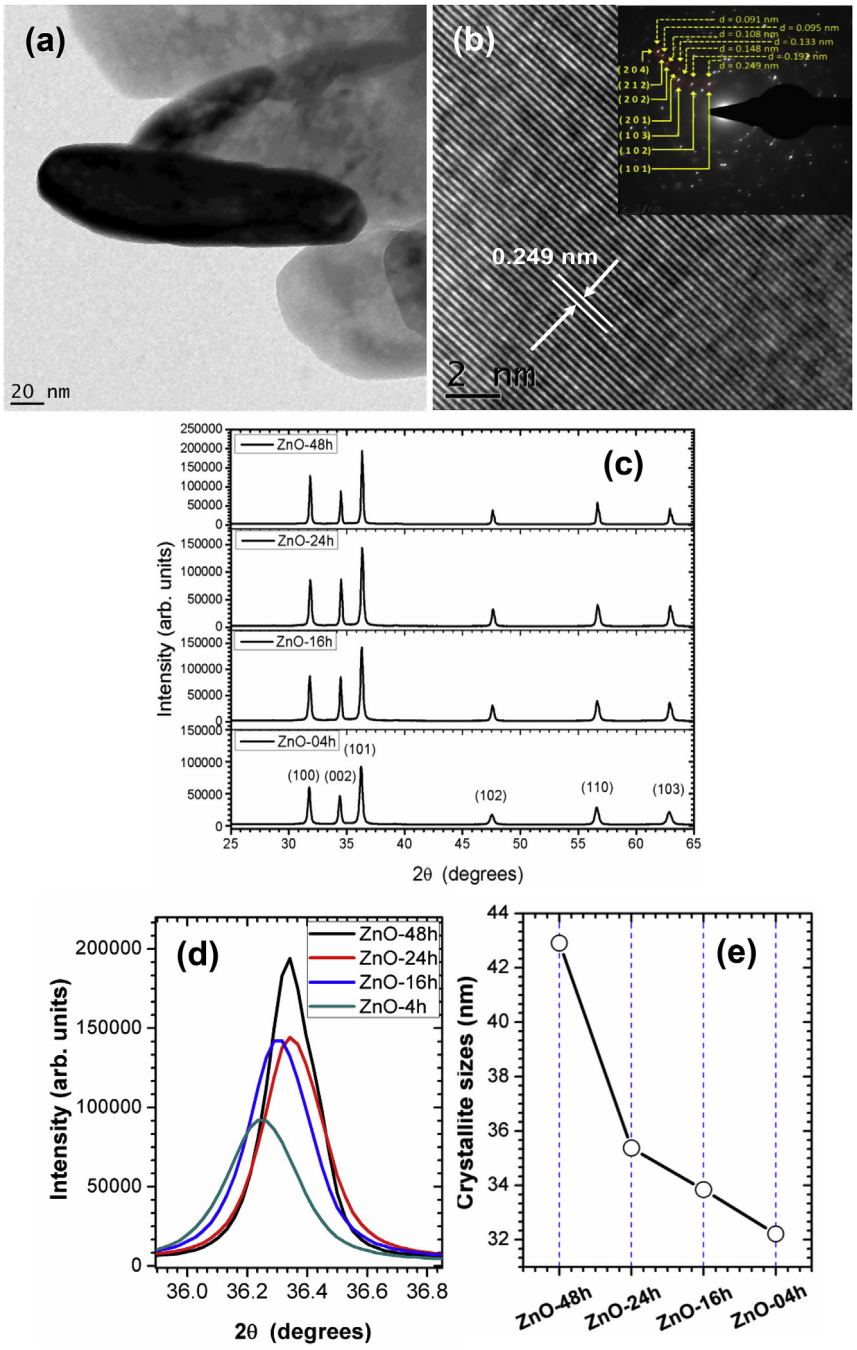


Fig. 1. (a–b) TEM micrographs and SAED, inset, of the ZnO-4h, (c) XRD diffraction patterns of ZnO nanostructures, (d and e) (101) peaks showing the shifting to higher angles and crystallite sizes growth with increased synthesis time.

