DEVELOPMENT OF SELECTED SULPHUR COMPOUNDS AND OXYGENATED VOLATILE ORGANIC COMPOUNDS REFERENCE GAS MIXTURES FOR AIR QUALITY MONITORING

By

NOMPUMELELO LESHABANE

Submitted in accordance with the requirements for the degree of

MASTER OF SCIENCE

in the

COLLEGE OF AGRICULTURE AND ENVIRONMENTAL SCIENCES

at the

UNIVERSITY OF SOUTH AFRICA
FLORIDA CAMPUS

SUPERVISOR: Dr. J. Tshilongo
CO-SUPERVISOR: Prof. S. J. Moja

JUNE 2020

DEDICATION

I dedicate this dissertation to my children, Phetolo Kedibone Kelebogile Leshabane and Motheo Moratile Leshabane and also
To my parents (my late father Mr Mandlakayise Jabulani Magubane and Mrs Julia Magubane) for teaching me life's values, principles, and humility. They valued education and encouraged me to achieve my goals and never forget that the sky is the limit.

Nkomose, Jiyane, Nhlunu, Ndlandla
Wena wakwaMpahl'emhlophe
Ingabamnyama yeza nomlandakazi
Wena wakwaNkom'inkone
Zinja zafulathelan'entabeni
YakwaMagubane
Wena wakwaThole
Kungesil'ithole lenkomo
Kodwa kuyithole lomuntu
NKOMOSE

DECLARATION

I, Nompumelelo Leshabane, hereby declare that the dissertation, which I hereby submit for the degree of Master of Science at the University of South Africa, is my own work and has not previously been submitted by me for a degree at this or any other institution.

I declare that the dissertation does not contain any written work presented by other persons whether written, pictures, graphs or data or any other information without acknowledging the source.

I declare that where words from a written source have been used the words have been paraphrased and referenced and where exact words from a source have been used the words have been placed inside quotation marks and referenced.

I declare that I have not copied and pasted any information from the internet, without specifically acknowledging the source and have inserted appropriate references to these sources in the reference section of the dissertation.

I declare that during my study, I adhered to the Research Ethics Policy of the University of South Africa, received ethics approval for the duration of my study prior to the commencement of data gathering, and have not acted outside the approval conditions.

I declare that the content of my dissertation has been submitted through an electronic plagiarism detection program before the final submission for examination.

Student signature: ________________ Date: __12 June 2020_______________

ACKNOWLEDGEMENT

Firstly, I would like to thank My God for being my rock, my pillar, my strength. He gave me so much guidance, wisdom, and knowledge in writing this dissertation. Without him I would not have the courage, perseverance, and encouragement to carry on with my studies. My soul finds rest in God alone; my salvation comes from him. He alone is my rock and my salvation; he is my fortress, I will never be shaken. (NIV bible, Psalms 62:1-2).

My greatest gratitude goes to my supervisor Dr. James Tshilongo, who encouraged me to register for my Master's degree. His guidance, expertise, support, assistance, patience, and understanding has kept me going and never give up. Thank you for your support, kindness and always availing yourself.

I would also like to thank my co-supervisor, Professor S J Moja, for believing in me, encouraging and being patient all the time. Thank you for your valuable input and guidance added to help me graduate.

I would like to further extend my appreciation to my family, my mother (Mrs Julia Magubane) who has played a very important role to my education. She worked very hard to make sure I am educated and lacked nothing, I thank you *Gasela elihle*.

To my one and only brother, Mr Bongumusa Mathews Magubane, thank you for always availing yourself to help me with anything.

To my beautiful children (my angel Phetolo Kedibone Kelebogile Leshabane) and (my handsome Motheo Moratile Leshabane), thank you for understanding when Mommy got home late and had to study during the weekends, you both inspired me physically and spiritually to never give up but keep going. Your understanding has really surpassed my expectations, this degree is for you to remember that nothing is impossible in life. I hope it will always remind you that it is never too late to achieve your dreams and that, the sky is your only limit.

My colleagues, Mr Napo Ntsasa, Ms. Mudalo Jozela and Kedibone Mashale for sharing knowledge and insight with me. I appreciate every advice given and encouragement to keep marching on this beautiful journey together. Your strength, willingness, and patience with me has kept my faith burning.

A big thank you to National Metrology Institute of South Africa (NMISA), my employer for providing resources and financial support to further my studies in Master's degree in Environmental science. I also appreciate the rest of the Gas Analysis team for their support during my studies.

ABSTRACT

Highly accurate analysis for the quantification of sulphur compounds and oxygenated volatile organic compounds are crucial for the adherence of the legislation in different environmental sectors. The sulphur compounds and oxygenated volatile organic compounds measurements are challenging, due to various factors such as molecules being adsorbed on the inner surfaces of cylinders. It is therefore important to produce accurate and reliable reference gas mixtures with mole fraction at ambient levels for the air quality monitoring and field of gas sensing in South Africa. The challenges in producing sulphur compounds and oxygenated volatile organic compounds reference gas mixtures are that the overall process from gravimetric preparation steps until the comparison analysis process and the stability of mixture in the gas cylinder, results in the large measurement uncertainties. In order to produce reference gas mixtures of the highest level, three important steps are followed: purity assessment of starting material, gravimetric preparation, and verification/validation of prepared gas mixtures. The purity analysis of high purity starting materials was determined using gas chromatography coupled with various detectors and Karl Fischer for determination of moisture content in high purity chemicals.

The sulphur compounds and oxygenated volatile organic compounds to be developed in this study were hydrogen sulphide, sulphur dioxide, acetone, methanol, ethanol, isopropanol, and n-butanol. These components were produced following the International Organisation for Standardisation documents at mole fraction of 10 µmol/mol for sulphur compounds and 5 µmol/mol for oxygenated volatile organic compounds. The preparation of sulphur compounds reference gas mixtures was done with a static gravimetric method using a direct method where a target component was transferred directly into the cylinder. The preparation of oxygenated volatile organic compounds used an indirect method whereby a target liquid component from high purity chemicals was transferred into a cylinder using a gas-tight syringe.The comparison between the reference gas mixtures was validated using Non-Dispersive Ultra-Violet analysers (NDUV), gas chromatograph coupled with pulsed discharge helium ionisation detector (GC-PDHID, UV fluorescence analysers for sulphur compounds and gas chromatograph coupled with flame ionisation detector (GC-FID) for the oxygenated volatile organic compounds. A multi-point calibration method was used to analyse sulphur dioxide and hydrogen sulphide on the NDUV analyser, and the single-point calibration method was used for analysis on the gas chromatography and UV fluorescence where a sample mixture is analysed against a reference mixture with a similar mole fraction. The statistical data considered during analysis included calculation of the instrument drift and percentage relative standard deviation to check measurements repeatability, reliability, and measurement uncertainty. The gravimetric results of prepared sulphur compounds at 10 µmol/mol gave a percentage relative expanded uncertainty of 0.041 % REU for hydrogen sulphide, 0.12 % REU for sulphur dioxide. The gravimetric results of prepared oxygenated volatile organic compounds at 5 µmol/mol showed a percentage relative expanded uncertainty 0.068 to 0.35 % REU for isopropanol and ethanol respectively and less than 2.4 % REU for multi-component of oxygenated volatile organic compounds. Finally, the primary standard gas mixtures of sulphur compounds and oxygenated volatile organic compounds were developed with the highest metrological measurement uncertainty level of (k=2).

Keywords: Sulphur compounds, oxygenated volatile organic compounds, reference gas mixtures, relative expanded uncertainty, internal consistency, gravimetric preparation, GC-PDHID, GC-FID, NDUV, UV fluorescence

INGQIKITHI YOCWANINGO

Ukuhlaziya ngokunemba okuphelele kokuhlanganiswa kwezakhi zesibabule (sulphur compound) kanye nokuhlanganiswa kwezakhi zemvelo eziguquguqukayo ezine-oxygen kubalulekile ukuze kulandelwe umthetho emikhakheni ehlukene yezemvelo. Izilinganiso zezithako ezihlanganisiwe zesibabule kanye nokuhlanganiswa kwezakhi zemvelo eziguquguqukayo ezine-oxygen ziyinselelo, ngenxa yezici ezahlukahlukene ezinjengamamolekyuli amunceka ngaphezulu kwengaphakathi lamasilinda. Ngakho-ke kubalulekile ukukhiqiza izingxube zegesi ezinembile okungathenjelwa kuzo ezihambisana neqhezu le-mole (mole fraction) yamazinga angaphandle emazingeni okuqapha ikhwalithi yomoya kanye nensimu yokuzwela igesi eNingizimu Afrika. Izinselelo ekwakhiweni kwezakhi zesibabule nokuxhunyaniswa kwegesi yemvelo eguquguqukayo ene-oxygen esuselwa engxubeni yegesi ukuthi, inqubo iyonke ukusuka kwizinyathelo zokulungiselela kwe-gravimetric kuze kube inqubo yokuhlaziya yokuqhathanisa kanye nokungaguquguquki kwengxube kusilinda yegesi, kuholela ekungaqinisekini ngesilinganiso esikhulu. Ukuze ukhiqize izingxube zegesi okususelwa kuzo ezisezingeni eliphakeme kakhulu, kulandelwa izinyathelo ezintathu ezibalulekile; ukuhlolwa kobumsulwa kwezinto okuqalwa ngazo, ukulungiswa kwe-gravimetric kanye nokuqinisekiswa/ukufakazelwa kokuhlanganiswa kwengxube yegesi okulungiselelwe. Ukuhlaziywa kobumsulwa bezinto zokuqala zokuhlanzeka okuphezulu kunqunywe kusetshenziswa igesi ye-chromatography ehlanganiswe nezihlonzi ezithola okuthile ezahlukahlukene kanye ne-Karl fischer ukuthola okuqukethwe komswakama kumakhemikhali anokuhlanzeka okuphezulu.

Izakhi zesibabule negesi yemvelo eguquguqukayo ene-oxygen azokwakhiwa kulolu cwaningo yi-hydrogen sulphide, i-sulfur dioxide, i-acetone, i-methanol, i-ethanol, i-isopropanol ne-n-butanol. Lezi zingxenye zakhiqizwa ngokulandela amadokhumenti e-International Organisation for Standardisation ngeqhezu le-mole le-10 µmol/mol yezakhi zesibabule kanye ne-5 µmol/mol yezakhi zemvelo eziguquguqukayo ezine-oxygen. Ukulungiswa kwezakhi zesibabule kwenziwa ngendlela ye-static gravimetric kusetshenziswa indlela eqondile lapho ingxenye ekhonjiwe idluliselwe ngqo kusilinda. Ukulungiswa kwezakhi eziguquguqukayo ezine-oxygen kusebenzise indlela engaqondile lapho okufakwa khona uketshezi oluhlosiwe kusuka kumakhemikhali ahlanzeke kakhulu langena kusilinda kusetshenziswa isirinji yegesi evala ngci. Ukuqhathaniswa phakathi kwezingxube zegesi okususelwa kuyo kwaqinisekiswa kusetshenziswa izihlaziyi ne-Non-Dispersive Ultra-Violet (NDUV), i-chromatograph yegesi ehambisana ne-pulsed discharge helium ionisation detector (GC-PDHID, i-UV fluorescence analyzers yezakhi zesibabule kanye ne-chromatograph yegesi ehambisana ne-flame ionisation detector (GC-FID) yezakhi zemvelo eziguquguqukayo ezine-oxygen. Indlela yokulinganisa enamaphoyinti amaningi isetshenziselwe ukuhlaziya i-sulphur dioxide ne-hydrogen sulphide esihlaziyini se-NDUV, futhi indlela yokulinganisa iphuzu elilodwa isetshenziselwe ukuhlaziywa kwi-chromatography yegesi kanye ne-

UV fluorescence lapho ingxube yesampula ihlaziywa ngokumelene nengxube eyinkomba ne ingxenyana yemvukuzane efanayo. Imininingo yezezibalo (statistical data) ebhekwe ngesikhathi sokuhlaziya ihlanganise isivinini sokuhamba kwewashi lensiza kusebenza (instrument drift) kanye nephesenti le-relative standard deviation ukuze kubhekwe ukuphindaphinda kokukaliwe, ukuthembeka kanye nokungaqiniseki ngokuphathelene nokukala. Imiphumela ye-gravimetric yezakhi ezilungiselelwe zesibabule ku-10 µmol/mol inikeze iphesenti isihlobo esikhulise ukungaqiniseki kwe-0.041% REU ye-hydrogen sulphide, i-0.12% REU ye-sulphur dioxide. Imiphumela ye-gravimetric yezakhi zemvelo eziguquguqukayo ezine-oxygen eziku-5 µmol/mol akhombise iphesenti elihlobene nokwandiswa kokungaqiniseki okungu-0.068 kuya ku-0.35% REU kwe-isopropanol ne-ethanol ngokulandelana nangaphansi kuka-2.4% REU wezakhi eziningi zemvelo eziguquguqukayo ezine-oxygen. Ekugcineni, izingxube eziyinhloko ezijwayelekile zegesi zesibabule kanye nezakhi zemvelo eziguquguqukayo ezine-oxygen zakhiwe ngezinga eliphakeme kakhulu lokukala le-metrology lezinga lokungaqiniseki kwe-(k = 2).

Amagama ayisihluthulelo: Izakhi zesibabule, izakhi zemvelo eziguquguqukayo ezine-oxygen, izingxube zegesi okususelwa kuzo, ukungaqiniseki okuhlobene okwandisiwe, ukungaguquguquki kwangaphakathi, ukulungiswa kwe-gravimetric, i-GC-PDHID, i-GC-FID, i-NDUV, i-UV fluorescence

INGABULA ZIGCAWU

Uhlalutyo oluchanekileyo lwemixube yokusetyenziswa kwesalfure / usibabule (*sulfur*) kunye nezomongomoya ezingazinzanga (*volatile oxygenated compounds*) zibaluleke kakhulu ekubambeleleni komthetho kumacandelo ahlukeneyo endalo. Ukubala ngokuchanekileyo kwemixube yesalfure / usibabule neye mongomoya ongazinzanga kumanyathelo ezinto eziphilayo ezinobunzima kungumceli mngeni, ngenxa yezinto ezahlukeneyo ezinjenge- molecules ezifunxwa kumphezulu wangaphakathi wesilinda (*inner surface of cylinder*). Kubalulekile ke ngoko ukuba kuveliswe umxube ochanekileyo kunye onokwethenjelwa kwerhasi yokuqonononondisa (reference gas) kunye neqhezu le-mole kumanqanaba oqwalaselo lomgangatho womoya kunye nomhlaba wokuva igesi eMzantsi Afrika (*South Africa*).

Ngelixa ukhona umceli mngeni ekuveliseni umxube wesalfure/ usibabule kunye neyomongomoya ongazinzanga yokwenza kwerhasi yokuqonononondisa, lenkqubo iyonke ukusuka kumanyathelo okulungiselela i-gravimetric kude kube yinkqubo yohlalutya lokuthelekisa kunye nokuzinza komxube kwisilinda segesi, kukhokelela kukungaqiniseki kwemilinganiselo (*measurement uncertainty*). Ukwenzela kuveliswe umxube wegesi wenqanaba eliphezulu, kufuneka kulandelwa amanyathelo amathathu abalulekileyo; Uvavanyo lokucoceka kwezinto zokuqalisa ezisetyenziswayo koluvavanyo, ulungiselelo lwe-gravimetric kunye nokungqinisisa komxube wegesi olungiselelweyo. Uhlalutyo lokucoceka kwezixhobo nobunyulu obuphezulu bukhangelwe ngokusebenzisa i-chromatography yerhasi edityaniswe nezixhobo zokuchonga kunye ne-Karl Fischer yokukhangela ubumanzi kwiikhemikhali (*chemical*) ezinonokucoceka okuphezulu.

Imixube ezihlanganayo yesalfure/ usibabule kunye nezomongomoya engazizanga ekufuneka zenziwe koluphando yi-hydrogen sulphide, sulfur dioxide, acetone, methanol, ethanol, isopropanol ne-n-butanol. Ezi zinto ziveliswe ngokulandela amacwecwe e-International Organisation for Standardisation okubekwa emgangathweni kwi-molecule ye-10 µmol / mol kwiisampulu zesulfure kunye ne-5 µmol / mol yeefomathi eziguqukayo engazinzanga yemixube kamongomoya. Ukulungiswa kokuxutywa kwerhasi yokuqonononondisa yesalfure/ kukusibabule kwenziwe ngendlela ye-static gravimetric kusetyenziswa indlela ethe ngqo apho icandelo lokujolisa lagqithiselwa ngqo kwisilinda.

Ukulungiswa kwemixube yomongomoya engazinzanga esetyenziziweyo ibe yindlela ejikelezayo (*indirect method*) apho kusetyenziswa umbhobho ojolise kwinto ethile evela kwiikhemikhali zokucoceka okuphezulu yagqithiselwa kwisilinda kusetyenziswa isirinji enegesi ethe ngci. Ukuthelekisa phakathi komxube wegesi ongqinisisiweyo kwaqinisekiswa ngohlalutyo lwe-Ultra-Violet (NDUV), irhasi

chromatograph edityaniswe nomtshisi wokutshixiza we-helium ionisation (GC-PDHID, umhlalutyi we-UV fluorescence womatshini wesulfure kunye negesi ye-chromatography edityaniswe nomatshini ionisation detector (GC-FID) yomxube kamongomoya ongazinzanga.
Kuye kwabalwa ngemimiselo eliqela (*multiple point calibration*) kubalwa i-sulfur dioxide ne-hydrogen sulphide kwi-NDUV yokuhlalutya, kwaye indlela yokujonga yinto enephuzu elinye yokumisela esetyenziswa kuhlalutyo kwi-chromatography yegesi kunye ne-fluorescence ye-UV apho umxube wesampulu uhlaluthelwa ngokuchasene nomxube wokuqonononondisa kunye nenxalenye efanayo.

Idatha yeenkcukacha-manani ethe yaqwalaselwa ngexesha lohlalutyo ibandakanya ukubalwa kokutenxa kwesixhobo zakulinganisela (*instrument drift*) kunye neepesenti zokutenxa kumgangatho (*relative standard deviation*) wokujonga ukuphindaphinda kwemilinganiselo, ukuthembeka kunye nokungaqiniseki kwemilinganiselo. Iziphumo ze-gravimetric zezihlanganisi ezilungiselelwe isalfure / usibabule kwi-10 µmol / mol inike isixa sepesenti eyandisiweyo yokungaqiniseki kwe-0,041% i-REU ye-hydrogen sulphide, i-0,12% i-REU ye- sulfure dioxide. Iziphumo ze-gravimetric zezixhobo ezilungiselelwe umongomoyo ongazinzanga eziguqukayo ze-5 µmol / mol zibonise ipesenti yesihlobo esikhulisiweyo sokungaqiniseki kwe-0.068% ukuya kwi-0.35% i-REU ye-isopropanol kunye ne-ethanol ngokulandelanayo kwaye ingaphantsi kwe-2.4% i-REU yezinto ezixubeneyo nemixube kamongomoya ongazinzanga.

Okokugqibela, ukuxutywa kwegesi esemgangathweni okuphezulu komxube wesalfure / usibabule kunye nesomxube womongomoya ongazinzanga yokuqina kwemozulu yaveliswa ngenqanaba eliphezulu kukho ukungaqiniseki komgangatho we (k = 2).

Amagama aphambili: *Imixube ye Salfure / kaSibabule, Imixube kamangomoya engazinzanga, Umxube werhasi yokuqonononondisa, ukungqinisisa okwandisiweyo, ukungqinisisa okungaphakathi, ukulungiswa kwegravimetric, GC-PDHID, GC-FID, NDUV, i-fluorescence ye-UV*.

PUBLICATIONS AND MANUSCRIPTS

1. **Nompumelelo Leshabane**, James Tshilongo, Shadung J Moja, Napo G. Ntsasa, Gumani Mphaphuli, Mudalo I Jozela; (March **2021**) "*Quantitation of hydrogen sulfide reference gas mixtures to provide traceability for indoor air quality monitoring"*, DOI: 10.1007/s00769-021-01461-z. Journal of Accred and Qual Assur (Manuscript published).

2. Dalho Kim, Young-Doo Kim, Sangil Lee, Damian Smeulders, Hai Wu, Judit Fuko, Janneke I.T. van Wijk, Adriaan M.H. van der Veen, James Tshilongo, Mudalo Jozela, **Nompumelelo Leshabane**, Gumani Mphaphuli, Florbela Dias, Carlos Costa, Leonid Konopelko, Olga Efremova, Sam Bartlett, Paul Brewer and Arul Murugan – CCQM-K41.2017 – "*International Comparison of hydrogen sulfide in nitrogen (10 µmol/mol)*", Metrologia, 2021. Vol.58, Number 1A.

3. Teboho P. Mokoena, Kenneth T. Hillie, Hendrik C. Swart, **Nompumelelo Leshabane**, James Tshilongo, David E. Motaung; (April **2020**) "*Fabrication of propanol gas sensor using p-type NiO nanostructures: The effect of ramping rate towards luminescence and gas sensing characteristics*", DOI:10.1016/j.matchemphys.2020.123316 *(Manuscript published).*

4. **Nompumelelo Leshabane**, James Tshilongo, Shadung J Moja, Napo Ntsasa, Gumani Mphaphuli, Mudalo I Jozela "*Improved measurements of hydrogen sulphide reference gas mixtures in support of indoor air quality monitoring"* Conference Proceedings of the Test and Measurement 2019 (T&M) conference and Workshop, Misty Hills, Johannesburg (Gauteng Province), 16th to 18th September 2019 (*Manuscript Reviewed and published on website*: http://www.nla.org.za/webfiles/conferences/2019/Proceedings/index.php?dir=Manuscripts/Tuesday%2C%2017%20September%202019).

5. **Nompumelelo Leshabane**, James Tshilongo, Shadung J Moja, Napo G. Ntsasa, Gumani Mphaphuli and Mudalo I. Jozela., "*Improved measurement capabilities for hydrogen sulphide reference gas mixtures in South Africa".* Conference Proceedings of the international school of physics Enrico Fermi, Villa Monastero, Varenna (Milano), Italy, 4 to 13 July 2019 (Manuscript accepted for publication).

6. Steven S. Nkosi, Ioannis Kortidis; David E. Motaung; **Nompumelelo Leshabane**; Muzi Ndwandwe; James Tshilongo; Napo Ntsasa; (**2019**) "*The effect of stabilized ZnO nanostructures green luminescence towards LPG sensing capabilities*". DOI:10.1016/j.matchemphys.2019.122452.(*Manuscript published*).

7. Ioannis Kortidis; Silindile Lushozi; **Nompumelelo Leshabane**; Steven S. Nkosi; O. Muzi Ndwandwe; James Tshilongo; Napo Ntsasa; David E. Motaung (**2019**) "*Selective detection of propanol vapour at low operating temperature utilizing ZnO nanostructures*", Ceramics International, Vol 45, 16417-16423 (*Manuscript published).*

8. Prelly Marebane, James Tshilongo, Tshepiso Mphamo, Mudalo Jozela, Napo Ntsasa, David Mogale, Silindile Lushozi, **Nompumelelo Leshabane** "*Continuous improvement of emission reference materials"* Conference Proceedings of the Test and Measurement 2019 and Workshop conference (T & M) Conference, Misty Hills, Johannesburg (Gauteng Province), 16 to 18 October 2018 (Manuscript Reviewed and published on website: http://www.nla.org.za/webfiles/conferences/2018/Proceedings/Manuscripts/Monday%2C%208%20October%202018/M308%20-%20Continuous%20improvement%20of%20emission%20reference%20materials_peer%20reviewed.pdf).

PRESENTATIONS AND PAPERS AT CONFERENCES

1. **Nompumelelo Leshabane**, James Tshilongo, Shadung J Moja, Napo Ntsasa, Gumani Mphaphuli, Mudalo I Jozela, "*Improved measurements of hydrogen sulphide reference gas mixtures in support of indoor air quality monitoring*" Conference proceedings of the Test and Measurement 2019 (T&M) conference and workshop, Misty Hills, Johannesburg (Gauteng Province), 16 to 18 September 2019.

2. James Tshilongo, Napo Ntsasa, **Nompumelelo Leshabane**, Mudalo I Jozela, "*Overview and current capabilities of NMISA gas analysis section in support of air quality monitoring*", Workshop proceedings of Asia Pacific Metrology Programme 17th APMP/TCQM Gas Analysis workshop, Royal Ambarrukmo, Yogyakarta, (Indonesia) 5 to 7 August 2019.

3. **Nompumelelo Leshabane**, Mudalo I Jozela, James Tshilongo, Napo Ntsasa, "*Development of sulphur dioxide reference gas mixtures at nanomole per mole levels*". Conference proceedings of National Association for Clean Air (NACA) conference, Riverside Sun, Vanderbijlpark, (Gauteng Province), 31st October to 2nd November 2018.

4. Mudalo Jozela, James Tshilongo, Mr Napo Ntsasa, **Nompumelelo Leshabane**, *"Development of multi-components volatile organic compounds reference gas mixtures"*, Conference proceedings of National Association for Clean Air (NACA) conference, Riverside Sun, Vanderbijlpark, (Gauteng Province), 31st October to 2nd November 2018.

5. **Nompumelelo Leshabane**, James Tshilongo, Shadung J Moja, Napo G Ntsasa, Mudalo I Jozela, *"Improved measurements of sulphur containing compounds in nitrogen reference gas mixtures",* Conference proceedings of National Association for Clean Air (NACA) conference, Cedarwoods of Sandton, Woodmead, (Gauteng Province), 4th to 6th October 2017.

6. **Nompumelelo Leshabane**, *"Development of fuel combustion alcohol reference gas mixtures"*. Conference proceedings of Test and Measurements conference, Saint George Hotel and Convention centre, Centurion, (Gauteng Province), 31st July to 1st August 2017.

7. Mudalo I. Jozela, James Tshilongo, Napo Ntsasa, **Nompumelelo Leshabane**, *"Development of multi-component volatile organic compound reference gas mixtures",* Conference proceedings of Test and Measurements conference, Saint George Hotel and Convention centre, Centurion, (Gauteng Province), 31st July to 1st August 2017.

8. Mudalo I. Jozela, James Tshilongo, Napo G Ntsasa, **Nompumelelo Leshabane**, David M Mogale, Tshepiso Mphamo, Silindile Lushozi, Goitsemang Lekoto, Prelly Marebane, Luke Chimuka, *“Measurement equivalence of national measurement standards, a carbon dioxide case study”,* Conference proceedings of National Association for Clean Air (NACA) conference, Cedarwoods of Sandton, Woodmead, (Gauteng Province), 4th to 6th October 2017.
9. **Nompumelelo Leshabane**, James Tshilongo, Napo G Ntsasa, Mudalo I Jozela, “*Stability study of hydrogen sulphide reference gas mixtures”.* Conference proceedings of National Association for Clean Air (NACA) conference, Riverside Mall, Mbombela (Mpumalanga Province), 5th to 7th October 2016.
10. James Tshilongo, Napo G. Ntsasa, **Nompumelelo Leshabane**, Mudalo I.Nemadzhilili, David M. Mogale, Gumani Mphaphuli; Goitsemang Lekoto; Tshepiso Mphamo, Prelly M. Marebane and Silindile L. Lushozi, “*Impact and shortening traceability chain for air quality monitoring industries in South Africa”*, Conference Proceedings of the National Association for Clear Air (NACA) conference, Riverside Mall, Mbombela (Province), 5th to 7th October 2016.
11. Jozela Mudalo. I, James Tshilongo, Napo Ntsasa, **Nompumelelo Leshabane**, *“Improvement of propane (C_3H_8) reference gas mixtures to support automotive and stack emission industries”,* Conference Proceedings of the National Association for Clear Air (NACA) conference, Riverside Mall, Mbombela (Mpumalanga Province), 5th to 7th October 2016.

ABBREVIATIONS AND ACRONYMS

AWS	Automated Weighing System
BIPM	International Bureau for Weights and Measures
CCQM	Consultative Committee for Amount of Substance
CCQM-GAWG	Consultative Committee for Amount of Substance-Gas Analysis Working Group
CIPM MRA	International Committee of Weights and Measures Mutual Recognition Arrangement
CMC	Calibration and Measurement Capability
CO	Carbon Monoxide
CoA	Certificate of Analysis
DI	Designated Institute
DQOs	Data Quality Objectives
ESDM	Estimated standard deviation of the mean
EURAMET	European Association of National Metrology Institutes
FID	Flame Ionisation Detector
GC-FID	Gas Chromatography coupled with a Flame Ionisation Detector
GC-MS	Gas Chromatography coupled with Mass Spectroscopy
ISO	International Organization for Standards
KCRV	Key Comparison Reference Value
KRISS	Korea Research Institute of Standards and Science
LOD	Limit of Detection
NACA	National Association of Clean Air
NMHCs	Non-methane Hydrocarbons
NMI	National Metrology Institutes
NMISA	National Metrology Institute of South Africa
NOMHICE	Non-methane Hydrocarbon Intercomparison Experiments
NPL	National Physical Laboratory
PAN	Peroxide and Peroxyacetyl Nitrate
PDHID	Pulsed Discharge Helium Ionisation Detector
POCP	Photochemical Ozone Creation Potential
PRGMs	Primary Reference Gas Mixtures
REU	Relative Expanded Uncertainty
RMM	Relative Molar Masses
RMO	Regional Metrology Organisation
RSD	Relative Standard Deviation
SADC	Southern African Development Community
SSV	Stream Selection Valve
TCD	Thermal Conductivity Detector
VIM	International Vocabulary of Metrology
VSL	Van Swinden Laboratory (Dutch Metrology Institute)
WMO-GAW	World Meteorological Organization-Global Atmosphere Watch

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1: INTRODUCTION

An overview background of the selected sulphur compounds and oxygenated volatile organic compound (OVOC) primary standard gas mixtures will be discussed. It then provides the significance of the study, problem statement, aims and objectives are discussed as well. It will also indicate the link between the develop primary reference gas mixtures with the applications towards the gas sensor.

1.1 BACKGROUND OF THE STUDY

Air pollution is a serious challenge to the environment and the health of human beings. Air pollutants are primarily composed of particulate matter and gaseous compounds suspended in air. The main air pollution sources are classified as either natural or anthropogenic. Natural sources include dust storms from deserts, emission from volcanoes, etc. Anthropogenic sources include activities such as domestic fuel burning, industrial emissions, etc. Even though most hazardous chemicals can be emitted to the environment unintentionally, many of air pollutants are released as by-products during burning activities. Thus, illness associated with air pollution could be nausea, headaches, skin and eye irritation and respiratory tract problems, birth defects, cancer and immune suppression (Kampa and Castanas, 2008). There are other sources of anthropogenic activities which include vehicle exhaust, fuel combustion or production, natural gas industry emissions and domestic fuel burning or biomass burning (Radzi Bin Abas *et al.*, 2004); (Lewtas, 2007). Burning or combustion of fuel results in many chemicals being produced or emitted in the air. Fuel consumption is the major contributor to air pollution including greenhouse gas emissions. Fuel combustion results in air pollutants such as particulate matter, nitrogen oxides, volatile organic compounds, benzene, metals, alcohols, and sulphur dioxide, among others; many of these contribute to the creation of smog.

Air pollution monitoring in South Africa focused is mainly on the primary pollutants such as oxides of nitrogen, sulphur dioxide and ground level ozone. Research activities into other air pollutants which contribute to global warming such as the greenhouse gases have increased. Gases that pose a threat to human health due to exposure in working environments (indoor air quality) such as sulphur containing compounds and Oxygenated volatile organic compounds (OVOCs) are not well documented.

The South African government implemented the National Environmental Management: Air Quality Act 2004 (Act No. 39 of 2004), due to the challenges of air quality issues cause to the human and environmental. The purpose of the Air Quality Act emphases the improvement of air quality through several laws and regulations, set standards for monitoring, managing, and controlling ambient air quality. It also set out fines and penalties for people who break the law and most important it makes air quality the responsibility of local government, through air quality management plans.

The legislature has led to the requirements for stable and accurate reference gas mixtures with mole fraction at ambient levels for the indoor and outdoor air quality monitoring in South Africa. To develop accurate mole fraction trends of selected sulphur and OVOC compounds for air pollution monitoring industry, it is important to produce accurate and stable reference gas mixtures which can be used to produce traceable, reliable, and accurate measurements.

In accordance with the Measurement Units and Measurement Standards Act no.18 of 2006, National Metrology Institute of South Africa (NMISA) provides dissemination for the measurement traceability from the national measurement standards to ambient air quality monitoring industries and other stakeholders through the provision of gravimetrically prepared primary reference gas mixtures (PRGMs).

1.1.1 SULPHUR CONTAINING COMPOUNDS

Accurate measurements for the determination of sulphur containing compounds are very critical for the compliance with legislation in various industries and environmental sectors such as natural gas industry and monitoring the quality of air. Sulphur containing compounds measurements are challenging because sulphur containing compounds tend to adsorb on the internal surfaces of the sample collection devices and transfer lines. Therefore, passivated sampling container should be used to minimise the loss of sulphur compounds, thus ensuring sample integrity during the collection, transportation, and storage of these compounds. These types of compounds can cause harm to human beings, animals and damage the equipment and the pipelines. Hence, metrological measurements of sulphur containing compounds are required to ensure that the gas injected into transmission network comply with national limits for concentration of these compounds (Martinez *et al.*, 2012); (Brown *et al.*, 2015).

Some of the sulphur containing compounds used as odorants are added to natural gas as odorants to enable any leaks of natural gas to be detected by the public for safety purposes (Brown *et al.*, 2015). Other sulphur containing compounds such as hydrogen sulphide, sulphur dioxide, mercaptans and thiophenes are highly reactive get adsorbed easily and their losses are within minutes or hours.

1.1.2 OXYGENATED VOLATILE ORGANIC COMPOUND

The studies in air pollution monitoring indicate that domestic fuel combustion in low-income settlements of South Africa is the major source of urban air pollution. Most of the low-income households in South Africa use large quantities of coal, wood, paraffin (Kerosene) for cooking to provide for their energy needs. These OVOCs are mostly produced from biomass Research shows that more work still needs to be done on domestic combustion emissions inventory in South Africa (Demirbas, 2008); (Naidoo, Piketh and Curtis, 2015).This is because there are still some several issues in relation to the following:

(a) There are different types of fuel combustions: Liquid fuels which are combustible or energy - generating molecules that can be used to create mechanical energy. Majority of liquid fuels are derived from fossil fuels such as hydrogen fuel, ethanol, and biodiesel. These liquid fuels contribute mainly towards the automotive fuel market and the socioeconomic related issues (Demirbas, 2008).
(b) Solid fuels which are mainly coal and wood, consumed during winter season.
(c) Gaseous fuels which are popular for cooking purposes but maybe too expensive for low income households (Naidoo *et al., 2015)*.

In accordance with the Measurement Units and Measurement Standards Act no.18 of 2006 (Government Gazette, 2007). National Metrology Institute of South Africa (NMISA) provides dissemination for the measurement traceability from the national measurement standards to ambient air quality monitoring industries and other stakeholders through the provision of gravimetrically prepared primary reference gas mixtures (PRGMs).

1.2 SIGNIFICANCE OF THE STUDY

Accurate and traceable reference gas mixtures are required for reliable measurements of sulphur containing compounds and oxygenated volatile organic compound alcohols for air quality monitoring in South Africa. There is currently no local provider for primary reference gas mixtures of sulphur containing compounds and OVOCs in South Africa and SADC region which are traceable to SI units. The industry imports these primary reference gas mixtures internationally at great expense and the time frame to receive the gases is long which leads to almost three months of the useful life of the primary reference gas mixtures lost before the PRGMs can be used.

The development of selected sulphur containing compounds and OVOC primary standard gas mixtures (PSGMs) during this study will provide a significant solution to the South African Industry and SADC region. Therefore, by providing measurement traceable primary reference gas mixtures to indoor and outdoor air quality monitoring industry in South Africa.

1.3 PROBLEM STATEMENT

Most selected sulphur containing compounds and oxygenated volatile organic compound alcohols are stable for a short period of time in the gas cylinders and therefore stability assessment of these compounds becomes a huge challenge and therefore need to be investigated. Indoor and outdoor air quality monitoring in South

Africa is primarily associated with industries such as biogas and natural gas. The sulphur containing compounds are also present in wastewater treatment and livestock operations. Existing plants and new plants need to comply with minimum emission standards in accordance with the Air Quality Act 2004 (Act No. 39 of 2004)

Analysis of selected sulphur containing compounds and OVOCs is very important for the protection of the life of human with the aim of providing the quality of life to the South African community. The quality of life in South Africa is being compromised by lack of accurate measurement data that is traceable to International System of units (SI) of measurements. Lack of sulphur containing compounds and OVOCs primary reference gas mixtures in South Africa results in inaccurate, unreliable, and large uncertainty measurements in the air pollution monitoring industry.

1.4 AIM OF THE STUDY

The aim of this study was to develop precise, accurate and traceable selected sulphur and oxygenated volatile compound alcohols compound primary reference gas mixtures for indoor and outdoor air quality monitoring in South Africa. The developed selected sulphur containing compounds and oxygenated volatile organic compound primary reference gas mixtures will be used in various applications which includes the stability and sensitivity test of the gas sensors. This application is for gas sensing in the nanostructures. It is envisaging that the success of stability test using this accurate gas mixtures will be part of monitoring safety environment in the field of mining industries. This is to support the South African air pollution monitoring industries, in accordance with the set regulations of the Air Quality Act 2004 (Act No. 39 of 2004) and Measurement Units and Measurement standard Act, 2006 with precise primary reference gas mixtures for accurately air pollutants measurements.

1.5 OBJECTIVES OF THE STUDY

To achieve the aim of the study, the following objectives were considered:

(a) Gravimetrically prepare and verify the selected sulphur containing compounds such as, sulphur dioxide (SO_2) and hydrogen sulphide (H_2S) and OVOC such ethanol (C_2H_5OH), butanol (C_4H_9OH), acetone (C_3H_6O) and isopropanol (C_3H_8O).

(b) The critical part of the work was to study the quantitative and qualitative analysis which included purity analysis of the high pure gases, static dilution methods and internal consistency (comparison) or verification of the primary standard gas mixtures.

(c) The research includes the adsorption and desorption study of selected sulphur compounds and oxygenated volatile organic compounds in the gas cylinders.

During the study, the evaluation of adsorption and desorption was done by using equal division method (Lee *et al.*, 2017).

(d) Participation in international key comparisons with other national metrology institute around the world with the aim to do the equivalence test for all the developed primary standard gas mixtures during this study was the final goal. This will lead to the NMISA being able to claim the calibration and measurement capabilities for these compounds in the global Bureau International des Poids et Mesures (BIPM) key comparison database. This was done with the aim of evaluating the capabilities of purity analysis, gravimetric preparation (includes weighing etc), analysis of the compounds and data evaluation which includes the uncertainty budgets for the respective measurements.

(e) Applications of the developed precise, accurate and traceable selected sulphur and oxygenated volatile organic compound primary reference gas mixtures in the field of gas sensing and gas metrology.

CHAPTER 2: LITERATURE REVIEW

This chapter reviews the existing information on the development of primary standard gas mixtures of selected sulphur containing compounds and oxygenated volatile organic compounds. The chapter will also give information on the different methods for gravimetric preparation and analysis of reference gas mixtures. It will highlight some of the metrological concepts such as measurement uncertainty, international equivalence, and traceability of measurements.

2.1 BACKGROUND ON SELECTED SULPHUR COMPOUNDS

The National Environmental Management of Air Quality Act 2004 (Act No. 39 of 2004) stipulates all the measures to follow and comply with for air pollution monitoring industries. The Act also sets rules and regulations for emission measurements. As the air pollution industry continuously measures emissions, they still have to comply to time frames set by the Air Quality Act 2004. Measurements for sulphur dioxide, oxides of nitrogen (nitrogen dioxide, nitric oxide) and particulate matter which are continuous measurements found in most subcategory of minimum emission standards. Hydrogen sulphide is also found in most subcategories for continuous measurements (Air Quality Act 2004 (Act No. 39) of 2004). Measurements of sulphur-containing compounds are critical for the compliance with legislation in various industries and environmental sectors such as natural gas and air pollution monitoring.

Sulphur pollutants contributes majorly to the air pollution challenges and thus sulphur containing compounds are considered significant in the air pollution monitoring industry. These sulphur compounds originate from natural environment and air pollution emissions. The sulphur components naturally occur as sulphate (SO_4^{2-}) aerosols from sea spray meanwhile hydrogen sulphide (H_2S) is produced from decomposition of organic matter such as swamp areas, bogs, and tidal flats. The emissions of SO_2 and H_2S come from air pollution sources and industrial origin respectively (Robinson and Robbins, 1970). Sulphur containing compounds are found to be the main cause for the environmental damage especially acid deposition, rapid acidification of lakes and corrosion of metal structures. They are highly recognised by their strong smell in sewage systems. They play a role in global chemical cycles such as Dimethyl Sulphide (DMS) which is found in sea water, DMS is produced in the ocean and is assumed to be important in global sulphur cycle and the radiation balance of the Earth. They are also present in trace amounts in foods, beverages and fragrances and are responsible for taste and odour. In order for the public to detect a natural gas leak, sulphur containing compounds are added as odorants (Brown *et al.*, 2015). This study will address the two selected sulphur containing compounds, sulphur dioxide (SO_2) and hydrogen sulphide (H_2S). Sulfinert treated transfer lines and well treated gas cylinders are used in the production of sulphur containing gas mixtures because these compounds tend to adsorb onto or reactions with internal surfaces of cylinders and transfer lines. They may react with water or oxygen when they are measured in biogas as shown in reaction 1 and 2 (Brown *et al.*, 2015).

$$2H_2S_{(g)} + 3O_{2(g)} \rightarrow 2SO_{2(g)} + 2H_2O_{(l)} \qquad (1)$$

$$COS_{(g)} + H_2O_{(l)} \rightarrow H_2S_{(g)} + CO_{2(g)} \qquad (2)$$

H_2S can easily react with water to form sulphuric acid (H_2SO_4) which is very corrosive and damaging to structural steel and concrete (Preece et al., 2012).

2.1.1 Health risks impact due to hydrogen sulphide emissions

Hydrogen sulphide (H_2S) is mainly monitored for occupational health and safety and indoor air quality. Most of the hydrogen levels set are for industrial emission sources and hence the high levels of hydrogen sulphide are properly documented. The standards such as Occupational Health and Safety (OSHA) and the National Institute for Occupational Safety and Health (NIOSH) cover mostly short-term maximum exposure levels for workers. Unfortunately, long-term exposure to low levels of H_2S is not well documented. The personal monitors for hydrogen sulphide have a detection limit of 1 µmol/mol which is above the odour threshold. These personal monitors are inadequate to detect low levels of H_2S which are below 1 µmol/mol. Human exposure mainly comes from nearby industrial and agricultural sources, oil and gas development and wastewater treatment plants which are mostly regulated. Drinking water contaminated by hydrogen sulphide is not yet regulated. However high levels of hydrogen sulphide in drinking water can cause stomach pains and nausea (Brewer *et al.*, 2014). Table 2.1 shows the exposure levels and the symptoms of exposure to hydrogen sulphide.

Table 2.1: Exposure levels symptoms (Source: Preece at al.,2012)

Concentrations levels	Exposure Symptoms
Above 250 µmol/mol	Laxative effect, dehydration, and olfactory paralysis
50 to 200 µmol/mol	Challenging respiratory tract irritation, eye irritation, shock, convulsion, comma, and death in severe cases
10 to 50 µmol/mol	Headaches, dizziness, nausea, stomach pains, vomiting, coughing, challenge in breathing
5 to 10 µmol/mol	Increased blood lactate concentration decreased skeletal muscle citrate synthase activity
2 µmol/mol	Bronchial constriction in asthmatic people, automatic abortion.
0 to 10 µmol/mol	Irritation of eye, nose, and throat

Hydrogen sulphide is not regulated in the Environmental Protection Agency's current drinking water standard as either primary or secondary contaminant. Hydrogen sulphide is found naturally in ground water through the following:

(a) Sulphur reducing bacteria during the decomposition process of the organic matter in low-oxygen areas
(b) Chemical reduction of the dissolved sulphate by sulphate -reducing bacteria in low-oxygen areas

Hydrogen sulphide can be generated from magnesium corrosion control rod present in electric hot water heaters. This converts naturally occurring sulphate in water to hydrogen sulphide and thus the odour will be mostly found in hot water (Brewer *et al.*, 2014).

2.1.2 Hydrogen sulphide and sulphur dioxide gas mixtures

Other international, National Metrology Institutes (NMIs) such as the Korean Research Institute of Standards and Science (KRISS), National Institute of Standards and Technology (NIST), National Physical Laboratory (NPL) in the United Kingdom and Dutch Metrology Institute (VSL) have already developed the standard reference materials of hydrogen sulphide and sulphur dioxide in nitrogen reference gas mixtures in the form of binary for some of the molecules studied in this thesis. However, accurate and traceable reference gas mixtures are required by the South African air pollution monitoring industry for reliable measurements. Currently there is no local provider for primary standard gas mixtures of hydrogen sulphide in nitrogen. The industry imports these reference gas mixtures internationally at great expense and the time frame to receive the gases is long which leads to almost three months of the stability of the reference gas mixtures lost before the gas mixtures can be used. The development of hydrogen sulphide in nitrogen reference gas mixtures during this study will provide a significant solution to the South African Industry and SADC region. Therefore, by providing measurement traceable reference gas mixtures to indoor and outdoor air quality monitoring industry in South Africa. Hydrogen sulphide is mainly monitored for occupational health and safety (Miller and Guenther, 2007) and sulphur dioxide for outdoor air pollution monitoring. To support the indoor and outdoor air quality monitoring industry in South African, in accordance with the set regulations of the Air Quality Act 2004 (Act No. 39 of 2004), the National Metrology Institute of South Africa (NMISA) has developed hydrogen sulphide and sulphur dioxide in a nitrogen as primary standard gas mixture (PSGMs).

2.2 BACKGROUND ON SELECTED OXYGENATED VOLATILE ORGANIC (OVOCs) COMPOUNDS

The main precursors for the production of ozone (O_3) are volatile organic compounds (VOCs) and nitrogen oxides (NO_x). Ozone plays an essential part in atmospheric chemistry and is also a significant greenhouse gas. The oxygenated volatile organic compounds (OVOCs) are significant fraction of the VOCs (Legreid *et al.*, 2007); (Mellouki *et al.*, 2015). OVOCs are more reactive than alkanes which are the starting material to form these compounds (Mellouki *et al.*, 2015). These compounds contribute to the sequence of chemical reactions for the troposphere of ozone formation in polluted environment. OVOCs are emitted in the atmosphere from four main sources (Legreid *et al.*, 2007); (Mellouki *et al.*, 2015):

(a) Atmospheric oxidation of hydrocarbons

(b) Emissions from biological sources such as growing plants, plant debris and biomass burning

(c) Evaporation of oxygenated solvents or fuels used in industrial processes, commercial operations, or consumer products

(d) Incomplete combustion of hydrocarbon-fuelled mobile or stationary sources

Methane is the simplest hydrocarbon which undergoes atmospheric oxidation by reaction with HO radicals to produce alcohols, aldehydes, and ketones. The use of OVOCs as blends with fuel have three main purposes: Firstly OVOCs such as ethanol, ethyl tert-butyl ether (ETBE) and methyl tert-butyl ether (MTBE) can make the antiknock value of fuel better by resisting autoignition. Secondly, they can physically substitute or dilute some fuel components and reduce harmful tailpipe emissions such as benzene (Legreid *et al.*, 2007); (Mellouki *et al.*, 2015) and thirdly OVOCs produced from renewable sources such as ethanol from corn, sugar cane, cellulose, fatty acid methyl esters from animal fats and vegetable oils displace, replace petroleum and can advance energy security and decrease greenhouse gas emissions.