2. Experimental details

2.1. Synthesis of ZnO nanostructures

All chemicals were procured from Sigma-Aldrich and used as received. ZnO nanostructures were prepared using hydrothermal method. Initially, 0.2 M of $Zn(NO_3)_2{\cdot}6H_2O$ (Zinc Nitrate Hexahydrate) was added in 125 mL of distilled water in 4 different round bottom flasks. Then, 1.0 M sodium hydroxide (NaOH) was added dropwise under vigorous stirring at room temperature, resulting to a pH of 12.5. The solutions were allowed to stir for 2 h. Then, the solutions were transferred to 200 mL volume stainless steel autoclave reactor vessels (Anton Parr instruments) and placed in an oven at 200 °C for 4, 16, 24 and 48 h. The achieved white solid precipitates were collected by several rinse-centrifugation cycles using distilled water. Then, the obtained ZnO products were dried at 90 °C for 12 h and annealed at 200 °C in air for 2 h.

2.2. Characterization

The ZnO structures were investigated using an X-ray diffractometer (XRD) (Panalytical X'pert PRO PW 3040/60) fixed with a Cu-Kα (λ = 0.15418 nm) monochromatized radiation source in the 2θ range of 25–70° and JEOL-2100 high-resolution transmission electron microscopy (HR-TEM). The PL spectra were measure using a Horiba Jobin-Yvon NanoLog spectrometer at an excitation wavelength of 330 nm at room temperature. The EPR analyses were examined using JEOL X-band at room temperature.

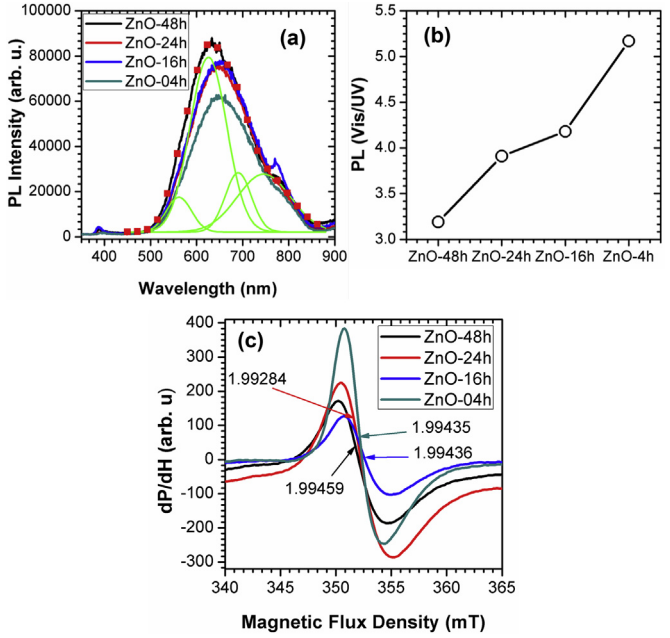


Fig. 2. PL spectra and (a) the relative intensity of the visible emission and ultraviolet (Vis/UV) extracted from the PL spectra as a function of synthesis reaction time and (c) EPR spectra of various ZnO nanostructures.

Sensors were prepared according to the procedure described in Ref. [11]. Gas-sensing characteristics were measured using KSGAS6S KENOSISTEC gas testing station. The fabricated ZnO sensors were exposed to various concentrations (5–100 ppm) of VOCs (ethanol (C_2H_5OH), propanol (C_3H_8O), acetone (C_3H_6O), benzene (C_6H_6) and toluene (C_7H_8)). The measurements were carried out at 75 °C and 125 °C in dry air and in the presence of 40% relative humidity. The sensor response was defined as $(I_g\text{-}I_a)/I_a$, where I_a and I_g are the current in air and I_g in tested gases, respectively. The response-recovery times were calculated as the time the sensor response needed to reach 90% of its maximum and when it reduced to 10% of its maximum [10].

3. Results and discussions

The low and high resolution TEM micrographs and the selected electron diffraction (SAED) patterns (inset) of ZnO grown for 4h are shown in Fig. 1. As illustrated in Fig. 1a, the nanoplatelets with diameter range of 30–60 nm are observed (see SEM, electronic supplementary information (ESI), Fig. S1). The lattice fringes with a d-spacing of 0.249 nm corresponding to (101) plane are observed, while the SAED patterns show that the nanostructures are highly crystalline. Fig. 1c illustrates the XRD patterns of ZnO grown at various times. The diffraction peaks are in agreement with the hexagonal ZnO (space group P63/mc, JCPDS file NO. 36–1451). The peaks shift to higher diffraction angles (Fig. 1d), while the intensity increases with an increase in preparation times as presented in Fig. 1e.

To quantify the defects involved in the gas sensing properties, the PL and EPR studies were carried out, as depicted in Fig. 2. All the nanostructures display minor and broad PL emission peaks positioned at 380 nm and 500–850 nm. The emission at 385 nm is associated to the near band edge (NBE) emission [12]. After deconvoluting the emissions in the range of 500–850 nm, four peaks were fitted as shown in Fig. 2. The peaks located at 548 nm and 600 are associated to oxygen vacancies (V_O) and doubly ionized oxygen vacancy [13,14]. The emission peak at 690 nm is associated to oxygen interstitials (O_i) [15]. According to Lupan et al. [16] and Gomi et al. [17] the near-IR emission at 750 nm is linked to the oxygen-related defects and interstitial zinc, respectively.

The relative intensity of the visible emission and ultraviolet (Vis/UV) extracted from the PL spectra in Fig. 2b demonstrates that the ZnO-4h has higher relative concentration of V_O, which decreases with an increase in reaction time. The EPR analyses presented in Fig. 2c validate that the intensity of the paramagnetic V_O defects with g-factors around 1.99 is improved for the ZnO-4h nanostructures compared to its

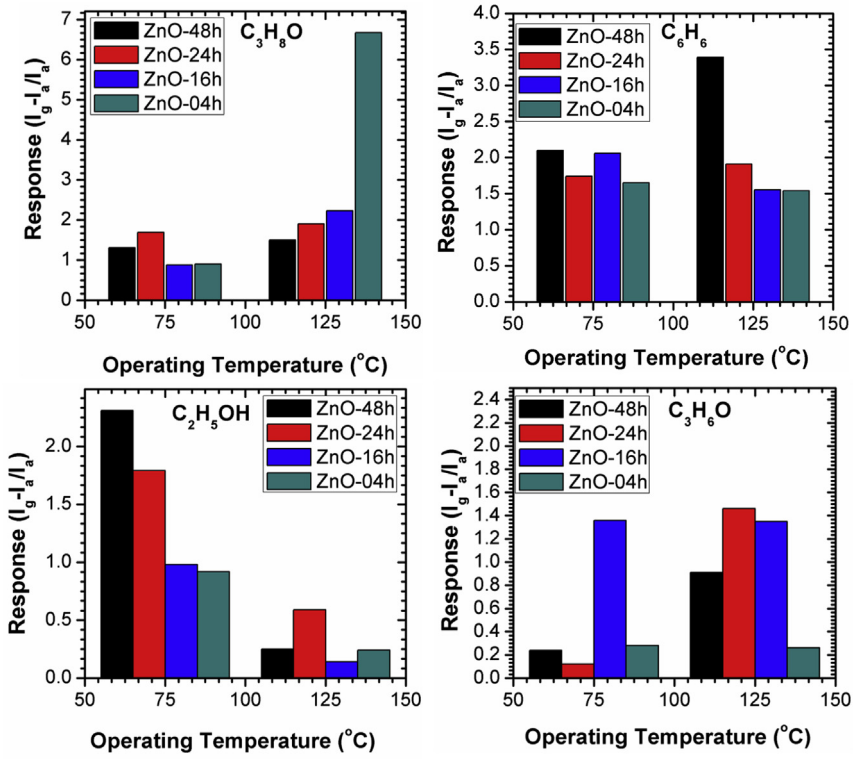


Fig. 3. (a) Response as a function of the operating temperature for various ZnO towards C_3H_8O vapour.