OVOCs generally have lower vapour pressure compared to corresponding alkanes. As oxidation increases with addition of oxygen atoms, vapour pressure decreases significantly. Thus lower volatility malfunctional oxygenated volatile compounds will change into existing atmospheric particles and hence increase the organic fraction of secondary organic aerosols (Mellouki *et al.*, 2015). In support to Indoor and outdoor air quality monitoring industry in South African, the study has developed OVOCs of acetone, methanol, ethanol, isopropanol, and n-butanol in a nitrogen as primary standard gas mixture.

2.3 DEVELOPMENT OF SELECTED SULPHUR COMPOUNDS AND OXYGENATED VOLATILE ORGANIC COMPOUNDS

Selected sulphur containing compounds and OVOCs gas mixtures can be challenging components to develop. Sulphur components has the tendency to adsorb on the inner surfaces of the cylinder and transfer lines and can be highly reactive such as hydrogen sulphide, mercaptans and thiophenes (Brown *et al.*, 2015). Therefore it is important to use properly treated aluminium cylinders and sulfinert treated tubing or transfer lines. OVOCs has limitations in preparation due to their vapour pressure which gives maximum amount of OVOCs to be vaporised in a cylinder (Grenfell *et al.*, 2010). Several methods in preparation and verification of selected sulphur containing compounds and OVOCs have been improved to resolve these challenges experienced when developing these compounds. In developing highest metrological reference gas mixtures, there are three major processes to be adhered to such as purity assessment of source materials, Gravimetric preparation methods to be used and verification of gravimetrically prepared gas mixtures. These processes will be major topics in the literature review.

2.3.1 Precise preparation of gas mixtures

The oxygenated volatile organic compounds (OVOCs) are mostly prepared from high pure chemicals as source. The quantified amount of liquid is transferred into an evacuated cylinder where it vaporises into the gas phase. The transferred liquid into the cylinder needs to fully vaporise into the gaseous phase in order to produce accurate and precise gas mixtures. Therefore extra precaution is required when preparing these gas mixtures to evade any condensation. For the preparation of OVOCs, a syringe method is used as in accordance with ISO 6142-1:2015 (ISO 6142-1:2015). Thus a gas-tight syringe is filled with the calculated amount of liquid to be transferred into the cylinder. The syringe is weighed with the liquid and then again after injection into the cylinder and the difference between these weighing will the mass of liquid transferred into the cylinder. The liquid is therefore transferred into an evacuated cylinder by injection through a closed off septum (ISO 6142-1:2015). The injected liquid is further pressurised with a matrix gas to ensure that all the liquid is transferred into the cylinder.

Other liquid introduction methods are described in ISO 6142-1:2015 in ANNEX D, however Grenfell *et al.*(2010) mentions improvements in the preparation which include the use of an evacuated single-valve sample loop transfer vessel studied at NPL. Research shows that sample loops that were used has valves at each end whereby the liquid was introduced from the loop by blowing into the evacuated cylinder, but this would leave an unknown amount of gas in the loop therefore inaccurate weighing of the amount of the sample left in the sample loop. The improved method uses an evacuated sample loop, which has only a valve at one end of sample the loop while the other end is sealed, and a liquid is still transferred into an evacuated cylinder. Thus no gas remaining left after transferring and the amount transferred can be weighed accurately (Grenfell *et al.*, 2010). Other improvements included the use of minimum dead volume (MDV) connector constructed by NPL. The MDV is made of modified silver-coated valco long series nut connector which fits directly to the centre of cylinder valve housing. This results in minimised dead volume and elimination of liquid loss during transferring and evades absorption of material throughout sampling.

2.3.2 Stability study of primary standard gas mixtures

One of the challenges in developing the accurate reference gas mixtures of selected sulphur containing compounds and oxygenated volatile organic compounds is the stability of the primary standard gas mixtures in the gas cylinders. Therefore to accurately produce these gases, the type of gas cylinder and its inner surface wall treatments that assists in maintaining the stability of gas mixtures over extended period which is measured in years (Rhoderick *et al.*, 2019). The sulphur containing compounds are highly reactive and also tend to adsorb on the inner surface of aluminium cylinders and transfer lines. Passivated and pre-treated aluminium cylinders will largely prevent reactions between surfaces and components (Brown *et al.*, 2015). Stability of a gas mixture needs to be assessed periodically by preparing new gravimetric mixtures, this is in interval of three (3) months, six (6) and then yearly depending on the component at test. The long-term stability assessment is done by comparing newly prepared standard to the mixture under study and its mole fraction determined from the new standards (Lee *et al.*, 2017); (Rhoderick *et al.*, 2019).

Rhoderick et al mentions that influence of pressure on the stability has not being addressed but observation have been made that many different types of compounds show either an increase or decrease in mole fraction as the pressure of the gas mixture decreases. Some compounds such as acetone and methyl ethyl ketone experiences both increase and decrease in mole fraction as pressure is reduced to range of 1MPa to 3MPa. Thus both adsorption and desorption occur.

Stability of a primary standard gas mixture is also influenced by the type of gas cylinder used such as stainless steel or aluminium cylinders. Leuenberger *et al*, (2015) studied the adsorption and desorption effect on gas cylinders for different components of CO_2, H_2O and CH_4. The aluminium gas cylinders gave significantly low adsorption and desorption energy values than the stainless steel and thus they might be least influenced by temperatures. Therefore, aluminium cylinders indicated that they are more robust against adsorption/desorption processes and recommended to be used for preparation of primary standard gas mixtures

(Leuenberger *et al.*, 2015). To be able to evaluate adsorption, the internal surface of different cylinders must have been compared to find the correct material cylinder for preparing specific components. Different components show different adsorption behaviours on different surfaces. Lee *et al*. (2017) describes a method used to evaluate physical adsorption loss and how to estimate the corrected mole fraction and its uncertainty for preparation of PSGMs. In this method, cylinder-to-cylinder division whereby a pre-mix cylinder (the mother) is used to transfer gas mixtures through a T-shape stainless steel connection to newly evacuated cylinder (daughter) (Lee *et al.*, 2017). The transferring process is done with care to prevent the Joule Thompson effect.

2.3.3 Analytical challenges

Sulphur containing compounds measurements are challenging because sulphur compounds tend to adsorb on the internal surfaces of the sample collection devices and transfer lines. Therefore passivated sampling container should be used to minimise the loss of sulphur containing compounds, thus ensuring sample integrity during the collection, transportation and storage of these compounds (Martinez *et al.*, 2012); (Brown *et al.*, 2015). Also other sulphur containing compounds are highly reactive such as hydrogen sulphide, mercaptans and thiophenes and get adsorbed easily and their losses are within minutes or hours.

The separation of OVOCs also gives challenges during verification of gas mixtures due to co-elution of components using gas chromatography coupled with a flame ionisation detector (GC-FID). Therefore the method to be used needs to be properly developed and optimised. Precision is a very critical factor for analysis of OVOCs in this study. The measurement uncertainty of the final binaries and multi-components of OVOCs and selected sulphur compounds is expected to be significantly high. Thus because of the major uncertainty contributor being analytical uncertainty which can be from the difficulties encountered during analysis of these components.

2.4 PURITY ANALYSIS OF HIGH PURITY STARTING MATERIAL

Purity analysis is a very important and a prerequisite step for the preparation of calibration gas mixtures. It can be very challenging because trace level amounts of various components need to be quantified in the matrix and the standards to be used are not readily available. The purity analysis data is used in the determination of the final composition of the calibration gas mixtures and essential in establishing metrological traceability of the certified gas composition. Impurities in high pure source material contribute majorly to the uncertainty associated with prepared gas mixtures. Different methods can be used to identify impurities present in high pure source materials such as using open literature, information from manufacturer's specification purity data, previous data from the same materials and knowledge on the process used to produce the materials (ISO 19229:2015). If the impurities are not quantified, the prepared reference gas mixture will have a wrong gravimetric mole fraction and thus contribute to the final uncertainty of the prepared reference gas mixture (Yang *et al.*, 2017). Therefore a comprehensive purity analysis of high pure source material needs to be done to reduce the uncertainties. Several national metrology institutes (NMIs) internationally have developed various measurement methods for purity analysis of high pure source materials as it is the key to measurement traceability of gases. Thus confidence in the high pure source materials to be used for gravimetric preparation of reference gas mixtures.

Different techniques have been used for analysis of impurities in the high pure source material. Cavity ring-down spectroscopy (CRDS) has been used in gas analysis for trace moisture analysis and precise measurements of greenhouse gases and isotope analysis (Persijn, 2018), but gas chromatography is commonly used due to its more reliable and sensitivity detectors for some components. The flame ionisation detector (FID) is widely used for the detection of hydrocarbons and trace amount analysis of carbon monoxide (CO) and carbon dioxide (CO_2) using methaniser as a catalyst to convert CO and CO_2 to CH_4 (Janse van Rensburg *et al.*, 2007); (Zuas and Budiman, 2016). Pulsed discharge helium ionisation detector (PDHID) is a universal detector and more sensitive than thermal conductivity detector (TCD) in detection of permanent gases (Janse van Rensburg *et al.*, 2007); (Hindayani *et al.*, 2019). FID has a disadvantage of no or minute response to permanent gases of O_2 and N_2 (Janse van Rensburg *et al.*, 2007). Two methods for purity analysis of high pure source materials have been defined in the International Organization for Standardization, ISO 19229 (ISO 19229:2015). These two methods are defined as follows:

a) Purity analysis with results that are traceable

Purity analysis results need to be traceable to the International System of Units (SI) and this can be accomplished by using reference gas mixtures with defined uncertainties. The impurities in high pure source material can be quantified by using the direct method comparison with the reference gas mixtures with similar composition as the impurities. There could also be available metrological traceable purity data from different sources such a certificate of analysis that could be utilised the purity analysis. However this data should be checked if it is not clear on the certificate or report and thus also including to check if certified reference materials were used with detailed uncertainty assessment leading to measurement results was performed.

b) Indicative purity analysis

This is purity analysis data which produces data which the traceability is not yet established. This is when an analysis is done using gas mixtures without metrological traceability, theoretical response factors, using data from a certificate analysis which does not mention metrological traceability. For indicative purity analysis, results should include suitable uncertainty component that will account for any bias. Most gas manufacturers provide the gas specifications especially for high pure source gases. The specification can also be used to calculate the amount of impurities present in high pure source gases where reference gas mixtures are not available. The method of quantifying these impurities using the specification is outlined in ISO 19229:2015. Therefore the purity analysis method that provides the metrological traceability is a preferred method.

2.4.1 Calculation of mole fraction for the pure component

High pure source materials are expected to have purity of 100 % mol/mol in concentration if impurities are not present in these high pure components. Unfortunately, the analogy is not possible give different impurities present in all high pure source materials and hence purity of 100 % mol/mol is not achievable. Therefore the final purity or mole fraction of high pure component is determined by subtracting the mole fraction of all impurities in the high pure component. Equation 2.1 shows how the mole fraction of high pure component was calculated (ISO 19229:2015).

$$\boldsymbol{x_c = 1 - \sum_{i=1}^{n} x_i} \qquad 2.1$$

where $\boldsymbol{x_c}$ is the mole fraction of the high purity component and $\boldsymbol{x_i}$ represents the mole fraction of the expected impurity $\boldsymbol{i}$ and $\boldsymbol{n}$ represents the total number of impurities in the high pure component.

The uncertainty evaluation techniques are used to calculate uncertainty of each impurity. The law of propagation of uncertainty described in ISO/IEC GUIDE 98-3 (GUM) is used to determine the standard uncertainty in the mole fraction of high pure component. Equation 2.2 is used to calculate standard uncertainty. The calculation should include all the uncertainty contributors such as analytical repeatability and reproducibility measurements, uncertainties in calibration gas mixtures and manufacturer's specification uncertainty evaluation.

$$\boldsymbol{u^2}\,(\boldsymbol{x_c}) = \textstyle\sum_{i=1}^{n} \boldsymbol{u^2}\,(\boldsymbol{x_{ic}}) \qquad 2.2$$

where $\boldsymbol{u^2}\,(\boldsymbol{x_c})$ is the standard uncertainty of the high purity component and $\boldsymbol{u^2}\,(\boldsymbol{x_{ic}})$ represents the standard uncertainty of the expected impurity $\boldsymbol{i}$ and $\boldsymbol{n}$ represents the total number of impurities in the high pure component.

The impurity present in the high pure source material is sometimes present below the limit of detection (LOD) levels of the optimised measurement method. Therefore the mole fraction of the impurity $(\boldsymbol{x_i})$ is calculated as half the LOD value and its related uncertainty is calculated by assuming the rectangular distribution as shown in both equations 2.3 and 2.4, respectively.

$$\boldsymbol{x_i} = \frac{\boldsymbol{LOD}}{\boldsymbol{2}} \qquad 2.3$$

$$\mathrm{U}\ (x_i)= \frac{x_i}{\sqrt{3}} \qquad 2.4$$

where $\boldsymbol{x_i}$ is the mole fraction of the impurity, $\mathbf{LOD}$ is the limit of detection of the analytical method used to quantify the impurity and *U* (x_i) is the associated uncertainty of the quantified impurity.

2.5 GRAVIMETRIC PREPARATION OF REFERENCE GAS MIXTURES

Reference gas mixtures are gravimetrically prepared in accordance with International Organization for Standardization. These gas mixtures are produced from diluting from high pure starting materials (gaseous or liquid components) or pre-mixtures gases into an evacuated cylinder. The method is based on mass calculation of each component to be transferred into a cylinder (ISO 19229:2015); (Milton *et al.*, 2011). Two methods can be used for gravimetric preparation of gas mixtures such as static gravimetric and dynamic gravimetric methods. Both gravimetric preparation methods are traceable to both SI unit of mass (kg) and amount of substance (mol). Each component to be added is accurately weighed during the preparation process. The mixture cylinder is weighed against a tare cylinder which has similar properties as the mixture cylinder, thus include the cylinder valve, cylinder material, cylinder volume and finishings. This is done to minimise the buoyance effect rising from cylinder expansion effect and the difference in air densities (Milton *et al.*, 2011). It is very critical for a gravimetrically prepared reference gas mixture to be verified after preparation. This is done by analytical comparison using ISO 6143 (*ISO 6143*, 2001) or a reference gas mixture of similar composition and verified before. Therefore, only after the prepared gravimetric gas mixture has been verified can be considered to have a mole fraction and uncertainty that is fully traceable to the SI unit. The ideal gas law equation is used to calculate the target mass from a parent gas can be determined with a derived equation from the ideal gas equation as shown in equation 2.5 (ISO 6142-1:2015).

$$\mathbf{m_i} = \frac{\mathbf{x_i P_{cyl} V_{cyl} M_i}}{\mathbf{RTZ_f}} \qquad 2.5$$

where $\boldsymbol{m_i}$ is the target mass of component $\boldsymbol{i}$, $\boldsymbol{x_i}$ is the mole fraction, $\boldsymbol{P_{cyl}}$ is the required pressure (Pa) of the mixture, $\boldsymbol{V_{cyl}}$ is the volume (m^3) of cylinder used, $\boldsymbol{M_i}$ is the molar mass of the major component ($g.mol^{-1}$), $\boldsymbol{R}$ is the gas constant (8.31451 $J.mol^{-1}.K^{-1}$), $\boldsymbol{T}$ is the temperature in Kelvin (°C + 273.15 K) and $\boldsymbol{Z_f}$ is the compressibility factor = 1.

The gravimetric preparation of a gas mixture is based on mass weighing, and hence first result will be a mass fraction of a gas mixture which is described by equation 2.6.

$$\boldsymbol{\omega_i} = \frac{\mathbf{m_i}}{\mathbf{m_{major}} + \sum_i \mathbf{m_i}} \qquad 2.6$$

where $\boldsymbol{\omega_i}$ is the mass fraction produced in a multi-component mixture, $\boldsymbol{m_i}$ is the mass of the minor component, $\boldsymbol{m_{major}}$ is the mass of the major component in the mixture and $\sum_i \boldsymbol{m_i}$ is the sum of all the components as the minor component.

The mole fraction refers to the composition of the gas mixture in their final results of preparation of gas mixtures. The relative molar masses (RRM) are used to convert mass fraction to amount of fraction or mole fraction. Equation 2.7 describes the amount of fraction (Milton *et al.*, 2011).

$$\boldsymbol{x_i} = \frac{\sum_i \boldsymbol{m_i/M_i}}{m_{major}/M_{major} + \sum_i m_{i/M_i}} \qquad 2.7$$

where $\boldsymbol{x_i}$ is the amount of fraction for component $\boldsymbol{i, m_i}$ and $\boldsymbol{m_{major}}$ the mass of all the minor components and the major component respectively, and $\boldsymbol{M_i}$ and $\boldsymbol{M_{major}}$ represent the RMM of all the minor components $\boldsymbol{i}$ and the major component, respectively.

The gravimetric preparation of reference gas mixtures is extensively known as having the potential to be a primary method and thus produce reference gas mixtures with value and uncertainty which are traceable to the SI unit (Milton *et al.*, 2011) ; (Brown *et al.*, 2017) ; (Milton and Quinn, 2001). The important criteria for a method to be considered as primary method are as follows:

a) It must be of the highest metrological qualities

b) The method's operation must be fully defined by a suitable measurement equation.

c) It must be fully understood with a complete uncertainty statement which can be written in terms of SI units.

d) It must yield traceable results without reference to a standard of the quantity being measured.

Therefore the gravimetric method for preparation of gas mixtures meets all the criteria described for a primary method and its principle of operation is defined by equation 2.5. Thus ISO 6142-1:2015 explains in detail the principle of operation for the gravimetric preparation with an equation for determining the target mass of each component for the final composition of the gas mixture. The gravimetric preparation has been studied over the years and has led to major improvements in the primary methods used for preparation of gas mixtures. All uncertainties associated with gravimetric preparation are well understood with overall gravimetric preparation traceable to the SI units for mass, kilogram, and the mole (amount of substance). Therefore gas mixtures prepared are produced independently of any other measurements' standards. These gas mixtures produced are directly traceable to the SI units for mass and mole. This concludes that the gravimetric method is indeed a primary method with all criteria being met.

Over the years, gravimetric preparation methods have advanced and new methods are accepted to improve the measurements uncertainties. The new methods make it possible to prepare gas mixtures in a single step dilution using transfer vessels such as small steel cylinders or loop (Milton *et al.*, 2011); (Zheng *et al.*, 2019). Thus a small transfer vessel is used to add the minor component and weigh it before transferring it to the cylinder. Major component is directly transferred to the cylinder as its mass to be transferred is large. Two different balances with different maximum weighing capacity are used to weigh both minor and major components, for minor component a more sensitive balance to weigh the small transfer vessels is used (Milton *et al.*, 2011). The method of using a small transfer vessel as an alternative preparation method has shown a huge improvement in the gravimetric method. The weighing of the minor component on a more sensitive balance with relatively small uncertainties has led to improvement in the gravimetric uncertainties. Using the small transfer vessels has minimised the need for multiple–step dilution methods and thus small uncertainties.

2.6 GRAVIMETRIC PREPARATION METHODS

ISO 6142-1:2015 describes different preparation methods for gravimetric preparation of reference gas mixtures. It is therefore important to choose a suitable preparation method for the intended gas mixture to be prepared, depending on factors such as mass of target component to be added and expected uncertainty. To produce gas mixtures of high metrological qualities, it is important to determine the smallest mass of the gas that can be weighed without contributing significantly to the measurement uncertainty. The minimum mass of a gas that can be added in a single-step dilution has added to some of the challenges of the gravimetric method. In order to ease this effect, other methods of preparation have adopted the use of multiple-step dilution until the final target composition of the gas mixture can be prepared. Therefore both single and multiple step dilution methods can be used to prepare gas mixtures.

2.6.1 Single - step dilution methods

The single-step dilution method is more preferred method because of its reduced final measurement uncertainty and preparation of low mole fraction can be achieved in one step (Milton *et al.*, 2011) ; (Zheng *et al.*, 2019). The mass of the target component must be significant enough to produce the desired small gravimetric uncertainties. The dilution factor is used to refer to different levels of dilution in the preparation of gas mixtures as demonstrated by Milton *et al*., (2011). The dilution steps are expressed by an equation derived from the mass fraction equation 2.6 to calculate the dilution factors. Thus dilution factor $\boldsymbol{D_i}$ is defined by equation 2.8 as

$$\boldsymbol{D_i} = \frac{\boldsymbol{m_a}}{\boldsymbol{m_a + m_b}} \qquad 2.8$$

where $\boldsymbol{D_i}$ is the dilution factor of gas A and gas B for a single-step dilution, with $\boldsymbol{m_a}$ being the mass required for minor component and $\boldsymbol{m_b}$ representing the mass required for the major component. The associated uncertainty of $\boldsymbol{D_i}$ was calculated by equation 2.9 (Milton *et al.*, 2011) as

$$\frac{u(\boldsymbol{D_i})^2}{\boldsymbol{D_i}^2} = \frac{\boldsymbol{m_b^2}}{(\boldsymbol{m_a}+\boldsymbol{m_b})^2}\left(\frac{\mathrm{u}(\boldsymbol{m_a}^2)}{\boldsymbol{m_a}^2} + \frac{\mathrm{u}(\boldsymbol{m_b}^2)}{\boldsymbol{m_b}^2}\right) \qquad 2.9$$

where $\frac{u(\boldsymbol{D_i})^2}{\boldsymbol{D_i}^2}$ is the relative uncertainty in $\boldsymbol{D_i}$ dilution factor of gas A and gas B for a single-step dilution, with $\frac{\mathrm{u}(\boldsymbol{m_a}^2)}{\boldsymbol{m_a}^2}$ being the uncertainty for mass required for minor component $\boldsymbol{m_a}$ and $\frac{\mathrm{u}(\boldsymbol{m_b}^2)}{\boldsymbol{m_b}^2}$ representing the uncertainty for mass required for major component $\boldsymbol{m_b}$.

Gravimetric preparation of gas mixtures is improving as weighing systems improve and methods using small vessels to introduce liquids and gases more accurately into cylinders are being developed. Thus both minor and major components can both be weighed into same vessels followed by use of a small vessel to obtain larger dilutions in one step and widely reported relative uncertainty as low as 0.02 % (Milton *et al.*, 2011); (Zheng *et al.*, 2019).

2.6.2 Multiple - step dilution methods

In preparation of low mole fraction gas mixtures, a multiple step dilution preparation method is preferred as it encourages addition of significant mass of each component in order to attain acceptable gravimetric uncertainties. The preparation strategy to gravimetrically prepare a 10 µmol/mol gas mixture which is too small to be directly prepared from a high pure source material. It is also noted from Milton *et al*., (2011) that more dilution steps used in preparation of gas mixtures can be optimised to attain the lowest relative uncertainty for total dilution. It is also noted that generally the mass of parent gas should be more than 10 g for each dilution step to ensure accurate weighing. Thus preparation of lower mole fractions at (ppb level) could require more than five steps dilution. Multiple step dilutions result to time consuming, more labour, use of many cylinders during preparation, more use of diluent gas and increased risk of errors in between the dilution steps during preparation process (Hu *et al.*, 2013). This method is adopted for preparation of gas mixtures from high pure gases or pre-mixtures, whereby a target component is transferred directly into the cylinder. For multiple dilutions, the total dilution of a gas mixture is expressed by equation 2.10 (Milton *et al.*, 2011) as

$$\boldsymbol{D_T} = \prod \boldsymbol{D_i} \qquad 2.10$$

where   is the total dilution factor of a gas and   the number of dilution factors in a multiple dilution mixture with the uncertainties in the dilution steps are given by equation 2.11 (Milton *et al.*, 2011) as

$$\frac{\mathbf{u(D_T)^2}}{\mathbf{D_T}^2} = \sum_{\mathbf{i}}^{i} \left(\frac{\mathbf{u(D_i)^2}}{\mathbf{D_i}^2} \right) \qquad 2.11$$

where $\frac{\mathbf{u(D_T)^2}}{\mathbf{D_T}^2}$ is the standard uncertainty of the total dilution factor of a gas $\boldsymbol{D_T}$ and $\mathbf{u(D_i)^2}$ is the standard uncertainty in the number of dilution steps $\boldsymbol{i}$ taken for a multiple-step dilution gas mixture.

Milton *et al*., (2011) emphasises that the preparation of high accurate gas mixtures by gravimetry is limited by the smallest target mass which can be weighed and added with acceptable uncertainty. Therefore this imposes a limit on the most dilute gas mixture that can be prepared by single step dilution. Milton *et al*.,(2011) also described a mathematical relationship between uncertainty in the weighing and optimal developed number of serial dilutions. This can be determined by calculating the ratio between the relative uncertainty in the total dilution and the relative uncertainty in the major weighing . This can be determined by calculating the ratio between the relative uncertainty in the total dilution $(\boldsymbol{u_r D_T})$ and the relative uncertainty in the major weighing $(\boldsymbol{u_r m_b})$. Therefore the relationship in the number of dilution steps and its associated uncertainty $(\boldsymbol{u_r D_T / u_r m_b})$ can be used to optimise the number of dilutions of dilution steps to attain small uncertainties in the preparation.

2.6.3 Preparation of gas mixtures using liquid introduction methods

Liquid introduction into a gas cylinder needs dedicated introduction methods and proper equipments. The amount of liquid needed to prepare gas mixtures is normally small and hence requires a highly sensitive and low-capacity balance which provides low uncertainty. This ISO standard describes different methods of liquid introduction which results in good reference gas mixtures. The liquid component introduced into an evacuated cylinder needs to completely vaporise into gaseous phase and remain in the gas phase with no or less condensation which affects the gravimetric mole fraction of the prepared gas mixture and its stability period. Therefore the liquid can be introduced using different vessels. The most commonly used vessels in literature are syringe method, loop injection method and glass tube method. Extra precautions need to be taken when preparing oxygenated volatile organic compounds. These include losses through evaporation of liquid the syringe needle and adsorption onto inner surfaces of transfer vessels. This effect is minimised by determining the amount of liquid added from the difference between the mass of the filled vessel and the mass of the empty vessel after transfer instead of calculating the amount of liquid from mass difference between empty vessel before filling and the filled vessel masses.

2.6.3.1 Syringe liquid preparation method

In this method, a gas -tight syringe is filled with the amount of liquid to be introduced into an evacuated cylinder. The syringe with graduated scale is more useful for estimating the quantity of liquid in the syringe. It is recommended to weigh the filled syringe before and after injection of the liquid. Therefore the difference between these two weighing amounts to the mass of liquid component introduced to the cylinder. It is critical to eradicate any loss of component in the syringe and especially in the needle when using this method. Hence it is advised to replace the needle after filling and before weighing and especially with very volatile components where the remaining liquid droplets may vaporize during weighing (ISO 6142-1:2015).

2.6.3.2 Glass tube liquid preparation method

This method uses a glass tube with one open end which is weighed and filled with a liquid. The glass tube is then sealed by melting off the open end and weighed again. The mass of liquid introduced corresponds to the mass difference between empty and filled glass tube. The glass tube is then connected in the filling line and transferred into the cylinder and the glass tube has been broken by high-pressure matrix gas (ISO 6142-1:2015). Some vaporisation of the liquid may occur during sealing of the glass tube especially with volatile components, therefore it is recommended to cool the tube before sealing it.

2.6.3.3 Loop injection method

In this method, a self-made volume adjustable loop is used as a vessel to transfer liquid to the cylinder (Hu *et al.*, 2013). The loop can be made of stainless steel with single-valve (Grenfell *et al.*, 2010). A weighed gas-tight syringe is used to transfer the target mass of a liquid component into an evacuated empty loop. The loop is weighed in a highly sensitive and low-capacity mass comparator balance. In this preparation, a reference loop is required for a comparison method used. The weighing of the loop is done against an identical reference loop. The loop is weighed before and after transferring the liquid component into an evacuated cylinder. The mass of liquid added is determined by subtracting the two weighing of the loop before and after addition (Zheng *et al.*, 2019).

2.7 VERIFICATION TECHNIQUES FOR SELECTED SULPHUR COMPOUNDS AND OVOCs

2.7.1 Gas chromatography coupled with a flame ionisation detector

Gas chromatography (GC) is a technique used to separate components in the gas phase. The separation is attained by using carrier gas as mobile phase to carry the sample in a column through a liquid or solid stationary phase. Thus the interface between the sample component and the stationary phase result in separation of the component in the sample mixture depending upon physical characteristics of the component. The quicker moving components exit the end of the column before the slower moving components. Flame ionisation detector (FID) is the most widely used universal and generally applicable detector for GC. It mainly detects the hydrocarbon compounds by using the number of carbons incoming the detector per unit of time hence more a mass-sensitive than concentration-sensitive device (Poole, 2015) ; (Skoog et al., 2007 book, page 788 to 794). This detector is mainly used for organic components because of its long-tern stability, fast response, linear response range and low detection limits (Poole, 2015). Analysis of OVOCs require sensitive and selective techniques such as gas chromatography with a universal and selective detection methods. Oxygenated selective flame ionisation detector (O-FID) is used for analysis of OVOCs but the O-FID contains a cracking reactor which converts any oxygenated component to carbon monoxide and use of special FID with a microreactor for the catalytic hydrogenation of CO and detection of methane hydrocarbon with no signal. Peaks observed in the chromatogram are mainly for oxygenated organic components. This detector quantifies higher concentration which disqualifies it for analysis of OVOCs at ppb or ppm level especially in wastewater (Makoś *et al.*, 2019). However analysis of OVOCs in nitrogen gas mixtures have been widely done using GC-FID because its linearity range and stability over a long period of time and known cost-effective (Schultz *et al.*, 2015).

2.7.2 Gas chromatography coupled with pulsed discharge helium ionisation detector

Gas chromatography techniques uses the pulsed discharge helium ionisation detector (PDHID) to analyse compounds with poor response to the flame ionisation detector and exist at very low concentration for detection by thermal conductivity detector. The PDHID is a very universal and ultra-sensitive detector to permanent gases such as hydrogen (H_2), oxygen (O_2), nitrogen (N_2), Argon (Ar), some volatile organic such carbon disulphide (CS_2), methane (CH_4) and inorganic compounds, carbon dioxide (CO_2), carbon monoxide (CO) especially analysing these components at trace level (Hindayani *et al.*, 2019); (Poole, 2015). The helium ionisation detector uses two common versions, either radioisotope or gas discharge as basis of ionisation radiation. The radioisotope source detectors use scandium tritide foil with high specific activity (0.2-1.0 Ci) which is stored in an ionisation chamber with parallel plate or co axial cylinder geometry of comparable design to early version of the electron-capture detector. A plasm containing metastable helium species is generated from the bombardment of helium gas molecules with high energy beta electrons and thus responsible for ionisation of analytes by collision. The gas discharge detectors will however employ high voltage discharge in helium to create photons that will ionise components in a separate ionisation region. The production of photons is separated and interacts with components in the column effluent which results in a very stable and robust detector that overcomes several difficulties related with radioisotope-based detectors (Poole, 2015). Due to its application remaining for inorganic gases and simple organic compounds and gas-solid columns are mostly used to obtain the expected separation and minimise contamination challenges. Thus the PDHID is used with a wider range of column types. Analysis of sulphur containing compounds is have been done using the GC-PDHID because of its sensitivity and covers wide range of compounds to be analysed.

2.7.3 Non-dispersive ultraviolet spectroscopy using Limas 11 UV

Non-dispersive ultraviolet (NDUV) spectroscopy is another technique used for analysis of selected sulphur containing compounds. This technique is based on the ultraviolet absorption characteristics of gases to measure gas concentration. Thus molecular electron transitions occur in this range. Emission wavelength will determine the emission absorption produced when the molecule transitions to a higher electron state. To measure the absorption quantitatively, Lambert-Beer absorption Law is used as per equation 2.12 (Davenport *et al.*, 2018).

$$\frac{I\,(\lambda)}{I_o(\lambda)} = e^{-\sigma(\lambda)lN} \qquad 2.12$$

where I is the final intensity of light transmitted through a sample at wavelength λ, I_o is the initial intensity at that wavelength, σ is the absorption cross-section per molecule of absorbing gas that wavelength, l is the light path length through the sample and N is the number of density of absorbing gas molecules (Davenport *et al.*, 2018).

2.7.4 Ultraviolet Fluorescence spectroscopy

Ultraviolet Fluorescence (UVF) spectroscopy is defined as the emission of light by a substance following absorption of light or other electromagnetic radiation of a different wavelength (Abdelhalim *et al.*, 2013) ; (Bose *et al.*, 2018). Generally the emitted light has longer wavelength which results in lower energy than the absorbed radiation. However it is likely for one molecule to absorb two photons when the absorbed electromagnetic radiation is intense and thus two-photon absorption which can lead to emission of radiation having shorter wavelength than the absorbed radiation (Abdelhalim *et al.*, 2013). UVF is mainly used because of its simplicity, extraordinary sensitive, high specificity, quickness, and low cost compared to other analytical techniques (Bose *et al.*, 2018). It can be affected by the following factors (Bose *et al.*, 2018):

a) Molecules must have the electrons to ensure that UV/Vis radiation is absorbed. No absorption of radiation results in no fluorescence

b) Rigid structures produce more fluorescence.

c) Substituents group like amino, hydroxyl groups enhance fluorescence activity while electron withdrawing groups such as Nitro, carboxyl group reduce fluorescence. No effect on fluorescence for groups of SO_3H and NH_4^+.

d) An increase in temperature results in decreased fluorescence intensity due to increase in collisions of molecules.

e) Increased viscosity results in enhanced fluorescence due to decreased collisions of molecules.

f) Oxygen present will decrease the fluorescence intensity due to its paramagnetic properties.

Fluorescence intensity is determined by equation 2.13 (Bose *et al.*, 2018).

$$\mathbf{F = Ql_{o}act} \qquad 2.13$$

where F is the Fluorescence intensity, Q is the constant for a particular substance, $\mathbf{l_o}$ is the intensity of incident light, a is the molecular extinction coefficient, c is the concentration of substance, t is the path length. Intensity of fluorescence is directly proportional to the substance.

2.8 TRACEABILITY OF REFERENCE GAS MIXTURES

Metrological traceability is described as a property of a measurement result which the results can be associated to a reference through a documented unbroken chain of calibrations, contributing to the measurement uncertainty (Brown *et al.*, 2017); (VIM, JCGM 200:2012). Brown *et al*., (2017) emphasis the production of measurement results traceable to the International System of Units (SI). However metrological traceability requires an established calibration hierarchy (VIM, JCGM 200:2012). It is also critical to mention that ILAC considers the elements for confirming the metrological traceability as the unbroken metrological traceability chain to an international measurement standard or national measurement standard, a documented measurement uncertainty , a documented measurement procedure, accredited technical competence, metrological traceability to the SI and calibration intervals (VIM, JCGM 200:2012). The metrological traceability chain is made of sequence of measurement standards and calibrations which are used to associate with measurement result to a reference. It is described through a calibration hierarchy. In this calibration hierarchy, measurement uncertainties are believed to increase at each level as it goes down the traceability chain with NMIs providing the highest metrological quality measurements and further disseminated down each level on the traceability chain (VIM, JCGM 200:2012). Thus measurements performed by industry will have the highest uncertainty. Figure 2.1 gives an example of uncertainties expected throughout the traceability chain with NMIs' uncertainty as low as 0.1 % and increased to 2 to 5 % relative uncertainty for measurements in the industry.

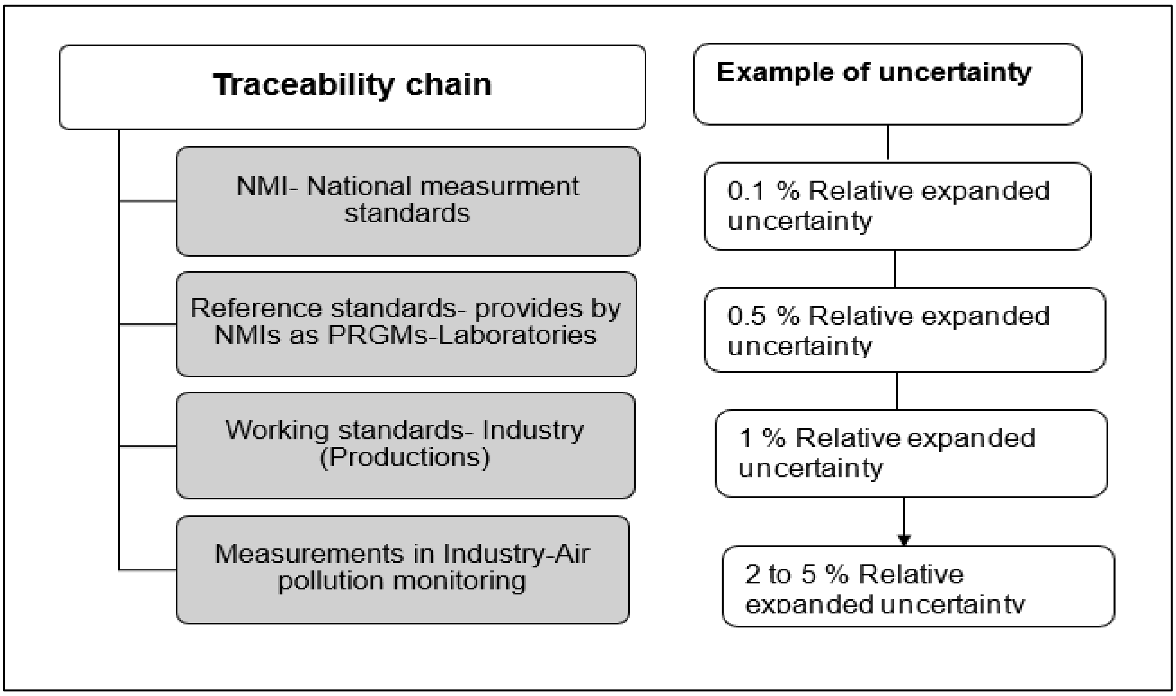


Figure 2.1: Traceability chain with an example of uncertainty at each level

Metrological traceability in chemical measurements can be a challenge because of the complexity of the measurement challenge in chemistry. This is due to the number of analyte -matrix combinations that is vast as compared to physical measurements which deals with the magnitude of a single quantity. Thus a challenge for NMIs to be able to meet all the traceability needs of the chemical and biological measurement communities. Traceability in physical measurement is disseminated through calibrated instruments or calibrated physical artefacts and in chemistry it disseminated through certified reference material or reference measurements (Brown *et al.*, 2017). Traceability chains from the SI to the end user are usually shorter for chemical measurements than the physical measurements. It is encouraged to have short traceability chain especially in the field measurements such as air quality and natural gas. This is to avoid the increased uncertainty which could be large at each comparison level in a traceability chain (Brown *et al.*, 2017.

2.9 MEASUREMENT UNCERTAINTY OF THE PREPARED GAS MIXTURES

Uncertainty of measurement is described as a parameter, related with the result of a measurement, that indicate the distribution of the values which could reasonably be attributed to the measurand (ISO GUIDE 98-3:2008); (VIM, JCGM 200:2012). Uncertainty in general is expressed as a measure of possible error in the estimated value of the measurand as provided by the result of a measurement and also can be an estimate characterising the range of values within which the true value of measurand lies (ISO GUIDE 98-3:2008). Uncertainty of measurement is derived from different effects such as systematic effects as contributor to the measurement uncertainty. Its equation is based on three parts which are measured value (y), coverage interval and coverage probability. The measured value (y) is also mentioned as a true value of the measurement and always expressed with an expanded uncertainty (U). Expanded uncertainty is defined as an interval of the result of a measurement which maybe expected to include a large fraction of the distribution of values that could reasonably be attributed to the measurand (ISO GUIDE 98-3:2008). Expanded uncertainty is based on a combined standard uncertainty multiplied by the coverage factor (K). Coverage interval contains a set of true quantity values of a measurand with a specified probability distribution (p), based on information available (VIM, JCGM 200:2012). Coverage probability indicates that the true value lies within stated coverage interval. ISO GUM:1995 lists possible sources of uncertainty in measurement such as measurement procedure, environmental conditions, analytical systems, measurement standards, personnel, calibration certificates and repeatability of the measurand. The measurement result is defined as measurement value y and its associated uncertainty. Thus the measurement of traceable result is reported by equation 2.14 (ISO GUIDE 98-3:2008).

$$\boldsymbol{Y} = \boldsymbol{y} \pm \boldsymbol{k}(\boldsymbol{u}) \qquad 2.14$$

where $\boldsymbol{Y}$ is the measurement result, $\boldsymbol{y}$ is the measured value, $\boldsymbol{k}$ is the coverage factor and $\boldsymbol{u}$ is the associated standard uncertainty of the measurement result. The coverage factor $\boldsymbol{k}$ produces the coverage interval, which depends on the level of confidence of the measurement result. Expanded uncertainty of the measurement is expressed by equation 2.15. This is illustrated graphically in Figure 2.2, with the oval shape showing the measurement value (y) and the final measurement result (Y) falling between $\boldsymbol{y} - \boldsymbol{U}$ and $\boldsymbol{y} + \boldsymbol{U}$.

$$\boldsymbol{U} = \boldsymbol{k}(\boldsymbol{u}) \qquad 2.15$$

where $\boldsymbol{U}$ is the measurement expanded uncertainty, $\boldsymbol{k}$ is the coverage factor and $\boldsymbol{u}$ is the associated standard uncertainty of the measurement result.

$$\boldsymbol{Y} = \boldsymbol{y} \pm \boldsymbol{U} \qquad 2.16$$

where $\boldsymbol{Y}$ is the measurement result, $\boldsymbol{y}$ is the measured value and $\boldsymbol{U}$ is the expanded uncertainty of the measured value.

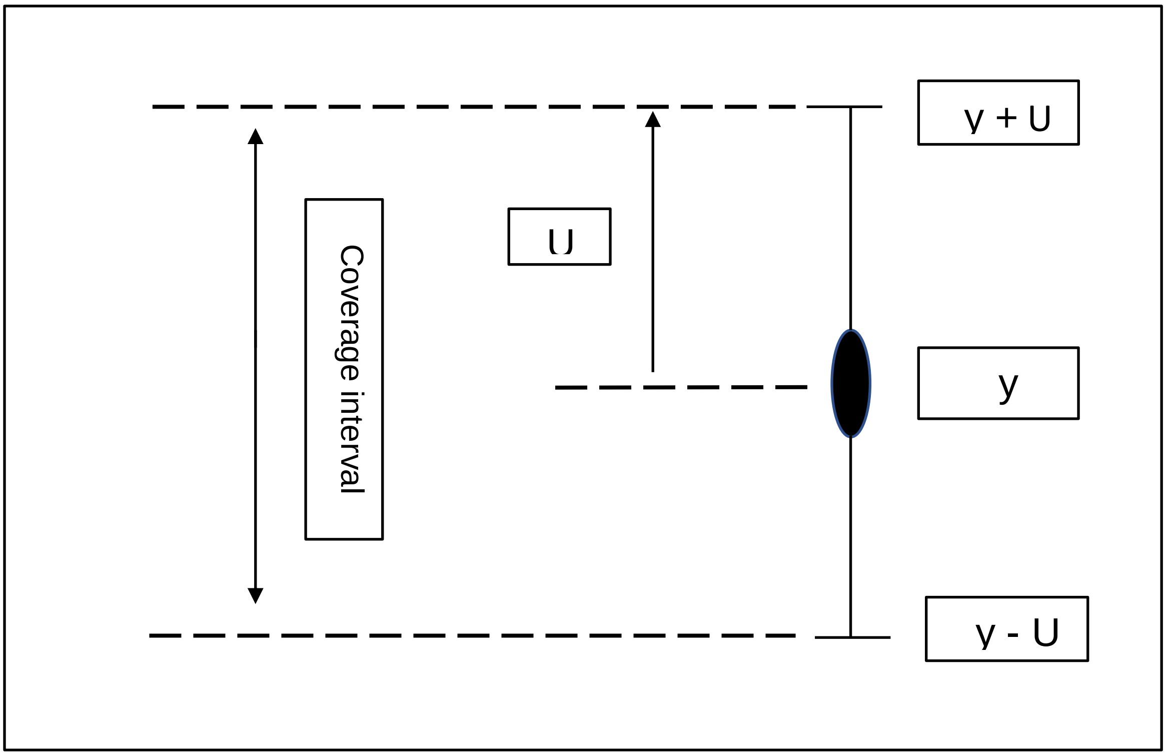


Figure 2.2: Measurement results with associated uncertainty

2.9.1 Evaluation of uncertainty

Evaluation of uncertainty depends mostly on known measurement model. The different parameters from the measurement model contribute to the uncertainty of the measurement result. Therefore uncertainty is evaluated based on measurement result. There are two types of uncertainty evaluation techniques that are used to calculate measurement uncertainty. It is type A and type B uncertainty evaluation (VIM, JCGM 200:2012; ISO GUIDE 98-3:2008). Type A uncertainty evaluation is when measurement uncertainty uses statistical tools to evaluate this type of uncertainty using standard deviation, mean and estimated standard deviation of the mean (ESDM) through repeated measurements. Type B uncertainty evaluation is when other method of evaluation is used than statistical analysis of observed measurements. Thus measurement data for evaluation of uncertainty is obtained elsewhere, either from a calibration certificate used to perform the measurement, uncertainty of reference material or manufacturer's specification values (ISO GUIDE 98-3:2008).

2.10 PROBABILITY DISTRIBUTION

Probability distribution is a statistical function that defines all the possible true values and the confidence in the reported measurement. It is used during uncertainty evaluation. The notion of uncertainty evaluation contains coverage interval, which specifies the range of the true value within the stated interval for a specific coverage probability distribution. Coverage probability is also included, and it highlights the probability that the true value lies with the stated coverage interval (VIM, JCGM 200:2012).

2.10.1 Normal distribution

Normal distribution is a continuous probability distribution which defines how the values of a variable are dispersed symmetrically on both sides of the mean value forming mirror image of right and left side of the centre. This distribution is used when uncertainty contributors are known, mostly from repeated measurements or specified uncertainty of a reference material. Figure 2.3 represents the normal distribution of the value (u) lying between interval A and interval B. Interval A is symbolised as $\mu \pm \sigma$, thus indicating the coverage probability at 68.27 %. Interval B symbolised as $\mu \pm 2\sigma$, indicating the coverage probability at 95.45 %. For the reported expanded uncertainty of the measurement, coverage probability of 95.45 % is mostly used (JCGM 100:2008).