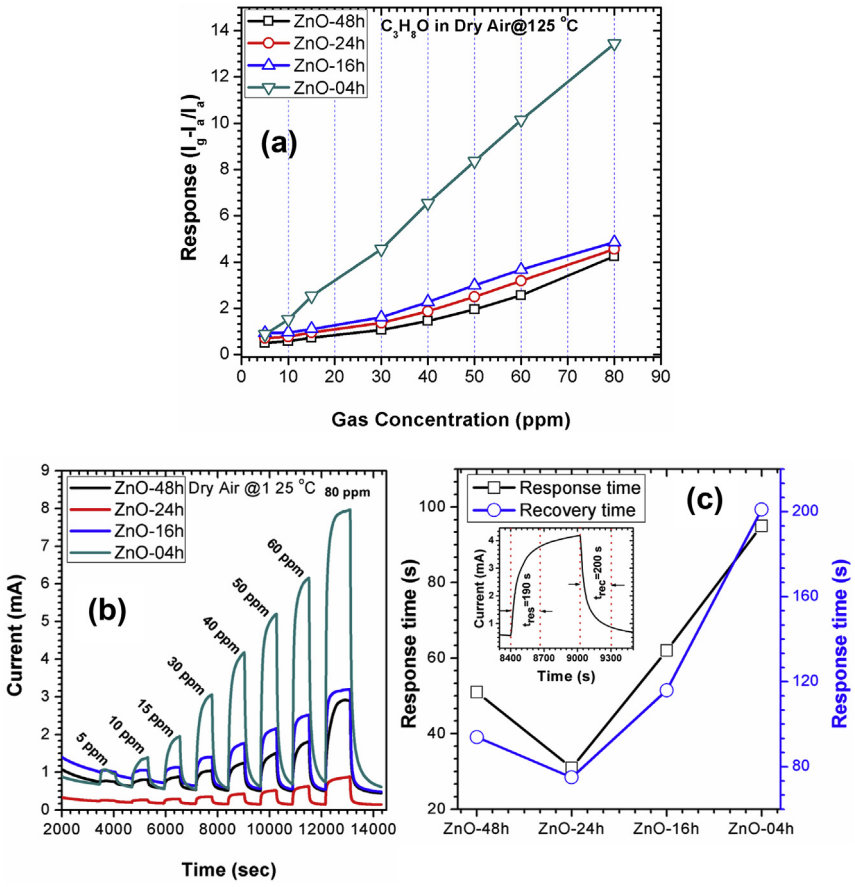


Fig. 4. (a) Response versus C_3H_8O gas concentration, (b) real-time response and (c) response-recovery times plot of various ZnO nanostructures.

Table 1
Comparison of C_3H_8O gas sensors based on ZnO nanostructures.

Sensing material/fabrication technique	Gas Concentration (ppm)	Operating Temp. (°C)	Response (ΔG/G*100)	t_{res} (s)	t_{rec} (s)	Refs.
ZnO-4h nanoplatelets/hydrothermal	40	125	6.6	190	200	In this work
ZnO nanowires/electrospinning	100	100	~2.5	–	–	Li et al. [27]
ZnO thin films/spray pyrolysis	150	250	~85	–	–	Prajapati et al. [28]
ZnO porous particles/Hydrothermal	100	320	~35	–	–	Huang et al. [29]
Au decorated ZnO nanowires	100	320	~14	–	–	Gu et al. [30]
CuO/ZnO flower-like nanostructures	100	220	28	–	–	Huang et al. [31]
ZnO hollow spheres	100	385	57.6	23	13	Han et al. [32]
ZnO nanotubes	700	25	62	~265	~220	Acharyya et al. [33]

counterparts and its intensity decreases with reaction time [18,19].

The response of the SMO based sensors is significantly influenced by working temperature [9–11]. To attain the optimum temperature, the sensors were tested at temperatures of 75 and 125 °C, Fig. 2. The ZnO-4h based sensor demonstrates a maximum response of 6.6 towards 40 ppm C_3H_8O vapour as the temperature increases to 125 °C. This response is higher than that of other gases (see Fig. 3). The increase in response for ZnO-4h can be justified by higher relative concentration of V_O offering additional active sites for adsorption of the gas molecules as confirmed by ESR and PL analyses in Fig. 2 [11]. Previous studies have reported that alcohols with increased -CH_2- groups are indeed easily decomposed and oxidized compared to those with lesser one [20,21]. Consequently, propan-2-ol containing the maximum number of -CH_2- groups is simply decomposed.

Therefore, this reacts efficiently with the adsorbed oxygen species, resulting to a release of electrons which, in turn, increases the sensing response. Thus, this justifies the high sensing response towards propanol, followed by ethanol and methanol, respectively. These findings are also consistent with those reported by Canevali et al. and D'Arienzo et al. [22,23] demonstrating that the quantity of the paramagnetic V_O is associated to that of the electrons reaching the conduction band of the SnO_2 and as a result it is equivalent to the enhanced sensing response.

Fig. 4a demonstrates the sensors response as a function of C_3H_8O concentrations at the optimal operating temperature of 125 °C. The responses of the sensors increased linearly with C_3H_8O concentration from 5 to 80 ppm. For all the gas concentrations, the ZnO-4h based sensor reveals higher responses, displaying a maximum response of 13.5 at 80 ppm. Based on the American Chemical Society guidelines [24] and refs. [25,26], the calculated limit of detection (LoD) for the ZnO-04h towards C_3H_8O is 0.13 ppm.

The electrical current change of the various ZnO based sensors tested towards C_3H_8O is displayed in Fig. 4b. All the sensors display a typical n-type gas sensing behaviour. Different morphologies have substantial effect on the baseline current (or resistance) of the gas sensors. The current of the ZnO-16h (1.76 mA) and 48 h (1.39 mA) is higher in air compared to other nanostructures showing values of 1.12 mA (ZnO-4h) and 0.44 mA (ZnO-24h). Besides, irrespective of the C_3H_8O concentration, the current of the ZnO based sensors recovers to