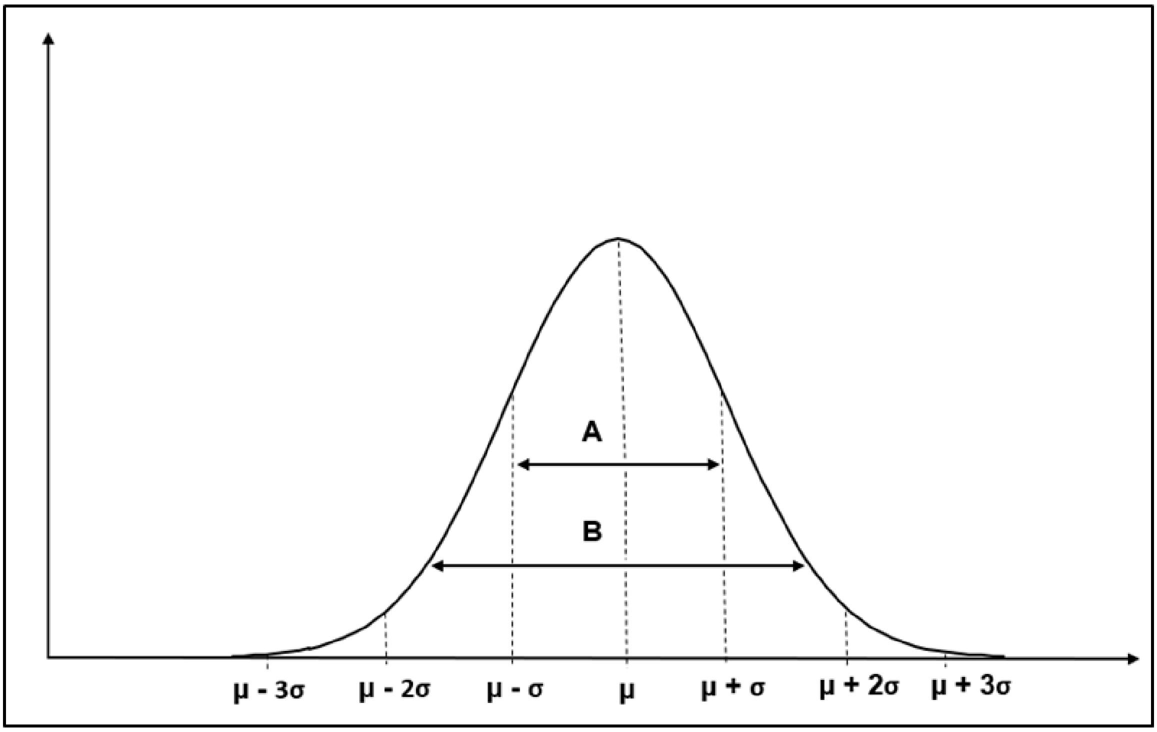


Figure 2.3: Normal distribution curve

JCGM 100:2008, assumes a normal distribution of the measurement result, the coverage interval at 95.4 % coverage probability is calculated as y ± 2u (GUM). The coverage factor (k_p) at a stated level of confidence (p) is shown in Table 2.2.

Table 2.2: Normal distribution coverage factor (k_p) values with its corresponding coverage interval at a stated level of confidence (p) (Source: JCGM 100:2008)

Coverage factor (k_p)	**Coverage probability (p)**	**Coverage interval**
1	68.27	$\boldsymbol{y \pm u}$
1.645	90	$\boldsymbol{y \pm 1.645u}$
1.960	95	Y$\pm\boldsymbol{1.960u}$
2	95.45	$\boldsymbol{y\ \pm 2u}$
2.576	99	$\boldsymbol{y\ \pm 2.576u}$
3	99.73	$\mathbf{y\ \pm 3u}$

2.10.2 Rectangular distribution

Rectangular distribution is used to calculate the value of if no information about the value of is known. Rectangular distribution assumes that the value ranges between and the probability of it falling outside this interval is zero. Thus the probability distribution is frequently used when determining impurities based on the manufacture's specification. This is shown in Figure 2.4. Value of is then calculated by equation 2.17, with its associated uncertainty calculated by equation 2.18 (JCGM 100:2008).

$$x_i = \frac{a_- + a_+}{2} \tag{2.17}$$

where x_i is the calculated amount fraction for component i and a_-, and a_+ is the interval of value x. This is also referred to as the midpoint of the interval and expressed as a. Uncertainty evaluation of x_i is calculated by equation 2.18

$$u_{xi} = \frac{\mathrm{a}}{\sqrt{3}} \tag{2.18}$$

where u_{xi} is the standard uncertainty of component i and a is the midpoint of the interval.

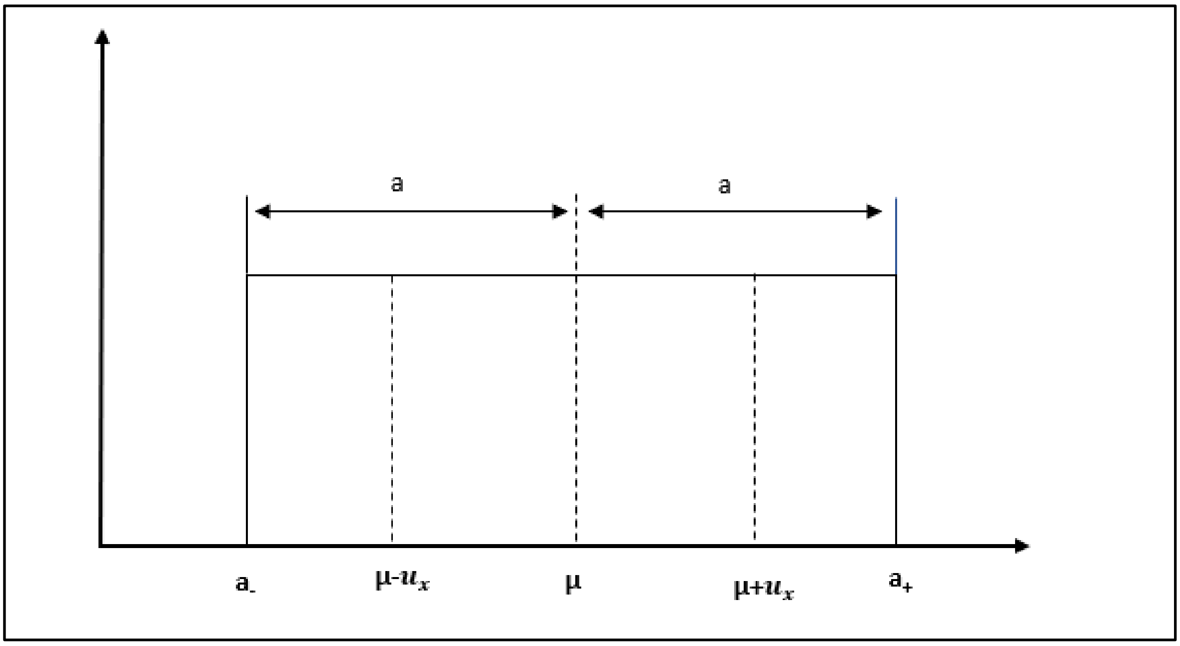


Figure 2.4: Rectangular distribution

2.10.3 Triangular distribution

In this probability distribution it is assumed that there is a probability that the value µ lies closer to the midpoint is higher than it is towards the edges. This probability distribution is also often used when determining impurities based on the manufacturer's specification. Thus is shown in Figure 2.5. Value of is then calculated by equation 2.17, with its associated uncertainty calculated by equation 2.19 (JCGM 100:2008).

$$\boldsymbol{u_{xi}} = \frac{\mathbf{a}}{\sqrt{6}} \qquad 2.19$$

where $\boldsymbol{u_{xi}}$ is the standard uncertainty of component $\boldsymbol{i}$ and $\boldsymbol{a}$ is the midpoint of the interval.

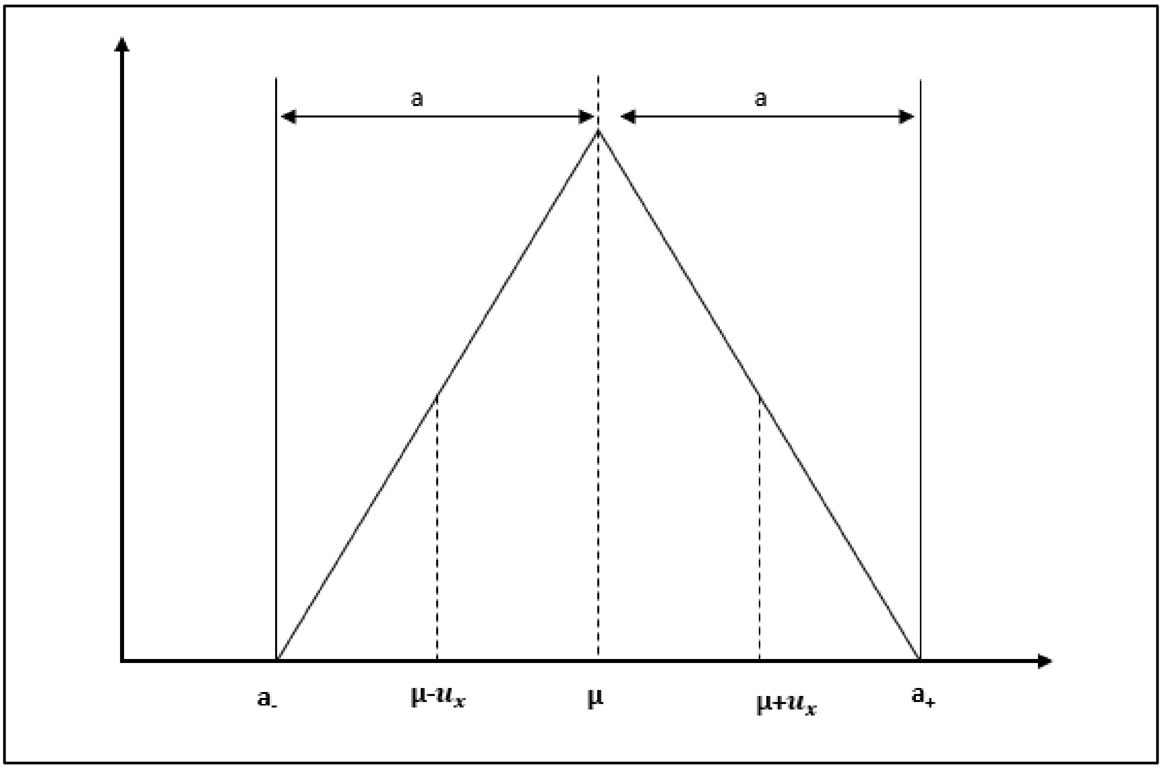


Figure 2.5: Triangular distribution curve

2.11 MEASUREMENT EQUIVALENCE

International key comparisons are technical basis of a mutual recognition of national measurement standards whereby arrangement prepared in conjunction with the National Metrology Institutes (NMIs). Therefore there's a worldwide workload to be undertaken by the International Committee of Weights and Measures (CIPM), its Consultative Committee for amount of Substance-Working Group on Gas analysis

(CCQM-GAWG) and the NMIs is large (CIPM MRA, 2010); (Kovalevsky and Kovalevsky, 2000). The CIPM has taken a responsibility to achieve something that is as nearby as possible to an international recognition in its own domain represented by the NMIs. Thus international key comparisons performed by the NMIs and Designated Institutes (DIs) are part of CCQM-GAWG and CIPM Mutual Recognition Arrangement (MRA) (CIPM MRA, 2010). This is to coordinate measurements in the gas analysis field worldwide. The key comparisons institute measurement capabilities of the NMIs and DIs in producing reliable and accurate national measurement standards (CIPM MRA, 2010). Participating in these key comparisons establish measurement equivalence of NMIs' primary standards at the highest metrological level. This confirms the whole understanding of the measurement method and the realisation of the SI unit for the amount of substance fraction in the produced gas mixtures. International key comparisons are driven by the participating NMI where they agree on a comparison to demonstrate measurement equivalence depending on different needs such as the industry need to demonstrate new capabilities, regulations, previously encountered measurement challenges and improvement on methods. Thus the NMIs capabilities to produced primary standards known to have the highest metrological quality using primary methods such as gravimetric preparation method is assessed by the CIPM MRA (Brown *et al.*, 2017).

The establishment of measurement equivalence between the CIPM MRA participants is regarded as being the highest metrological level as it is directly linked to the SI unit (Brown *et al.*, 2017); (CIPM MRA, 2010). International key comparison can either be provided to determine analytical capabilities where the participants receive a comparison sample and analyse it against their own national measurement standards or preparative capabilities where participants prepare one or two standards and send it to one laboratory for analysis. The NMIs' capabilities are based on their measurement result agreeing with the key comparison reference value (KCRV) (Brown *et al.*, 2017) and measurement uncertainties stated are referred to as calibration and measurement capabilities (CMC). These international comparisons can be organised in CCQM level or at regional metrology organisations (RMOs). Thus then cab be linked to CCQM level by means of one participant who participated in a CCQM level comparison such as coordinating and providing the link to the RMOs level (CIPM MRA, 2010).

2.11.1 International Key Comparison for hydrogen sulphide in nitrogen

The international key comparisons of hydrogen sulphide have been conducted to compare the primary standards for hydrogen sulphide (H_2S) in nitrogen. Its main intention was to compare the capabilities of the preparation and value assignment of gas standard of H_2S. The comparison sample's range of nominal amount of substance fractions is 10 µmol/mol and this is closer to the regulatory levels in most countries.

2.11.1.1 International Comparison CCQM-K41 (2005)

The National Institute of Standards and Technology (NIST) coordinated the CCQM-K41 comparison of hydrogen sulphide (H_2S) in nitrogen measurements (Guenther *et al.*, 2005). The comparison was aimed at assessing the analytical capabilities of different NMIs and DIs of the CIPM MRA with seven (7) participants. NIST obtained ten 6 litre gas mixtures of 10 µmol/mol H_2S in nitrogen from its gas company in the USA. The purchased gas mixtures were monitored for 6 months for stability preceding to the start of the key comparison. Each gas standard was verified and reference to a nominal 10 µmol/mol NIST stable reference cylinder (SRC), which has history of stability over the years.

Several methods are used globally for the analysis of hydrogen sulphide, which was evident in this comparison, as different participants used various analytical methods. But the mostly used method in this comparison was gas chromatography. The key comparison indicated the use of national measurement standards of each NMIs to analyse the comparison sample using diverse measurement methods. Additionally the key comparison indicated that even though different methods can be used, the measurement equivalence will always be achieved using traceable, reliable, and accurate national primary gas standards.

The degrees of freedom of each participating laboratory are calculated as an indication of how well the measurements agree with the KCRV. The degree of equivalence of each laboratory with respect to the reference value is given by equation 2.20 and its expanded uncertainty is stated by equation 2.21. The Overall comparison results for CCQM-K41 is illustrated in Figure 2.6. However NMISA did not participate in this comparison in 2005.

$$\boldsymbol{D_i = (x_i - x_{igrav})} \qquad 2.20$$

where $\boldsymbol{D_i}$ is the degree of equivalence of component $\boldsymbol{i}$, $\boldsymbol{x_i}$ is the analytical results reported for component $\boldsymbol{i}$ and $\boldsymbol{x_{igrav}}$ is the gravimetric value of component $\boldsymbol{i}$. The degree of equivalence is expressed with expanded uncertainty. This is calculated by equation 2.19.

$$\boldsymbol{U_i = k\sqrt{(u_i^2 + u_{igrav}^2)}} \qquad 2.21$$

where U_i is the expanded uncertainty, k is the coverage factor, u_i is the reported standard uncertainty and u_{igrav} is the gravimetric uncertainty.

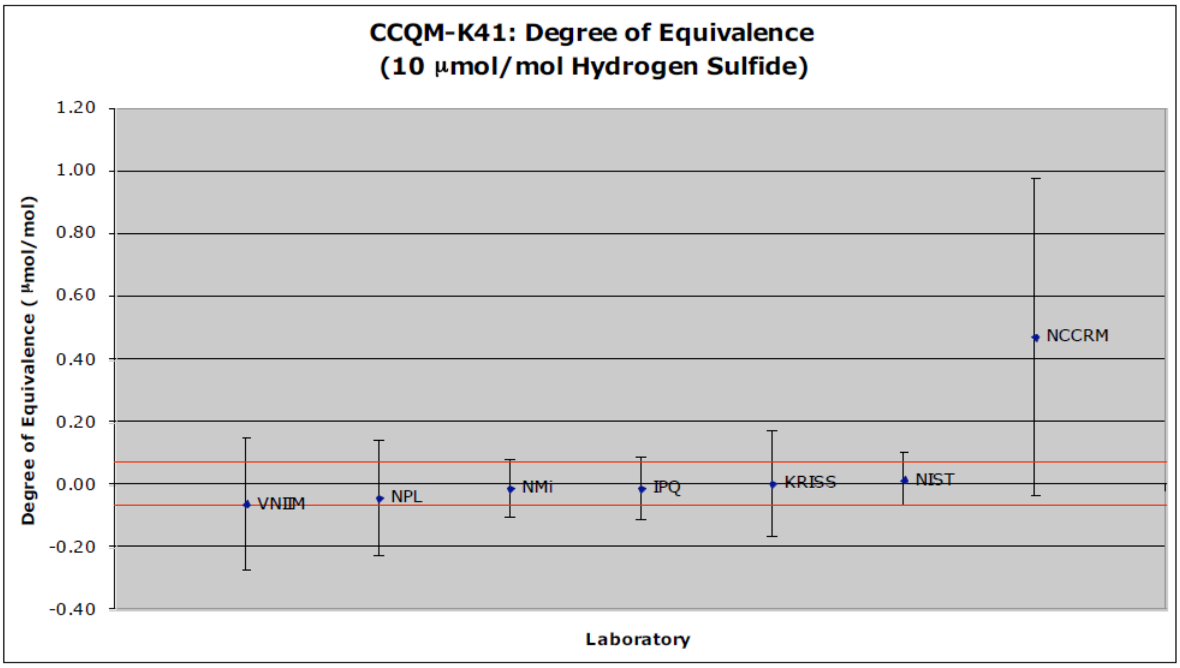


Figure 2.6: Degrees of equivalence in CCQM-K41 international comparison (Source: Guenther *et al.*, 2005)

The KCRV is within the uncertainty limits of all the participants' measurement value for the stability reference cylinder. Most of the participants, excluding NRCCRM, agreement is outstanding for this reactive compound and indicates excellent comparability (Guenther *et al.*, 2005)

2.11.1.2 International key Comparison APMP.QM-K41 (2014)

An international comparison of hydrogen sulphide in nitrogen at an amount of substance fraction of 10 µmol/mol was made. The comparison was coordinated by Korea Research Institute of Standards and Science (KRISS) with a total of four (4) participants in 2009. This comparison was intended at evaluating the analytical capabilities of various NMIs of the CIPM MRA. KRISS gravimetrically prepared all the comparison samples and compared them to a nominal 10 µmol/mol KRISS reference cylinder before shipping them to the participants to value assign the comparison sample. The measurement technique of choice for most participants was a gas chromatography coupled with different detector. The comparison was intended to determine the analytical capabilities of the NMIs employing their own gravimetrically prepared standards to analyse the comparison sample. For method analysis, NMISA used GC-PDHID with sulfinert tubing, multi-position gas switching valves, gas sampling for analysis of H_2S. The separation was achieved by a Hayesep-Q column. Standards ranging from 8 to 100 µmol/mol hydrogen sulphide in nitrogen were used for calibration.

The degree of equivalence of each laboratory with respect to the reference value is given by equation 2.20 and its expanded uncertainty is stated by equation 2.21. The Overall comparison results for APMP.QM-K41 is illustrated in Figure 2.7. Three participants' results out of the four (4) were consistent with their KCRV in this comparison. Their results agree with the KCRV within their uncertainties. It is possible with this comparison to offer good traceability and harmonisation amongst the worldwide distribution data of hydrogen sulphide. Thus supporting the measurement capability of H_2S in the range of 1 to 500 µmol/mol in air, nitrogen or methane (Kim *et al.*, 2014). Kim *et al*. (2014) states that the results of the regional QM key comparison are linked to CCQM key comparison through the gravimetric values.

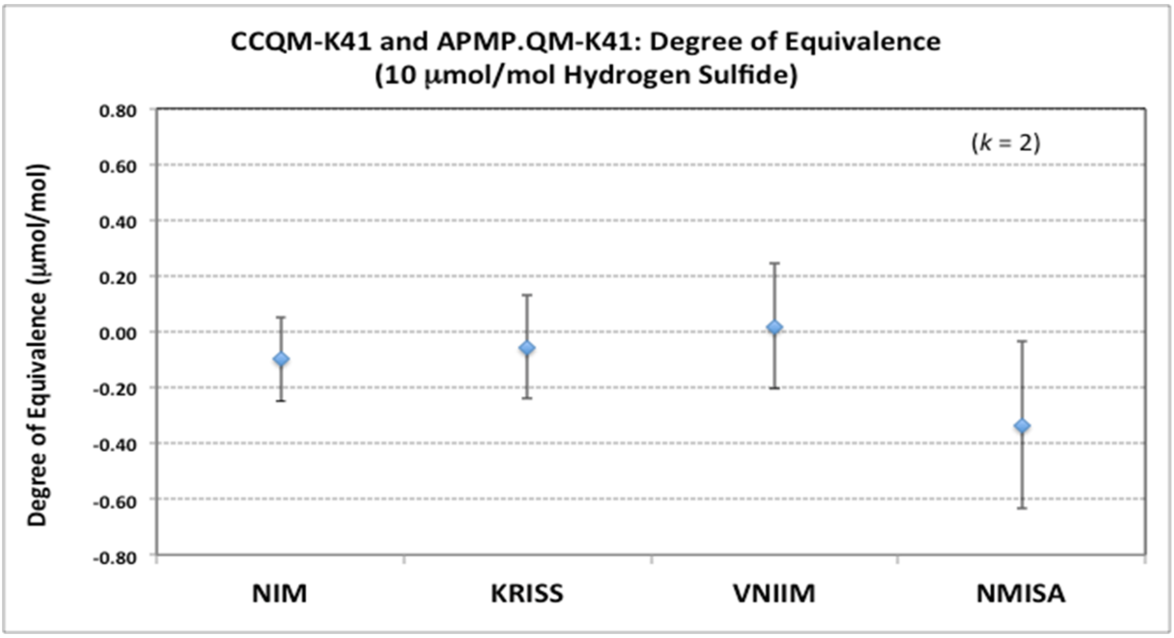


Figure 2.7: Degrees of equivalence in APMP.QM-K41 international comparison (Source: Kim *et al.*, 2014)

NMISA's reported results did not agree with the KCRV, which shows unacceptable results. This directed to improvements in the method being used. The improvement method for the analysis of hydrogen sulphide was adopted in this study and discussed in detail in section 4 on the verification of hydrogen sulphide gas mixtures with improvements in the purity analysis and calibration standards. Thus the improved measurements led to the development of new hydrogen sulphide standards at NMISA. Then the laboratory prepared itself to participate in the repeated key comparison of the CCQM-K41.2017 linked to the CCQM-K41 (2005) to demonstrate the improvement and therefore measurement equivalence for hydrogen sulphide measurements.

2.11.2 International comparison CCQM-K93

This international key comparison was conducted to assess the capability of the NMIs to prepare standard gas mixtures of ethanol at a nominal amount of fraction of 120 µmol/mol in nitrogen. The amount of fraction is a representative level used to calibrate evidential breath analysers in most countries. These standards fulfil the approved requirements of the International Organisation of Legal Metrology (OIML) for the calibration of evidential breath-alcohol analysers (Brown *et al.*, 2013).
The National Physical Laboratory (NPL) coordinated the CCQM-K93 comparison of ethanol in nitrogen measurements (Brown *et al.*, 2013). The comparison employs the preparative model designed by the CCQM-GAWG and used formerly for key comparisons of oxygen (CCQM-K53) and hexane (CCQM-K54) Participants are expected to prepare a standard mixture of ethanol in nitrogen and submit the gas mixture to coordinating laboratory for analysis. This is direct test of the capability of the participants to be able to prepare accurate reference materials of this type of measurements (Brown *et al.*, 2013). This comparison is linked to previous key comparison of ethanol in nitrogen or air. The previous comparison was aimed at assessing the analytical capabilities of various NMIs of the CIPM MRA and hence standards were prepared by the coordinating laboratory (NPL) and distributed to participating laboratories for them to analyse.

Several methods of adding ethanol to the cylinder were used by the participants but syringe method was mostly used in this comparison. It was noted that many participants did not apply the buoyancy correction to the mass of ethanol added. For this comparison, each participant had to submit a mixture together with its value for the amount fraction of ethanol in nitrogen and its standard uncertainty . The submitted mixtures from participants were analysed with Agilent 6890 Gas chromatograph coupled with a flame ionisation detector (GC-FID) using a DB-624 column which is 75m x 0.535 mm in diameter and film thickness of 3 µm and a sample loop of 0.5 ml. Helium was used as the carrier gas. A comparison method used consisted alternating injection between unknown NMI standard and the NPL working reference standard (WRS) until each six injections of NMI standard and WRS were achieved. This is done to compensate for any instrument drift during the measurements (Brown *et al.*, 2013).

The degree of equivalence of each laboratory with respect to the reference value is given by equation 2.22 and its expanded uncertainty is stated by equation 2.23. The Overall comparison results for CCQM-K93 is illustrated in Figure 2.8.

$$D_oE_i = \frac{x_i{}^{NMI}}{r_i} - x_{KCRV} \qquad 2.22$$

where D_oE_i is the degree of equivalence of participants, x_{KCRV} is the KCRV obtained from the deduced amount fractions of ethanol in the NMI standards, $x_i{}^{NMI}$ is the submitted amount fraction of ethanol and r_i is the ratio of the mean of NMI standard to the mean of WRS.

$$u(D_oE_i) = \sqrt{u^2\left(\frac{x_i{}^{NMI}}{r_i}\right) - u^2(x_{KCRV})} \qquad 2.23$$

Where $u(D_oE_i)$ is the uncertainty in the degrees of equivalence.

Most of the participants measurement value agreed with the calculated KCRV with its uncertainty at k =1. NMISA’s reported results overlapped with the KCRV which showed satisfactory results

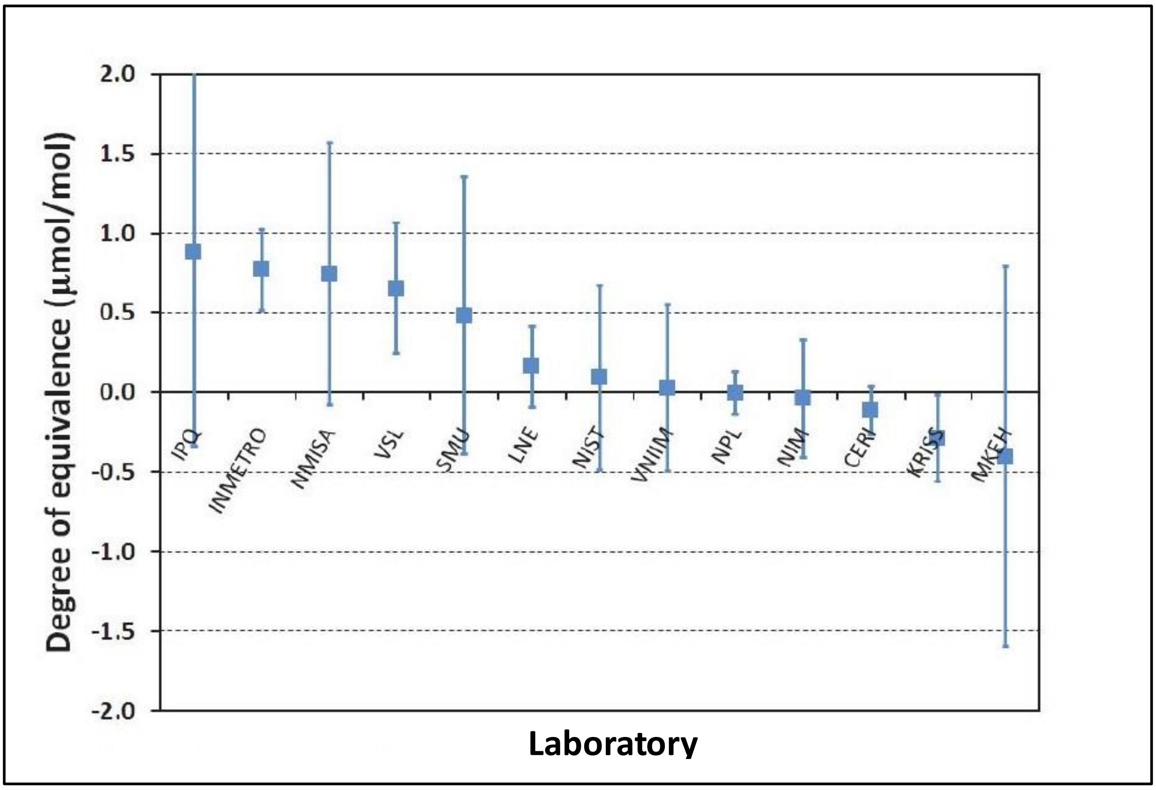


Figure 2.8: Degrees of equivalence in CCQM-K93 international comparison (Source: Brown *et al.*, 2013).

2.11.3 International comparison CCQM-K76 for sulphur dioxide in nitrogen at 100 µmol/mol

The international key comparison of sulphur dioxide (SO_2) was conducted to assess the capabilities of the participants to be able to measure and analyse sulphur dioxide in nitrogen. This comparison was done to offer supporting evidence for the CMCs of institutes for sulphur dioxide. The component of sulphur dioxide is regarded as a core compound and the amount of fraction of 100 µmol/mol is within the designated core compound concentration range. It will be also intended to establish core capabilities of institutes which are under Gas Analysis Working Group rules.

The National Institute of Standards and Technology (NIST) coordinated the CCQM-K76 comparison of sulphur dioxide in nitrogen measurements (Guenther *et al.*, 2009). The comparison was aimed at assessing the analytical capabilities of different NMIs and DIs of the CIPM MRA with sixteen (16) participants. NIST purchased thirty (30) aluminium cylinders with internal volume of approximately 6 litres to be used for preparation of comparison samples. The comparison samples were prepared gravimetrically. NIST chose one parent gas cylinder of nominal amount of fraction of 1500 µmol/mol to use as the control standard. Each gas standard of SO_2 comparison sample was verified preceding to shipment to the participants using pulsed fluorescence process analyser. A control gas cylinder at amount of fraction nominal 100 µmol/mol was also gravimetrically prepared and data analysis was evaluated using ISO 6143.

Several methods are used globally for the analysis of sulphur dioxide, which was evident in this comparison, as different participants used various analytical methods. But the mostly used methods in this comparison were Non-dispersive Infrared (NDIR) and Pulsed Fluorescence techniques. The key comparison indicated the use of national measurement standards of each NMIs to analyse the comparison sample using diverse measurement methods. Additionally the key comparison indicated that even though different methods can be used, the measurement equivalence will always be achieved using traceable, reliable, and accurate national primary gas standards.

The degrees of freedom of each participating laboratory are calculated as an indication of how well the measurements agree with the KCRV. The degree of equivalence of each laboratory with respect to the reference value is given by equation 2.20 and its expanded uncertainty is stated by equation 2.21. The Overall comparison results for CCQM-K41 is illustrated in Figure 2.9. NMISA's reported results overlapped with the KCRV which showed satisfactory results.

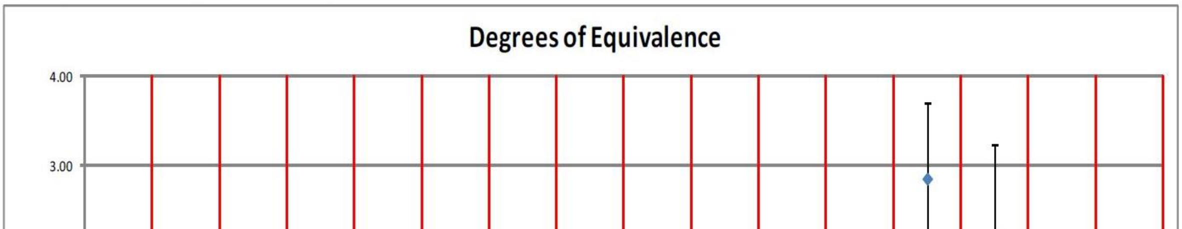


Figure 2.9: Degrees of equivalence in CCQM-K76 international comparison
(Source: Guenther *et al.*, 2009)

Most of the participants, except for three, were consistent with their KCRV in this comparison. Their results agree with the KCRV within their uncertainties. This key comparison was used to determine core analytical capabilities in accordance to the rules and measures of the CCQM GAWG (Guenther *et al.*, 2009).

CHAPTER 3: METHODOLOGY AND EXPERIMENTAL FOR PREPARATION OF REFERENCE GAS MIXTURES

This chapter details the research methods and experiments followed for the development of the selected sulphur compounds and the OVOCs. It briefly discusses the purity analysis of the source material, gravimetric preparation of reference gas mixtures, stability assessment, adsorption/desorption study, internal consistency and analytical techniques used for selected sulphur compounds and OVOCs reference gas mixtures.

3.1 GRAVIMETRIC PREPARATION PROCESS

The primary standard gas mixtures were produced following the International Organization for Standardization ISO 6142 (ISO 6142-1:2015). There are various gravimetric techniques that can be used such as static and dynamic volumetric methods (Słomińska *et al.*, 2014). The static technique is when gas mixtures are prepared by transferring high pure gases, high pure liquids, or pre-mixtures of known mole fraction quantitatively into a sample mixture cylinder (ISO 6142-1:2015). In this technique multi-step dilutions for preparation of low mole fraction gas mixtures at high pressure are required. This require the mass of parent gas to be added to the cylinder to be more than 10 g considering the mass resolution of the balance and to weigh accurately (Hu *et al.*, 2013). The dynamic technique involves introduction of a gas at volume or mass flow rate into a constant flow rate of a diluent gas. The introduced gas can either be high pure component or a pre-mixture. This technique produces a continuous flow rate of the reference gas mixture directly to the analyser without any build-up of a reserve by storage under pressure (ISO 6145-1:2003). The dynamic volumetric methods can be used to produce accurate low mole fractions of reactive gas mixtures that are unstable in the cylinders (Słomińska *et al.*, 2014). Table 3.1 shows the comparison between the static and dynamic techniques. In this study, static gravimetric technique was used to gravimetrically prepare reference gas mixtures.

Table 3.1: Comparison of dynamic and static techniques for producing reference gas mixtures (Słomińska *et al.*, 2014).

	Static Techniques	Dynamic Techniques
Benefits	a) Inexpensive apparatus b) Easy to carry out	a) No adsorption challenges b) Prepared gas mixtures can be introduced directly to the measuring system c) Stable and homogenous prepared reference gas mixtures.
Challenges	a) Time consuming b) Inaccurate procedure c) Adsorption and condensation problems d) Stability issues e) Not suitable for reactive and unstable components	a) It requires high pure gases b) Necessity of controlling flow rate of the diluent gas c) Problems in stopping the generation of reference gas mixture

The gravimetric preparation process included pre-treatment, cleaning, evacuation, weighing and filling of the gas cylinder, then homogenization of the gas mixtures. The pre-treatment of cylinders through fluorination process is important to ensure no chemical reactions occur on the inner surface of the cylinders. This process is illustrated by Figure 3.1.

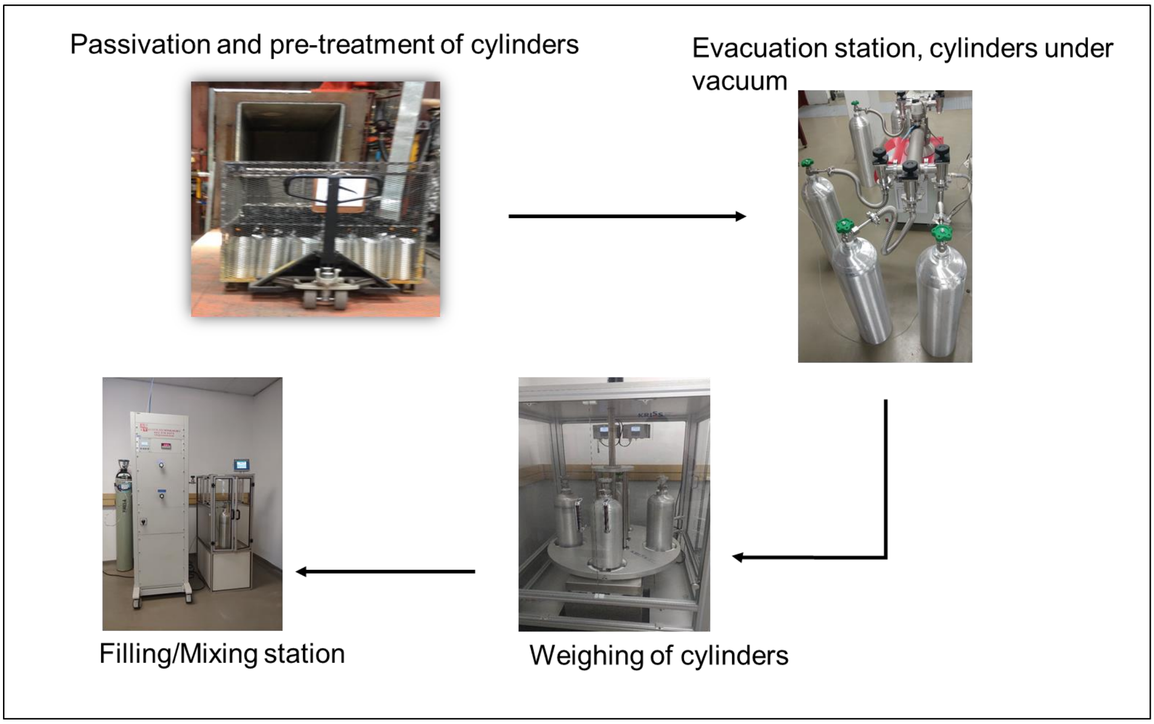


Figure 3.1: Gravimetric preparation processes

3.2 THE SOURCE MATERIAL OF HIGH PURITY GASES

Purity analysis is a critical step for the gravimetric preparation of the primary standard gas mixtures (PSGMs). The accuracy of the gravimetrically prepared reference gas mixtures depends significantly on the purity of the parent gases used to prepare the PSGMs. Uncertainty contributions from the impurities of the pure or parent gases contribute majorly on the uncertainty of the final mixture composition. Accurate measurement of diluent gas (nitrogen) in high pure hydrogen sulphide and sulphur dioxide is critical because errors in the measurement of nitrogen gas can influence the quality of reference material produced (ISO 6142, 2015). Therefore, the amount of nitrogen in the high purity H_2S and SO_2 was analysed before the preparation of reference gas mixtures.

The high purity gases and liquid chemicals used for the gravimetric preparation of reference gas mixtures were purchased from both international and national suppliers. High purity H_2S gas purchased from Takachiho Chemical Industrial

(99.99 %) and SO_2 (99.98 %) purchased from Air Liquide. The high pure Built-in purifier (BIP^{TM}) nitrogen was purchased from Air Products, South Africa and used as a diluent gas during the gravimetric preparation of reference gas mixtures. High purity chemicals (C_2H_5OH, CH_3OH, C_4H_9OH and C_3H_6O) with purity higher than 99 % were purchased from Sigma Aldrich South Africa. For the high purity gases, they were stored in an external gas cage with proper safety conditions. The high purity liquid chemicals were stored inside a cupboard designated for flammable chemicals.

3.3 CYLINDER TREATMENT

Aluminium gas cylinders with the water capacity volume of 5 and 10 litres were purchased from Luxfer in the United Kingdom and were used for the gravimetric preparation of reference gas mixtures. Both sulphur containing compounds and OVOCs can be lost due to adsorption onto surfaces or reactions with surfaces. Passivated and pre-treated aluminium gas cylinders will largely prevent reactions between inner surfaces and components (Brown *et al.*, 2014). The gas cylinder and its valves were fluorinated prior to use to render the internal surfaces non-reactive. When the gas cylinders have been received by the laboratory, they are visually inspected using the swing-prism boroscope to check the inner surface of the gas cylinder. If the inner surface is scratched or uneven, the gas cylinder is returned to manufacturer for replacement. The gas cylinders are then taken to Air products for valving and leak checked with Helium gas after valving to ensure that the valving was done according to specification. When this process is completed, the gas cylinders are sent to Pelchem for fluorination process whereby the fluorine gas is used to coat the inner surface of the gas cylinders to improve corrosion resistance.

3.4 INSTRUMENTATION USED

A Radwag mass comparator balance with capacity of 26 kg and serial number: 512121 was used to target the calculated amount of pre-mixture and diluent gases to be added into the gas cylinder. An Automated weighing system (AWS) fitted with a Mettler Toledo AG (model XP26003L, serial number M4630072 mass comparator balance with highest capacity of 26.1 kg was used for accurate weighing of gas cylinders (manufactured by the Korean Research Institute of Standards and Science (KRISS)), with a readability of 1 mg (Park *et al.*, 2004). Prior to use, an external adjustment was performed on the AWS mass comparator balance using a 10 kg calibrated mass piece.

For introduction of liquids into gas cylinder, the calculated amount of liquid to be added into the cylinder, was weighed using an analytical semi-micro-Sartorius balance with capacity of 210 g and readability of 0.01 mg. Hamilton gas-tight syringes were purchased from Sigma Aldrich (Pty) Ltd of different volumes such as 50 µl, 100 µl, 250 µl, 500 µl and 1 000 µl for this purpose. Internal calibration of the Sartorius balance was performed prior to use and at least once per week.

All the weighing measurements are directly traceable to the SI unit of mass (kilogram). 10 ml vials were used for the addition of multi-component liquid solutions of OVOCs. To evacuate the cylinders before preparation process, a Pfeiffer Turbo Molecular pump was used to remove any residual gas or moisture that could be left inside the cylinders. The filling station used was fitted with Pfeiffer vacuum pump, shut-off and needle valves, pressure readout and a vent out system to release gases out into scrubbers, before being released to the atmosphere outside the laboratory

The gravimetrically prepared cylinders were homogenised on a roller bench for minimum of four hours. An Agilent 7890B with serial number: CN16193149 gas chromatography with three channels, sulphur chemiluminescence detector, thermal conductivity detector and pulsed discharged helium ionisation detector (GC-SCD/TCD/PDHID) was used to analyse hydrogen sulphide (H_2S), sulphur dioxide (SO_2). For analysis measurements of acetone, methanol, ethanol, propanol, and butanol, a Varian CP-3800 gas chromatography coupled with flame ionisation detector (GC-FID) was used.

3.5 PURITY ASSESSMENT OF HIGH PURITY GASES AS THE STARTING MATERIAL

Impurities analysis in high pure source material is the first step in producing calibration gas mixtures. The analysis is done following the international standard ISO 19229 (Gas analysis - Purity analysis and treatment of purity data) (ISO 19229:2015). It is therefore very important to choose high quality source material to minimise considerable compositions of these components and their contributions to the mole fraction of the gravimetrically prepared reference gas mixtures. Purity analysis of impurities can be very challenging because trace levels of components need to be quantified in a matrix whereby no measurement standards are easily available (ISO 19229:2015). In this work, traceable gravimetrically prepared PSGMs were used to quantify the impurities and other impurities were used as per manufacturer's specifications. These PSGMs were prepared very close to the impurities level in the high pure source materials. The purity analysis was done using gas chromatography coupled with various detectors. This includes Varian CP-3800 (model) gas chromatography coupled with two detectors, the TCD and FID with methaniser and Agilent 7890B gas chromatography coupled with three detectors (SCD/TCD/PDHID).

The manufacturer's specification for high purity hydrogen sulphide (H_2S) was 99.99 % (cylinder number: 3K-37622) and for high purity sulphur dioxide (SO_2) was 99.99 % (cylinder number: GU-82571). The purity of high pure Built-in-Purifier (BIP^{TM}) nitrogen diluent gas used was 99.9999 %. The purity assessment was done using Gas Chromatography (GC) coupled with Thermal Conductivity Detector (GC-TCD), for impurities such as hydrogen (H_2), nitrogen (N_2) and oxygen (O_2). GC coupled with Flame Ionisation Detector (GC-FID) was used for impurities of carbon monoxide (CO), methane (CH_4) as total hydrocarbons (THCs). GC coupled with pulsed discharged helium ionisation detector (PDHID) was used for analysis of carbon dioxide (CO_2) and argon (Ar) impurities. Sulphur containing compounds impurities such as ethyl mercaptans (CH_3CH_2SH), carbon disulphide (CS_2) and carbonyl sulphide (COS) were assessed using GC coupled with sulphur chemiluminescence detector (GC-SCD) because they are the main impurities components in both high pure sulphur dioxide (SO_2) and H_2S. Other main components checked in the high pure H_2S and SO_2 were N_2, H_2, O_2, CO, Ar and moisture as shown in Table 4.1 and Table 4.2.

3.5.1 Purity analysis of high purity gases using thermal conductivity detector/flame ionisation detector

Varian CP-3800 gas chromatography coupled with a TCD detector and FID detector with a methaniser in series, was used to analyse the impurities of CO_2, CH_4, C_2H_6 and CO in both high pure gases of nitrogen and sulphur dioxide. Columns used were molecular sieve 5Å and Hayesep N, whereby molecular sieve 5Å analysed smaller components due to its small porous stationary phase and Hayesep N with a backflush configuration analysed heavier components. Galaxie chromatography software was used to control the valve switching and sample introduction through multi-position VICI Serial Stream Selection valve (SSV) array enabled by a Varian Serial SSV 5.31 control software as shown in Figure 3.2

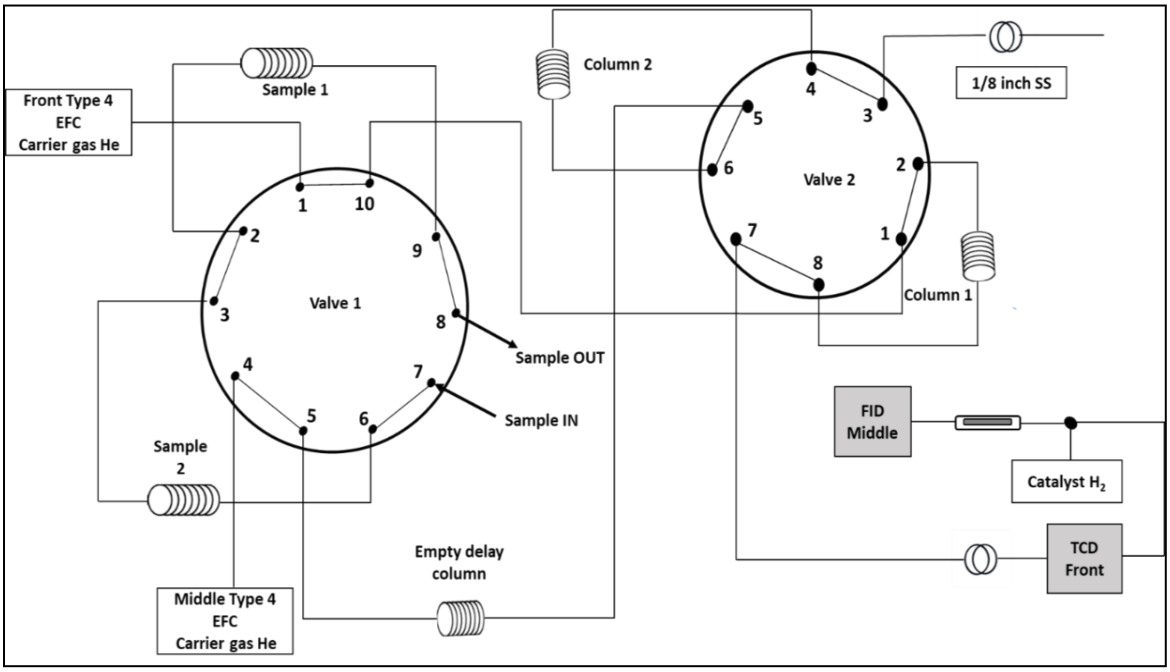


Figure 3.2: GC configuration of the Varian CP3800 GC-FID/TCD used for purity analysis of CO, CH_4, CO_2 and C_2H_6

The analytical conditions for analysis of CO, CH_4, CO_2 and C_2H_6 impurities in the high pure nitrogen and sulphur dioxide gases are shown in Table 3.2.

Table 3.2: Analytical conditions for analysis of CO, CH_4, CO_2 and C_2H_6 impurities in the high pure nitrogen and sulphur dioxide gases using GC-FID/TCD

Parameter	Experimental conditions
TCD temperature	200 ^{o}C and filament at 290 ^{o}C
FID temperature	300 ^{o}C and methaniser at 380 ^{o}C
Column 1	1.83 m x 1/8-inch OD x 2.1 mm ID Molecular sieve 5Å, 60/80 mesh Packed column for CO and CH_4
Column 2	1.83 m x 1/8-inch x 2 mm ID, Haysep N 80/100 mesh Packed column for CO_2 and C_2H_6
Temperature programming	60 ^{o}C for 3.2 minutes, ramp to 90 ^{o}C for 3.8 minutes
Sample flow	100 ml/min
Sample loop	2 ml
Total run time	9 minutes

To quantify H_2, N_2 and O_2 in high pure sulphur dioxide, a TCD detector was used. Molecular sieve 5Å column was used for analysis of N_2 and O_2 at the oven temperature of 30 ºC with argon as a carrier gas. For hydrogen impurity analysis, the same molecular sieve 5Å column was used but at an oven temperature of 180 ºC with using nitrogen as carrier gas. Standards containing CO, CO_2, CH_4, C_2H_6 and argon in Helium were gravimetrically prepared, ranging from 0.1 to 100 µmol/mol.