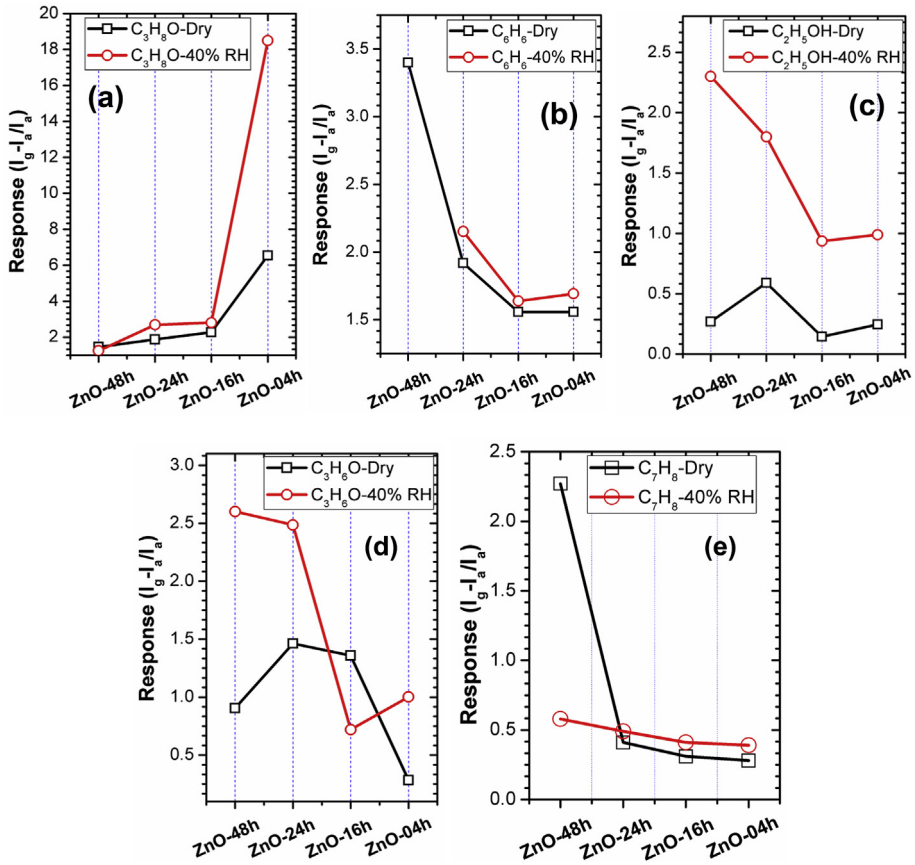


Fig. 5. Responses of ZnO sensors toward 40 ppm of (a) C_3H_8, (b) C_6H_6, (c), C_2H_5O, (d) C_3H_6O and (e) C_7H_8 in dry air and in the presence of 40% RH at 125 °C.

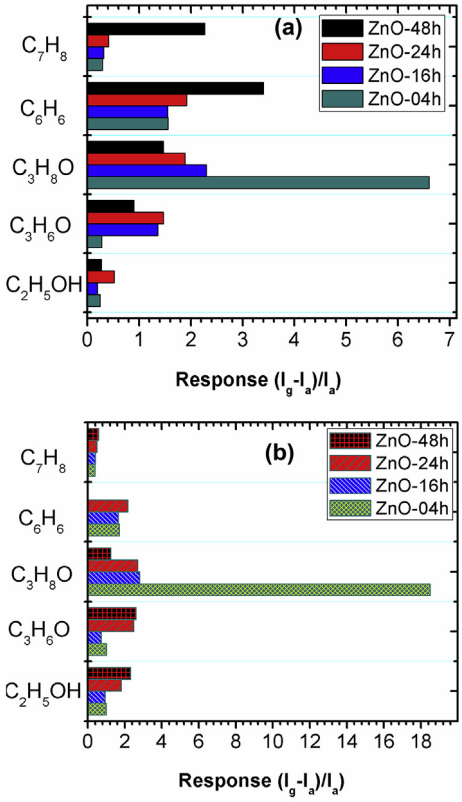


Fig. 6. Selectivity plots of various ZnO toward 40 ppm of various gases (a) in dry air and (b) in the presence of 40% RH at 125 °C.

the baseline level after stopping the target gas. The response (t_{res}) and recovery (t_{rec}) times of the sensors exposed to various C_3H_8O vapour in air are shown in Fig. 4c, while the t_{res} and t_{rec} of ZnO-4h are 190 and 200 s as shown in the inset of Fig. 4c.

Table 1 compares the response of the current sensors with that in the literature. As listed in Table 1, it evident that our ZnO-04h based sensor has higher response compared to other sensors, more remarkably it low operating temperature and gas concentration its response is competitive.

Relative humidity (RH) is one of the main credible features, especially for low operating temperatures that are commonly affecting the gas sensing performances considerably in comparison to that in dry air conditions [34]. Fig. 5 compares the response of various ZnO based sensors tested toward various gases at 40 ppm in dry air and in the presence 40 %RH. The response of the ZnO-4h (Fig. 5a) decreases by roughly 8.5% towards 40 ppm C_3H_8O in the presence of 40 %RH, while that of 16 and 24 h increases with RH. When the sensors are exposed to C_6H_6, C_2H_5OH, C_3H_6O and C_7H_8 (see Fig. 5a–e), their responses increased in the presence of 40 %RH compared in dry air. Except that no response was observed for ZnO-48h sensor towards 40 ppm C_6H_6 in the presence of 40 %RH. The slight decrease of the ZnO-48h sensor in Fig. 5a and e towards humidity is probably because of the physisorbed water occupying the active sites of the sensing material [34].