3.5.2 Purity analysis of high purity gases using pulsed discharge helium ionisation detector

From the manufacturer’s specification, argon has been reported to be high in mole fraction in high purity nitrogen and therefore requires quantification. A Varian CP-3800 gas chromatograph coupled with a PDHID detector with a 30 m capillary molecular sieve 5Å column with 0.53 mm ID and 50 µm film thickness at an oven temperature of 25 ºC was used to analyse argon in high purity nitrogen. This GC-PDHID was also used to quantify oxygen impurity in high purity nitrogen. A 6-port diaphragm valve was used to introduce the sample into the system using a 250 µl sample loop. The carrier gas used was helium passed through a helium purifier before entering the gas chromatography system. The GC configuration is shown in Figure 3.3.The sample is introduced to the GC through valve 1. The sample enters the GC on port 3 where the sample loop connected in port 2 and 5 is then filled with the sample with the valve in the OFF position. Valve 1 then switches to the ON position to move the sample together with the mobile phase helium carrier gas to the molecular sieve column through port 6 where oxygen, argon and nitrogen were separated and detected by the PDHID.

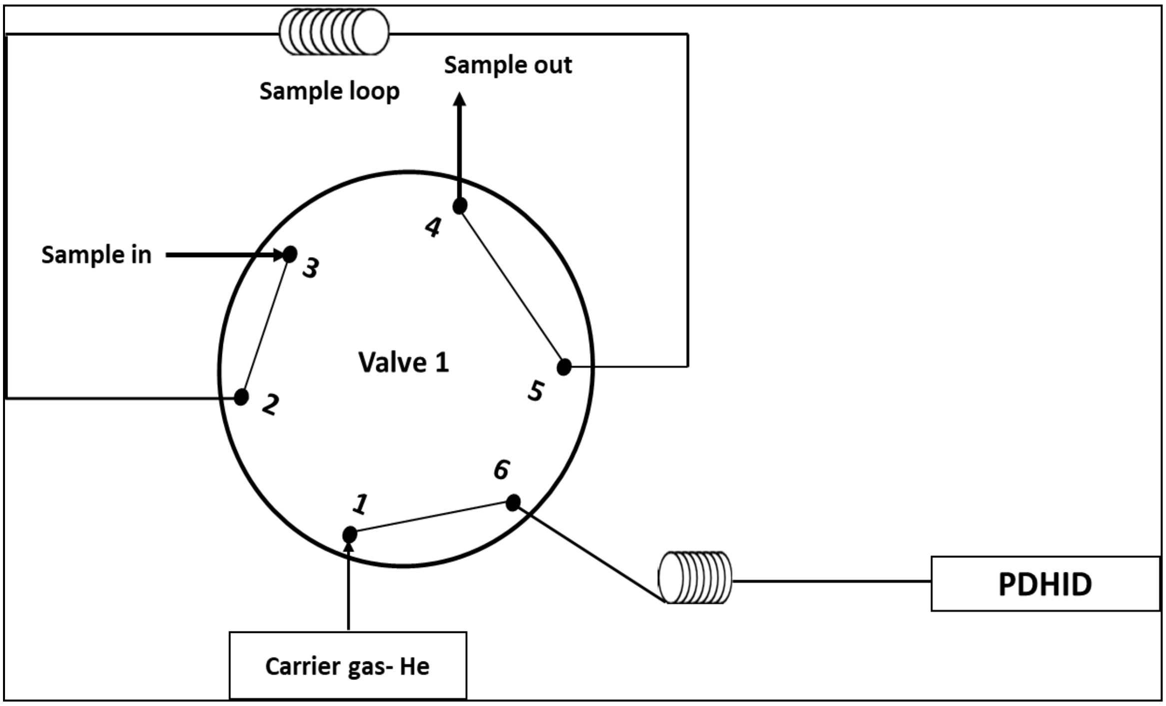


Figure 3.3: The configuration of Varian GC-PDHID used to quantify impurities of argon, oxygen, and nitrogen.

3.5.3 Purity analysis of high purity source gases using pulse discharge ionisation detector/sulphur chemiluminescence detector/thermal conductivity detector

The purity assessment for high purity hydrogen sulphide gas was done using Agilent 7890B gas chromatography coupled with three channel detectors (GC-TCD/SCD/PDHID). Impurities of sulphur dioxide (SO_2) and ethyl mercaptans (CH_3CH_2SH) were analysed on the SCD channel and impurities of hydrogen (H_2), nitrogen (N_2) Argon (Ar), oxygen (O_2) were analysed on the TCD and PDHID channels. Columns used were DB Sulfur SCD (40 m x 0.320 mmm ID x 0.75 µm) to analyse sulphur components and ShinCarbon ST (80/100 mesh, 2 m x 2 mm ID, 1/8-inch OD) to analyse N_2, H_2, Ar and O_2. The analysis of impurities was done on valve 4 and valve 1 of the GC-SCD/TCD/PDHID as per illustration in Figure 3.4. Open lab software was used to control the valve switching and sample introduction through multi-position VICI Serial Stream Selection Valve (SSV) array by Agilent Serial SSV5.31 control software to selected valves for different columns as shown in Figure 3.4.

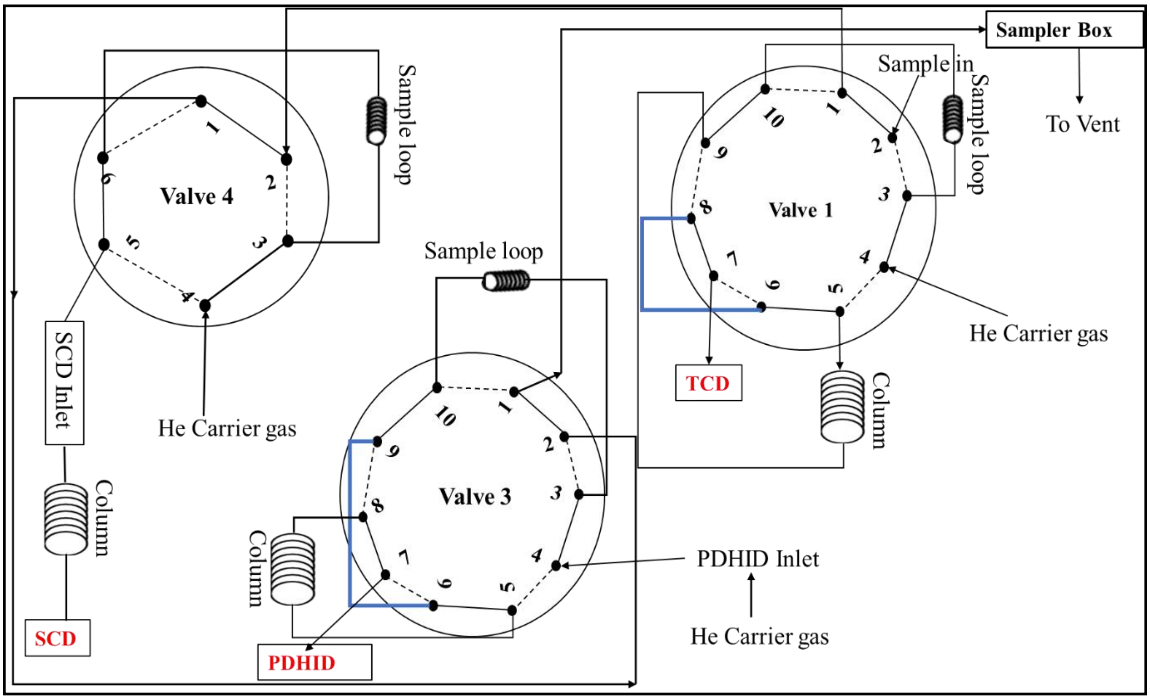


Figure 3.4: Configuration of GC-SCD/TCD/PDHID used to the analyse impurities of SO_2, C_2H_5SH, N_2, H_2, Ar and O_2.

3.6 PURITY ASSESSMENT OF HIGH PURITY LIQUID CHEMICALS (ETHANOL, ACETONE, METHANOL, PROPANOL AND N-BUTANOL)

Moisture is the major impurity contributor to the high purity liquids such as ethanol, acetone, methanol, propanol, and n-butanol. High purity ethanol was checked for moisture content. Manufacturer specifications were used for acetone, methanol, butanol, and other impurities of ethanol.

3.6.1 Purity analysis of high purity ethanol using Karl Fischer Titration

To determine the moisture content in high purity ethanol, the following reactions were followed in accordance with American Society for Testing and Material (ASTM E 1064-08: Standard test method for water in organic liquids by coulometric Karl Fischer titration) is shown in reaction 2 and reaction 3.

$$ROH + SO_2 + RN \rightarrow (RNH).SO_3R \qquad (2)$$

$$(RNH).SO_3R + 2RN + I_2 + H_2O \rightarrow (RNH).SO_4R + 2\,(RNH)I \qquad (3)$$

Iodine and sulphur dioxide will react with water in the presence of an alcohol and a base (RN), and Iodine is produced electrochemically by oxidation at the generator electrode which has no-diaphragm.

The balance used for this analysis was first exercised using 10 g mass piece then measurements of the mass piece were taken using a substitution method whereby one mass piece used as reference and the other as sample are weighed one after the other (Alink and Van Der Veen, 2000). To verify the coulometric measurement, a pre-titration determination was performed on the Karl Fischer instrument and the drift determined to ensure that not much drift is experience during the measurements. The amount of moisture (H_2O) expected was calculated prior to the measurement. For example if high purity ethanol is 99.9 % then assuming that 0.1 % of H_2O is in the high purity ethanol, the expected amount of moisture will be 0.790 µg/ml. A 5 ml graduated scale syringe was used to inject 2 to 3 aliquots of ethanol (using 1 ml per injection). For this study, a calibrated Mettler Toledo balance with a model AX205 Delta Range®, Max 81/220g was used for weighing of the syringe. A syringe was filled with the required amount of ethanol and capped with a septum. The syringe was then weighed. The needle of the syringe was then inserted through the white plug (septum-sealed) on the titration cell. Ethanol was gently injected into the reagent while avoiding splashing on the sides of the cell. The syringe was immediately removed and weighed with a septum on the needle. Then the automatic titration was started and left for10 minutes to run as shown in Figure 3.5. All the masses from the balance were printed out directly from the balance's built-in printer. Readings from the Karl Fischer titration were obtained from the desktop computer connected to Karl Fischer apparatus.

Figure 3.5: Karl Fischer titration used to analyse moisture content in high purity ethanol.

3.7 GRAVIMETRIC PREPARATION OF SELECTED SULPHUR CONTAINING COMPOUNDS AND OVOCS REFERENCE GAS MIXTURES

The selected sulphur containing compounds and OVOCs reference gas mixtures were prepared by gravimetry primary method in accordance with International Organization for Standardization ISO 6142-1:2015. The substitution method was used whereby a gas mixture cylinder was weighed against a reference cylinder during a weighing cycle. The gas mixture cylinders were weighed before and after each addition of components. The difference in weighing is equal to the mass of the component added. The method is mass-based which is directly traceable to the SI unit of mass (Kg). The evacuation process is critical in gravimetric preparation method because any residuals gases or moisture in the cylinder is removed and hence a minimum or less vacuum of 2 x 10^{-6} hPa is required. For uncertainty evaluation, the contribution of weighing process, the purity of the starting material, stability of the reference gas mixture and verification of the reference gas mixture were considered. An automated gravimetric weighing system balance was used in this work as described by (Lee *et al.*, 2006); (Park *et al.*, 2004) as shown in Figure 3.6, whereby a cylinder loading system is automated.

Figure 3.6: The Automatic weighing system (AWS) used to weigh cylinders on the Mettler Toledo balance.

The process is repeated until all components of gases and the diluent gas have been added to the cylinder. For permanent gases, each component is added directly into the cylinder using the direct method and for condensable gases such as ethanol, components are transferred using intermediate transfer vessels for example a metal loop or syringe. When all components have been transferred into the cylinder, the gas mixture is homogenised through rolling the cylinder on the roller bench for a minimum of two hours. The gravimetric mole fraction of the prepared gas mixture is calculated based on the actual masses added into the cylinder. The gas mixture is verified with in-house gravimetrically prepared gas mixtures of similar mole fraction.

The Gravimetric method is recognised as the highest metrological level method for preparation of gas mixtures by weighing and is traceable to the SI unit, mass (Kg) (Alink and Van Der Veen, 2000) .

The ideal gas law is assumed in order to calculate the mass of the components to be prepared. Equation 3.1 describes the behaviour of the gas where volume, temperature, pressure, and number of moles of the gas are considered.

$$\mathbf{PV = nRT} \tag{3.1}$$

where P is the pressure of the gas in *Pa*, V is the volume of the gas in the cylinder in M^3, n is the number of moles of the gas in mole, R is the gas constant defined as R = 8.31451 $J.mol^{-1}. K^{-1}$ and T is the temperature measured in kelvin (K).

GravCalc software (Brown, 2009) was developed by National Physical Laboratory (NPL) in the United Kingdom (UK) for the calculation of target masses based on the derived ideal gas law equation (Holland *et al.*, 2001). Mass pieces for all the balances such as top loading and the mass comparator balances, were calibrated by the NMISA Mass laboratory who is traceable to the SI unit mass (Kg).

3.7.1 Preparation of the cylinder

The cylinders used to prepare the selected sulphur compounds and OVOCs reference gas mixtures were aluminium from the United Kingdom (UK) with a water capacity of 5.0 and 10.0 Litres. These cylinders were pre-treated through the fluorination process before use. The outside surface of the cylinder was cleaned with water and soap to remove any dust particles and material that could interfere with the weighing process. The cylinders were then evacuated overnight to reach < 9 x 10^{-7} hPa vacuum pressure using a Pfeiffer turbomolecular pump to remove any residual gas and moisture or any contaminants that could be left inside the cylinder as shown in Figure 3.7. Once the cleaning and evacuation process were completed, the cylinders were kept in the weighing room to allow for the cylinders to reach same environmental conditions of temperature and humidity as the tare cylinders. Tare cylinders used had the similar volume, shape and make as the sample or mixture cylinder to be weighed. The weighing system is shown in Figure 3.6.

Figure 3.7: Evacuation station with a turbomolecular pump used for interior cleaning of cylinders

3.7.2 The weighing process of the cylinder during the preparation.

The substitution method (Alink and Van Der Veen, 2000) was used to weigh a reference cylinder and gas mixture before and after each filling of the targeted mass into a cylinder. All the targeted mass measurements of gas introduced into a cylinder were done on the automated weighing system (AWS) as shown in Figure 3.6. The AWS consists of the following:

(a) High precision mass comparator balance (XPE-S/XPE-L models) with a resolution of 1 mg, with a capacity of 26 kg.
(b) It has a robotic automated cylinder loading system which supports four cylinders.
(c) A computer integrated with LabView software to control the weighing process and automatically records the weighing data.
(d) The balance is installed in an isolated box mounted in a granite stone plate with a glass shield to minimise any vibration and fluctuations. The balance is calibrated with a 10 kg or 20kg mass pieces of class E_2 (Matsumoto *et al.*, 2004) weights before use to ensure its measurement accuracy. The environmental conditions in the balance or weighing room such as temperature and humidity were controlled at 20 ± 2 °C and 45 ± 10 % RH, respectively. In this study the weighing sequence followed was weighing the reference cylinder first, followed

by the gas mixture cylinder and this sequence was repeated 10 times. This was done to minimise any variation in air density during the weighing process.

3.7.3 The weighing process of a syringe used for liquid introduction into the cylinder.

To introduce a liquid component into a gas cylinder, normally a small amount of liquid is required because of vapour pressure, where the liquid vaporizes into a gas phase. Hence a highly sensitive and low-capacity analytical balance is used. In this study, a Sartorius MC 210 S balance was used to weigh the calculated amount of liquid required to be introduced into a gas-tight syringe as shown in Figure 3.8. The gas-tight syringe filled with the amount of liquid was weighed before and after transferring the liquid into a cylinder.

Figure 3.8: Sartorius balance used for weighing transfer vessels during the liquid preparation process.

3.7.4 Filling of the cylinder with the gas molecules

A static gravimetric method was used to prepare reference gas mixtures of selected sulphur containing compounds and OVOCs. The reference gas mixtures were diluted from high purity starting material to nominal mole fraction of 10 µmol.mol^{-1} for sulphur containing compounds and 5 µmol.mol^{-1} for OVOCs. The mixing of the gases was done using the filling station as shown in Figure 3.9 where both the pre-mix gas cylinder and gas mixture cylinders were connected to the transfer lines on the opposite sides of the filling station. The gas mixture cylinder was connected on the target balance side of the filling station and the pre-mix gas cylinder connected to the left side of the filling station. The high-pressure nitrogen gas was purged through the filling station to check for any gas leak, which would be indicated by a pressure drop. If there is any pressure drop, then a chemical such as Swagelok SNOOP^{TM} was used to check for a leak in the filling station. The filling station was then purged with a pre-mix gas cylinder several times to minimise and avoid any contamination. The pressure of the gas in the filling station was released through a venting system. The transfer lines were evacuated to a vacuum pressure of less than 2,5 x 10^{-5} hPa through a turbomolecular pump. The calculated target mass was added to the gas mixture cylinder using the mass comparator Radwag balance.

The filling station is in a closed system with stainless steel tubing connection from the pre-mix gas cylinder on the left side to the gas mixture cylinder on the right side of the filling station. It has a needle valve for controlling the gas flow from the pre-mix, a pressure gauge indicator and a turbomolecular pump to achieve the required vacuum pressure for filling purposes. The filling station is flushed several times with pre-mix component gas mixture to avoid any contamination from other gases that might have been present in the filling station lines.

Figure 3.9: Filling station used to introduce gas components into sample cylinder

For transferring liquids into gas cylinders, the filling station is connected to a liquid introduction system for injection through a septum using a gas-tight syringe as shown in Figure 3.10. A minimum dead volume (MDV) bullnose or connector was connected to the gas mixture cylinder which was the connected to the liquid introduction system. The MDV connector was used to minimise the losses of liquids during transferring process as illustrated in Figure 3.10. This MDV connector was designed by the NPL, and has been extensively used for the preparation of liquid components (Grenfell *et al.*, 2010). The high purity nitrogen gas cylinder was connected to the left side of the filling station and was used to purge any excess liquid that could be left in the liquid introduction system into the cylinder. This process was done at low pressure to protect the septum in the liquid introduction system from leaking. Nitrogen was used to purge excess liquid because it was used as the diluent gas in the preparation of these gas mixtures. The gas mixture cylinder with liquid and nitrogen was weighed to determine how much nitrogen gas was already added in the gas mixture cylinder. The final amount of nitrogen required was determined by subtracting the already added amount of nitrogen from the total calculated target amount of nitrogen using the GRAVCALC software (Brown, 2009). The amount of liquid added in the cylinder was determined by weighing the gas-tight syringe before and after transferring the liquid into a cylinder using the analytical balance as shown in Figure 3.8.

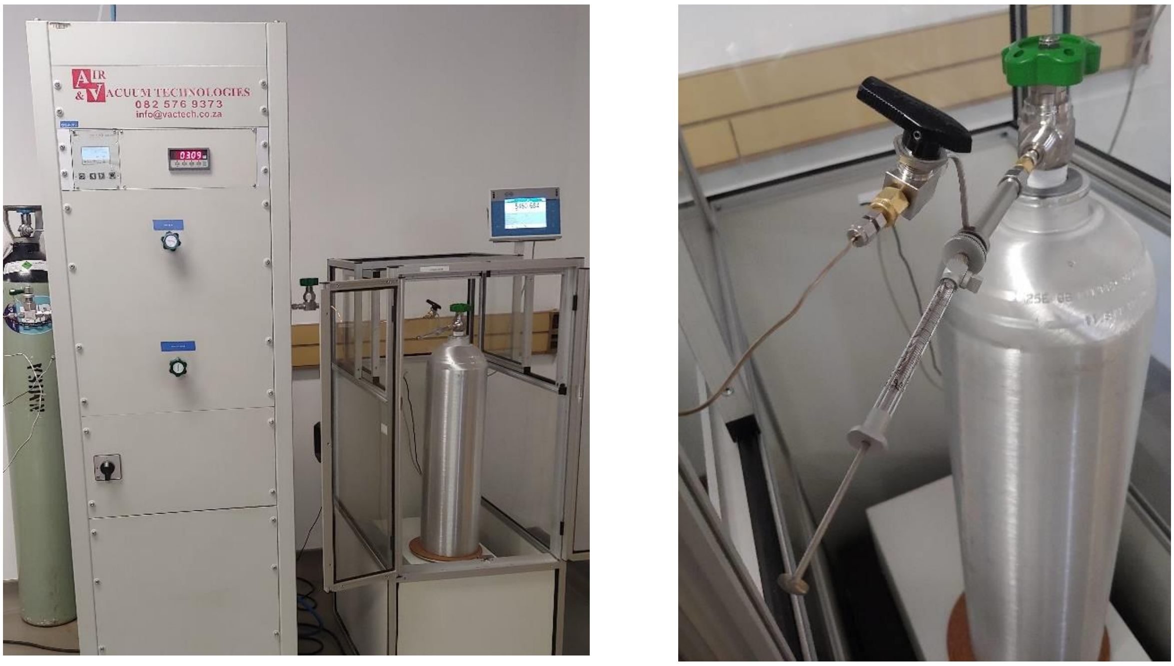
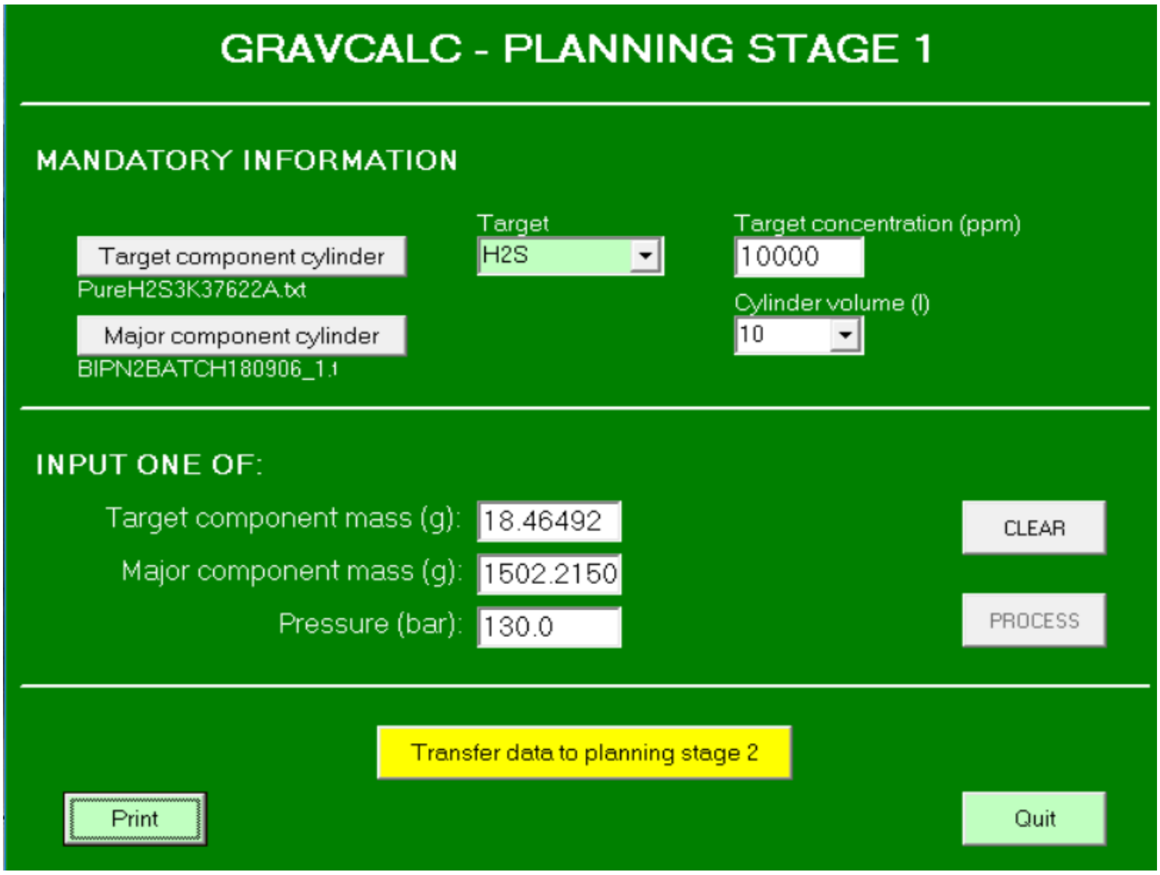


Figure 3.10: Liquid introduction system for transferring liquid sample to the cylinder

3.8 GRAVIMETRIC PREPARATION OF BINARY PRIMARY STANDARD GAS MIXTURES

During gravimetric preparation, the GravCalc software (Brown, 2009) was used to calculate the target amount of gas when diluting from pre-mixtures or high pure source material. This is done in the planning stage 1 as illustrated in Figure 3.11, where the target component cylinder is the pre-mix component that will be used to dilute from, and a major component is the diluent gas to be used. For this study, nitrogen was used as diluent gas for all the gravimetrically prepared gas mixtures. Target referred to the component that is of interest for example H_2S, and target concentration being 10 000 µmol/mol with a cylinder volume of 10 L.



PureH2S3K37622A.txt

BIPN2BATCH180906_1.1

Target: H2S

Target concentration (ppm): 10000

Cylinder volume (l): 10

Target component mass (g): 18.46492

Major component mass (g): 1502.2150

Pressure (bar): 130.0

Figure 3.11: GravCalc software (Brown, 2009) planning stage 1 for hydrogen sulphide gas mixtures

The first weighing was the empty evacuated cylinder on the AWS balance (Mettler Toledo AG (Model XP26003L) with highest capacity of 26.1 kg and readability of 1 mg). Then the filled gas mixture cylinder was then weighed accurately using the AWS balance in the weighing room. The actual added mass was calculated by subtracting the weighing difference of the empty cylinder and filled cylinder. After the gas mixture cylinder was filled with nitrogen gas (balance gas), the gas mixture cylinder was left in the weighing room until it has reached same conditions as the reference cylinder (Milton *et al.*, 2011). When the final weighing was completed the gas mixture cylinders were rolled for the minimum of two hours on the roller bench to ensure homogeneity of the gas mixtures. Milton *et al.*, 2011, gives detailed gravimetric method on “Gravimetric methods for preparation of standard gas mixtures”.

3.8.1 Accurate preparation of hydrogen sulphide reference gas mixtures in nitrogen

The primary standard gas mixtures of hydrogen sulphide in nitrogen were produced following International Organization for Standardization (ISO 6142-1:2015) using high pure hydrogen sulphide as the starting material. These PSGMs were diluted from the high purity H_2S (99.99 %) to a range of 8 to 12 µmol. mol^{-1} mole fractions of hydrogen sulphide reference gas mixtures. Each subsequent concentration level was prepared from the previous hydrogen sulphide pre-mix gases and diluted with nitrogen. The first step was to weigh an empty evacuated cylinder with a reference cylinder of similar material to the gas mixture cylinder. Four-step dilution was used for the preparation of PSGMs of hydrogen sulphide in nitrogen as illustrated in Figure 3.13. The first dilution were two times nominal 2 % mol/mol and one 1 % mol/mol from the high purity 99.99 % H_2S.

The weighed empty evacuated cylinder was connected to the filling station together with the pre-mix gas as shown in Figure 3.9. High pure nitrogen gas was purged through the filling station to check for any gas leaks, which would be indicated by a pressure drop. If there was a pressure drop, then the Swagelok SNOOP^{tM} was used to check for the specific leaks in the filling station and any leaking connection was re-tightened. The filling station was then purged with the high purity hydrogen sulphide several times to remove any residual gas in the filling station lines. The pressure of the gas in the filling station was released through a venting system. The transfer lines were evacuated to pressure of less than 2,5 x 10^{-5} through a turbomolecular pump. After flushing several times, then the calculated amount of high purity hydrogen sulphide was transferred into the empty evacuated gas mixture cylinder. The gas mixture cylinder was weighed accurately using the AWS mass comparator balance as illustrated in Figure 3.6. The actual amount of hydrogen sulphide added in the cylinder is calculated the weighing difference between the mass of the filled gas mixture cylinder and the empty evacuated gas mixture cylinder. The actual mass of hydrogen sulphide in the cylinder is used to re-calculate the amount of nitrogen diluent gas to be added into the gas mixture cylinder.

The weighed gas mixture cylinder with hydrogen sulphide added was then re-connected to the filling station to be filled with the nitrogen diluent gas as shown in Figure 3.8. The filling station was flushed with high purity nitrogen several times to remove any residuals of high purity hydrogen sulphide gas in the filling station lines. The calculated amount of nitrogen diluent gas was added to the gas mixture cylinder with hydrogen sulphide. After the gas mixture cylinder was added with nitrogen, it was left for minimum of two hours to reach the ambient temperature before weighing the nitrogen added into the cylinder because the gas mixture cylinder had released heat during filling the nitrogen diluent gas due to high pressure. When the gas mixture cylinder has reached the ambient temperature, it was weighed again on the AWS mass comparator balance as illustrated in Figure 3.6 to determine the amount of nitrogen gas added. This was achieved by calculating the weighing difference between the mass of the gas mixture cylinder filled with both hydrogen sulphide and nitrogen and the mass of gas mixture cylinder filled with hydrogen sulphide. The gas bench for the minimum of two hours to homogenise the gas mixtures as shown in Figure 3.12. The overall production diagram for hydrogen sulphide gas mixtures is shown in Figure 3.13.

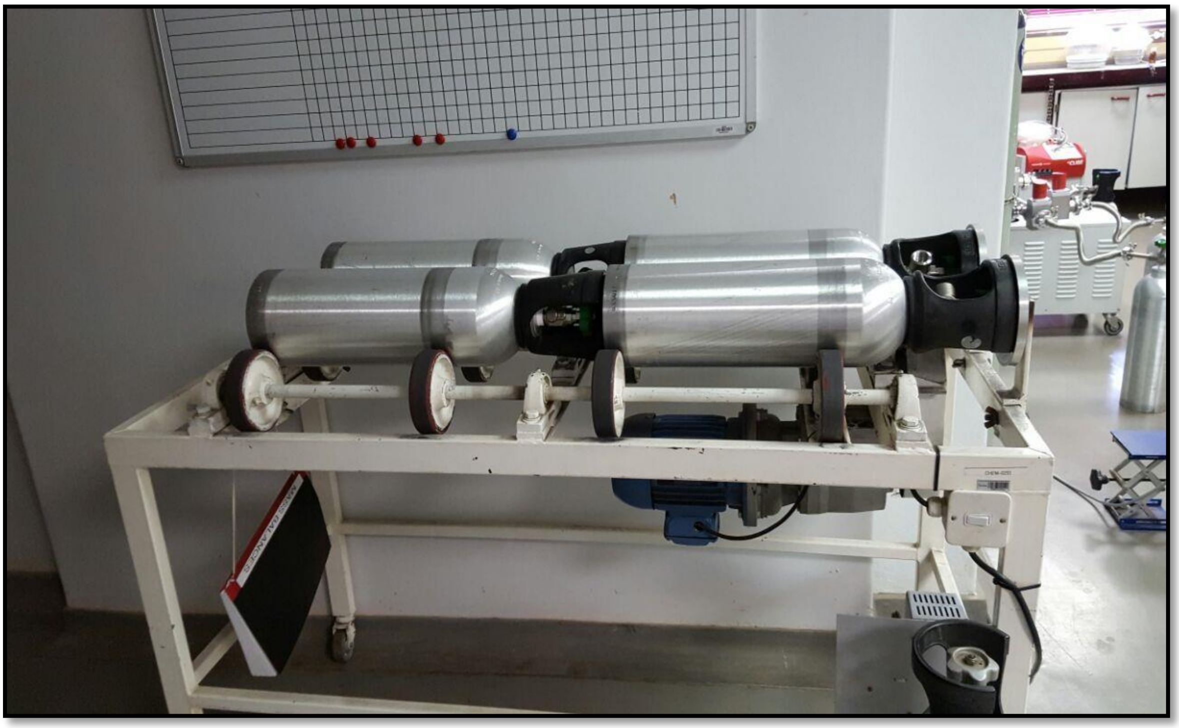


Figure 3.12: Roller bench used to homogenise the prepared gas mixtures

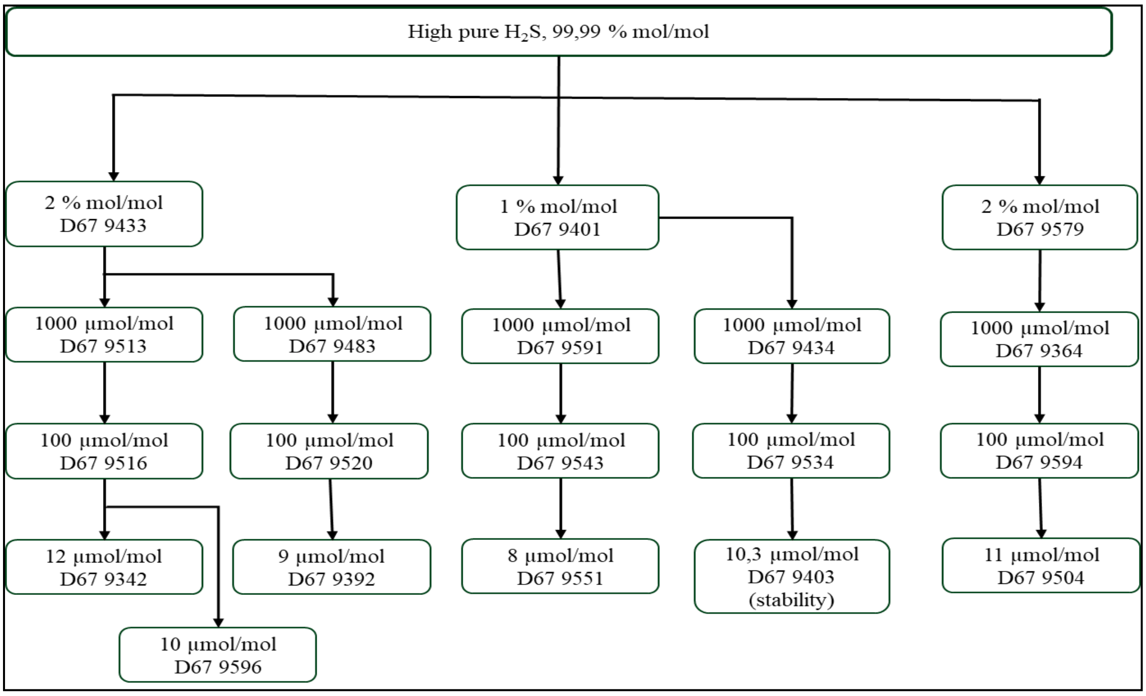


Figure 3.13: Schematic diagram of the production of the hydrogen sulphide (H_2S) in nitrogen primary standard gas mixtures.

3.8.2 Precise preparation of sulphur dioxide in nitrogen reference gas mixtures

Sulphur dioxide in nitrogen reference gas mixtures were prepared in four dilution steps. Figure 3.14 illustrates the dilution steps followed to prepare the desired 10 µmol/mol of sulphur dioxide. High purity sulphur dioxide (99.98 % mol/mol) was diluted into two cylinders of 3.5 % mol/mol. Each subsequent concentration level was prepared from the previous sulphur dioxide pre-mix gases and diluted with nitrogen. The preparation process for sulphur dioxide followed that of hydrogen sulphide with differences in the dilution mole fractions for hydrogen sulphide.
“D62 6445’’ refers to the cylinder identification number.

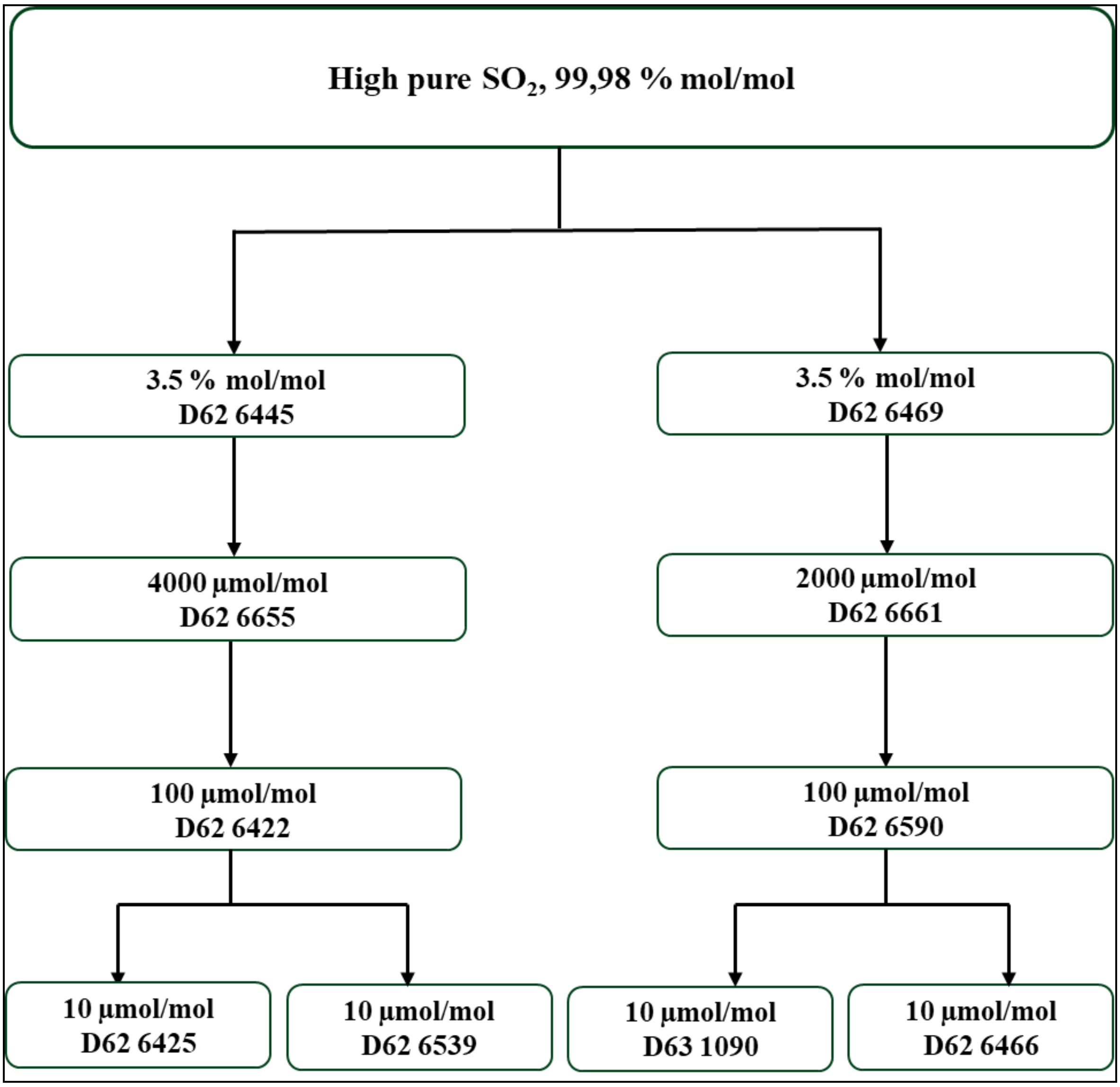


Figure 3.14: Schematic diagram of the production of the sulphur dioxide (SO_2) in nitrogen primary standard gas mixtures.

3.8.3 Isopropanol (C_3H_8O) in nitrogen reference gas mixtures prepared by gravimetric technique

Gravimetric preparation of gas mixtures from liquid phase requires known vapour pressures to ensure that the liquid fully vaporises into the gas phase at a specific volume and pressure according to the ideal gas law and to prevent condensation of the liquid in the cylinder. The ideal gas law in equation 3.2 is assumed in determining the maximum amount of the liquid that will vaporise to gas phase inside the cylinder.

$$\boldsymbol{m_i} = \frac{\boldsymbol{P_{Vap}} \times \boldsymbol{V_{Cyl}} \times \boldsymbol{M_i}}{\boldsymbol{R} \times \boldsymbol{T}} \qquad 3.2$$

where $\boldsymbol{m_i}$ is the maximum mass of the liquid component (g) of component, $\boldsymbol{P_{Vap}}$ *is the* vapour pressure of component (Pa), $\boldsymbol{V_{Cyl}}$ is the volume (m^3) of cylinder used, $\boldsymbol{M_i}$ is the molar mass of component to be prepared ($g.mol^{-1}$), R is the gas constant (8.31451 $J.mol^{-1}.K^{-1}$) and T is the temperature in Kelvin (°C + 273.15 K).

In addition, the isopropanol in nitrogen primary standard gas mixtures were prepared in accordance with ISO 6142 (ISO 6142-1:2015). In this study, the isopropanol PSGMs were prepared in one dilution steps as illustrated in Figure 3.14. to a mole fractions of two times 200 µmol/mol. The syringe method for liquid introduction in Annex D of ISO 6142 was followed. A gas-tight graduated scale syringe was used to estimate the amount of liquid in the syringe. The syringe was capped with the septum to minimise any evaporation of liquid during the weighing process of the syringe. Through its vapour pressure, the maximum amount of liquid to be introduced into a gas cylinder was calculated and considered during gravimetric preparation.

The calculated amount of isopropanol from high pure source material was transferred into a gas-tight syringe. The filled gas-tight syringe was weighed on the analytical balance as illustrated in Figure 3.7 before transferring into the evacuated cylinder. The liquid was transferred into the gas cylinder by injection through a closed off septum using the liquid introduction system and an MDV connector as shown in Figure 3.9. High pressure nitrogen of about 0.8 MPa was used to purge the liquid into the cylinder. This was done to minimise any adsorption of liquid in the liquid introduction system. After injection, the gas-tight syringe was weighed, and the amount of isopropanol added into the cylinder was calculated by the weighing difference of the filled syringe and empty syringe after injection into the cylinder.
The gas mixture cylinder filled with C_3H_8O and 0.8 MPa of nitrogen was weighed on the AWS balance to determine the amount of nitrogen already added into the cylinder and then calculate the balance of nitrogen to be added. This was done by subtracting the initially added nitrogen to push the liquid component from the total target nitrogen to be added to achieve the mole fraction of 200 µmol/mol isopropanol prepared. The gas mixture cylinder was then filled with the calculated balance nitrogen and finally weighed on the AWS balance. The gas mixture cylinder was rolled for minimum of two hours on the roller bench to ensure homogenisation of the gas mixture.

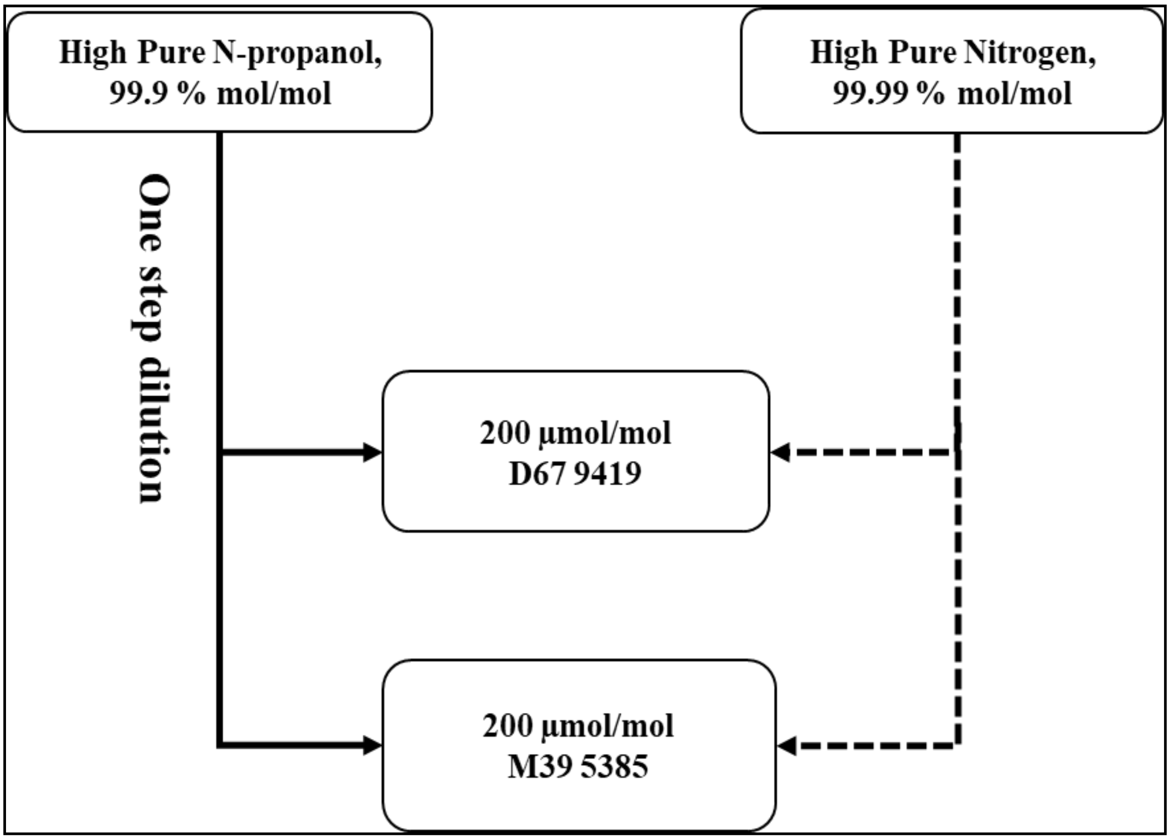


Figure 3.15: Schematic diagram of the production of isopropanol in nitrogen primary standard gas mixtures.

3.8.4 Ethanol (C_2H_5OH) in Nitrogen reference gas mixtures prepared by gravimetric method.

Ethanol in nitrogen reference gas mixtures were prepared in two dilution steps. Figure 3.16 illustrates the dilution steps followed to prepare the desired 5 µmol/mol of ethanol. High purity ethanol (99.95 % mol/mol) was diluted into four cylinders in the range of 82 to 213 µmol/mol. Each subsequent concentration level was prepared from the previous ethanol pre-mix gases and diluted with nitrogen. The preparation process for ethanol in the range 82 to 213 µmol/mol followed that of isopropanol with differences in the dilution mole fractions for isopropanol. The four cylinders of mole fractions of 5 µmol/mol were diluted directly from the pre-mix of 82 to 213 µmol/mol as shown in Figure 3.16.

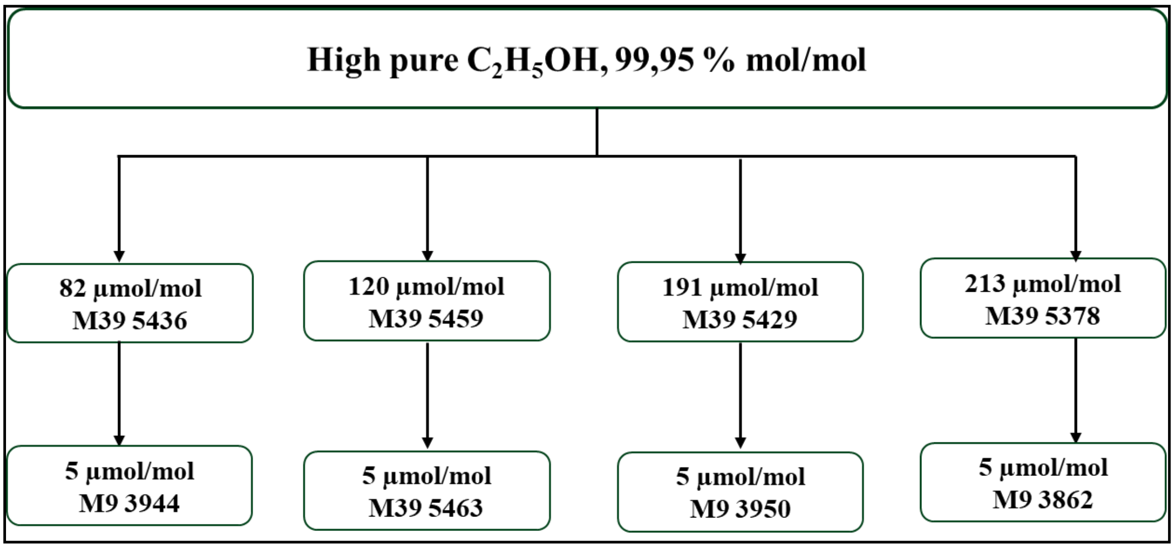


Figure 3.16: Schematic diagram of the production of ethanol in nitrogen primary standard gas mixtures.

3.8.5 The preparation of multi-component OVOCs in nitrogen reference gas mixtures using gravimetric preparation technique.

Four multi-components primary standard gas mixtures of (C_3H_6O/CH_3OH/C_2H_5OH/C_4H_9OH) in nitrogen with nominal mole fraction of 5 µmol/mol were gravimetrically prepared in accordance with ISO 6142. For this study, the PSGMs were prepared in one dilution steps as illustrated in Figure 3.17. The syringe method for liquid introduction in Annex D of ISO 6142-1:2015 was followed to prepare two times multi-component gas mixtures directly into the cylinder as compared to addition in a vial for pre-mix. The preparation process followed was the same as that of gravimetrically preparing isopropanol in section 3.7.3, but the addition of the liquid into the cylinder was done based on the vapour pressure with components with lower vapour pressure added first. This was done to minimise differential vapour losses during the transfer of these liquids while transferring Grenfell *et al.*, 2010). The other two times multi-component gas mixtures were prepared by first adding the calculated amount of each liquid into a gas-tight syringe and then transferred into an empty weighed vial. The gas-tight syringe filled with target component was weighed before transferring the liquid into a vial to determine if enough mass will be added. The addition of the liquid into the vial was done based on the vapour pressure with components of lower vapour pressure being added first as per Table 3.3.

Table 3.3: Vapour pressures for OVOCs Source: PubChem website[a]

Component	Vapour pressures (kPa) at 20°C
Acetone	23.998
Methanol	12.799
Ethanol	5.866
Isopropanol	4.399
n-Butanol	2.068

[a](https://pubchem.ncbi.nlm.nih.gov assessed date 14 November 2019)

The first component to be added was n-butanol and acetone being the last to be added based on their vapour pressures. The vial was then weighed after all the components were added to confirm the weighing of the vessels used during liquid introduction following the gravimetric method. Once all the components were added into the vial and mixed, the gas-tight syringe with a graduated scale was filled with the calculated amount of pre-mix of acetone, methanol, ethanol, and n-butanol. The syringe was weighing before transferring the liquid into the gas mixture cylinder. The liquid was transferred into the gas cylinder by injection through a closed off septum using the liquid introduction system and an MDV connector as shown in Figure 3.10. High pressure nitrogen of about 0.8 MPa was used to push the liquid into the cylinder. This was done to minimise any adsorption of liquid in the liquid introduction system. After injection, the gas-tight syringe was weighed, and the amount of multi-component mixture added into the cylinder was calculated by the weighing difference of the filled syringe and empty syringe after injection into the cylinder.

The gas mixture cylinder filled with ($C_3H_6O/CH_3OH/C_2H_5OH/C_4H_9OH$) and 0.8 MPa of nitrogen was weighed on the AWS balance to determine the amount of nitrogen already added into the cylinder and then calculate the balance of nitrogen to be added. This was done by subtracting the initially added nitrogen to push the liquid component from the total target nitrogen to be added. The gas mixture cylinder was then filled with the calculated balance nitrogen and finally weighed on the AWS balance. The gas mixture cylinder was rolled overnight on the roller bench to ensure homogenisation of the gas mixture especially at mole fraction of 5 µmol/mol.

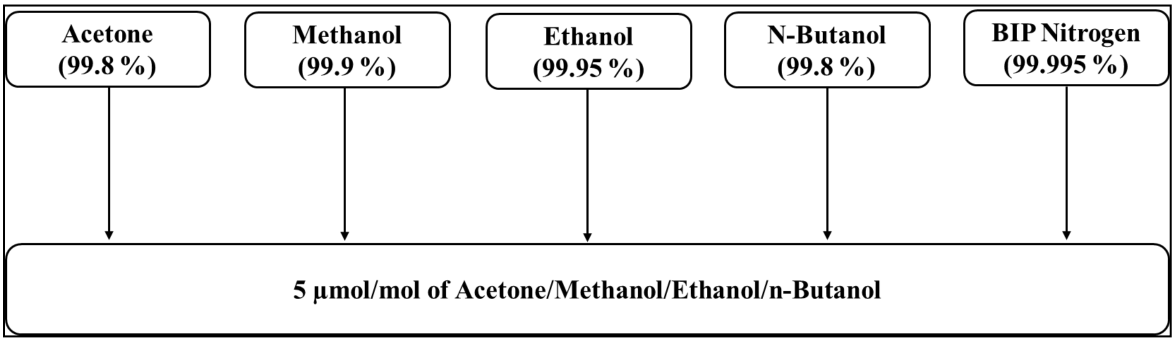


Figure 3.17: Schematic diagram of the production of multi-component of acetone, methanol, ethanol, and n-butanol in nitrogen primary standard gas mixtures.

3.9 VERIFICATION OF GRAVIMETRICALLY PREPARED PRIMARY STANDARD GAS MIXTURES

Gravimetrically prepared reference gas mixtures need to be validated to confirm their consistent gravimetric composition with the analytical values obtained during verification of these gas mixtures using a suitable analytical method. After the prepared gas mixtures have been rolled, they were validated using different techniques to determine the accuracy of the gravimetric mole fraction. Validation of reference gas mixtures was done in accordance with ISO 6143- Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures (*ISO 6143*, 2001). ISO 6143 states that a reference gas mixture is reliable and validated when it meets the criteria given by equation 3.3 for each component in the gas mixture.

$$\left|x_g - x_a\right| \leq 2\sqrt{u\left(x_g\right)^2 + u(x_a)^2} \tag{3.3}$$

where x_g is the gravimetric mole fraction from preparation and x_a is the analytical mole fraction of the component, $u\left(x_g\right)$ is the gravimetric standard uncertainty and $u(x_a)$ is the analytical standard uncertainty from analytical measurements.

Several calibration methods are used to determine the accuracy of the gas mixtures; the most commonly used are the following:

1) *One-point calibration method*: One reference gas mixture with similar mole fraction to the sample is used. This calibration method assumes that the detector behaves similarly to both sample and reference gas mixtures. The linearity factor can be ignored if the sample and reference mixtures are within <1% relative of each other.

2) *Two-point calibration method*: This is mostly known as bracketing technique during which two reference gas mixtures with mole fraction (± 10% relative) of the sample mole fraction are used to analyse the sample.
3) *Multi-point calibration method*: A calibration method in which a minimum of 3 to 10 standards are used to assign value to one or more samples. A set of standards with known mole fraction are used to draw a calibration curve. This is further detailed in ISO 6143 (ISO 6143, 2001).

In this study both one-point and multi-point calibration methods were used for the validation of the reference gas mixtures. The analytical techniques used in this study were Non-Dispersive Ultra-Violet (NDUV) spectroscopy, Ultra-Violet (UV) Fluorescence spectroscopy, Gas Chromatography (GC) coupled with pulsed discharged helium ionisation detector (PDHID), sulphur chemiluminescence detector (SCD) and flame ionisation detector (FID).

1) For Gas Chromatography (GC) technique: The separation is achieved through the interaction of the target components with the mobile and stationary phase. Separation of the sample occurs in the column, which is referred to as the stationary phase that is packed with different packing material with affinity for certain components depending on various physical properties of the component such as on boiling point, polarity, and molecular size. The most commonly used carrier gases for GC are hydrogen, helium, and nitrogen. It is therefore critical to choose a good column for identification and quantification of components. Hence for OVOCs have different boiling points lower boiling points components such as acetone eluting very quick due to its low affinity for the stationary phase, therefore a specific column is required to achieve the separation of the components.

2) For Ultra-Violet (UV) spectroscopy: This technique is based on the Ultraviolet absorption characteristics of gases to measure gas concentration. The gas filter correlation is specific to different gases absorbing light at different wavelengths. Thus happens when light is guided through the sample gas cell and measuring gas cell at suitable wavelengths, providing information of the gas composition (Tirpitz *et al.*, 2019). The absorption cross-section $\sigma(\lambda)$ explains the absorption efficiency of a gas component at wavelength λ. Through the measurement of light's attenuation, component mole fraction can be determined (Tirpitz *et al.*, 2019). This technique was used to confirm the gravimetrically prepared mole fraction of reference gas mixtures. for hydrogen sulphide and sulphur dioxide as shown in Figure 3.18

Figure 3.18: Non-Dispersive ultraviolet (NDUV) spectroscopy analysers used for analysis of hydrogen sulphide and sulphur dioxide in nitrogen primary standard gas mixtures

3.9.1 Validation of reference gas mixtures

Validation is one of the key requirements in ensuring the quality of results obtained and thus providing confidence in the measurement system. To determine the reliability, consistency, and accuracy of prepared gas mixtures with their gravimetric values, the mixtures were validated against other independently prepared gas mixtures. Table 3.4 shows the validation criteria for the validated parameters in this study.

Table 3.4: Validation criteria for the validated parameters

Validation parameters	Acceptance criteria
Percentage difference (% Diff)	Less than 1 % difference between gravimetric and analytical value
Percentage relative expanded uncertainty (% REU)	Less than 3 % for all the new reference gas mixtures
Percentage Relative Standard Deviation (% RSD)	Less than 1 % repeatability measurements
Percentage drift (Drift %)	Less than 1 % instrument drift

3.10 ANALYSIS OF BINARY PRIMARY STANDARD GAS MIXTURES

The mole fraction of gravimetrically prepared binary reference gas mixtures for selected sulphur components and OVOCs were verified using different techniques. For hydrogen sulphide three techniques used were gas chromatography coupled with PDHID, NDUV and UV Fluorescence. For sulphur dioxide, NDUV and UV Fluorescence techniques were used to verify the gravimetric mole fraction of the prepared reference gas mixtures. GC-FID was used to verify the gravimetric mole fraction of isopropanol and ethanol reference gas mixtures.

3.10.1 Analysis of gas mixtures using gas chromatography coupled with pulsed discharge helium ionisation detector

For analysis on the GC, the sample is injected in the column for separation. The reference gas mixtures were purged a minimum of three times under extraction in the laboratory to remove any dust particles that could be present at the cylinder valve outlet. To introduce the sample to the GC column, a regulator with a Swagelok quick fit connector was connected to the cylinder valve and purged several times under the extraction in the laboratory to flush any contaminants or moisture that could have been present. The cylinder was then connected to a 1/16-inch sulfinert treated tubing which is connected on the sampler box of the GC. The sample flow rate of the gas set was between 30 ml/min and 200 ml/min on the MFC using the *get red-y* software (Vögtlin instruments, 2013). The sample was then injected into the GC through a sample loop, which was initially in the fill state where sample loop is flushed before injection into the GC. The sample loop then changes to the inject state after 0.5 minutes where the sample together with the carrier gas moves to the column for separation. This process is repeated until both reference and sample are analysed as per set number of injections. For this study one-point or single calibration for analysis on the GC was used. This method is also known as substitution following a sequence of A-B-A, where A is chosen as reference or standard and B as the sample. Therefore one of the gas mixtures with similar mole fraction was chosen as a reference cylinder. Thus the sequence on the GC followed analysing the reference cylinder before and after analysis of the sample cylinder. This method is used for correction of the drift during the analysis.

3.10.2 Non-dispersive ultraviolet analyser: analysis of gas mixtures.

The NDUV technique was also used to verify gravimetrically prepared primary standard gas mixtures of selected sulphur compounds on the Limas 11 NDUV analyser. The system was purged using high purity nitrogen after every sample analysis using LabView software to control the sampling gas system. Sample introduction was done with Teflon tubing. The LabView software allowed for any number of sampling combinations, number of runs per sample, and number of cycles. The determination of gas mixture was done using multi-point calibration method to correct for linearity on the NDUV analyser since the analyser can be non-linear. Calibration standards and comparison sample were connected randomly on the Limas 11 UV analyser. The generated data was analysed using a generalized least square method.

The reference gas mixtures were purged a minimum of three times under extraction in the laboratory to remove any dust particles that could be present at the cylinder valve outlet. To introduce the sample on the Limas 11 UV s analyser, a regulator was connected to the cylinder valve and purged several times under the extraction in the laboratory to flush any contaminants or moisture that could have been present, close the black knob of the regulator after flushing. The cylinders were randomly connected to a 1/8-inch Teflon tubing which is connected on the sampler box of the analyser. The sample line was flushed by opening and closing the cylinder valve and regulator (fill and empty cycles) at least three times. The sample flow of all the cylinders connected to the sampler box and the nitrogen was set to the optimized sample flow for each sulphur compound, by opening the cylinder valve and opening the regulator knob slowly until the flow on the cylinder gets to the set flow. After all the connection a leak check (using SNOOP^{TM} solution) was done for all the connections.

3.10.3 Ultraviolet (UV) fluorescence analyser: analysis of gas mixture

In order to compare the analysis by Non-dispersive Ultraviolet analyser, the Teledyne T101 UV fluorescence analyser was used for the analysis of the gravimetrically prepared primary standard gas mixtures. The PSGMs were introduced through the sample stream of Molbloc system and mass flow controllers to control sample flow and directly to the UV fluorescence. Data was recorded manually. Optimised conditions for the H_2S UV fluorescence analyser are shown on Table 3.5.

Table 3.5: Analytical conditions for the analysis of hydrogen sulphide in T101 UV Fluorescence Analyser

Parameters	Method conditions
Purging time	10 minutes
Sample measurements taken	50 readings
Number of repeats	3
Sample flow	200 ml/min
Sample pressure	341KPa

3.10.4 Comparison of analytical techniques: hydrogen sulphide reference gas mixtures

In order to compare the analysis results from various techniques, hydrogen sulphide reference gas mixture was analysed using three different analytical techniques such as Non-Dispersive Ultraviolet (NDUV) spectroscopy, Ultraviolet Fluorescence spectroscopy and gas chromatography coupled with three detectors – PDHID, TCD and SCD. Only the PDHID channel was used for the analysis of hydrogen sulphide in nitrogen reference gas mixture and this channel is connected on valve 3 of the GC-SCD/TCD/PDHID.

3.10.4.1 Validation of hydrogen sulphide using GC-PDHID channel

The mole fraction of gravimetrically prepared H_2S reference gas mixture was analysed with Agilent 7890B gas chromatography coupled with Pulsed Discharged Helium Ionisation Detector (GC-PDHID). The PDHID was switched on for overnight before starting the analysis to allow the base line to stabilise. The regulator was connected to a cylinder and flushed several times and then connected to the cylinder with a regulator to a sulfinert treated tubing sample line on the sampler box of the GC. Both the sample and reference lines were purged for few minutes before the analysis started. The GC-PDHID conditions are shown on Table 3.6. The 1ml stainless steel treated sample loop was used to introduce the sample into the column through a 16-port stainless steel gas sampling valve of the sampler box.

The prepared H_2S primary standard gas mixture of 10,3 µmol/mol was analysed using A-B-A, where A and B represents the reference and sample, respectively. One of the previously prepared and analysed H_2S gas mixture was used as a reference cylinder. The sequence followed as: A, B, A1…with repeats of minimum five sets. This was done to ensure the correction of the drift during the analysis. Data acquisition was done using Open Lab software program.

Table 3.6: Analytical conditions for the analysis of hydrogen sulphide in nitrogen reference gas mixtures using GC - PDHID

Parameters	Method conditions
Column	Hayesep Q, 80/100, 2m, ID(2.1mm), 1/8"
Oven temperature	120 º C isothermal
Detector temperature	150 º C
Sample loop	1 ml
Carrier gas	Helium
Run time	2 minutes
Sample flow (mass flow controller)	50 ml/min
Number of injections	15

Figure 3.19 and Figure 3.20 show the PDHID channel configuration in both fill and inject positions. The sample is introduced to the GC through port 2 of valve 3. The sample loop connected on port 3 and 10 is filled with the sample in the fill position as illustrated in Figure 3.19. Valve 3 then switches to the inject position moving the sample together with the helium carrier gas to the Hayesep Q column through port 5 where H_2S is separated and detected by the PDHID as shown in Figure 3.20.

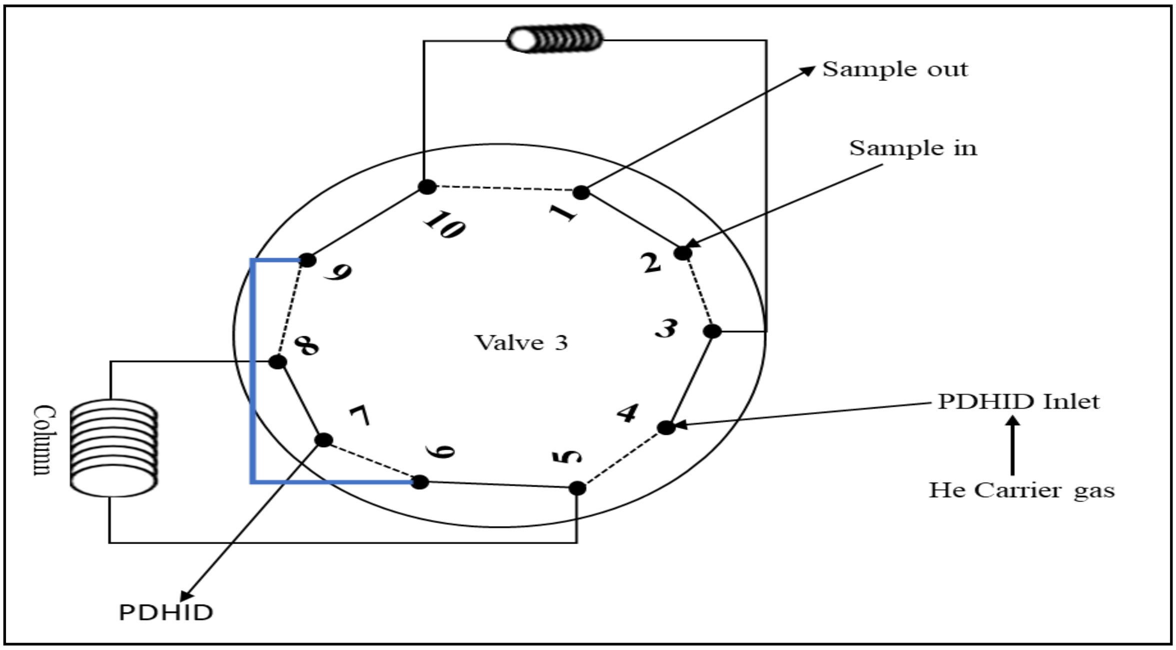


Figure 3.19: Valve configuration for Agilent gas chromatography with the PDHID channel in the fill position used to analyse the hydrogen sulphide reference gas mixtures.

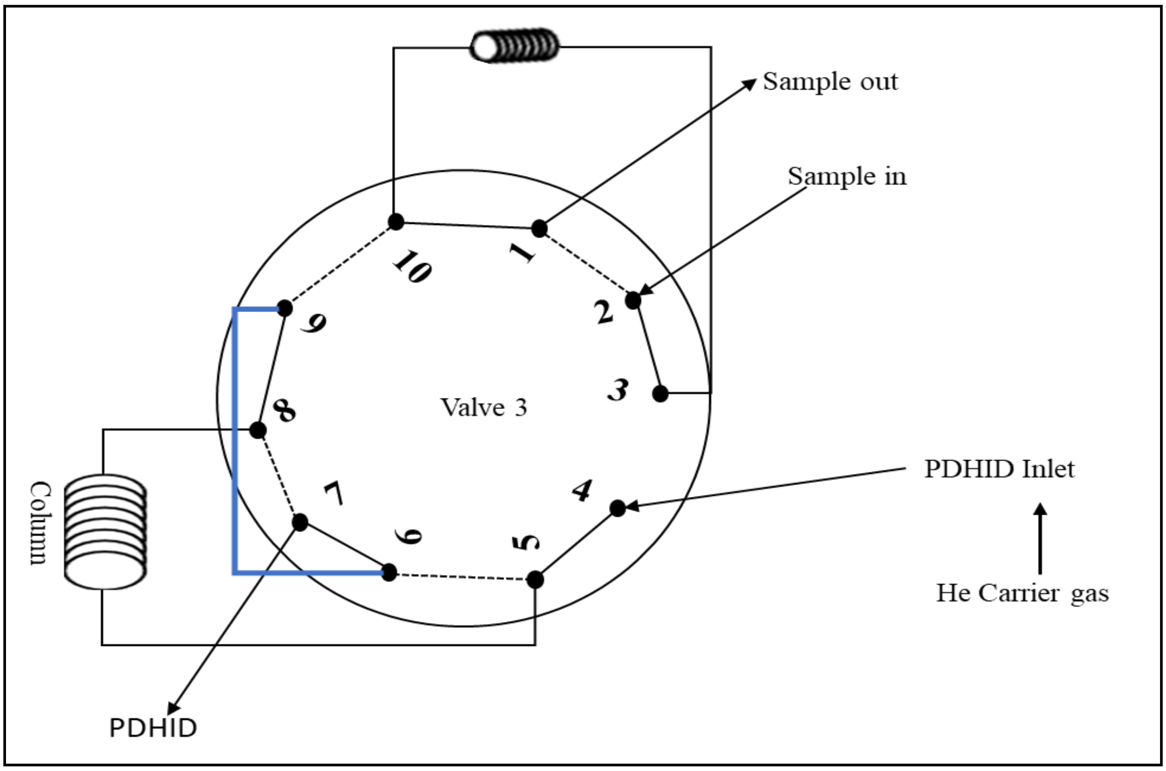


Figure 3.20: Valve configuration for Agilent gas chromatography with the PDHID channel in the inject position used to analyse the hydrogen sulphide reference gas mixtures.

3.10.4.2 Validation of hydrogen sulphide using NDUV Spectroscopy

The Gravimetrically prepared primary standard gas mixtures of H_2S were verified using the ABB Limas 11 UV H_2S analyser as shown in Figure 3.17. The system was purged using high purity nitrogen after every sample analysis using LabView software to control the sampling gas system. Sample introduction was done with Teflon tubing. The LabView software allowed for any number of sampling combinations, number of runs per sample, and number of cycles. Optimised conditions for the Limas 11 UV H_2S analyser are shown on Table 3.7.

Table 3.7: Analytical conditions for the analysis of hydrogen sulphide in nitrogen using the ABB Limas 11 UV H_2S analyser

Parameters	Method conditions
Purging time	180s
Number of measurements taken	30 samples
Number of cycle repeats	4
Sample flow	200 ml/min

The analysis of hydrogen sulphide reference gas mixtures was done using multi-point calibration curve which ranged from a mole fraction of 8 to 12 µmol/mol. Calibration standards and samples were connected randomly on the ABB Limas 11 UV H_2S analyser. The generated data was analysed using a generalized least square method.

3.10.4.3 Verification of hydrogen sulphide using UV Fluorescence Spectroscopy

Hydrogen sulphide reference gas mixtures were analysed on the Teledyne T101 UV H_2S fluorescence analyser. To introduce the sample to the UV fluorescence H_2S analyser, a regulator with a Swagelok quick fit connector was connected to the cylinder valve and purged several times under the extraction in the laboratory to flush any contaminants or moisture that could have been present. The cylinder was then connected to a 1/16-inch sulfinert treated tubing and connected to the sample stream of molbloc B system and mass flow controllers to control sample flow and directly to the H_2S UV fluorescence as illustrated in Figure 3.21. Data was recorded manually. Optimised conditions for the UV fluorescence H_2S analyser are shown on Table 3.5

Figure 3.21: UV fluorescence analysers with the Molbloc system used to introduce the sample to the analysers.

3.10.5 Spectroscopy comparison of Non-Dispersive Ultraviolet (NDUV) spectroscopy and Ultraviolet Fluorescence spectroscopy: Verification of sulphur dioxide reference gas mixtures

The sulphur dioxide reference gas mixtures were analysed using two different analytical techniques such as Non-Dispersive Ultraviolet (NDUV) spectroscopy and Ultraviolet Fluorescence spectroscopy.

3.10.5.1 Verification of sulphur dioxide using NDUV Spectroscopy

The Gravimetrically prepared primary standard gas mixtures of sulphur dioxide were verified using the ABB Limas 11 UV SO_2 analyser as shown in Figure 3.16. The system was purged using high purity nitrogen after every sample analysis using LabView software to control the sampling gas system. Sample introduction was done with Teflon tubing. The LabView software allowed for any number of sampling combinations, number of runs per sample, and number of cycles. Optimised conditions for the Limas 11 UV SO_2 analyser are shown on Table 3.8.

Table 3.8: Analytical conditions for the analysis of sulphur dioxide in nitrogen reference gas mixtures using ABB Limas 11 NDUV analyser

Parameters	Method conditions
Purging time	300s
Number of measurements taken	30 samples
Number of cycle repeats	4
Sample flow	300 ml/min

The analysis of sulphur dioxide in nitrogen reference gas mixtures was done using multi-point calibration curve which ranged from a mole fraction of 10 to 100 µmol/mol. Calibration standards and samples were connected randomly on the ABB Limas 11 UV SO_2 analyser. The generated data was analysed using a generalized least square method.

3.10.5.2 Verification of sulphur dioxide using UV Fluorescence Spectroscopy

Sulphur dioxide reference gas mixtures were verified on the Teledyne T100 UV fluorescence analyser. To introduce the sample to the UV fluorescence analyser, a regulator with a Swagelok quick fit connector was connected to the cylinder valve and purged several times under the extraction in the laboratory to flush any contaminants or moisture that could have been present. The cylinder was then connected to a 1/16-inch sulfinert treated tubing and connected to the sample stream of Molbloc B system and mass flow controllers to control sample flow and directly to the SO_2 UV fluorescence as illustrated in Figure 3.21. The LabView software was used to control the number of sampling combinations, number of runs per sample, and number of cycles. Data was collected automatically using the LabView software. Optimised conditions for the UV fluorescence analyser are shown on Table 3.9

Table 3.9: Analytical conditions for the analysis of sulphur dioxide in nitrogen reference gas mixtures using T100 UV Fluorescence

Parameters	Method conditions
Purging time	6 minutes
Sample measurements taken	30 readings
Number of repeats	5
Sample flow	400 ml/min
Sample pressure	342KPa

3.10.6 Gas chromatography coupled with flame ionisation detector: analysis of isopropanol and ethanol reference gas mixtures

Isopropanol and ethanol reference gas mixtures were verified using gas chromatography coupled with flame ionisation detector (GC-FID). Figure 3.22 and Figure 3.23 show the configuration for the GC-FID used to verify the isopropanol and ethanol reference gas mixtures with both sample and reference in the inject position. The FID was connected to valve 2 from the GC. The GC is configured with two sampling valves which can be used for online drift compensation method for multiple injections and thus correcting or minimising the instruments drift. Alternate filling and injection of reference and sample was achieved within 0.5 minutes interval. The sample was introduced on port 2 of valve 1 and the reference was introduced on port 6 of valve 1, then both sample and reference exit on port 1 alternatively and went through the mass flow controller where they entered port 2 of valve 2. The sample and reference will then enter the column through a stainless steel treated 1.0 ml sample loop which was connected on port 3 and 6. This sequence is repeated six (6) times until 12 peaks on the chromatogram are achieved with a run time of 7.5 min. The six peaks each will be for both reference and sample alternatively. The measurements of ethanol and isopropanol were done using SUPELCOWAX^{TM}10, fused silica capillary column, 60 m x 0.25 mm x 0.25 µm for separation. Sample loops used for isopropanol was 500 µl for verification of 200 µmol/mol and for ethanol was 2.0 ml for verification of 5 µmol/mol of ethanol. The column temperature of 145 ºC with helium carrier gas flow of 40 ml/min fuelled with synthetic air at 400 mL/min, hydrogen at 40 mL/min and nitrogen used as the make-up gas at 10 ml/min.

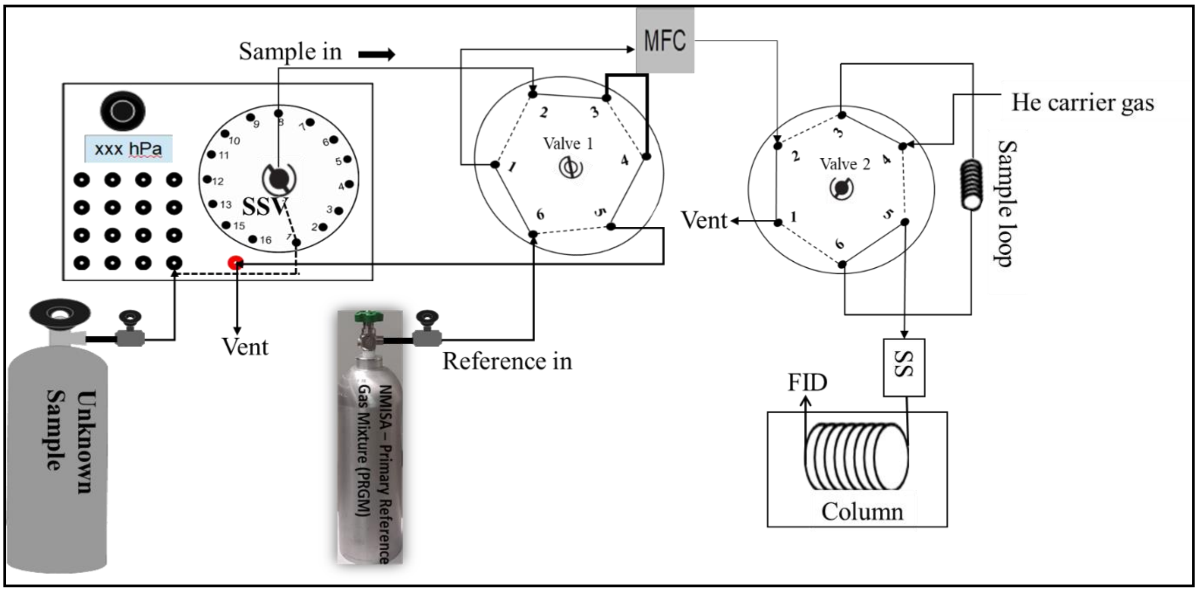


Figure 3.22: Experimental configuration schematic diagram for analysis ethanol and isopropanol when the injection position is analysing a reference gas mixture using Varian CP 3800 GC-FID

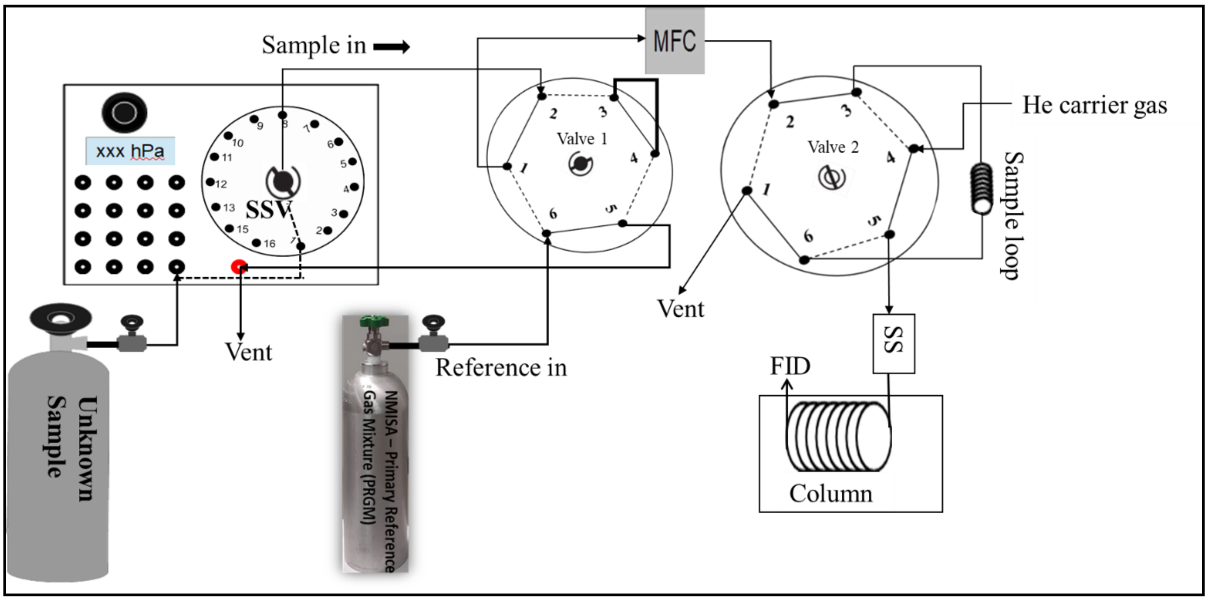


Figure 3.23: Experimental configuration schematic diagram for analysis ethanol and isopropanol when the injection position is analysing a sample gas mixture using Varian CP 3800 GC-FID

3.10.7 ANALYSIS MULTI-COMPONENT OF OVOCS REFERENCE GAS MIXTURES

The verification of the multi-component oxygenated volatile organic compounds (OVOCs) reference gas mixtures was done using the Varian CP 3800 GC-FID as shown in Figure 3.24 and Figure 3.25. The measurements of multi-components of OVOCs were optimised as illustrated in table 3.8. Nitrogen was used as the make-up gas at 10ml/min fuelled with hydrogen at 40 ml/min and synthetic air at 400ml/min. The sample line and the regulator of each cylinders were purged several times before the analysis. Samples were introduced into the column through a 6-port stainless steel valve which was equipped with a 2 ml sample loop connected on port 3 and 6 of the 6-port valve for reference gas mixtures of OVOCs. The 2 ml sample loop was used as more sample is needed to be injected for verification of low mole fraction of 5 µmol/mol multi-component of OVOCs. The sample flow for the verification was set at 100 mL/min. The split ratio used for verification of the OVOCs was a 50:1 split ratio. **Table 3.10** shows the conditions of the GC-FID used to analyse the OVOCs.

Table 3.10: Analytical conditions for the analysis of OVOCs in nitrogen reference gas mixtures using GC – FID

Parameters	Method conditions
Column	Restek, Rtx-Wax, capillary column, 60 m x 0.32 mm ID x 1µm thickness
Oven temperature	Temperature programme, Initial 75 ºC, hold for 2.0 min and ramped at 20 ºC/min to 100 ºC and hold for 1 min
Detector temperature	270 º C
Sample loop	2 ml
Carrier gas	Helium @ 20 mil/min
Run time	4.25 minutes
Sample flow (mass flow controller)	100 ml/min
Number of injections	10

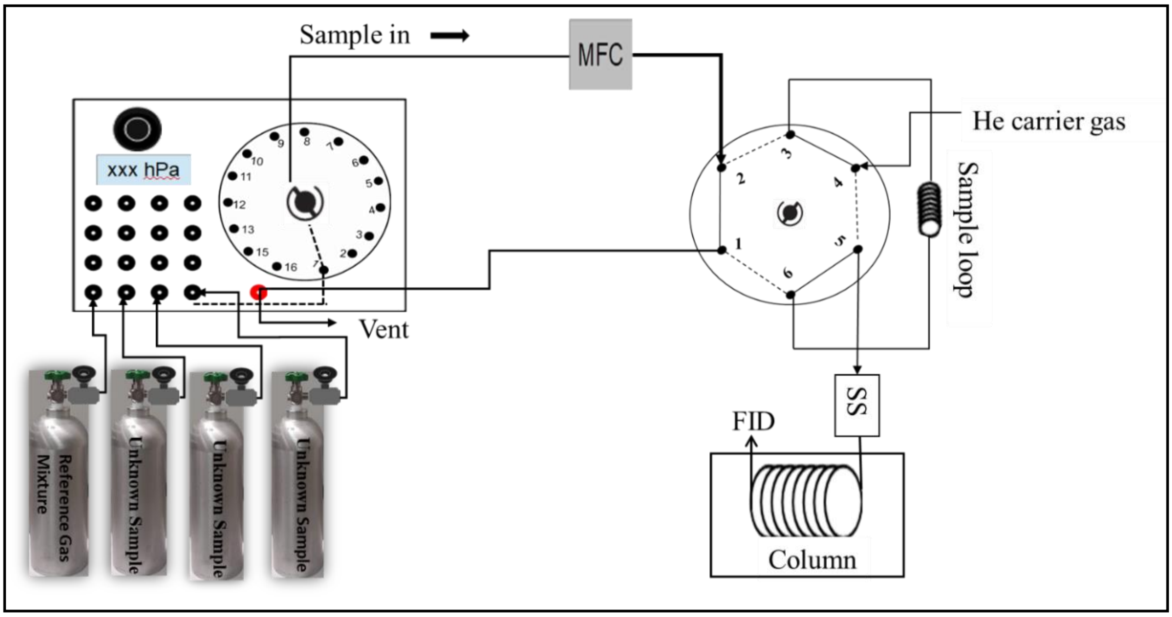


Figure 3.24: Experimental configuration schematic diagram for analysis of the acetone, methanol, ethanol, and n-butanol when the injection position is analysing a reference gas mixture using Varian CP 3800 GC-FID

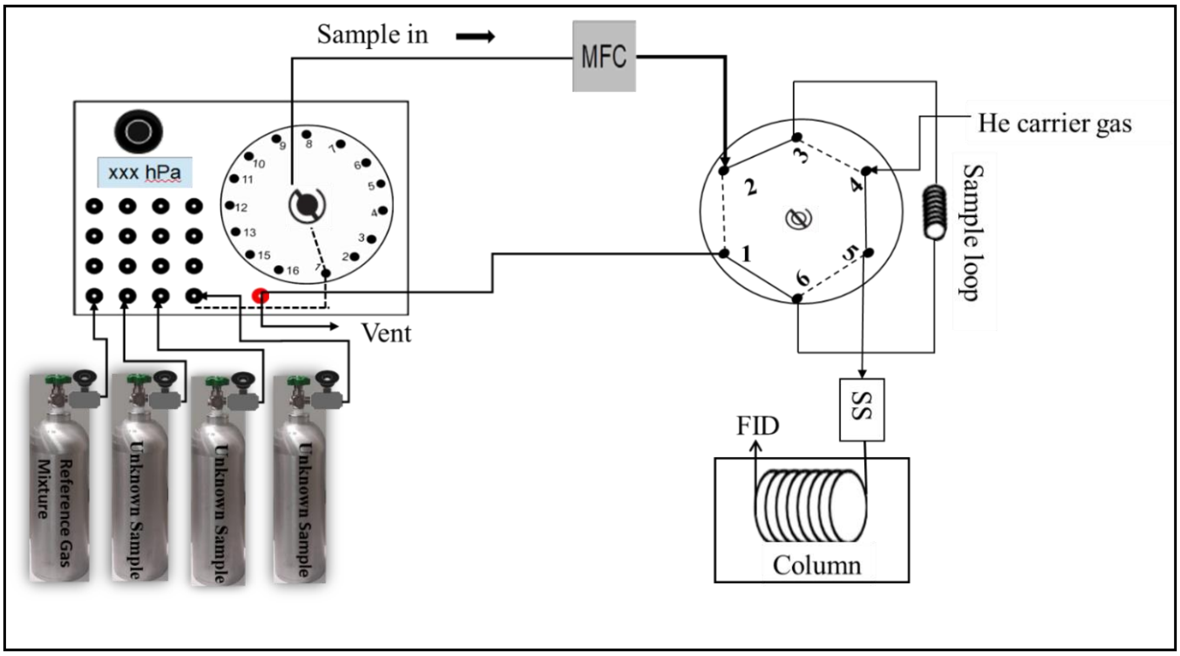


Figure 3.25: Experimental configuration schematic diagram for analysis of the acetone, methanol, ethanol, and n-butanol when the injection position is analysing sample gas mixture using Varian CP 3800 GC-FID

3.11 STABILITY STUDY OF THE PREPARED REFRENCE GAS MIXTURES

All reference material producers are required to state the period of stability of the reference material they are producing. The knowledge of previously determined measurements for specific gas mixtures and concentrations assists in establishing long term and short-term stability periods (ISO 17034:2016); (Trapmann *et al.*, 2017). Therefore, stability of reference gas mixture in the cylinder becomes a huge challenge in developing accurate reference gas mixtures for selected sulphur compounds and oxygenated volatile organic compounds (OVOCs). Mixtures needs need to be certified with the validity period before the mixtures show signs of degradation. To investigate the short-term stability of the standard gas mixtures, both reference gas mixtures of selected sulphur compounds and OVOCs were analysed immediately after preparation. The OVOCs and selected sulphur compounds were verified for a minimum of three measurements to test for short-term stability.

Stability assessment was done by monitoring the primary standard gas mixtures (through analysis) at different intervals after preparation throughout this study. This investigated other factors that might lead to instability of the gas mixtures such as adsorption/desorption on the inner surface of the cylinders. To assess the long-term stability, for H_2S a newly prepared gas mixtures of mole fraction of 8 to 12 µmol/mol H_2S were used to analyse the previously prepared 10 µmol/mol H_2S reference gas mixture. The analysis was done on the ABB Limas 11 UV H_2S analyser. For SO_2 and OVOCs, the primary standard gas mixtures were re-analysed periodically on the specific UV spectroscopy and gas chromatography techniques.

3.12 ADSORPTION AND DESORPTION STUDY FOR REFERENCE GAS MIXTURES

Adsorption or desorption plays a very important role in the stability of the reference gas mixture. Adsorption tends to increase with lower pressures and hence determination of minimal end pressure of the cylinder to be used for calibration purposes is critical. The effect of adsorption is minimal on the surface of aluminium cylinders as compared to the steel surface. It is therefore recommended to use aluminium cylinders and thus to minimise temperature fluctuations in order to limit desorption and thermal diffusion effects (Leuenberger *et al.*, 2014). Hydrogen sulphide, sulphur dioxide and some OVOCs such as ethanol tend to adsorb on the inner surface of aluminium cylinders and transfer lines. Thus, the loss increases with decreasing amount of fraction. Passivated and pre-treated aluminium cylinders will largely prevent reactions between surfaces and components (Brown *et al.*, 2014). The adsorption/desorption test for this study was only done for hydrogen sulphide. The adsorption/desorption effect was not tested for sulphur dioxide, acetone, methanol, ethanol, isopropanol, and n-butanol. Thus the test was done by using the Equal division method (Lee *et al.*, 2017) as shown in Figure 3.26. This was done in order to assess the effect of adsorption/desorption of hydrogen sulphide on the inner surface of aluminium cylinder.

In this method, a gas mixture cylinder with a known mole fraction of 10.01 µmol/mol and pressure of 9.0 MPa (mother cylinder) was connected to two evacuated empty cylinders (daughter cylinders) as shown in Figure 3.26. Both mother and daughter cylinders are connected to the vacuum pump through a transfer line to evacuate all the transfer lines connections. The gas mixture in the mother cylinder was transferred to the daughter cylinders until all cylinders reach equal pressure. The transferring process was done gradually to prevent the Joules Thompson effect (Marić, 2005)**.** The mother and daughter cylinders were analysed with ABB Limas 11 UV analyser to compare the concentration of the daughter cylinders to that of the mother cylinder.

Figure 3.26: Cylinder setup for the Equal division method for adsorption/desorption test

3.13 INTERNAL CONSISTENCY OF REFERENCE GAS MIXTURES

Same mole fraction reference gas mixtures of each components were gravimetrically prepared (except for hydrogen sulphide which was a range of mole fractions) and verified using a one or single-point calibration comparison method whereby one reference gas mixture with same mole fraction is chosen as the reference and used to analyse the other samples. This sequence is followed: reference$_1$-sample$_1$-reference$_1$ sample$_2$-reference$_1$, until all the samples are verified (ISO 12963:2017). This was done to ensure the repeatability and correction of the drift during the verification. The model equation used to calculate the mole fraction of the sample is showed in equation 3.4.

$$\boldsymbol{C_{sample}} = \frac{\boldsymbol{A_{Sample}}}{\boldsymbol{A_{Reference}}} \times \boldsymbol{C_{reference}} \qquad 3.4$$

where the C$_{\text{sample}}$, A$_{\text{sample}}$, A$_{\text{reference}}$, and C$_{\text{reference}}$ represent mole fraction of the sample, area of the sample, area of the reference and the mole fraction of the reference, respectively.

The sensitivity ratio factors were used to evaluate the internal consistency of prepared gas mixtures with similar mole fraction shown in equation 3.5. Reference gas mixtures with similar mole fraction will give similar calculated sensitivities, as the instrument response will ideally be similar if mixtures are consistent with each other. This is calculated as a function of instrument response and the mole fraction of the gas mixture as illustrated in equation 3.5 and 3.6.

$$\boldsymbol{Sensitivity\ reference} = \frac{\boldsymbol{Area_{Ref}}}{\boldsymbol{C_{Ref}}} \qquad 3.5$$

where $\boldsymbol{Sensitivity_{reference}}$ is the sensitivity of the reference, $\boldsymbol{Area_{Ref}}$ and $\boldsymbol{C_{Ref}}$ represents the average peak area from the instrument response and the mole fraction of the reference cylinder.

$$\boldsymbol{Sensitivity\ sample} = \frac{\boldsymbol{Area_{Sample}}}{\boldsymbol{C_{Sample}}} \qquad 3.6$$

where $\boldsymbol{Sensitivity_{sample}}$ is the sensitivity of the sample, $\boldsymbol{Area_{Sample}}$ and $\boldsymbol{C_{Sample}}$ represents the average peak area from the instrument response and the mole fraction of the sample cylinder.

$$\boldsymbol{Sensitivity\ ratio} = \frac{\boldsymbol{Sensitivity_{Sample}}}{\boldsymbol{Sensitivity_{Reference}}} \qquad 3.7$$

where $\boldsymbol{Sensitivity_{ratio}}$ is the ratio of the sensitivity calculated for the sample and the reference, $\boldsymbol{Sensitivity_{Sample}}$ is the sensitivity of the sample and $\boldsymbol{Sensitivity_{Reference}}$ is the sensitivity of the reference.

3.14 DATA ANALYSIS TREATMENT

The data analysis considered during the verification of gravimetrically prepared reference gas mixtures included the following:

(a) The average peak areas of both reference and sample from the instrument's response.
(b) The standard deviation of measurements during the analysis.
(c) The repeatability of the measurements during analysis expressed as percentage relative standard deviation (% RSD).
(d) The estimated standard deviation of the mean (ESDM).
(e) The drift of the instrument during analysis.
(f) The uncertainties from the verification of reference gas mixtures.

For the highest quality reference gas mixtures to be produced, all the uncertainty contributors during gravimetric preparation process needed to be considered. This includes uncertainty from weighing process and uncertainty from the purity of high pure source materials. In this study, all major uncertainty contributors for the gravimetric preparation of selected sulphur compounds and OVOCs reference gas mixtures were addressed.