For practical applications, gas sensors are obligated not only to show rapid response-recovery times, however also extraordinary selectivity towards the target gas molecules. Consequently, the responses of the four ZnO sensors towards 40 ppm of various VOCs gases, such as C_2H_5OH, C_3H_8O, C_3H_6O, C_6H_6 and C_7H_8, at 125 °C were calculated to assess the selectivity of the sensors in dry air and in the presence of 40% RH.

As presented in Fig. 6a, the ZnO-4h based sensor response towards C_3H_8O in dry air is higher (resistance ratio of ~6.6) compared to other

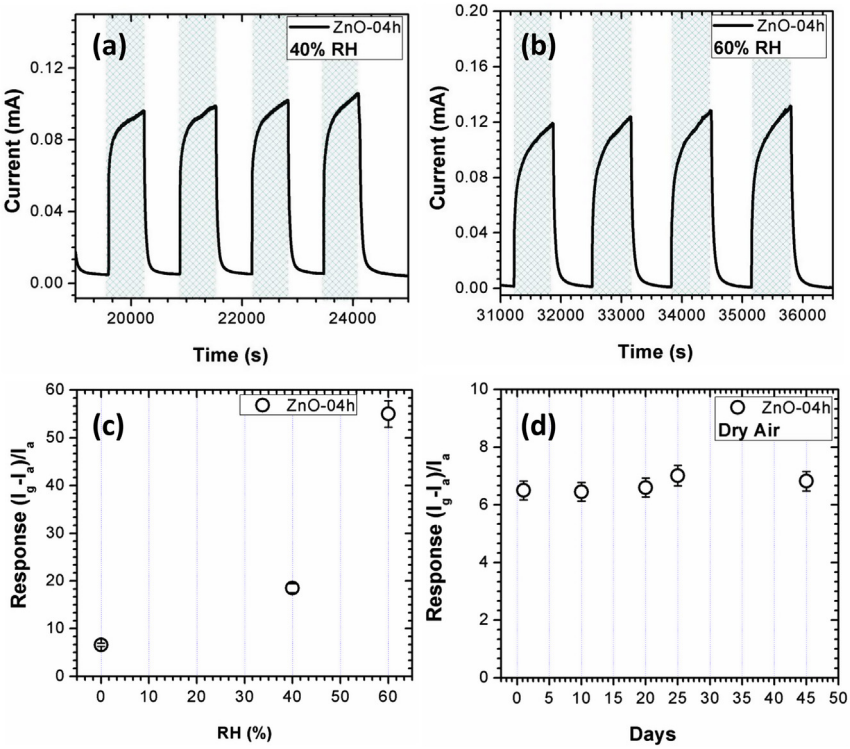


Fig. 7. (a and b) The dynamic responses of the ZnO-4h based sensor upon exposure to 40 ppm C_3H_8O for four successive cycles in the presence of various RH of 40 and 60% at 125 °C, (c) Response of ZnO-4h towards 40 ppm C_3H_8O versus RH, and (d) Lon-term stability of ZnO-4h towards 40 ppm C_3H_8O at 125 °C.

gases, showing a great selectivity. This response is 2 times higher than that of other tested gases, indicating an exceptional selectivity to C_3H_8O. When the sensors are tested towards 40 ppm in various gases in the presence of 40% RH, the ZnO-04h based sensor demonstrates higher response of approximately 18 towards 40 ppm C_3H_8O as shown in Fig. 6b. This signifies that the ZnO-4h based sensor can be considered as an effective gas sensing material to detect C_3H_8O in real environment.