3.14.1 The standard deviation of measurements

Standard deviation is the dispersion of the results in measurements and given by equation 3.8 (Bipm, 2012). It is used to estimate the standard uncertainty of the analytical measurements (ISO 12963:2017).

$$\boldsymbol{s} = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \bar{x})^2}{(n-1)}} \qquad 3.8$$

Where, $\boldsymbol{s}$ is the standard deviation, $\boldsymbol{x_i}$ is the measurement *i*th results, $\overline{\boldsymbol{x}}$ is the average of all the measurements and $\boldsymbol{n}$ is the total number of measurement results

3.14.2 Measurement precision

Precision is the closeness of the agreement between the results of successive measurements of the measurand carried out under the same or similar specified conditions. It is normally expressed by means of standard deviation, variance, or coefficient of variation under the same or similar conditions. The same conditions can be repeatability conditions of measurements or reproducibility conditions of measurements (Bipm, 2012). The coefficient of variation (CV) is an estimate of standard deviation from the total number of measurement results divided by the average of all the measurements and it is expressed as percentage (%CV). The % CV is often also expressed as the percentage relative standard deviation (%RSD). A lower %RSD value indicates a higher precision of measurements during the analysis. Equation 3.9 shows how the %RSD is calculated during measurements.

$$\% \boldsymbol{RSD} = \frac{\boldsymbol{s}}{\bar{\mathbf{x}}} \times \mathbf{100} \qquad 3.9$$

Where $\% \boldsymbol{RSD}$ is the percentage relative standard deviation, $\boldsymbol{s}$ is the standard deviation and $\bar{\mathbf{x}}$ is the average of the total number ($\boldsymbol{n}$) of measurement results.

3.14.3 The estimated standard deviation of the mean (ESDM)

The ESDM is used in measurement as an expression of the standard uncertainty in the analytical measurement and calculated by equation 3.10 (JCGM, 2008).

$$\boldsymbol{ESDM} = \frac{\boldsymbol{s}}{\sqrt{\boldsymbol{n}}} \qquad 3.10$$

Where ESDM is the estimated standard deviation of the mean, $\boldsymbol{s}$ is the standard deviation and $\boldsymbol{n}$ is the total number of measurement results.

3.14.4 The instrument drift

Instrument drift is a continuous difference over a period of time in instrument responses of the measurand due to changes affecting the measuring instrument (Bipm, 2012). Therefore any changes occurring during the analysis process need to be noted and precautionary measures taken to reduce or monitor the changes. In this study, the reference mixture was verified before and after the sample mixture to monitor the changes during the analysis, thus considering the drift of the instrument during measurement process. The instrument drift was calculated using equation 3.11 as a percentage difference between the instrument response of the reference mixture before and after sample mixture monitored by their peak areas.

$$\boldsymbol{Drift}_{\%} = \frac{\boldsymbol{Peak\ area}_{\boldsymbol{Ref\ (B)}} - \boldsymbol{Peak\ area}_{\boldsymbol{Ref\ (A)}}}{\boldsymbol{Peak\ area}_{\boldsymbol{Ref\ (A)}}} \times \mathbf{100} \qquad 3.11$$

Where $\mathbf{Drift}$; is the measure of the changes during analysis, $\boldsymbol{Peak\ area}_{\boldsymbol{Ref\ (B)}}$ is the peak area of the reference mixture analysed after the sample mixture and $\boldsymbol{Peak\ area}_{\boldsymbol{Ref\ (A)}}$ is the peak area of the reference mixture analysed before the sample mixture.

3.15 METHOD DEVELOPMENT AND VALIDATION

In order to successfully develop the selected sulphur compounds and oxygenated volatile organic compounds, optimisation of the method development is critical, and its method validation is one of the key requirements in ensuring quality of results obtained. It provides confidence in the measurement system thus proving that the method is acceptable for its intended purpose or use. Pre-set acceptable values for measurement criteria should be demonstrated as being met.

3.15.1 Precision

Precision is the closeness of the agreement between the results of successive measurements of the measurand carried out under the same or similar specified conditions. It is normally expressed by means of standard deviation, variance, or coefficient of variation (CV) under the same or similar conditions. The % CV is often also expressed as the percentage relative standard deviation (%RSD). A lower % RSD value indicates a higher precision of measurements during the analysis. Equation 7 shows how the % RSD for precision of run-to-run is calculated during the verification of reference gas mixtures using GC, NDUV and UV fluorescence, thus the repeatability of measurements. Repeatability is the closeness of the agreement between the results of successive measurements of the same measurand carried out under the same conditions of measurement (Bipm, 2012). Repeatability of a measuring instrument is an expression of the most optimistic expected precision of the method. It gives ideas of the sort of variability to be expected when a method performed by a single analyst on one piece of equipment over a short timescale, for example when a sample is analysed in duplicate.

3.15.2 Measurement accuracy

Accuracy is important during the development of reference gas mixtures. It is defined as the closeness of agreement between a measurement result and its true value.

3.15.3 Instrument bias

The bias is defined as the difference between the expectation of the results and the reference or true value. The deviation between the gravimetric value and the analytical value can be measured through using statistical methods as described in ISO 17043: 2010. Thus measuring the difference between the gravimetric value and the analytical value as described in equation 3.12.

$$\boldsymbol{D} = \boldsymbol{x_{Grav}} - \boldsymbol{x_{Analy}} \qquad 3.12$$

Where $\mathbf{D}$ is the difference between the gravimetric and analytical value, $\boldsymbol{x_{Grav}}$ is the gravimetric value (true value) and $\boldsymbol{x_{Analy}}$ is the analytical value.

The difference between the gravimetric and analytical value can be expressed as a percentage difference ($D_{\%}$) or relative deviation from the true value. Equation 3.13 is used to determine the percentage difference between the gravimetric and analytical value.

$$\boldsymbol{D}_{\%} = \frac{\boldsymbol{x_{Grav}} - \boldsymbol{x_{Analy}}}{\boldsymbol{x_{Analy}}} \times \mathbf{100} \qquad 3.13$$

Where $\boldsymbol{D}_{\%}$ is the percentage difference between the gravimetric and analytical value, $\boldsymbol{x_{Grav}}$ is the gravimetric value (true value) and $\boldsymbol{x_{Analy}}$ is the analytical value.

3.15.4 Measurement uncertainty

To gravimetrically prepare reference gas mixtures of highest metrological quality, all uncertainty contributors are considered. This includes all the uncertainties in weighing, uncertainties in the purity of the high purity starting material, any uncertainties from the diluent gases as they can contribute majorly to the gravimetric preparation of selected sulphur compounds and OVOCs reference gas mixtures and lastly, uncertainties from the verification of reference gas mixtures. For any measurement method used in this study, a fully detailed uncertainty budget is required to understand the measurement result from gravimetric preparation of the reference gas mixtures to the verification of the prepared reference gas mixtures. All the uncertainty contributors are calculated as combined standard uncertainties which contribute to the developed reference gas mixtures. Combined standard uncertainties of a gravimetrically prepared reference gas mixtures are calculated from the gravimetric preparation (Alink and Van Der Veen, 2000); (ISO 6142-1:2015) and the uncertainties from the verification measurements of the reference and the sample verified which is measured as repeatability of the measurement technique. (ISO 6143:2001) The combined standard uncertainty is expressed as and is calculated as a combination of all the uncertainty contributors as the sum of square of all the uncertainty contributors as shown in equation 3.14 (Bipm, 2012) .

$$\boldsymbol{u_c}\ (\mathrm{y}) = \sqrt{\sum_{\boldsymbol{i=1}}^{\boldsymbol{N}} [\boldsymbol{c_i u(x_i)}]^2} \qquad 3.14$$

Where $\boldsymbol{u_c}\ (\boldsymbol{y})$ represents the combined standard uncertainty, $\boldsymbol{c_i}$ is the sensitivity coefficient for input *i*, $\boldsymbol{u(x_i)}$ represents the uncertainty estimates for input $\boldsymbol{x_i}$

The sensitivity coefficient describes how the changes in the input affects the output value (JCGM 100: 2008). This is calculated using partial derivatives as shown by equation 3.15. Sensitivity coefficient is calculated for all the uncertainty contributors for input .Sensitivity coefficient are useful in converting the individual uncertainty value to standard uncertainty with same units that can be summed together to obtain the combined standard uncertainty.

$$\boldsymbol{c_i} = \boldsymbol{\partial f / \partial x_i} \qquad 3.15$$

Other sources of uncertainties include the gravimetric uncertainties of the reference gas mixture used, the purity of the high purity starting materials (Zuas and Budiman, 2016). A schematic representation of the uncertainty contributors identified in the preparation of the selected sulphur compounds and OVOCs is shown in Figure 3.27.

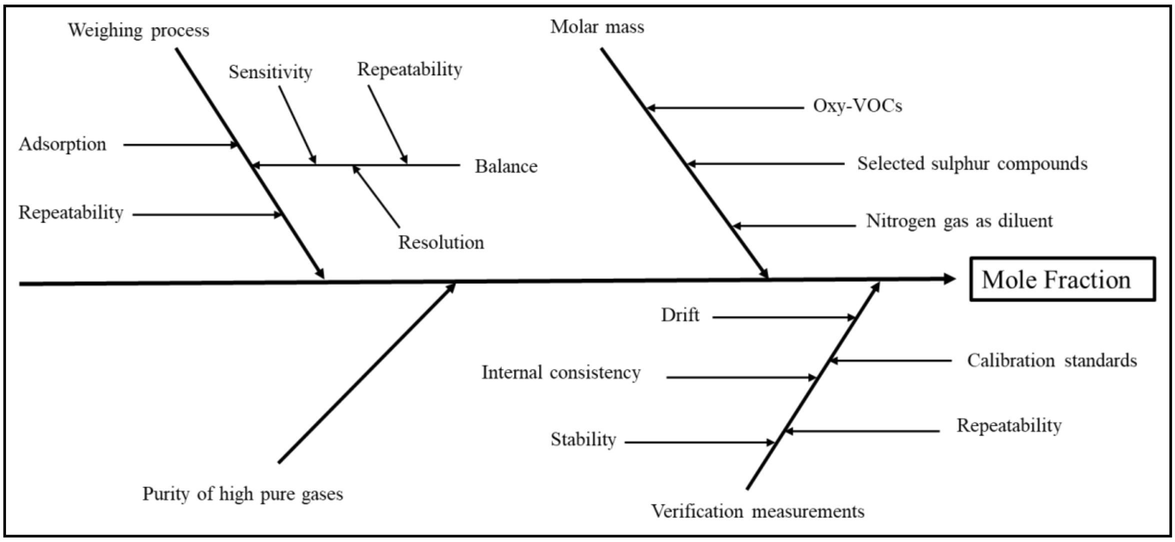


Figure 3.27: The “fishbone” diagram showing the uncertainty contributors in the preparation of selected sulphur compounds and OVOCs reference gas mixtures

The Gravcalc software (Brown, 2009) from NPL, is used to calculate the mole fraction and uncertainty of all components in the gravimetrically prepared reference gas mixtures with the method in ISO 6142. The gravimetric uncertainty contributors arises from those of pre-mix gas mixtures used and the weighing repeatability. For example to prepare 10 µmol/mol hydrogen sulphide in nitrogen, usually a pre-mix gas mixture of 100 µmol/mol will be used with 10:1 dilution factor and plus a diluent gas to prepare the hydrogen sulphide reference gas mixture. Therefore the prepared hydrogen sulphide reference gas mixture consists of uncertainties in 100 µmol/mol pre-mix gas mixture of H_2S and diluent gas nitrogen including all the impurities.

For Gas Chromatography, uncertainty calculation was based on the peak areas obtained during the analysis from the sample and reference cylinders and the gravimetric uncertainty of the reference gas mixture used to verify the prepared gas mixtures. For NDUV spectroscopy, the XLGENLINE1.1 software (Smith and Onakunle, 2007) was used for manupulating data from multi-point calibration and the calculations used polynomial degree of the order of two for regression analysis when non-linearity is assumed. The XGENLINE1.1 software (Smith and Onakunle, 2007) is a normal microsoft excel spreadsheet used to convey ordinary least-squares and generalised least-squares polynomial fitting and inverse polynomial evaluation. The software also included calculation for estimation of uncertainties selected sulphur compounds. The gravimetric uncertainty is expressed in relation to the gravimetric mole fraction and this is expressed as percentage relative expanded uncertainty (%REU) and thus calculated by equation 3.16.

$$\% \boldsymbol{REU} = \frac{\boldsymbol{Expanded\ uncertainty}}{\boldsymbol{Gravimetric\ value}} \times \mathbf{100} \qquad 3.16$$

CHAPTER 4: RESULTS AND DISCUSSION

This chapter discuss and presents the results of the research methodology and experimental work employed in this study. The results will include purity analysis of the impurities in high pure starting materials, gravimetric preparation of both binary and multi-components reference gas mixtures, stability assessment done on some of the reference gas mixtures, adsorption study of hydrogen sulphide. The verification of selected sulphur compounds and OVOCs is presented and discussed in this chapter.

4.1 PURITY ASSESSMENT OF HIGH PURITY GASES

Impurities analysis in high pure source material is the first step in producing calibration gas mixtures. The analysis is done following the International Organisation for Standardisation ISO 19229 (Gas analysis - Purity analysis and treatment of purity data). It is important that these impurities are identified and quantified to ensure that gravimetrically prepared reference gas mixtures will have a correct mole fraction. A certificate of analysis (CoA) is obtained from the manufacturers of high purity starting materials, but the CoA is only an indication of the impurities that are present in the high pure starting material, but it does not give accurate measurements of impurities' mole fractions. Some impurities are present in the high purity starting material but are not quantified by the manufacturer. These impurities can affect the overall purity of the high pure starting material (ISO 19229) and hence quantification of these impurities is important so that the purity of the high purity starting material is corrected accordingly.

4.1.1 Purity analysis of high purity gases using GC- TCD/GC-FID

Both high purity Built-in purifier (BIP^{TM}) nitrogen and sulphur dioxide were analysed for impurities using gas chromatography. Their manufacturer specifications for high purity nitrogen and sulphur dioxide were 99.9999 % and 99.99 % respectively. The BIP^{TM} nitrogen purchased from Air Products, SA was used as diluent gas during gravimetric preparation for the development of selected sulphur compounds and OVOCs reference gas mixtures. Assessment of impurities on both high purity nitrogen and sulphur dioxide were done on a two channel GC-TCD/FID. The final mole fractions of both sulphur dioxide and nitrogen as starting materials for this study are shown in Table 4.1 and Table 4.2. Equation 2.1 was used to calculate the final mole fraction of nitrogen and sulphur dioxide with associated uncertainties calculated by equation 2.2. The purity analysis was done following the International Organisation for Standardisation ISO 19229 (Gas analysis - Purity analysis and treatment of purity data), whereby gravimetrically prepared reference gas mixtures are used, yielding purity analysis results that are traceable to national standards.

For the H_2 impurities analysis in sulphur dioxide, a gas chromatography coupled with a TCD detector was used. A reference gas mixture of 500 µmol/mol H_2 in nitrogen was utilised to quantify the H_2 impurity in the high pure sulphur dioxide. The impurities in high purity sulphur dioxide and nitrogen were quantified using both binaries and multi-components in nitrogen reference gas mixtures of Ar, O_2, N_2, CO_2, CO and CH_4 in the range of 1 µmol/mol to 1 % mol/mol depending on component being analysed. GC-FID was used to quantify CH_4 and CO. For Ar and CO_2, GC-PDHID was used. To quantify O_2 and H_2, GC-TCD was used.

Table 4.1: Purity analysis results of high purity sulphur dioxide

Components	**Analysis concentration (µmol/mol)**	**Distribution types**	**Standard Uncertainty (µmol/mol)**	**Expanded Uncertainty (µmol/mol), k = 2**	**Analytical Methods**
CH_4	0.766464	Normal	0.038323	0.077	FID
CO	0.759	Normal	0.037960	0.076	FID
H_2	1096.311	Normal	54.815545	110	TCD
CO_2	14.380	Normal	0.71920	1.4	PDHID
N_2	46836.534	Normal	1170.913359	2342	TCD
Ar	3349.380	Normal	167.469025	335	PDHID
O_2	9.351	Normal	0.467573	0.94	TCD
SO_2[1]	94.869[1]	% mol/mol	0.00118	0.0024	

[1] The final purity of sulphur dioxide was calculated by using the equation 2.

Nitrogen was the largest in the purity analysis of high pure sulphur dioxide given that it was used as the diluent gas for the development of sulphur dioxide component and other selected sulphur compounds in this study. Nitrogen was the largest impurity in the high pure sulphur dioxide, followed by hydrogen impurity. Both hydrogen and nitrogen are constituents of a natural gas stream or source (Brown *et al.*, 2015). The amount of nitrogen in natural gas differs depending on the gas reservoirs. Therefore nitrogen can be found higher in concentration as it naturally occurs in some gas fields (Mokhatab and Mak, 2015). High amount of nitrogen and hydrogen impurities in high purity sulphur dioxide concludes that the source area to produce high purity sulphur dioxide contained higher concentrations of nitrogen and hydrogen. The impurity amount of Argon was also observed to be high which could be the same reason of source area for high pure sulphur dioxide. These large impurities led to the purity of sulphur dioxide being significantly reduced and making it important for quantification of impurities to be accurate. Other sulphur compounds such as hydrogen sulphide, mercaptans, dimethyl sulphide is expected as impurities in high pure sulphur dioxide when its produced. These sulphur components were analysed using the three-channel gas chromatography coupled with SCD/TCD/PDHID as per Figure 3.3. The SCD channel was used to analyse the impurities of sulphur compounds and they were not detected or identified. Other impurities that were quantified, their uncertainties were less than 1 µmol/mol. The final purity analysis value for sulphur dioxide was 94.869 % after quantification of all the impurities in high purity sulphur dioxide.

Table 4.2: Purity analysis results of high purity BIP^{TM} nitrogen

Component	Analysis concentration (µmol/mol)	Distribution types	Mole fraction (µmol/mol)	Standard Uncertainty (µmol/mol)	Expanded Uncertainty (µmol/mol), k = 2	Analytical Methods
Ar	63.64	Normal	63.64000	3.1820	6.40	PDHID
CO	0.05	Normal	0.05000	0.0025	0.005	FID
CO_2	0.050	Normal	0.05000	0.0025	0.005	PDHID
CH_4	0.01	Normal	0.01000	0.0005	0.0010	FID
C_2H_6	<0,010	Rectangular	0.00500	0.0029	0.0060	N/A
O_2	0.004	Normal	0.00400	0.0002	0.00040	TCD
H_2O	<0,02	Rectangular	0.01000	0.0058	0.012	N/A
H_2	<1	Rectangular	0.50000	0.2887	0.58	N/A
N_2		% mol/mol	99.994	0.000320	0.00064	

The analytical value of the impurity is determined by assuming rectangular distribution was calculated by (equation 2.15) with uncertainty calculated by (equation 2.16).

Similar impurities in high purity nitrogen were observed as those present in high purity sulphur dioxide with argon content being the largest impurity in high purity nitrogen. Argon was not specified in the CoA for high purity nitrogen, but it was identified and contribute significantly to the final purity of nitrogen. During purity analysis, it is important to do a fully detailed analysis of impurities even those that are expected to be in high purity gases, but not mentioned by the manufacturer. Where possible, reference gas mixtures and methods available should be used to quantify these impurities and not rely on manufacturer's specification. The amount of ethane, water and H_2 impurities were calculated assuming a rectangular distribution which assumed at the half of limit of detection value of the specific analytical method. When all the impurities in high purity nitrogen were quantified, the final purity value was 99.994 % mol/mol using (equation 2.2).

4.1.2 Purity analysis of high purity hydrogen sulphide using GC-SCD/TCD/PDHID

High purity hydrogen sulphide was analysed for impurities using gas chromatography. The manufacturer's specification was 99.99 % purity. The BIP^{TM} nitrogen purchased from Air Products, SA was used as diluent gas during gravimetric preparation for the development of hydrogen sulphide reference gas mixtures. Assessment of impurities on high pure hydrogen sulphide was done on a three-channel GC-SCD/TCD/PDHID. The final mole fraction of hydrogen sulphide as starting materials is shown in Table 4.3. Equation 2.1 was used to calculate the final mole fraction of hydrogen sulphide with associated uncertainties calculated by equation 2.2.

Table 4.3: Purity analysis results of high purity hydrogen sulphide

Components	Analysis concentration (µmol/mol)	Distribution types	Standard Uncertainty (µmol/mol)	Expanded Uncertainty (µmol/mol) , k = 2	Analytical Methods
H_2	2800.395518	Normal	70.009888	140	TCD
N_2	2.371033505	Normal	0.059	0.12	TCD
Ar + O_2	61.63785201	Normal	3.082	6.2	PDHID
H_2S	99.713560	% mol/mol	0.000070	0.00014	

For the high purity hydrogen sulphide, only H_2, N_2 and Ar + O_2, impurities were analysed. For both H_2 and N_2 were analysed on the GC-TCD channel and Ar + O_2 co-eluted on the GC-PDHID channel. H_2 was the largest impurity in high pure hydrogen sulphide. Hydrogen is the constituent of natural gas stream or source and the amount depends on the gas reservoir used (Mokhatab and Mak, 2015). High amounts of hydrogen impurity in the high purity hydrogen sulphide concludes that there was higher concentration of hydrogen in the source area used to produce hydrogen sulphide. Impurities of sulphur dioxide and ethyl mercaptans were analysed on the SCD channel but not detected or identified. When all the impurities in high purity hydrogen sulphide were quantified, the final purity value was 99.714 % mol/mol using (equation 2.2).

4.2 PURITY ANALYSIS OF HIGH PURITY CHEMICALS

Purity analysis in high purity chemicals is also a critical first in producing condensable calibration reference gas mixtures. Following the same standard of ISO 19229 for purity analysis and treatment of purity data, it is important that these impurities are identified and quantified to ensure that gravimetrically prepared reference gas mixtures will have a correct mole fraction. Certificate of analysis (CoA) is obtained from the manufacturers of high purity starting materials, but the CoA is an indication of the impurities that are present in the high pure starting material but does not give accurate measurements of impurities' mole fractions.

Moisture is the major impurity contributor to the high purity chemicals such as ethanol, acetone, methanol, propanol, and n-butanol. In this study, only high purity ethanol was analysed for moisture content. Manufacturer specifications were used for acetone, methanol, butanol ethyl mercaptans and other impurities of ethanol.

4.2.1 Moisture assessment in high purity ethanol using Karl Fischer Titration

Moisture content impurity in high purity ethanol was determined by following the ASTM E 1064-08:Standard test method for water in organic liquids by coulometric Karl Fischer titration as shown in reactions 2 and 3. Other impurities in the high purity ethanol were quantified using the manufacturer's specification. Table 4.4 shows the final mole fraction of ethanol as source chemical used in this study. Equation 2.1 was used to calculate the final mole fraction of ethanol with associated uncertainties calculated by equation 2.2. When all the impurities in high pure ethanol were quantified, the final purity value was 99.918 % mol/mol using equation 2.2.

Table 4.4: Purity analysis results of high purity ethanol

Component	Analysis concentration (µmol/mol)	Distribution types	Analysis concentration (µmol/mol	Standard Uncertainty (µmol/mol)	Expanded Uncertainty (µmol/mol), k = 2
Water	319.636	Normal	0.00031960	0.000006	0.000013
2-propanone	<10	Rectangular	0.000005	0.000002887	0.000006
isopropanol	<100	Rectangular	0.000050	0.00002887	0.000058
3-methyl-1-butanol	<500	Rectangular	0.00025	0.00014434	0.000289
n-hexanol	<100	Rectangular	0.000050	0.00002887	0.000058
ethylmethylketone	<200	Rectangular	0.000100	0.00005774	0.000115
methanol	<100	Rectangular	0.000050	0.00002887	0.000058
Ethanol		% mol/mol	99.918	0.00016088	0.000322

The mole fraction of the impurity is determined by assuming rectangular distribution calculated using (equation 2.15) with uncertainty calculated by = (equation 2.16).

4.2.2 Assessment of impurities in high purity chemicals using manufacturer's specification

Purity analysis of high purity chemicals was determined using manufacturer's specifications except for moisture content impurity in ethanol as shown in Table 4.4. For high purity methanol, high purity acetone and high purity isopropanol, water was the main impurity identified by the manufacturer's specification and it was calculated by assuming rectangular distribution. Table 4.5 to Table 4.7 show the purity table of high purity acetone, isopropanol, and water, respectively. High purity n-butanol had other impurities identified by the manufacturer's specification other than water only. The specifications of impurities identified were H_20, n-Butyraldehyde and DI-Butyl Ether. These impurities were also calculated by assuming rectangular distribution as per purity table of n-butanol shown in Table 4.8.

Table 4.5: Purity analysis results of high purity CH_3OH

Component	Analysis concentration (µmol/mol)	Distribution types	Analysis concentration (µmol/mol	Standard Uncertainty (µmol/mol)	Expanded Uncertainty (µmol/mol), k = 2
H_2O	<0.01	Rectangular	0.00000001	0.000000003	0.000000006
Methanol		% mol/mol	99.999999	0.0000000029	0.000000006

Table 4.6: Purity analysis results of high purity C_3H_6O

Component	Analysis concentration (µmol/mol)	Distribution types	Analysis concentration (µmol/mol	Standard Uncertainty (µmol/mol)	Expanded Uncertainty (µmol/mol), k = 2
H_2O	<0.5	Rectangular	0.00000025	0.000000144	0.000000289
Acetone		% mol/mol	99.99997500	0.000000144	0.000000289

Table 4.7: Purity analysis results of high purity C_3H_8O

Component	Analysis concentration (µmol/mol)	Distribution types	Analysis concentration (µmol/mol	Standard Uncertainty (µmol/mol)	Expanded Uncertainty (µmol/mol), k = 2
H_2O	<0.05	Rectangular	0.000000025	0.0000000144	0.0000000289
Isopropanol		% mol/mol	99.999997500	0.0000000144	0.0000000289

Table 4.8: Purity analysis results of high purity $CH_3(CH_2)_3OH$

Component	Analysis concentration (µmol/mol)	Distribution types	Analysis concentration (µmol/mol	Standard Uncertainty (µmol/mol)	Expanded Uncertainty (µmol/mol), k = 2
H_20	<0.015	Rectangular	0.00000001	0.000000004	0.000000009
n-Butyraldehyde	<0.02	Rectangular	0.00000001	0.000000006	0.000000012
DI-Butyl Ether	<0.10	Rectangular	0.00000005	0.000000029	0.000000058
Isobutyl alcohol	<0.015	Rectangular	0.00000001	0.000000004	0.000000009
n-Butanol		% mol/mol	99.99999250	0.000000030	0.000000060

4.3 HYDROGEN SULPHIDE BINARY REFERENCE GAS MIXTURES RESULTS

In order for NMISA to demonstrates its international measurement equivalence, it has to participate in International key comparisons as organised by the Consultative Committee for amount of substance (CCQM). For hydrogen sulphide in nitrogen reference gas mixtures, NMISA participated in the CCQM-K41.2017 which forms part of this study. The hydrogen sulphide primary standard gas mixtures prepared in the range of 8 to 12 µmol/mol were used for the analysis of the comparison sample of CCQM-K41.2017 with nominal value of 10 µmol/mol. These PSGMs were also used to analyse newly prepared 10.3 µmol/mol hydrogen sulphide in nitrogen reference gas mixture for stability.

4.3.1 Gravimetric preparation of hydrogen sulphide reference gas mixtures

For the development of hydrogen sulphide in this study, a total of five 10 µmol/mol hydrogen sulphide reference gas mixtures were prepared for CCQM-K41.2017 as shown in Table 4.9. On verification of the comparison sample, the mole fraction was estimated at 10.3 µmol/mol. To confirm the predicted mole fraction of the comparison sample, six reference gas mixtures in the range of 8 to 12 µmol/mol hydrogen sulphide in nitrogen reference gas mixtures were prepared to bracket the comparison sample inclusive of the sixth gas mixture used to monitor the short-term stability of hydrogen sulphide reference gas mixture in this range. The percentage relative expanded uncertainty of these prepared reference gas mixtures was found to be < 2.1 %. The newly prepared hydrogen sulphide reference gas mixtures are indicated in Table 4.10, with % REU < 0.041 %.

Table 4.9: Gravimetric mole fraction and expanded uncertainties results of the prepared hydrogen sulphide primary standard gas mixtures

Cylinder Number	Gravimetric Mole Fraction (µmol/mol)[1]	Gravimetric Expanded uncertainty (µmol/mol)[2], k=2	Relative Expanded Uncertainty (% REU)[3]
D62 6475	10.0089	0.10094816	1.0
D62 6559	9.9996	0.21046392	2.1
D62 6572	10.0098	0.21067848	2.1
D62 6633	10.0173	0.1010799	1.0
D19 4914	10.0065	0.215526176	2.1

[1]Gravimetrically prepared mole fraction of hydrogen sulphide was calculated using equation 2.7 in accordance with ISO 6142-1:2015. [2]Gravcalc software (Brown, 2009) was used to determine the expanded uncertainty of the gravimetrically prepared hydrogen sulphide in nitrogen reference gas mixtures at 95 % confidence level with coverage factor of $k = 2$. [3]Equation 3.16 was used to determine the percentage relative expanded uncertainty (%REU) expressed as relative value of gravimetric uncertainty to the gravimetric mole fraction.

Table 4.10: Gravimetric mole fraction and expanded uncertainties of the newly prepared hydrogen sulphide primary standard gas mixtures used for the CCQM-K41.2017 inter-comparison

Cylinder Number	Gravimetric Mole Fraction (µmol/mol)[1]	Gravimetric Expanded uncertainty (µmol/mol)[2], k=2	Relative Expanded Uncertainty (% REU)[3]
D67 9551	7.9777	0.0033	0.041
D67 9596	9.9860	0.0036	0.036
D67 9392	8.9689	0.0032	0.036
D67 9504	10.9815	0.0040	0.036
D67 9342	11.9977	0.0043	0.036
D67 9403	10.3113	0.0021	0.020

[1]Gravimetrically prepared mole fraction of hydrogen sulphide was calculated using equation 2.7 in accordance with ISO 6142-1:2015. [2]Gravcalc software (Brown, 2009) was used to determine the expanded uncertainty of the gravimetrically prepared hydrogen sulphide in nitrogen reference gas mixtures at 95 % confidence level with coverage factor of $k = 2$. [3]Equation 3.16 was used to determine the percentage relative expanded uncertainty (%REU) expressed as relative value of gravimetric uncertainty to the gravimetric mole fraction.

4.3.2 Verification of hydrogen sulphide reference gas mixtures using gas chromatography

Measurements of hydrogen sulphide reference gas mixtures were developed to value assign the comparison sample of CCQM-K41.2017 International comparison. The comparison sample and the stability reference gas mixtures were verified using gas chromatography coupled with PDHID using a previously prepared 10 µmol/mol H_2S gas mixture as a reference cylinder. Substitution method (Alink and Van Der Veen, 2000) (A-B-A), where ‘A’ and ‘B’ represent the reference and sample respectively was used to verify the reference gas mixture and the comparison sample. The hydrogen sulphide verification on GC was done with statistical analysis of data which included calculation of average peak areas, standard deviation, and percentage relative standard deviation (% RSD) for each mixture verified. These were determined by using data from a minimum of 15 injections for each mixture.

The repeatability of H_2S measurements is shown in Table 4.11 and Table 4.12 when prepared 10 µmol/mol H_2S in nitrogen reference gas mixtures (D19 4914 and D62 6572) were used as a reference gas cylinders, respectively. The overall verification results were found to be repeatable, with % RSD less than 0.34 % and 0.41 % when using reference D19 4914 and D62 6572, respectively. The instrument drift was observed to be higher when D19 4914 was used as reference during verification with a drift % range from 0.09 to 0.82 % absolute values. The instability of the instruments in the beginning of measurements could be the reason for the slightly higher drift. When D62 6572 was used as reference it gave the instrument drift of less than 0.37 % absolute values.

Table 4.11: Verification results of the analysis of 10 µmol/mol H_2S in nitrogen reference gas mixtures using D19 4914 as a reference

Number of Injections	D19 4914	D62 6559	D19 4914	D62 6559	D19 4914	D62 6559	D19 4914
1	12886.87	13103.60	13006.72	13202.98	12998.02	13237.63	12986.84
2	12863.67	13146.21	12962.96	13222.59	13010.96	13250.98	13034.88
3	12852.95	13179.43	12952.34	13234.39	13004.17	13252.06	13021.25
4	12854.30	13203.02	12967.10	13253.53	13015.78	13210.77	13037.92
5	12891.95	13215.59	12991.26	13222.79	13034.83	13189.24	13044.40
Average[1]	12869.95	13169.57	12976.07	13227.26	13012.75	13228.13	13025.06
standard deviation[2]	18.33	45.36	22.28	18.52	14.06	27.38	22.97
%RSD[3]	0.14	0.34	0.17	0.14	0.11	0.21	0.18
ESDM[4]	8.20	20.29	9.97	8.28	6.29	12.25	10.27
Sensitivity[5]	1286.15	1317.01	1296.76	1322.78	1300.43	1322.87	1301.66
% Difference[6]		-2.34		-1.97		-1.70	
Gravimetric value[7]	10.01	10.00	10.01	10.00	10.01	10.00	10.01
Analytical value[8]		10.24		10.20		10.17	
Drift (%)[9]			0.82		0.28		0.09

[1] Average obtained using five consecutive peak area responses for each measurement, [2] Standard deviation of the measurement results calculated using equation 3.8, [3] Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5] Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6] Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8] Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

Table 4.12: Verification results of the analysis of 10 µmol/mol H_2S in nitrogen reference gas mixtures using D62 6572 as a reference.

Injections	D62 6572	D62 6559	D62 6572	D62 6559	D62 6572	D62 6559	D62 6572	D62 6559	D62 6572
1	14204.30	14116.75	14155.95	14177.57	14113.43	14173.92	14177.74	14274.65	14259.04
2	14098.35	14146.24	14136.28	14189.09	14169.37	14164.56	14219.82	14300.92	14218.19
3	14070.35	14148.93	14096.64	14167.78	14159.53	14186.06	14195.89	14303.98	14235.55
4	14065.36	14139.44	14123.22	14197.22	14153.82	14160.75	14200.17	14278.89	14227.79
5	14083.42	14206.68	14056.46	14166.79	14140.34	14150.90	14202.13	14311.12	14205.13
Average[1]	14104.36	14151.61	14113.71	14179.69	14147.30	14167.24	14199.15	14293.91	14229.14
standard deviation[2]	57.32	33.29	38.58	13.31	21.65	13.37	15.05	16.15	20.21
%RSD[3]	0.41	0.24	0.27	0.09	0.15	0.09	0.11	0.11	0.14
ESDM[4]	25.63	14.89	17.25	5.95	9.68	5.98	6.73	7.22	9.04
Sensitivity[5]	1409.05	1415.22	1409.99	1418.02	1413.34	1416.78	1418.52	1429.45	1421.52
% Difference[6]		-0.44		-0.57		-0.24		-0.76	
Gravimetric value [7]	10.01	10.00	10.01	10.00	10.01	10.00	10.01	10.00	10.01
Analytical value [8]		10.04		10.06		10.02		10.08	
Drift (%)[9]			0.07		0.24		0.37		0.21

[1] Average obtained using five consecutive peak area responses for each measurement, [2] Standard deviation of the measurement results calculated using equation 3.8, [3] Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5] Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6] Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8] Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis

The hydrogen sulphide reference gas mixtures in the range of 8 to 12 µmol/mol were used to validate the gravimetrically prepared 10.3 µmol/mol stability gas mixture using three different techniques. One of the techniques used was gas chromatography using a previously prepared and verified 10 µmol/mol hydrogen sulphide reference gas mixture. The stability gas mixture was verified using a GC with three detector channels (SCD/TCD/PDHID), but for this study the PDHID channel was used for validation of H_2S reference gas mixtures. This was done to check consistency of the stability reference gas mixture with the existing hydrogen sulphide reference gas mixtures. Table 4.13 shows the results when D67 9596 was used as the reference to verify the newly prepared stability reference gas mixture. The analysis data for the stability reference gas mixture shows that the mixture does not differ significantly with its gravimetric and verification mole fraction with % difference between 0.03 to 1.16 % absolute value. The high 1.16 % difference could have been influenced by variation in the environmental conditions. Therefore the stability reference gas mixture was kept for monitoring stability behaviour of hydrogen sulphide in nitrogen reference gas mixtures in the similar mole fraction range.

Table 4.13: Verification results of the analysis of 10.3 µmol/mol H_2S reference gas mixtures using D67 9596 as a reference

Injection	D67 9596	D67 9403	D67 9596	D67 9403	D67 9596	D67 9403	D67 9596	D67 9403	D67 9596
1	11274.01	11870.96	11366.06	11864.57	11467.37	11859.60	11421.20	12021.43	11481.57
2	11316.88	11815.12	11367.39	11855.88	11438.53	11911.85	11414.74	12096.83	11401.87
3	11314.39	11906.09	11369.92	11938.16	11390.96	11954.88	11425.85	12054.69	11510.12
4	11346.67	11888.36	11356.26	11924.56	11441.50	11846.00	11385.05	12035.01	11452.00
5	11291.35	11828.25	11394.83	11956.74	11440.59	11903.35	11469.21	12046.81	11458.57
Average[1]	11308.66	11861.75	11370.89	11907.98	11435.79	11895.14	11423.21	12050.95	11460.83
standard deviation[2]	27.59	38.91	14.35	45.17	27.70	43.57	30.23	28.56	40.06
%RSD[3]	0.24	0.33	0.13	0.38	0.24	0.37	0.26	0.24	0.35
ESDM[4]	12.34	17.40	6.42	20.20	12.39	19.49	13.52	12.77	17.92
Sensitivity[5]	1142.65	1150.36	1148.93	1154.85	1155.49	1153.60	1154.22	1168.71	1158.02
% Difference[6]		-0.67		-0.51		0.16		-1.24	
Gravimetric Value[7]	9.90	10.31	9.90	10.31	9.90	10.31	9.90	10.31	9.90
Analytical Value[8]		10.38		10.36		10.29		10.44	
Drift (%)[9]			0.55		0.57		-0.11		0.33

[1]Average obtained using five consecutive peak area responses for each measurement, [2]Standard deviation of the measurement results calculated using equation 3.8, [3]Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5]Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6]Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7]Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8]Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

For the repeatability study, a minimum of two repeated measurements were performed for each sample verified over a week. The repeatability data of the existing hydrogen sulphide and the newly prepared hydrogen sulphide stability reference gas mixtures are shown in Figure 4.1 with % RSD less than 0.50 % for all the measurements done. Thus concludes that the measurements of hydrogen sulphide using the gas chromatography developed method are repeatable and fit for purpose.

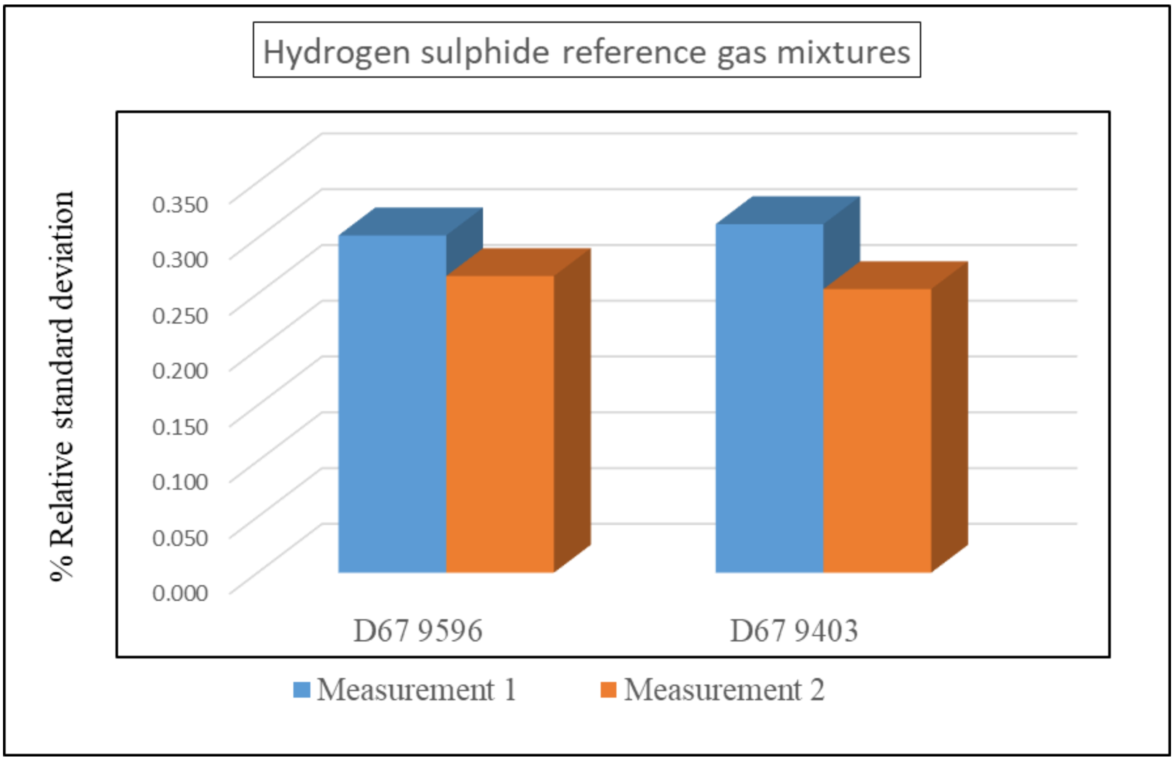


Figure 4.1: Repeatability measurements for 10 and 10.3 µmol/mol hydrogen sulphide reference gas mixtures using GC.

4.3.3 Verification of hydrogen sulphide reference gas mixtures using NDUV spectroscopy

The verification was done using the multi-point calibration method. Newly prepared H_2S reference gas mixtures of 8 to 12 µmol/mol were used to analyse the previously prepared 10 µmol/mol hydrogen sulphide mixtures and the new 10.3 µmol/mol H_2S stability reference gas mixture . Data acquisition was done with LabView in-house program for each analyser. XGENLINE1.1 software (Smith and Onakunle, 2007) was used to calculate the mole fraction of hydrogen sulphide reference gas mixtures. The results obtained from the verification of H_2S using NDUV analyser is shown in Table 4.14. Analytical data of D62 6633, D62 6572 and D62 6559 shows these reference gas mixtures differ significantly from their gravimetric and analytical values with % difference of 2.03 %, 1.99 % and 2.06, respectively. This showed significant inconsistencies between the gravimetric value and the analytical values and did not agree well with the multi-point calibration references used. Therefore the three reference gas mixtures were not used further for either preparation or verification of H_2S reference gas mixtures. Mixtures D62 6475 and D67 9403 did not differ significantly to their gravimetric and analytical values with % difference of 0.36 % and 0.49 % respectively, thus no significant inconsistency between their gravimetric and analytical values.

Table 4.14: Results obtained from NDUV analyser

Cylinder Number	**D62 6633**	**D62 6572**	**D62 6559**	**D62 6475**	**D67 9403**
Gravimetric mole fraction (µmol/mol)	10.017	10.010	10.000	10.009	10.311
Average verification mole fraction (µmol/mol)	10.225	10.213	10.210	9.973	10.362
Standard deviation (µmol/mol)	0.006	0.006	0.010	0.006	0.013
ESDM	0.003	0.003	0.006	0.003	0.005
% Difference	-2.028	-1.986	-2.063	0.361	-0.492
Combined uncertainty	0.053	0.106	0.107	0.055	0.020
Expanded uncertainty (U) (k=2)	0.107	0.212	0.214	0.110	0.039
% Relative expanded uncertainty (%REU)	1.04	2.08	2.09	1.10	0.38

For repeatability study, a minimum of three repeated measurements were performed for each sample verified over a short period of two days. The repeatability data of the existing hydrogen sulphide reference gas mixtures are shown in Figure 4.2 with % RSD less than 0.36 % for all the measurements done. Thus concludes that the measurements of hydrogen sulphide using the NDUV developed method are repeatable and fit for purpose.

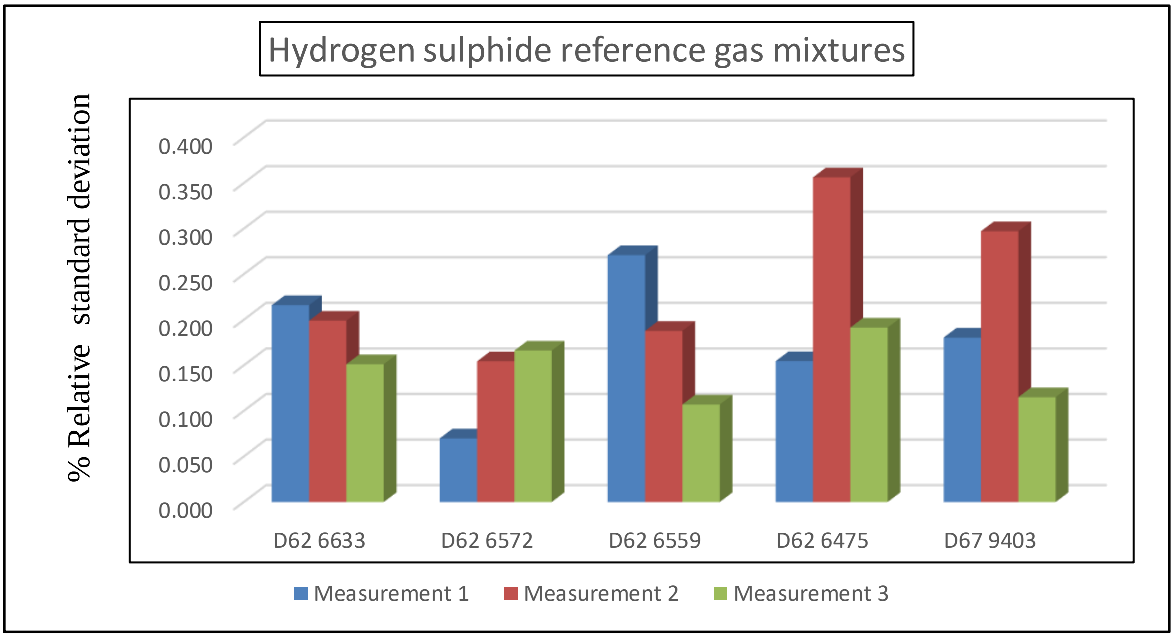


Figure 4.2: Repeatability measurements for 10 and 10.3 µmol/mol hydrogen sulphide reference gas mixtures using NDUV

4.3.4 Verification of hydrogen sulphide reference gas mixtures using UV Fluorescence spectroscopy

Substitution method (A-B-A) (Alink and Van Der Veen, 2000), where 'A' and 'B' represent the reference and sample respectively was used to verify the reference gas mixture and the stability mixture. The verification was done using the one-point or single point calibration, where the reference standard was analysed before and after the sample. The results obtained from the verification of H_2S using UV fluorescence analyser are shown in Table 4.15. The verification of the 10.3 µmol/mol H_2S stability reference gas mixture was done using a previously prepared and verified 10 µmol/mol hydrogen sulphide reference gas mixture. Table 4.15 shows the results when D67 9596 was used as the reference to verify the newly prepared stability reference gas mixture. The verification data for the stability reference gas mixture showed no significant inconsistency with its gravimetric and analytical values with % difference between 0.01 to 0.14 % absolute value. The instrument drift was observed between 0.01 to 0.23 % absolute values during the verification. This indicates the stability of the instruments during analysis which results in less deviation in measurements. Therefore the UV Fluorescence technique confirms the stability reference gas mixture being used to monitor stability behaviour of hydrogen sulphide in nitrogen reference gas mixtures in the similar mole fraction range.