The long-term stability, as one of the utmost significant benchmarks for assessing the performance of the gas sensors, was also examined. The transient sensing responses of the ZnO-04h based sensor to 40 ppm C_3H_8O for four successive cycles in the presence of various RH of 40 and 60% at 125 °C are presented in Fig. 7a and b. It is observed that the ZnO-4h based sensor is stable, showing clear repeatability behaviour in the presence of 40 and 60%RH. Moreover, there was little variation in the initial current in air (I_a), 0.0055 mA at 40% RH and 0.002 mA at 60% RH which suggested that the ZnO-4h has a strong robustness. It is further observed in Fig. 7c that the sensor response increases with an increase in RH. This behaviour is consistent with the previous study that reported the response of the CuO based sensor increases with an increase in H_2S concentration in the presence of 50% RH [35]. Oosthuizen et al. [36] also stated that the response of the CuO based sensor towards 40 ppm CO increases with the RH percentage. From our previous work, we observed that the response of the Mn_3O_4 increases with an increase in RH % [37]. This behaviour points out that the C_3H_8O does not compete with humidity (i.e. water vapour) for reaction partners (i.e. oxygen vacancies) on the surface of the ZnO. In actual fact, the interaction of the ZnO with the C_3H_8O appears to be promoted by humidity and this behaviour was previous observed by Staerz et al. [38], Choi et al. [39] and Wicker et al. [40] using operando diffused-reflectance infrared Fourier transform infrared spectroscopy for WO_3, Ni doped SnO_2 and pure SnO_2 nanostructures, respectively. According to Choi et al. [39], the DRIFT findings revealed that the water vapour in Ni doped SnO_2 based sensor will mostly interact with the Ni related surface sites such as NiO clusters or Ni atoms contained within in the surface lattice of the SnO_2 matrix. Thus, the water vapour was not competing with the CO for the pre-adsorbed oxygen ions, as a result its interfering influences in the CO sensing was considerably reduced. The ZnO-4h based sensor was further tested for long term stability in dry air for 45 days (see Fig. 7d) at 40 ppm C_3H_8O at 125 °C. It is clear in Fig. 7d that the sensor is very stable after 45 days, without showing any indication of drifting. These findings indicating that the fabricated sensor has a potential detection and monitoring of C_3H_8O vapour.

A commonly recognised gas sensing mechanism for ZnO is constructed on the change of the sensor current (or resistance) because of the surface adsorption/desorption reaction. When the sensor is exposed in air; adsorbed oxygen molecules on ZnO surface result into ionized oxygen species, such as O^- (ads) in the current work, leading in a development of an electron depletion layer. When exposed to C_3H_8O vapour, adsorbed C_3H_8O molecules capture the electrons from both ZnO and O^- (ads), see reaction 1, leading to an increase in electron depletion layer and consequently increased sensor resistance [10,11,34]. The enhancement in the number of surface adsorption sites might enable the C_3H_8O adsorption and result in improved sensor response. The considerably superior C_3H_8O response for the ZnO 4h based sensor compared to other sensing materials is linked to the higher V_O resulting to more surface adsorption sites as confirmed by EPR and PL studies.

$$C_3H_8\ O + 9O^-_{(ads)} \rightarrow 4H_2\ O + 3CO_2 + 9e^- \quad (1)$$

4. Conclusion

ZnO nanostructures were successfully prepared via hydrothermal method and tested towards various VOCs at various operating temperatures. The ZnO-4h based sensor revealed high response, sensitivity and selectivity towards C_3H_8O gas at low operating temperature of 125 °C. The response of ZnO-4h sensor to 40 ppm C_3H_8O was approximately 2 times higher than that of other sensing materials. A response and recovery times of approximately 190 and 200 s were recorded. The exceptional C_3H_8O -sensing performance of ZnO-4h is related to more

C_3H_8O adsorption sites provided by Vo. An excellent repeatability towards 40 ppm C_3H_8O for four successive cycles in the presence of various RH of 40 and 60% at 125 °C was witnessed using ZnO-4h based sensor. Our sensor displayed a clear increase in response in the presence of RH humidity indicating that the water vapour was not competing with the C_3H_8O for the pre-adsorbed oxygen ions, as a result its interfering effect in the C_3H_8O sensing was considerably reduced. The long-term stability findings showed that the ZnO-4h based sensor was very stable after 45 days.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ceramint.2019.05.172.

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