Table 4.15: Verification results of 10.3 µmol/mol H_2S reference gas mixtures using UV Fluorescence analyser

Number of runs	D67 9596	D67 9403	D67 9596	D67 9403	D67 9596	D67 9403	D67 9596	D67 9403	D67 9596
1	9888.27	10298.15	9888.30	10310.34	9896.07	10310.25	9896.17	10318.87	9891.51
2	9892.21	10299.52	9885.74	10308.95	9894.61	10308.70	9897.67	10320.23	9892.28
3	9893.85	10299.95	9886.97	10308.46	9895.96	10311.83	9899.52	10319.27	9889.24
4	9890.86	10299.97	9888.50	10311.39	9894.43	10310.43	9903.06	10316.14	9889.13
5	9890.44	10304.37	9891.73	10312.40	9896.44	10309.07	9907.59	10315.82	9884.82
6	9889.35	10306.79	9895.03	10313.72	9894.27	10305.92	9911.38	10315.38	9882.16
7	9891.20	10305.39	9893.04	10311.95	9897.57	10309.21	9913.76	10315.91	9881.41
Average[1]	9890.88	10302.02	9889.90	10311.03	9895.62	10309.35	9904.16	10317.37	9887.22
std deviation[2]	1.83	3.40	3.41	1.89	1.23	1.84	6.89	2.00	4.41
% RSD[3]	0.02	0.03	0.03	0.02	0.01	0.02	0.07	0.02	0.04
ESDM[4]	0.69	1.28	1.29	0.72	0.46	0.70	2.60	0.76	1.67
Sensitivity[5]	999.39	999.10	999.29	999.97	999.87	999.81	1000.73	1000.59	999.02
% Difference[6]		0.03		-0.07		0.01		0.01	
Grav. Conc[7]	9.90	10.31	9.90	10.31	9.90	10.31	9.90	10.31	9.90
Ver. Conc[8]		10.31		10.32		10.31		10.31	
Drift (%)[9]			-0.01		0.06		0.09		-0.17

[1] Average obtained using five consecutive peak area responses for each measurement, [2] Standard deviation of the measurement results calculated using equation 3.8, [3] Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5] Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6] Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8] Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

For repeatability study, a minimum of three repeated measurements were performed for each sample verified over a short period of a day. The repeatability data of the newly prepared 10.3 µmol/mol hydrogen sulphide stability reference gas mixtures are shown in Figure 4.3 with % RSD less than 0.070 % for all the measurements done. Thus concludes that the measurements of hydrogen sulphide using the UV Fluorescence developed method are repeatable and fit for purpose.

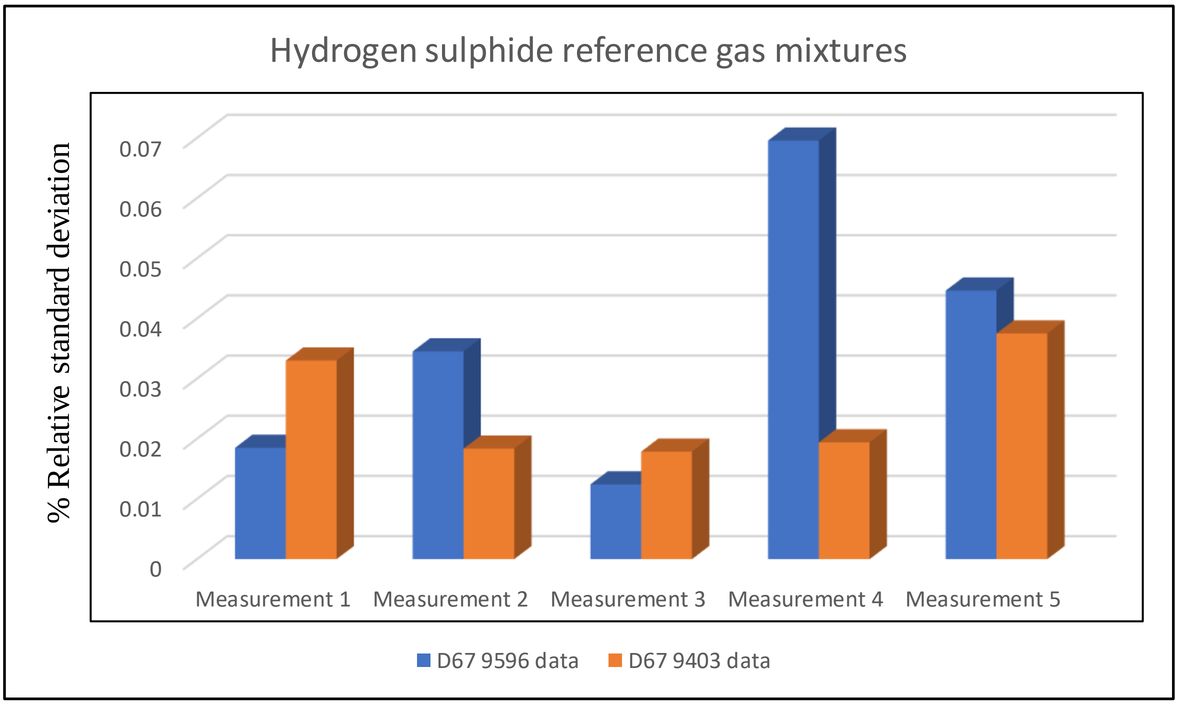


Figure 4.3: Repeatability measurements for 10 µmol/mol hydrogen sulphide reference gas mixtures using UV Fluorescence

4.3.5 International comparison CCQM-K41.2017 for hydrogen sulphide in nitrogen at nominal value of 10 µmol/mol

This comparison of CCQM-K41.2017 was aimed at improving the hydrogen measurements which were not satisfactory when NMISA participated in APMP.QM-K41 in 2009. Results Obtained in the initial participation at APMP.QM-K41 and also in CCQM-K41.2017 are both presented in Figure 4.4 and Figure 4.5.

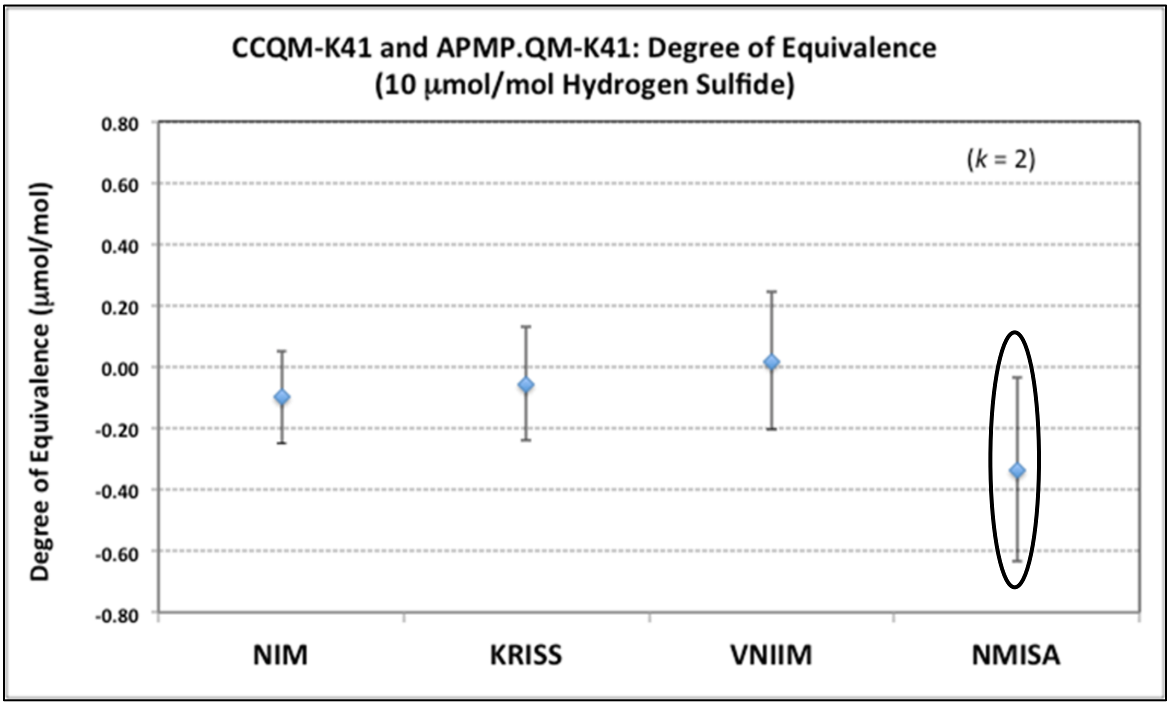


Figure 4.4: Degrees of equivalence for APMP.QM-K41 (Source: Heo and Kim, 2009) 10 µmol/mol hydrogen sulphide in nitrogen

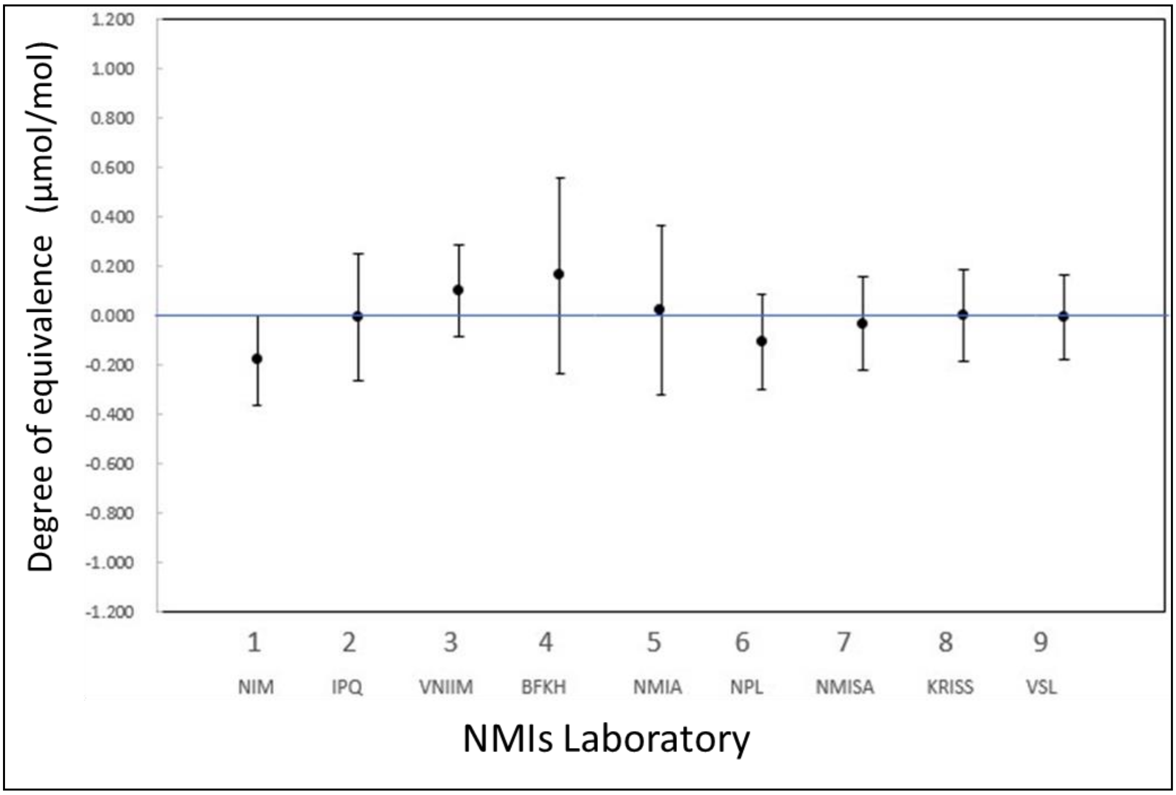


Figure 4.5: Degrees of equivalence for CCQM-K41.2017 (Source: Kim et al., 2019)

The CCQM-K41.2017 measurement results demonstrate a substantial improvement from that of former comparison APMP.QM-K41 for NMISA. The NMISA reported value overlapped with the KCRV, which indicates international equivalence for the hydrogen sulphide measurements. The improved H_2S measurements were achieved through a detailed purity analysis of all the source materials of high pure hydrogen sulphide and nitrogen. Purity analysis that is not done correctly results in giving incorrect mole fractions of gravimetrically prepared reference gas mixtures. The new techniques that were used for gravimetric preparation and verification of reference gas mixtures contributed to the improved measurements of hydrogen sulphide. The single-point calibration method was used to compensate for the instrument drift which has an effect on instrument responses during verification measurements.

4.3.6 Stability of hydrogen sulphide (H_2S) reference gas mixtures

The long-term stability of hydrogen sulphide reference gas mixtures was assessed by comparing the newly prepared hydrogen reference gas mixtures with the previously prepared and verified hydrogen sulphide primary standard gas mixture. The newly prepared 8 to 12 µmol/mol hydrogen sulphide reference gas mixtures were used to verify the previously prepared stability reference gas mixture. The minimum of three measurements were achieved using the NDUV spectroscopy as illustrated in Figure 4.6 and Figure 4.7 for both short-term, over five (5) days and long-term, over two (2) years stability of H_2S primary standard gas mixtures.

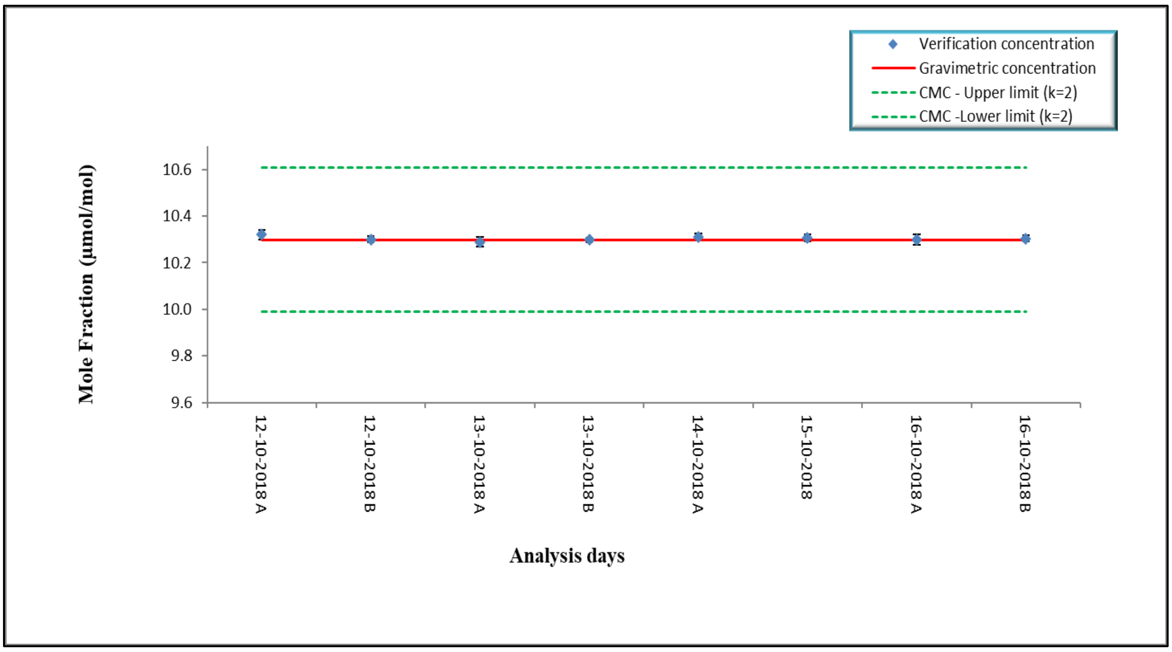


Figure 4.6: Short-term stability results of hydrogen sulphide primary standard gas mixture

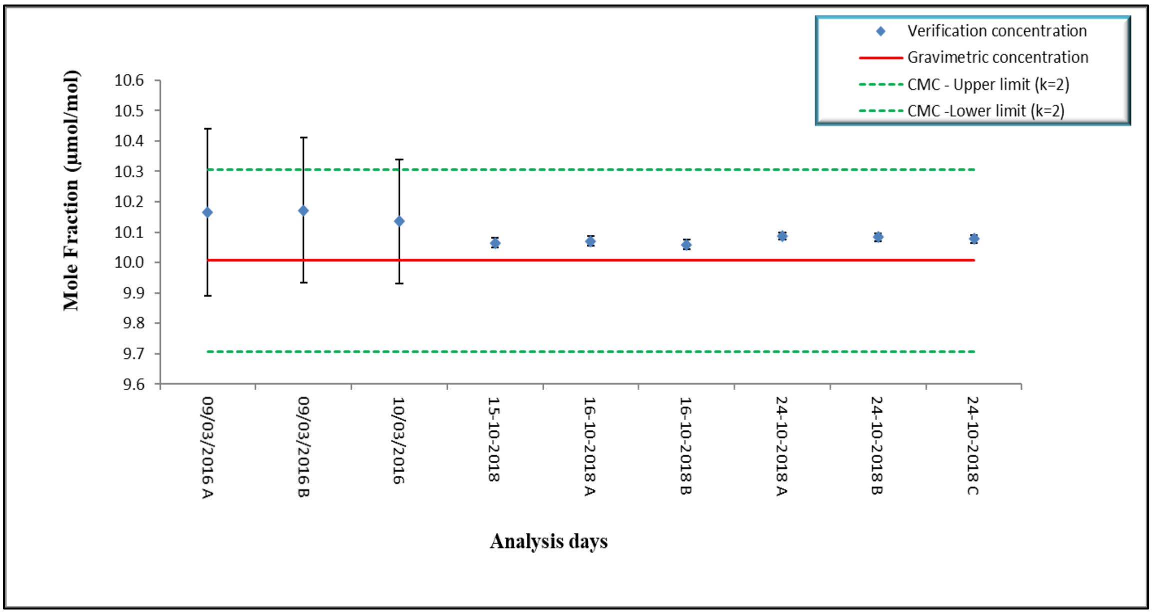


Figure 4.7: Long-term stability results of hydrogen sulphide primary standard gas mixture

The calculated percentage difference between the gravimetric and the analytical value is used to monitor if the hydrogen sulphide reference gas mixtures showed any significant nonconformity to the gravimetric value. This concept is used as a measure of the component stability valuation over a specified period. Table 4.16 shows the long-term stability results with % difference of the new hydrogen sulphide reference gas mixture prepared to be 0.50 % absolute value and the previously prepared hydrogen sulphide reference gas mixture to be 0.20 % absolute value. Thus, indicate that the previously prepared reference gas mixture of hydrogen sulphide is stable for a period of two (2) years within the measurement uncertainty of 1 %.

Table 4.16: Long term stability results of the H_2S in nitrogen reference gas mixture

Cylinder number	Mole Fraction (µmol/mol)	Analytical value	% RSD	% Difference	Preparation dates
D67 9596	9.99	9.94	0.271	-0.501	09/10/2018
D19 4914	10.01	9.99	0.146	-0.200	09/03/2016

4.3.7 Adsorption and desorption study of hydrogen sulphide reference gas mixtures

The adsorption/desorption effect is expected to be larger on the lower concentrations of hydrogen sulphide (Lee *et al.*, 2017). The mother cylinder was at 9.0 MPa before the equal division experiment. The results of the adsorption/desorption effect are shown in Table 4.17. Uncertainty measurement of adsorption/desorption was calculated to be 0.039 %. The percentage difference for adsorption results were less than 0.34 % absolute value and negligible to show no adsorption of H_2S reference gas mixtures on the inner surfaces of the aluminium cylinder (Lee *et al.*, 2017).

Table 4.17: Adsorption and desorption study of hydrogen sulphide in the aluminium cylinder

Cylinder numbers	Gravimetric Concentration (µmol/mol)	Means of analyser response	% RSD From Excel	Response factor	% Difference	Cylinder pressure After division
(Mother cylinder) D62 6475	10.01	9.992	0.076	0.998	0.168	3.01 MPa
(Daughter 1) D67 9548	10.01	9.993	0.121	0.998	0.157	3.01 MPa
(Daughter 2) D67 9397	10.01	9.975	0.117	0.997	-0.338	3.01 MPa

4.3.8 Validation of hydrogen sulphide reference gas mixtures

In order to determine the accuracy, consistency, and reliability of gravimetrically prepared reference gas mixtures with their gravimetric mole fractions, the reference gas mixtures were validated against other independently prepared reference gas mixtures. The hydrogen sulphide reference gas mixtures were validated with three techniques of GC, NDUV spectroscopy and UV Fluorescence spectroscopy. The validation criteria for all the several parameters such as precision (repeatability and reproducibility), percentage difference and relative expanded uncertainties for all the techniques in this study were set as per Table 3.4 for the method to be considered fit for purpose.

For validation, using both GC and UV fluorescence one gas mixture was used as a reference to validate other prepared gas mixtures with similar mole fraction. Verification mole fractions of each sample was calculated using equation 3.4 for single-point calibration method. For NDUV, multi-point calibration method in the range of 8 to 12 µmol/mol hydrogen sulphide reference gas mixtures were used to verify the previously and newly prepared hydrogen sulphide gas mixtures. Verification mole fractions was calculated using the XGENLINE1.1 software (Smith and Onakunle, 2007).

All the uncertainty contributions of each sample were calculated from the repeatability measurements of the reference used and the sample together with the gravimetric uncertainty of the reference mixture. The gravimetric and verification mole fractions' comparison of hydrogen sulphide are shown in Table 4.18 to Table 4.20.

Using gas chromatography, the validation results in Table 4.18 show a percentage difference of above 1% absolute values for previously prepared hydrogen sulphide reference gas mixtures with an overall uncertainty between 0.23 to 0.31 µmol/mol. There is a significant deviation between the gravimetric and verification values which is more than the overall uncertainty for the previously prepared reference gas mixtures and therefore these mixtures fail the validation criteria as per Table 3.4. Therefore these reference gas mixtures were not used further for either preparation or as references in this study. The newly prepared H_2S reference gas mixture gave a % difference of 0.11 % absolute value and the % REU for the newly prepared hydrogen sulphide gas mixtures is observed to be ten times less than the previously prepared hydrogen sulphide gas mixtures. Therefore there was no deviation between the gravimetric and the verification value and the mixture meets the validation criteria set in Table 3.4 and can be used for either preparation or as a reference.

Table 4.18: Validation data of hydrogen sulphide reference gas mixtures using gas chromatography

Cylinder Number	Gravimetric mole fraction (µmol/mol)[1]	Gravimetric uncertainty (µmol/mol)[2]	Verification mole fraction (µmol/mol)[3]	Verification uncertainty (µmol/mol)[4]	% Difference[5]	Combined Expanded uncertainty (U) (k=2)[6]	% Relative expanded uncertainty (%REU)[7]
D62 6633	10.0173	0.05505	10.1698	0.1281	-1.499	0.2562	2.5187
D62 6572	10.0098	0.1053	10.1322	0.1526	-1.2077	0.3052	3.0123
D62 6559	9.9996	0.1052	10.1835	0.1530	-1.8062	0.3059	3.0041
D62 6475	10.0089	0.0505	9.8235	0.1179	1.8869	0.2359	2.4010
D67 9403	10.3113	0.0021	10.2999	0.0103	0.1106	0.0249	0.2415

[1] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7 and represented by $\boldsymbol{x_g}$. [2] Associated standard uncertainty determined using the GRAVCALC software (Brown, 2009) and represented by $\boldsymbol{u_{xg}}$. [3] Verification mole fraction obtained from the verification results calculated using equation 3.4 and represented by $\boldsymbol{x_a}$. [4] Associated verification standard uncertainty obtained from the measurement repeatability and represented by $\boldsymbol{u_{xa}}$. [5] Percentage difference between the gravimetric and analytical value calculated using equation 3.13. [6] Combined expanded uncertainty from the gravimetric and analytical uncertainties calculated as ($\sqrt{\boldsymbol{2(u(x_g)^2 + u(x_a)^2}}$) using equation 2.19 and equation 3.14. [7] Percentage relative expanded uncertainty calculated using equation 3.16

Table 4.19: Validation data of hydrogen sulphide reference gas mixtures using UV Fluorescence

Cylinder Number	D67 9403
Gravimetric mole fraction (µmol/mol)[1]	10.3113
Gravimetric uncertainty (µmol/mol)[2]	0.0021
Verification mole fraction (µmol/mol)[3]	10.3110
Verification uncertainty (µmol/mol)[4]	0.0087
% Difference[5]	0.0035
Combined Expanded uncertainty (U), (k = 2)[6]	0.0186
% Relative expanded uncertainty (% REU)[7]	0.18

[1] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7 and represented by $\boldsymbol{x_g}$. [2] Associated standard uncertainty determined using the GRAVCALC software (Brown, 2009) and represented by $\boldsymbol{u_{xg}}$. [3] Verification mole fraction obtained from the verification results calculated using equation 3.4 and represented by $\boldsymbol{x_a}$. [4] Associated verification standard uncertainty obtained from the measurement repeatability and represented by $\boldsymbol{u_{xa}}$. [5] Percentage difference between the gravimetric and analytical value calculated using equation 3.13. [6] Combined expanded uncertainty from the gravimetric and analytical uncertainties calculated as $(\sqrt{\boldsymbol{2(u(x_g)^2+u(x_a)^2)}})$ using equation 2.19 and equation 3.14. [7] Percentage relative expanded uncertainty calculated using equation 3.16

Using the single- point calibration method for UV Fluorescence spectroscopy, the results in Table 4.19 shows the % difference of 0.0036 % absolute value indicating no significant deviation between the gravimetric and verification values. The expanded uncertainty was achieved at 0.019 µmol/mol and thus the newly prepared hydrogen sulphide reference gas mixture met the validation criteria, and the mixture could be used further in this study for preparation or verification purposes.

Table 4.20: Validation data of hydrogen sulphide reference gas mixtures using NDUV

Cylinder Number	D67 9403
Gravimetric mole fraction (µmol/mol)	10.3113
Gravimetric uncertainty (µmol/mol)	0.0021
Verification mole fraction (µmol/mol)	10.3623
Verification uncertainty (µmol/mol)	0.0203
% Difference	-0.4924
Combined Expanded uncertainty (U), (k = 2)	0.0422
% Relative expanded uncertainty (% REU)	0.41

[1]Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7 and represented by x_g. [2]Associated standard uncertainty determined using the GRAVCALC software (Brown, 2009) and represented by u_{xg}. [3]Verification mole fraction obtained from the verification results calculated using equation 3.4 and represented by x_a. [4]Associated verification standard uncertainty obtained from the measurement repeatability and represented by u_{xa}. [5]Percentage difference between the gravimetric and analytical value calculated using equation 3.13. [6]Combined expanded uncertainty from the gravimetric and analytical uncertainties calculated as ($\sqrt{2(u(x_g)^2 + u(x_a)^2}$) using equation 2.19 and equation 3.14. [7]Percentage relative expanded uncertainty calculated using equation 3.16.

The validation results of hydrogen sulphide reference gas using NDUV are illustrated in Table 4.20 where a multi-point calibration method in the range of 8 to 12 µmol/mol was used and the percentage difference obtained was 0.49 % absolute. This indicates no significant difference between the gravimetric and the verification values. The overall uncertainty was 0.042 µmol/mol which was less than the calculated percentage deviation of this mixture. The verification mole fraction was determined with the XGENLINE1.1 software. Thus the newly prepared hydrogen sulphide reference gas mixture met the validation criteria and gas mixture was further used in this study for preparation of lower mole fractions of hydrogen sulphide or used as reference.

4.3.9 Internal consistency of results of the gravimetrically prepared hydrogen sulphide reference gas mixtures

Internal consistency gives an indication of how the prepared gas mixtures with similar mole fraction agree relative to one another. An internal consistency study was carried out to determine the consistency of the hydrogen sulphide reference gas mixtures with similar mole fraction. The nominal mole fraction of prepared 10 µmol/mol hydrogen sulphide was used for the internal consistency study using cylinder D19 4914 and D62 6572 as reference and results are shown in Table 4.21 and Table 4.22, respectively. Figure 4.8 and 4.9 illustrates graphically the calculated sensitivity and sensitivity ratios for each sample and the reference when D19 4914 and D62 6572 were used as reference, respectively.

The percentage deviation of the sensitivity ratios between the mixture samples and the reference mixture was more than 1.04 % absolute values for reference gas mixtures of cylinder D62 6572, D62 6633, D62 6559 and D62 6475 when cylinder D19 4914 was used as a reference. When cylinder D62 6572 was used as a reference, the percentage deviation in the sensitivity ratios between the mixture samples and the reference mixture was less than 0.18 % absolute value for reference gas mixture of D62 6633 and but more than 1.27 % absolute value for reference gas mixture of cylinder D62 6559. All the previously prepared hydrogen sulphide reference gas mixtures showed poor internal consistency amongst each other with significant difference from the gravimetric value.

Table 4.21: Internal consistency results of the analysis of 10 µmol/mol using D19 4914 as a reference

Cylinder number	Gravimetric mole fraction (µmol/mol)[1]	Average Response[2]	Sensitivity[3]	Sensitivity ratio[4]	% Difference[5]
D19 4914	10.010	12995.903	1298.318	1.000	Reference
D62 6572	10.010	13248.945	1323.597	0.982	-1.910
D62 6633	10.017	13142.407	1311.970	1.011	-1.041
D62 6559	10.000	13208.320	1320.884	1.018	-1.708
D62 6475	10.009	12765.807	1275.445	1.015	1.793

[1]Gravimetric value from the gravimetric preparation in accordance with ISO 6142 calculated using equation 2.7. [2]instrument response from the verification measurements represented by peak area. [3]Sensitivity is calculated by considering the peak area divide it by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [4]Sensitivity ratio is calculated by dividing the sensitivity of the sample by sensitivity of the reference calculated using equation 3.7. [5]Percentage difference between the sensitivity ratios of the reference and the sample.

Table 4.22: Internal consistency results of the analysis of 10 µmol/mol using D62 6572 as a reference

Cylinder number	Gravimetric mole fraction (µmol/mol)[1]	Average Response[2]	Sensitivity[3]	Sensitivity ratio[4]	% Difference[5]
D62 6572	10.010	14032.426	1401.869	1.000	Reference
D62 6633	10.017	14017.611	1399.339	1.006	0.18
D62 6559	10.000	14198.112	1419.867	1.004	-1.27

[1]Gravimetric value from the gravimetric preparation in accordance with ISO 6142 calculated using equation 2.7. [2]instrument response from the verification measurements represented by peak area. [3]Sensitivity is calculated by considering the peak area divide it by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [4]Sensitivity ratio is calculated by dividing the sensitivity of the sample by sensitivity of the reference calculated using equation 3.7. [5]Percentage difference between the sensitivity ratios of the reference and the sample.

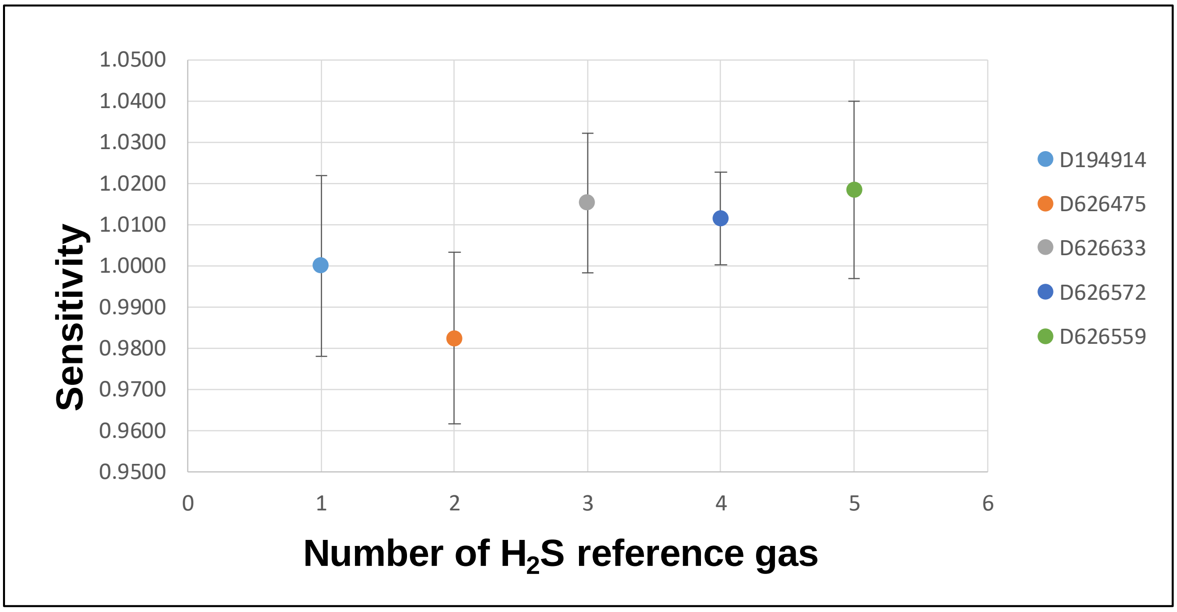


Figure 4.8: Internal consistency graph results for hydrogen sulphide reference gas mixtures using D19 4914 as a reference

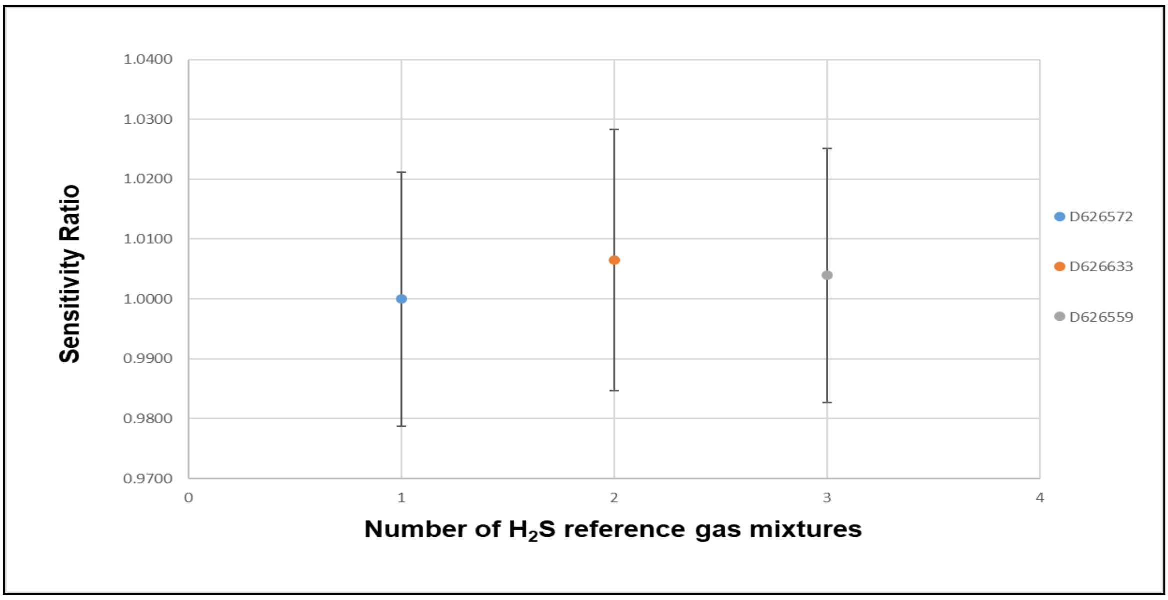


Figure 4.9: Internal consistency graph results for hydrogen sulphide reference gas mixtures using D62 6572 as a reference

4.4 SULPHUR DIOXIDE BINARY REFERENCE GAS MIXTURES RESULTS

4.4.1 Gravimetric preparation of sulphur dioxide reference gas mixtures

There were ten sulphur dioxides in nitrogen reference gas mixtures that were gravimetrically prepared. The first dilution step included diluting from high purity sulphur dioxide to 3.5 % mol/mol and 2.0 % mol/mol of SO_2. These high mole fractions were prepared to ensure no limitations by the smallest mass that can be added and weighed on the mass comparator balance with an acceptable uncertainty of the reference gas mixtures. Dilution of high purity starting material gases depend on the component and its mole fraction that is desired to be prepared since it impacts on the gravimetric uncertainty (Milton *et al.*, 2011). Four step dilution was applied to gravimetrically prepare reference gas mixtures of 10 µmol/mol as final sulphur dioxide in nitrogen reference gas mixtures for this study. Table 4.23 represents the results of sulphur dioxide in nitrogen binary reference gas mixtures prepared. The relative expanded uncertainties of the gravimetric reference gas mixtures were found to be less than 0.115 % REU.

Table 4.23: Gravimetric mole fraction and expanded uncertainties results of the prepared sulphur dioxide reference gas mixtures

Cylinder Number	Mole Fraction (µmol/mol)^1	Expanded uncertainty (µmol/mol)^2, k=2	Relative Expanded Uncertainty (% REU)^3
D62 6469	20064.992	22.426	0.112
D62 6445	34883.701	26.941	0.077
D62 6661	1992.457	2.294	0.115
D62 6655	3983.227	3.254	0.082
D62 6422	99.917	0.082	0.082
D62 6590	100.113	0.115	0.115
D62 6425	9.953	0.008	0.082
D63 1090	10.016	0.012	0.115
D62 6539	10.023	0.008	0.082
D62 6466	9.954	0.011	0.115

[1]Gravimetrically prepared mole fraction of sulphur dioxide was calculated using equation 2.7 in accordance with ISO 6142-1:2015. [2]Gravcalc software (Brown, 2009) was used to determine the expanded uncertainty of the gravimetrically sulphur dioxide in nitrogen reference gas mixtures at 95 % confidence level with coverage factor of *k = 2*. [3]Equation 3.16 was used to determine the

percentage relative expanded uncertainty (%REU) expressed as relative value of gravimetric uncertainty to the gravimetric mole fraction.

4.4.2 Verification of sulphur dioxide reference gas mixtures using NDUV spectroscopy

The verification was done using the multi-point calibration method. Previously prepared SO_2 in nitrogen reference gas mixtures of 10 to 100 µmol/mol range were used to analyse the newly prepared 10 µmol/mol sulphur dioxide in nitrogen reference gas mixtures. Data acquision was done with LabView in-house programmed for each analyser. XGENLINE1.1 software (Smith and Onakunle, 2007) was used to calculate the mole fraction of sulphur dioxide reference gas mixtures. The results obtained from the verification of SO_2 using NDUV analyser is shown in Table 4.24. Analytical data of D62 6425, D62 6539, D62 6466 and D63 1090 shows these reference gas mixtures differ significantly from their gravimetric and analytical values with % difference 5.584 to 6.213 % absolute values. This showed significant inconsistencies between the gravimetric value and the analytical values and did not agree well with the multi-point calibration references used. Therefore the reference gas mixtures were not used further for either preparation or verification of SO_2 reference gas mixtures. This could have been affected by the multi-point calibration standards that were used or the inadequate evacuation of the cylinders.

Table 4.24: Results obtained from the verification of sulphur dioxide using NDUV analyser

Cylinder Number	D62 6425	D62 6539	D63 1090	D62 6466
Gravimetric mole fraction (µmol/mol)	9.953	10.023	10.016	9.954
Average verification mole fraction (µmol/mol)	10.541	10.645	10.637	10.614
Standard deviation (µmol/mol)	0.023	0.007	0.011	0.004
Estimated standard deviation (ESDM)	0.013	0.004	0.006	0.002
% Difference	-5.584	-5.839	-5.840	-6.213
Combined uncertainty	0.027	0.028	0.027	0.026
Expanded uncertainty (U) (k=2)	0.055	0.056	0.054	0.052
% Relative expanded uncertainty (%REU)	0.52	0.52	0.51	0.49

The repeatability study of sulphur dioxide in nitrogen reference gas mixtures was done with a minimum of three repeated measurements for each sample verified over three days. The repeatability data of the prepared sulphur dioxide reference gas mixtures are shown in Figure 4.10 with % RSD less than 0.49 % for all the measurements done. Thus concludes that the measurements of sulphur dioxide using the NDUV developed method are repeatable and fit for purpose.

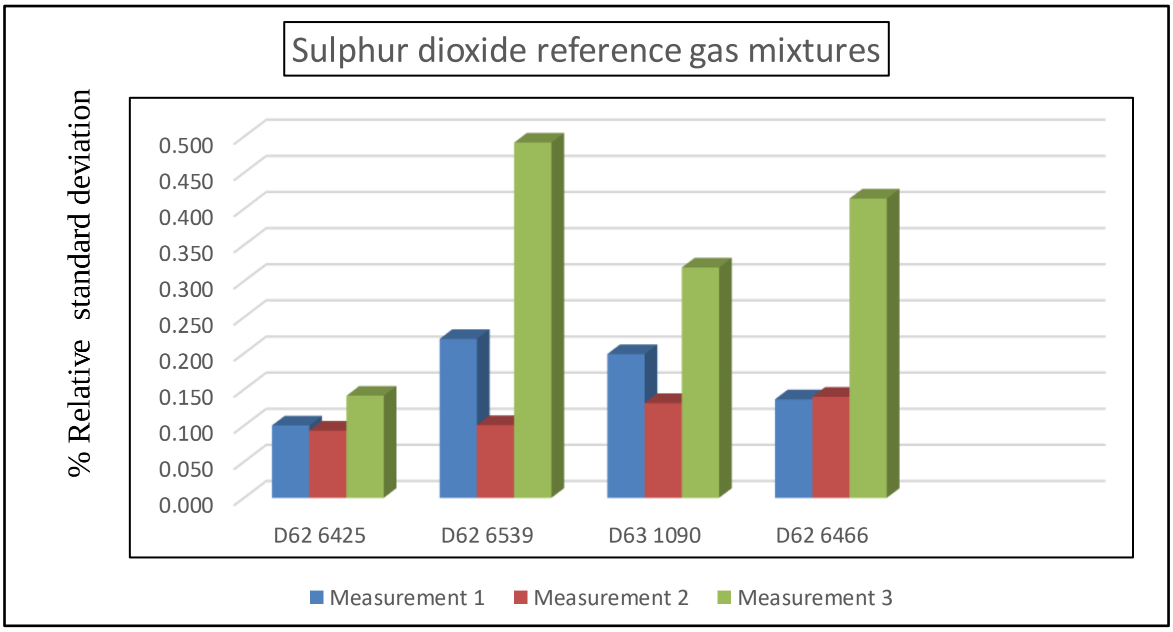


Figure 4.10: Repeatability measurements for 10 µmol/mol sulphur dioxide reference gas mixtures using NDUV analyser

4.4.3 Verification of sulphur dioxide reference gas mixtures using UV Fluorescence spectroscopy

Substitution method (A-B-A), where ‘A’ and ‘B’ represent the reference and sample respectively was used to verify the reference gas mixtures using UV fluorescence spectroscopy. The verification was done using the one-point or single point calibration, where the reference standard was analysed before and after the sample. For this study, a gas mixture of sulphur dioxide in nitrogen was used as a reference to monitor the changes during the verification to compensate for the drift of the instrument during the analysis. Thus the consistency of the prepared reference gas mixture with similar mole fraction is measured using the comparison method. These prepared reference gas mixtures have similar mole fractions which differ by less than 1 % relative to another. This is an important aspect when doing analysis with non-linear instruments because the uncertainty contribution from any deviation from linearity of the instrument response can then be ignored and considered negligible. Data calculations included average concentration response, standard deviation, % RSD and ESDM for each reference gas mixture analysed. The calculations were performed on a minimum number of runs of six per gas cylinder. The results of SO_2 using the single-point calibration method are presented in Table 4.25 to Table 4.27 for all sulphur dioxide measurements.

The instrument drift was monitored through reference gas mixtures used to ensure no significant changes in the instrument responses over time, which might lead to incorrect analytical measurements and decrease in the reliability of measurements being performed. The instrument drift was observed to be in the range of 0.01 to 0.49 % absolute values when D62 6466, D62 6539 and D62 6425 were used as reference mixtures thus indicating acceptable stability of the instrument used during the analysis run. The verification data for the reference gas mixtures showed no significant inconsistency with their gravimetric and analytical values with the % difference ranging between 0.03 to 0.73 % absolute value. Therefore the reference gas mixtures could be used further for analysis or preparation of lower mole fractions of sulphur dioxide.

Table 4.25: Verification results of the analysis of 10 µmol/mol SO_2 reference gas mixtures using D62 6466 as a reference

Number of runs	**D62 6466**	**D63 1090**	**D62 6466**	**D63 1090**	**D62 6466**	**D63 1090**	**D62 6466**	**D63 1090**	**D62 6466**
1	9835.20	9885.96	9844.23	9872.95	9864.12	9901.52	9857.07	9888.33	9831.09
2	9833.13	9889.44	9845.43	9876.53	9863.63	9899.97	9853.94	9880.31	9832.58
3	9833.43	9890.89	9842.04	9880.43	9863.24	9901.11	9847.76	9875.08	9837.33
4	9835.03	9894.91	9836.81	9876.40	9863.31	9902.04	9846.02	9867.23	9839.66
5	9837.96	9894.73	9836.31	9872.46	9866.51	9903.38	9847.20	9867.51	9842.93
6	9838.07	9899.38	9835.80	9869.37	9869.48	9899.77	9851.18	9867.70	9837.79
Average[1]	9835.47	9892.55	9840.10	9874.69	9865.05	9901.30	9850.53	9874.36	9836.90
standard[2]	2.14	4.75	4.31	3.89	2.49	1.35	4.33	8.64	4.42
% RSD[3]	0.02	0.05	0.04	0.04	0.03	0.01	0.04	0.09	0.04
ESDM[4]	0.87	1.94	1.76	1.59	1.02	0.55	1.77	3.53	1.80
Sensitivity[5]	988.06	987.68	988.53	985.90	991.03	988.56	989.58	985.87	988.21
% Difference[6]		0.04		0.27		0.25		0.38	
Gravimetric [7]	9.95	10.02	9.95	10.02	9.95	10.02	9.95	10.02	9.95
Verification[8]		10.01		9.99		9.99		9.98	
Drift (%)[9]			0.05		0.25		-0.15		-0.14

[1]Average obtained using five consecutive peak area responses for each measurement, [2]Standard deviation of the measurement results calculated using equation 3.8, [3]Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5]Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6]Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7]Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8]Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

Table 4.26: Results of the analysis of 10 µmol/mol SO_2 in nitrogen using D62 6539 as a reference

Number of runs	**D62 6539**	**D63 1090**	**D62 6539**	**D63 1090**	**D62 6539**	**D63 1090**	**D62 6539**	**D63 1090**	**D62 6539**
1	9993.71	9985.54	9996.20	9977.17	9995.76	9976.84	10051.41	10032.37	10057.86
2	9994.62	9983.24	9997.76	9981.18	9999.09	9981.55	10051.30	10030.54	10054.81
3	9997.38	9982.55	9998.97	9981.19	10004.55	9981.32	10050.35	10031.05	10053.86
4	9993.47	9983.20	9998.74	9984.63	10005.10	9982.61	10049.65	10031.14	10055.70
5	9994.10	9984.17	9992.61	9981.52	10005.05	9978.49	10049.89	10032.20	10062.40
6	9991.20	9984.34	9996.92	9981.91	10001.62	9979.47	10052.27	10034.11	10064.67
Average[1]	9994.08	9983.84	9996.87	9981.27	10001.86	9980.04	10050.81	10031.90	10058.22
standard deviation[2]	2.00	1.06	2.34	2.39	3.82	2.17	1.01	1.29	4.39
% RSD[3]	0.02	0.01	0.02	0.02	0.04	0.02	0.01	0.01	0.04
ESDM[4]	0.82	0.43	0.95	0.98	1.56	0.88	0.41	0.53	1.79
Sensitivity[5]	997.11	996.80	997.39	996.54	997.89	996.42	1002.77	1001.60	1003.51
% Difference[6]		0.03		0.09		0.15		0.12	
Gravimetric Concentration[7]	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02	10.02
Verification Concentration[8]		10.01		10.01		10.00		10.00	
Drift (%)[9]			0.03		0.05		0.49		0.07

[1]Average obtained using five consecutive peak area responses for each measurement, [2]Standard deviation of the measurement results calculated using equation 3.8, [3]Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5]Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6]Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7]Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8]Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

Table 4.27: Verification results of the analysis of 10 µmol/mol SO_2 reference gas mixtures using D62 6425 as a reference

Number of runs	D62 6425	D63 1090	D62 6425	D63 1090	D62 6425	D63 1090	D62 6425	D63 1090	D62 6425
1	9508.85	9618.80	9510.38	9632.24	9505.72	9624.05	9502.22	9623.90	9499.50
2	9506.33	9616.54	9508.22	9627.41	9509.54	9624.62	9503.91	9623.89	9498.77
3	9502.84	9613.86	9507.22	9624.76	9514.95	9627.19	9501.86	9626.05	9498.14
4	9504.70	9615.70	9508.39	9624.58	9515.42	9628.51	9499.29	9630.24	9495.67
5	9505.50	9614.56	9509.52	9621.86	9514.61	9626.32	9500.51	9634.95	9494.80
6	9502.64	9615.73	9510.99	9625.81	9507.74	9622.38	9501.65	9633.16	9492.44
Average[1]	9505.14	9615.86	9509.12	9626.11	9511.33	9625.51	9501.57	9628.70	9496.55
standard deviation[2]	2.33	1.72	1.43	3.51	4.20	2.25	1.57	4.79	2.72
% RSD[3]	0.02	0.02	0.02	0.04	0.04	0.02	0.02	0.05	0.03
ESDM[4]	0.95	0.70	0.58	1.43	1.71	0.92	0.64	1.95	1.11
Sensitivity[5]	955.01	960.06	955.41	961.08	955.63	961.02	954.65	961.34	954.15
% Difference[6]		-0.53		-0.59		-0.56		-0.70	
Gravimetric Concentration[7]	9.95	10.02	9.95	10.02	9.95	10.02	9.95	10.02	9.95
Verification Concentration[8]		10.07		10.08		10.07		10.09	
Drift (%)[9]			0.04		0.02		-0.10		-0.05

[1]Average obtained using five consecutive peak area responses for each measurement, [2]Standard deviation of the measurement results calculated using equation 3.8, [3]Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5]Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample,

respectively, [6]Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7]Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8]Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

For repeatability study, a minimum of three measurements were performed for each sample verified over a short period of a day. The repeatability data of the prepared 10 µmol/mol sulphur dioxide reference gas mixtures are shown in Figure 4.11 with % RSD less than 0.070 % for all the measurements done. Thus concludes that the measurements of sulphur dioxide using the UV Fluorescence method are repeatable and fit for purpose.

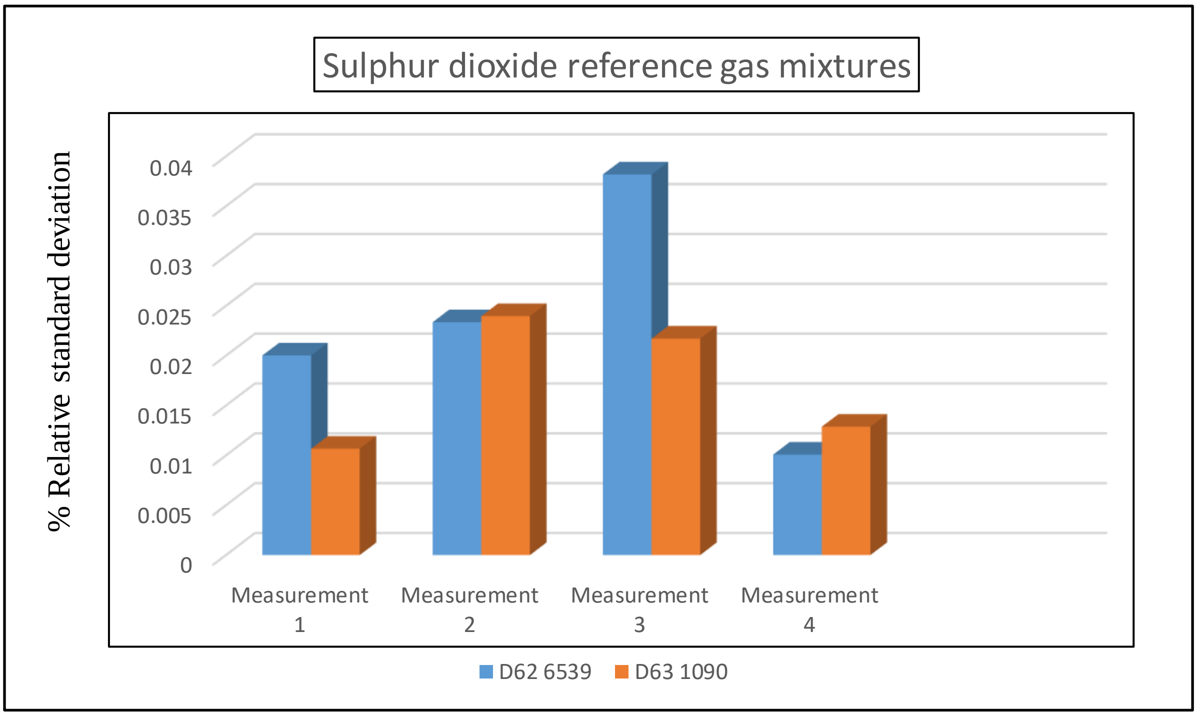


Figure 4.11: Repeatability measurements for 10 µmol/mol sulphur dioxide reference gas mixtures using UV Fluorescence analyser

4.4.4 Validation of sulphur dioxide in nitrogen reference gas mixtures

In order to determine the accuracy, consistency, and reliability of gravimetrically prepared reference gas mixtures with their gravimetric mole fractions, the reference gas mixtures were validated against other independently prepared reference gas mixtures. The sulphur dioxide reference gas mixtures were validated using two techniques of NDUV spectroscopy and UV Fluorescence spectroscopy.

Validation of reference gas mixtures on UV fluorescence, one or single-point calibration method was applied whereby one gas mixture was used as a reference to validate other prepared gas mixtures with similar mole fraction. Verification mole fractions of each sample were calculated using equation 3.4 for single-point calibration method. For validation using NDUV, a multi-point calibration method in the range of 10 to 100 µmol/mol sulphur dioxide reference gas mixtures were used to verify the prepared sulphur dioxide reference gas mixtures. Verification mole fractions were calculated using the XGENLINE1.1 software (Smith and Onakunle, 2007).

The uncertainty contribution of each sample was calculated from the repeatability measurements of the reference used and the sample together with the gravimetric uncertainty of the reference mixture. The gravimetric and verification mole fractions' comparison of sulphur dioxide are shown in Table 4.28 to Table 4.29.

Using Non-dispersive ultraviolet spectroscopy, the validation results in Table 4.28 show a % difference of above 6 % absolute values for prepared sulphur dioxide reference gas mixtures with an overall uncertainty between 0.052 to 0.056 µmol/mol. There is a significant deviation between the gravimetric and verification values which is more than the overall uncertainty for the prepared reference gas mixtures and therefore these mixtures fail the validation criteria as per Table 3.4. These reference gas mixtures could have been affected by the multi-point calibration standards used during the analysis.

Using the single- point calibration method for UV Fluorescence spectroscopy, the results in Table 4.29 shows the % difference of less than 0.77 % absolute value indicating no significant deviation between the gravimetric and verification values. The expanded uncertainty was achieved between 0.016 to 0.026 µmol/mol and thus the prepared sulphur dioxide reference gas mixture met the validation criteria shown in Table 3.4 and the mixtures could be used further in this study for preparation or verification purposes.

Table 4.28: Validation data of sulphur dioxide reference gas mixtures using NDUV spectroscopy

Cylinder Number	Gravimetric mole fraction (µmol/mol)[1]	Gravimetric uncertainty (µmol/mol)[2]	Average verification mole fraction (µmol/mol)[3]	Verification uncertainty[4]	% Difference[5]	Combined Expanded uncertainty (U) (k=2)[6]	% Relative expanded uncertainty (%REU)[7]
D62 6425	9.953	0.004	10.541	0.027	-5.584	0.055	0.517
D62 6539	10.023	0.004	10.645	0.028	-5.839	0.056	0.523
D63 1090	10.016	0.006	10.637	0.027	-5.840	0.054	0.508
D62 6466	9.954	0.006	10.614	0.026	-6.213	0.052	0.486

[1]Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7 and represented by $\boldsymbol{x_g}$. [2]Associated standard uncertainty determined using the GRAVCALC software (Brown, 2009) and represented by $\boldsymbol{u_{xg}}$. [3]Verification mole fraction obtained from the verification results calculated using equation 3.4 and represented by $\boldsymbol{x_a}$. [4]Associated verification standard uncertainty obtained from the measurement repeatability and represented by $\boldsymbol{u_{xa}}$. [5]Percentage difference between the gravimetric and analytical value calculated using equation 3.13. [6]Combined expanded uncertainty from the gravimetric and analytical uncertainties calculated as $(\sqrt{\boldsymbol{2(u(x_g)^2+u(x_a)^2}})$ using equation 2.19 and equation 3.14. [7]Percentage relative expanded uncertainty calculated using equation 3.16.

Table 4.29: Validation data of sulphur dioxide reference gas mixtures using UV Fluorescence spectroscopy

Cylinder Number	Gravimetric mole fraction (µmol/mol)[1]	Gravimetric uncertainty (µmol/mol)[2]	Average verification mole fraction (µmol/mol)[3]	Verification uncertainty[4]	% Difference[5]	Combined Expanded uncertainty (U) (k=2)[6]	% Relative expanded uncertainty (%REU)[7]
D62 6425	9.953	0.004	9.877	0.008	0.769	0.016	0.163
D62 6539	10.023	0.004	10.061	0.013	-0.381	0.026	0.255
D63 1090	10.016	0.006	10.021	0.013	-0.046	0.025	0.250
D62 6466	9.954	0.006	9.991	0.012	-0.363	0.025	0.246

[1] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7 and represented by $\boldsymbol{x_g}$. [2] Associated standard uncertainty determined using the GRAVCALC software (Brown, 2009) and represented by $\boldsymbol{u_{xg}}$. [3] Verification mole fraction obtained from the verification results calculated using equation 3.4 and represented by $\boldsymbol{x_a}$. [4] Associated verification standard uncertainty obtained from the measurement repeatability and represented by $\boldsymbol{u_{xa}}$. [5] Percentage difference between the gravimetric and analytical value calculated using equation 3.13. [6] Combined expanded uncertainty from the gravimetric and analytical uncertainties calculated as $(\sqrt{\boldsymbol{2(u(x_g)^2 + u(x_a)^2}})$ using equation 2.19 and equation 3.14. [7] Percentage relative expanded uncertainty calculated using equation 3.16.

4.4.5 Internal consistency results of the gravimetrically prepared sulphur dioxide reference gas mixtures

An internal consistency study was carried out to determine the consistency of the sulphur dioxide reference gas mixtures with similar mole fraction. The nominal mole fraction of prepared 10 µmol/mol sulphur dioxide was used for the internal consistency study using cylinder D62 6425, D62 6539, D63 1090 and D62 6466 as reference and results are shown in Table 4.30 to Table 4.33, respectively. Figure 4.12 to 4.15 illustrates graphically the calculated sensitivity and sensitivity ratios for each sample and the reference when D2 6425, D62 6539, D63 1090 and D62 6466 were used as reference, respectively.

The percentage deviation of the sensitivity ratios between the mixture samples and the reference mixture was more than 7.88 % absolute values for reference gas mixtures of D62 6466, D62 6539 and D63 1090 when D62 6425 was used as a reference. When D62 6539 and D63 1090 were used as a reference, percentage deviation in the sensitivity ratios between the mixture samples and the reference mixture was more than 1.12 % absolute value for reference gas mixture of D62 6425 and but less than 0.66 % absolute value for reference gas mixtures of D62 6466, D62 6539 and D63 1090. Using D62 6466 as a reference, the percentage difference in the sensitivity ratios between the mixture samples and the reference mixture was between 0.51 to 3.8 % absolute values. The prepared 10 µmol/mol sulphur dioxide in nitrogen reference gas mixtures showed poor internal consistency amongst each other with significant difference from the gravimetric value.

Table 4.30: Internal consistency results of the analysis of sulphur dioxide in nitrogen using D62 6425 as a reference mixture

Cylinder number	Gravimetric mole fraction (µmol/mol)[1]	Average Response[2]	Sensitivity[3]	Sensitivity ratio[4]	% Difference[5]
D62 6425	9.953	9899.923	994.682	1.000	Reference
D62 6539	10.023	9673.832	965.155	1.008	3.059
D63 1090	10.016	9624.603	960.932	1.006	3.512
D62 6466	9.954	10749.274	1079.860	1.009	-7.888

[1]Gravimetric value from the gravimetric preparation in accordance with ISO 6142 calculated using equation 2.7. [2]instrument response from the verification measurements represented by peak area. [3]Sensitivity is calculated by considering the peak area divide it by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [4]Sensitivity ratio is calculated by dividing the

sensitivity of the sample by sensitivity of the reference calculated using equation 3.7. [5]Percentage difference between the sensitivity ratios of the reference and the sample.

Table 4.31: Internal consistency results of the analysis of sulphur dioxide in nitrogen using D62 6539 as a reference mixture

	Gravimetric mole fraction (µmol/mol)[1]	Average Response[2]	Sensitivity[3]	Sensitivity ratio[4]	% Difference[5]
D62 6539	10.023	9945.998	992.309	1.000	Reference
D62 6425	9.953	9731.693	977.779	0.991	1.486
D63 1090	10.023	10003.351	998.747	0.998	0.645
D62 6466	9.954	9859.183	990.443	1.001	0.188

[1]Gravimetric value from the gravimetric preparation in accordance with ISO 6142 calculated using equation 2.7. [2]instrument response from the verification measurements represented by peak area. [3]Sensitivity is calculated by considering the peak area divide it by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [4]Sensitivity ratio is calculated by dividing the sensitivity of the sample by sensitivity of the reference calculated using equation 3.7. [5]Percentage difference between the sensitivity ratios of the reference and the sample.

Table 4.32: Internal consistency results of the analysis of sulphur dioxide in nitrogen using D63 1090 as a reference mixture

Cylinder number	Gravimetric mole fraction (µmol/mol)[1]	Average Response[2]	Sensitivity[3]	Sensitivity ratio[4]	% Difference[5]
D63 1090	10.016	9859.413	984.376	1.000	Reference
D62 6425	9.953	9908.211	995.515	0.994	-1.119
D62 6539	10.023	9815.091	979.248	1.002	0.524
D62 6466	9.954	9734.010	977.868	1.003	0.666

[1]Gravimetric value from the gravimetric preparation in accordance with ISO 6142 calculated using equation 2.7. [2]instrument response from the verification measurements represented by peak area. [3]Sensitivity is calculated by considering the peak area divide it by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [4]Sensitivity ratio is calculated by dividing the sensitivity of the sample by sensitivity of the reference calculated using equation 3.7. [5]Percentage difference between the sensitivity ratios of the reference and the sample.

Table 4.33: Internal consistency results of the analysis of sulphur dioxide in nitrogen using D62 6466 as a reference mixture

Cylinder number	Gravimetric mole fraction (µmol/mol)[1]	Average Response[2]	Sensitivity[3]	Sensitivity ratio[4]	% Difference[5]
D62 6466	9.954	9989.401	1003.524	1.000	Reference
D62 6425	9.953	10039.415	1008.697	0.995	-0.513
D63 1090	10.016	9857.025	984.138	0.998	1.970
D62 6539	10.023	9687.822	966.550	1.000	3.825

[1]Gravimetric value from the gravimetric preparation in accordance with ISO 6142 calculated using equation 2.7. [2]instrument response from the verification measurements represented by peak area. [3]Sensitivity is calculated by considering the peak area divide it by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [4]Sensitivity ratio is calculated by dividing the sensitivity of the sample by sensitivity of the reference calculated using equation 3.7. [5]Percentage difference between the sensitivity ratios of the reference and the sample.

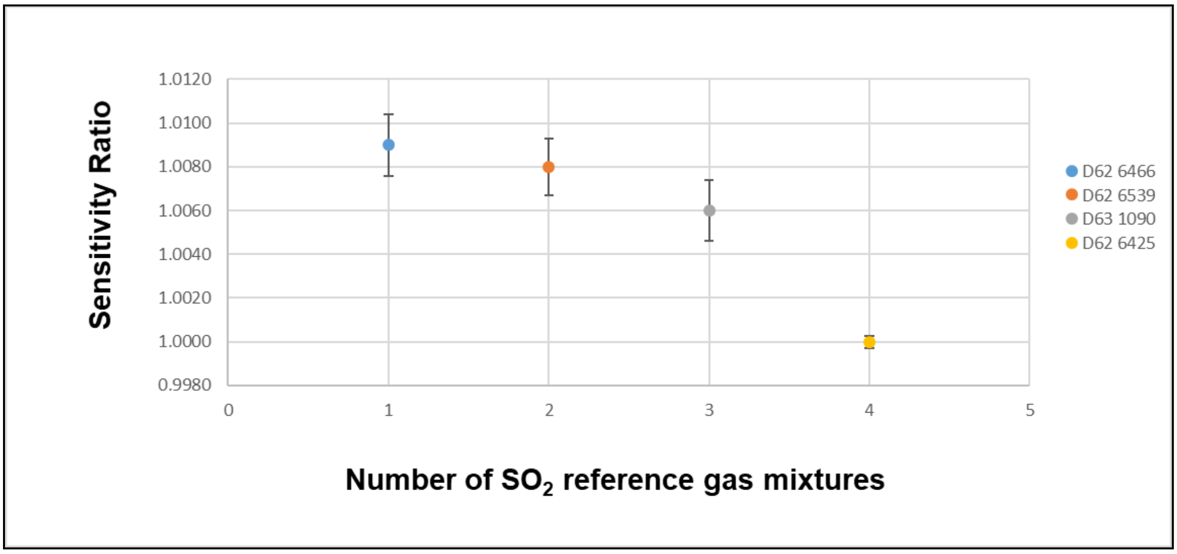


Figure 4.12: Internal consistency graph for sulphur dioxide in nitrogen reference gas mixtures using D62 6425 as a reference

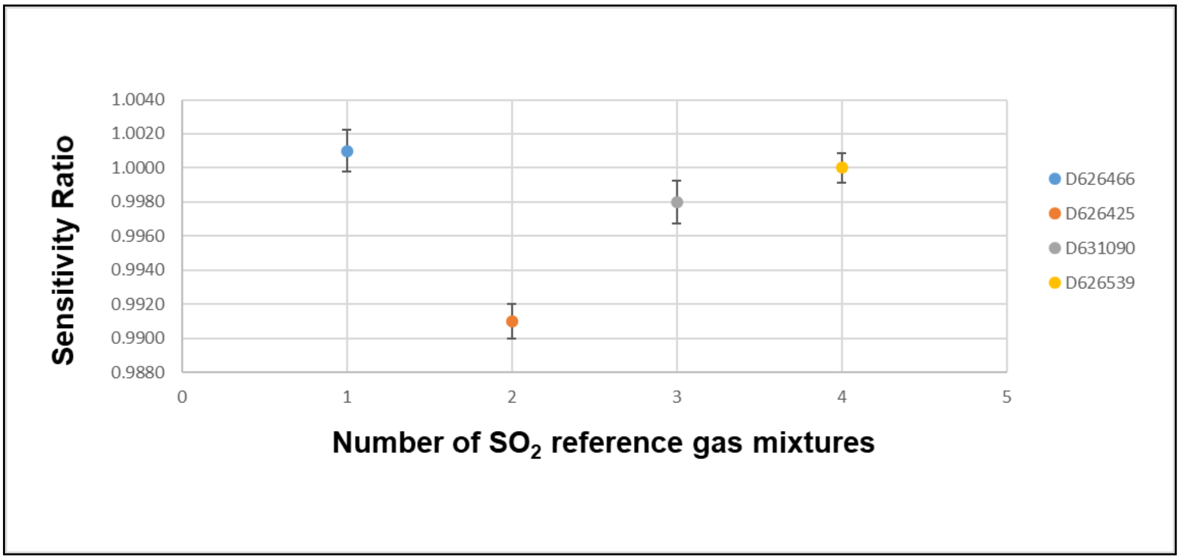


Figure 4.13: Internal consistency graph for sulphur dioxide in nitrogen reference gas mixtures using D62 6539 as a reference

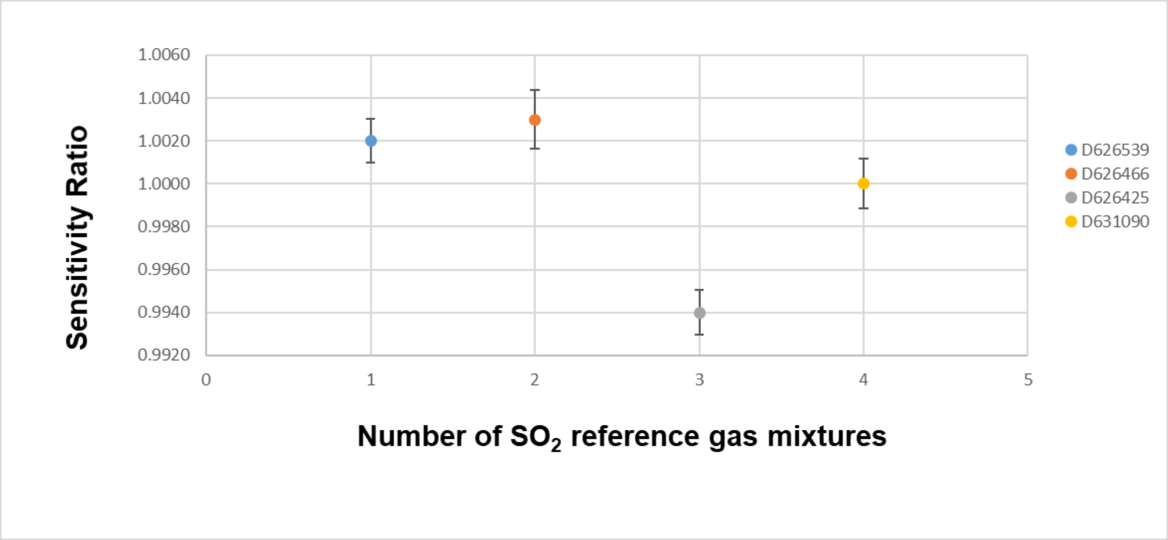


Figure 4.14: Internal consistency graph for sulphur dioxide in nitrogen reference gas mixtures using D63 1090 as a reference

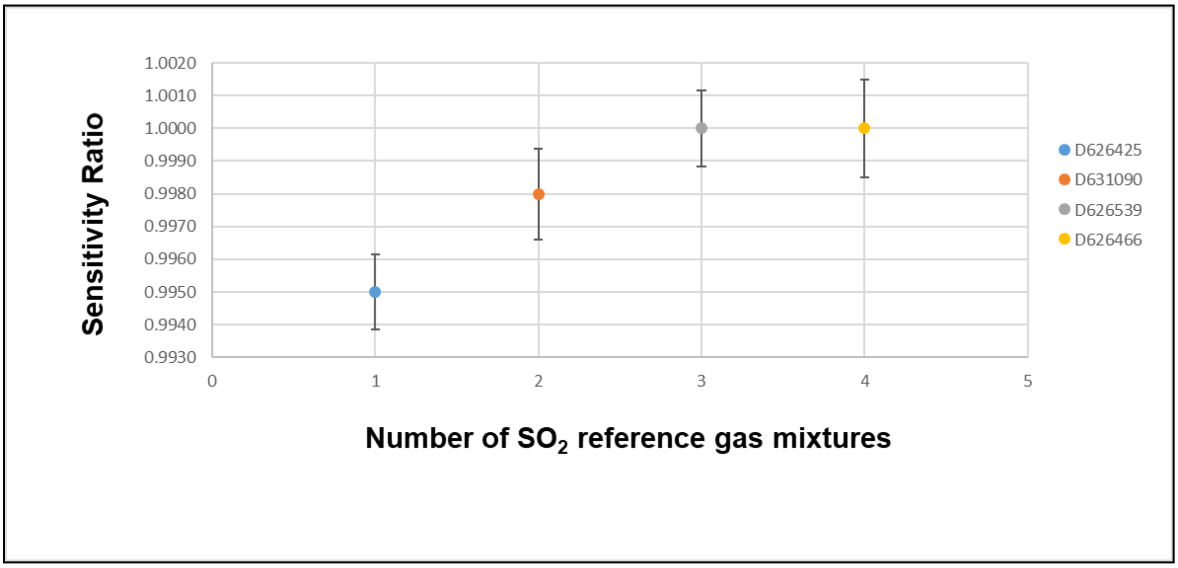


Figure 4.15: Internal consistency graph for sulphur dioxide in nitrogen reference gas mixtures using D62 6466 as a reference

4.5 RESULTS FOR BINARY ISOPROPANOL IN NITROGEN REFERENCE GAS MIXTURES

4.5.1 Gravimetric preparation of isopropanol reference gas mixtures

Two isopropanol in nitrogen reference gas mixtures were gravimetrically prepared in accordance with ISO 6142 method. The isopropanol reference gas mixtures were prepared in one step dilution from high purity isopropanol to a mole fraction of 200 µmol/mol. Using the ideal gas law equation 3.2 in chapter 3, the maximum amount of the liquid that will vaporise to gas phase inside the cylinder was calculated and hence a one-step dilution was applied for isopropanol in nitrogen reference gas mixtures. Table 4.34 shows the concentrations and uncertainties of prepared isopropanol in nitrogen reference gas mixtures. The relative expanded uncertainties of the gravimetric reference gas mixtures were found to be less than 0.068 % REU.

Table 4.34: Gravimetric mole fraction and expanded uncertainties results of the prepared isopropanol reference gas mixtures

Cylinder Number	Gravimetric mole fraction (µmol/mol)[1]	Expanded uncertainty (µmol/mol)[2], k=2	Relative Expanded Uncertainty (% REU)[3]
M39 5385	200.431	0.136	0.068
D67 9419	200.240	0.071	0.035

[1] Gravimetrically prepared mole fraction of isopropanol was calculated using equation 2.7 in accordance with ISO 6142-1:2015. [2] Gravcalc software was used to determine the expanded uncertainty of the gravimetrically isopropanol in nitrogen reference gas mixtures at 95 % confidence level with coverage factor of *k = 2*. [3] Equation 3.16 was used to determine the percentage relative expanded uncertainty (%REU) expressed as relative value of gravimetric uncertainty to the gravimetric mole fraction.

The final composition of the prepared 200 µmol/mol isopropanol in nitrogen reference gas mixtures is shown in Table 4.35. The purity table consists of the main component isopropanol, nitrogen diluent gas and all the impurities that are present in the isopropanol and nitrogen as starting materials. Therefore, starting materials with many unquantified impurities leads to a significant amount of these impurities in the prepared reference gas mixtures and thus mole fraction cannot be accurately established.

Table 4.35: Final composition of gravimetrically prepared isopropanol in nitrogen primary standard gas mixtures

Component	cylinder number: M39 5385		Cylinder number: D67 9419	
	Mole fraction (µmol/mol)[1]		Mole fraction (µmol/mol)[1]	
Isopropanol	200.4308	0.0680	200.2403	0.0355
N_2	999733.2886	3.2190	999733.4811	3.2184
Ar	63.6271	3.1814	63.6271	3.1814
H_2	0.4999	0.2889	0.4999	0.2889
H_2O	0.0707	0.0355	0.0707	0.0355
CO	0.0500	0.0025	0.0500	0.0025
CO_2	0.0500	0.0025	0.0500	0.0025
CH_4	0.0100	0.0005	0.0100	0.0005
C_2H_6	0.0050	0.0029	0.0050	0.0029
O_2	0.0040	0.0002	0.0040	0.0002

[1] The mole fraction (µmol/mol) of the prepared isopropanol reference gas mixtures was determined using equation 2.7

4.5.2 Verification of isopropanol reference gas mixtures using gas chromatography

For verification of isopropanol, one of the gas mixtures was used as the reference following the substitution method (A-B-A), where ‘A’ and ‘B’ represent the reference and sample mixtures, respectively. The comparison method is used to measure the consistency of the prepared reference gas mixtures with similar mole fraction that differ by less than 1 % relative to each other. The verification was done using the one-or single point calibration, where the reference mixture was analysed before and after the sample mixture. The isopropanol verification using gas chromatography was done with statistical analysis of data which included calculation of average peak areas, standard deviation, and percentage relative standard deviation (%RSD) for each mixture verified. These were determined by using data from a minimum of 5 injections for each mixture.

The results obtained from the verification of isopropanol using gas chromatography are shown in Table 4.36 and. The reference mixture is also used to monitor any changes of the instrument drift during the analysis. The instrument drift was observed between 0.01 to 1.01 % absolute values during the verification. This indicates the stability of the instruments during analysis which results in less deviation in measurements.

The isopropanol in nitrogen repeatability study was completed with a minimum of three repeated measurements for each sample verified over a brief period of a day. Figure 4.16 shows the repeatability data of the prepared isopropanol reference gas mixtures with % RSD less than 0.65 % for all the measurement done. The % RSD was observed to be decreasing which meant the instrument was getting more stable because it was not in use prior to isopropanol measurements and the more repeatable measurements were done, it became more stable. This concludes that measurements of isopropanol using the GC-FID method are repeatable and fit for purpose.

Table 4.36: Measurement results of isopropanol obtained from the gas chromatography coupled with flame ionisation detector

Injection	D67 9419	M39 5385	D67 9419	M39 5385	D67 9419	M39 5385	D67 9419
1	280.2	278.6	276.9	278.5	277.2	278.7	277.1
2	280.2	279.2	277.0	278.3	277.7	278.4	277.3
3	280.0	279.1	278.1	278.9	277.7	279.4	277.4
4	279.8	278.5	277.0	278.7	277.1	279.3	277.4
5	280.8	278.2	277.5	278.1	276.6	278.8	276.6
Average[1]	280.20	278.72	277.30	278.50	277.26	278.92	277.16
Standard deviation[2]	0.37	0.42	0.50	0.32	0.46	0.42	0.34
% RSD[3]	0.13	0.15	0.18	0.11	0.17	0.15	0.12
ESDM[4]	0.17	0.19	0.23	0.14	0.21	0.19	0.15
Sensitivity[5]	1.40	1.39	1.38	1.39	1.38	1.39	1.38
% Difference[6]		-0.11		0.34		0.52	
Gravimetric concentration[7]	200.24	200.43	200.24	200.43	200.24	200.43	200.24
Verification concentration[8]		200.22		201.12		201.48	
Drift (%)[9]			1.05		0.01		0.04

[1] Average obtained using five consecutive peak area responses for each measurement, [2] Standard deviation of the measurement results calculated using equation 3.8, [3] Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5] Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6] Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8] Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

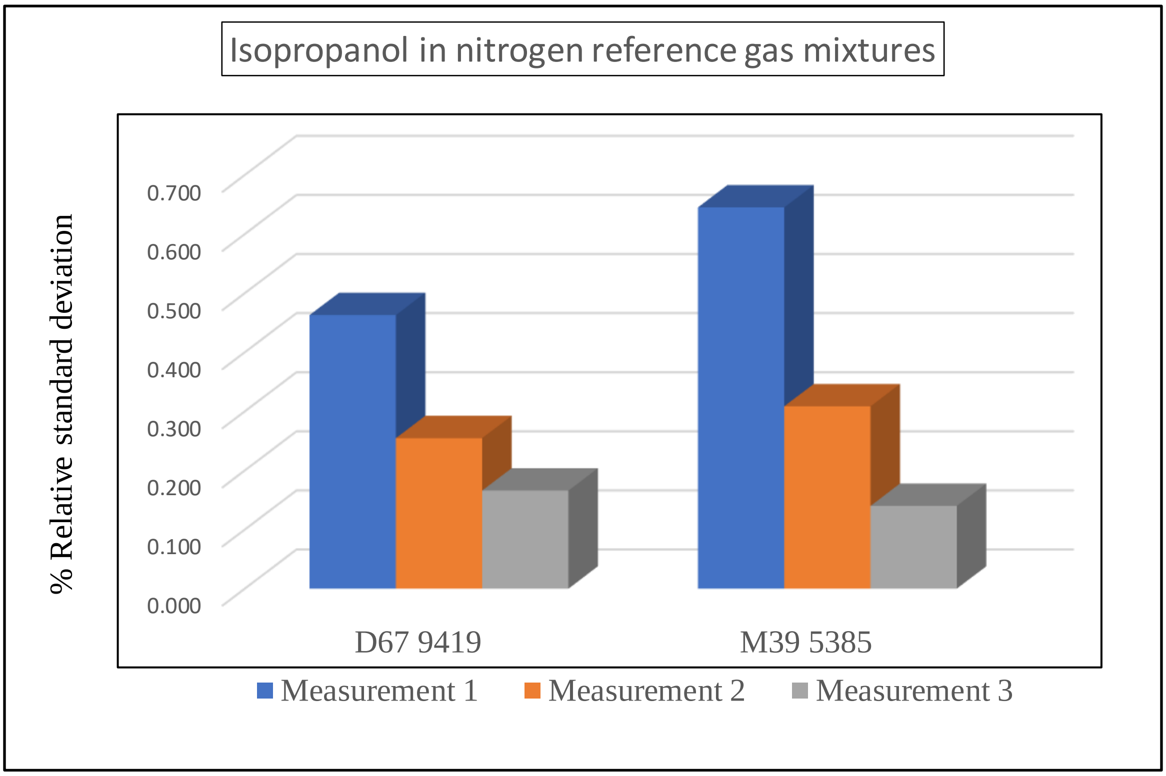


Figure 4.16: Precision measurements for 200 µmol/mol isopropanol in nitrogen using gas chromatography

4.5.3 Validation of isopropanol in nitrogen reference gas mixtures

To verify the consistency, reliability, and accuracy of the prepared reference gas mixtures with their gravimetric mole fractions, the reference gas mixtures were validated against other independently prepared reference gas mixtures. The isopropanol reference gas mixtures were validated with the gas chromatography coupled with flame ionisation detector. One gas mixture was chosen as a reference to validate other prepared gas mixtures of isopropanol with similar mole fraction. Using the single- or one-point calibration method, verification mole fraction was determined using equation 3.4. The uncertainty contribution of each sample was calculated from the repeatability measurements of the reference used and the sample together with the gravimetric uncertainty of the reference mixture. The gravimetric and verification mole fractions' comparison of isopropanol are shown in Table 4.37.

The validation results in Table 4.37 show a % difference of less than 0.43 % absolute values for prepared isopropanol reference gas mixtures with an overall uncertainty between 0.74 to 1.00 µmol/mol. The percentage relative expanded uncertainty gave values of less than 0.50 % for isopropanol reference gas mixtures. Therefore there was no deviation between the gravimetric and the verification value and the mixtures met the validation criteria as per Table 3.4 and can be further used for either preparation or as a reference.

Table 4.37: Data for validation of isopropanol in nitrogen reference gas mixture using gas chromatography

Cylinder Number	**Gravimetric mole fraction (µmol/mol)[1]**	**Gravimetric uncertainty (µmol/mol)[2]**	**Average verification mole fraction (µmol/mol)[3]**	**Verification uncertainty (µmol/mol)[4]**	**% Difference[5]**	**Combined Expanded uncertainty (U) (k=2)[6]**	**% Relative expanded uncertainty (%REU)[7]**
D67 9419	200.24	0.04	199.41	0.37	0.42	0.74	0.37
M39 5385	200.43	0.07	201.31	0.50	-0.43	1.00	0.50

[1] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7 and represented by $\boldsymbol{x_g}$. [2] Associated standard uncertainty determined using the GRAVCALC software (Brown, 2009) and represented by $\boldsymbol{u_{xg}}$. [3] Verification mole fraction obtained from the verification results calculated using equation 3.4 and represented by $\boldsymbol{x_a}$. [4] Associated verification standard uncertainty obtained from the measurement repeatability and represented by $\boldsymbol{u_{xa}}$. [5] Percentage difference between the gravimetric and analytical value calculated using equation 3.13. [6] Combined expanded uncertainty from the gravimetric and analytical uncertainties calculated as $(\sqrt{\boldsymbol{2(u(x_g)^2 + u(x_a)^2}})$ using equation 2.19 and equation 3.14. [7] Percentage relative expanded uncertainty calculated using equation 3.16.

4.6 ETHANOL IN NITROGEN REFERENCE GAS MIXTURES RESULTS

4.6.1 Gravimetric preparation of ethanol reference gas mixtures

The ethanol reference gas mixtures were prepared in two step dilution from high purity ethanol to a mole fraction of 5 µmol/mol. Using the ideal gas law equation 3.2 in chapter 3, the maximum amount of the liquid that will vaporise to gas phase inside the cylinder was calculated and each subsequent concentration level was prepared from the previous ethanol pre-mix gases and diluted with nitrogen to target mole fraction of 5 µmol/mol. Table 4.38 illustrates the concentrations and uncertainties of prepared ethanol in nitrogen reference gas mixtures. The % REU for the prepared ethanol gas mixtures were found to be less than 0.35 %.

Table 4.38: Gravimetric mole fraction and expanded uncertainties results of the prepared ethanol reference gas mixtures

Cylinder Number	Gravimetric mole fraction (µmol/mol)[1]	Expanded uncertainty (µmol/mol)[2], k=2	Relative Expanded Uncertainty (% REU)[3]
M9 3950	4.997	0.015	0.309
M9 3944	5.001	0.011	0.224
M9 3862	4.984	0.018	0.351
M39 5463	4.994	0.016	0.320

[1] Gravimetrically prepared mole fraction of ethanol was calculated using equation 2.7 in accordance with ISO 6142-1:2015. [2] Gravcalc software was used to determine the expanded uncertainty of the gravimetrically ethanol in nitrogen reference gas mixtures at 95 % confidence level with coverage factor of $k = 2$. [3] Equation 3.16 was used to determine the percentage relative expanded uncertainty (%REU) expressed as relative value of gravimetric uncertainty to the gravimetric mole fraction.

The composition of the gravimetrically prepared 5 µmol/mol ethanol in nitrogen reference gas mixtures is presented in Table 4.39. The main components in the purity table are ethanol, nitrogen as diluent gas and all the impurities from the starting materials of ethanol and BIP^{TM} nitrogen. Unidentified and unquantified impurities in the starting material led to significant amount of these impurities in the prepared reference gas mixtures and thus the mole fraction of gas mixtures cannot be accurately established.

Table 4.39: Composition of prepared ethanol in nitrogen primary standard gas mixtures

Component	**cylinder number: M9 3950**		**Cylinder number: M9 3944**		**Cylinder number: M9 3862**		**Cylinder number: M39 5463**	
	Mole fraction (µmol/mol)[1]		**Mole fraction (µmol/mol)[1]**		**Mole fraction (µmol/mol)[1]**		**Mole fraction (µmol/mol)[1]**	
Ethanol	4.997	0.008	5.001	0.006	4.984	0.009	4.994	0.008
N_2	999940.129	2.632	999944.328	2.541	999942.319	2.638	999939.588	2.595
Ar	54.808	2.632	53.900	2.541	53.900	2.638	55.343	2.595
H_2	0.022	0.009	0.009	0.005	0.009	0.005	0.029	0.013
H_2O	0.012	0.006	0.012	0.005	0.012	0.006	0.012	0.006
CO_2	0.010	0.001	0.010	0.001	0.010	0.001	0.010	0.001
CO	0.007	0.004	0.007	0.004	0.007	0.004	0.007	0.004
C_2H_6	0.006	0.004	0.006	0.003	0.006	0.004	0.006	0.003
O_2	0.005	0.003	0.005	0.003	0.005	0.003	0.005	0.003
CH_4	0.004	0.002	0.004	0.002	0.004	0.002	0.004	0.002

[1] The mole fraction (µmol/mol) of the prepared isopropanol reference gas mixtures was determined using equation 2.7

4.6.2 Verification of Ethanol reference gas mixtures using gas chromatography

Substitution method (A-B-A), where ‘A’ and ‘B’ represent the reference and sample respectively was used to verify the ethanol reference gas mixtures using gas chromatography coupled with flame ionisation detector. The verification was done using the one- or single-point calibration, where the reference standard was analysed before and after the sample. For this study one of the ethanol reference gas mixtures was used as a reference to monitor the changes during the verification to compensate for the drift of the instrument during the analysis. Thus the consistency of the prepared reference gas mixture with similar mole fraction is measured using the comparison method. These prepared reference gas mixtures have similar mole fractions which differ by less than 1 % relative to another. This is an important aspect when doing analysis with non-linear instruments because the uncertainty contribution from any deviation from linearity of the instrument response can be ignored and considered negligible.

Data calculations included average concentration response, standard deviation, % RSD and ESDM for each reference gas mixture analysed. The calculations were done from a minimum of four injections per gas cylinder. The results of ethanol using single-point calibration method are presented in Table 4.40 and Table 4.41 for all ethanol in nitrogen measurements using different reference gas mixtures.

The instrument drift was monitored through reference gas mixtures used to ensure no significant changes in the instrument responses. The instrument drift was observed to be in the range of 0.47 to 0.82 % absolute values when M9 3944 was used as reference mixture, thus indicating the acceptable stability of the instruments during analysis. The verification data for the reference gas mixtures when M9 3944 was used, showed no significant inconsistency with their gravimetric and analytical values with % difference ranging between 0.20 to 0.90 % absolute value. When M39 5463 was used, the % drift was observed to be more than 2.69 % absolute value which indicates the instability of the instrument during analysis.

Table 4.40: Results of the analysis of 5 µmol/mol Ethanol in nitrogen using M9 3944 as a reference

Injections	M9 3944	M9 3950	M9 3944	M9 3950	M9 3944	M9 3950	M9 3944
1	20.80	21.20	20.90	21.00	21.50	21.30	20.90
2	21.10	21.90	21.30	21.30	20.40	21.00	20.80
3	21.40	21.20	21.80	21.50	21.60	21.50	21.50
4	21.40	21.10	21.10	21.40	22.30	21.30	21.90
Average[1]	21.18	21.35	21.28	21.30	21.45	21.28	21.28
standard deviation[2]	0.29	0.37	0.39	0.22	0.79	0.21	0.52
% RSD[3]	1.36	1.73	1.82	1.01	3.66	0.97	2.44
ESDM[4]	0.14	0.19	0.19	0.11	0.39	0.10	0.26
Sensitivity[5]	4.23	4.27	4.25	4.2	4.29	4.26	4.25
% Difference[6]		-0.90		-0.20		0.74	
Gravimetric Concentration[7]	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Verification Concentration[8]		5.04		5.01		4.96	
Drift (%)[9]			0.47		0.82		-0.82

[1] Average obtained using five consecutive peak area responses for each measurement, [2] Standard deviation of the measurement results calculated using equation 3.8, [3] Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5] Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6] Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8] Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

Table 4.41: Results of the analysis of 5 µmol/mol Ethanol in nitrogen using M39 5463 as a reference

Injections	M9 3944	M9 3950	M9 3944	M9 3950	M9 3944	M9 3950	M9 3944
1	19.90	20.70	20.60	20.80	19.50	19.20	20.80
2	19.90	20.60	20.60	20.50	20.60	20.70	21.00
3	20.00	20.60	20.10	21.00	21.00	20.10	21.20
4	20.10	20.50	20.90	19.50	19.20	20.80	20.80
5	20.10	20.50	21.20	21.20	19.60	20.90	20.70
6	20.10	20.90	21.20	21.00	20.80	21.10	21.10
Average[1]	20.04	20.62	20.80	20.64	20.24	20.72	20.96
standard deviation[2]	0.09	0.16	0.46	0.69	0.79	0.38	0.21
% RSD[3]	0.45	0.80	2.23	3.33	3.92	1.82	0.99
ESDM[4]	0.04	0.07	0.21	0.31	0.35	0.17	0.09
Sensitivity[5]	4.01	4.13	4.16	4.13	4.05	4.15	4.20
% Difference[6]		-2.76		0.83		-2.27	
Gravimetric Concentration[7]	4.99	5.00	4.99	5.00	4.99	5.00	4.99
Verification Concentration[8]		5.14		4.96		5.11	
Drift (%)[9]			3.79		-2.69		3.56

[1] Average obtained using five consecutive peak area responses for each measurement, [2] Standard deviation of the measurement results calculated using equation 3.8, [3] Percentage relative standard deviation (%RSD) calculated using equation 3.9, [4] ESDM is the estimated standard deviation of the mean calculated by equation 3.10, [5] Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively, [6] Percentage difference between the gravimetric and analytical value calculated using equation 3.13, [7] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7, [8] Analytical value obtained from the analytical results calculated using equation 3.4, [9] Percentage Drift calculated using equation 3.11 to monitor the changes during analysis.

To determine repeatability of ethanol in nitrogen reference gas mixtures, a minimum of three repeated measurements were performed for each sample verified over a short period of a week. The repeatability data of the prepared 5 µmol/mol ethanol reference gas mixtures is shown in Figure 4.17 and Figure 4.18 with % RSD more than 1.27 % for all the measurements done. Low mole fraction reference gas mixtures are expected to give higher repeatability value because of the expected larger uncertainties. The increased uncertainties result from different effects such as losses during gravimetric preparation of gas mixtures, contribution of interferences to the measurements and the unstable baseline during verification of gas mixtures. Therefore as gas mixtures mole fraction drop, their relative uncertainties associated with the results usually increase (Eurachem/CITAC Working Group. *et al.*, 2000).

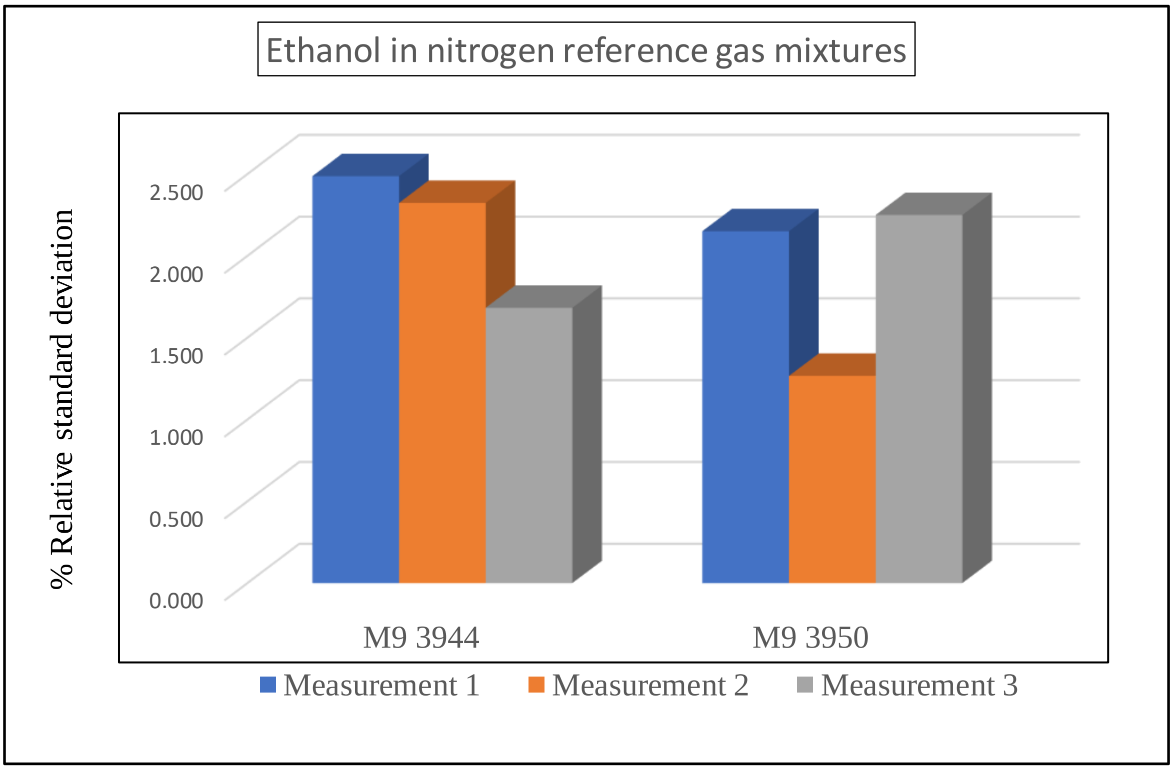


Figure 4.17: Repeatability measurements for 5 µmol/mol ethanol reference gas mixtures using M9 3944 as reference

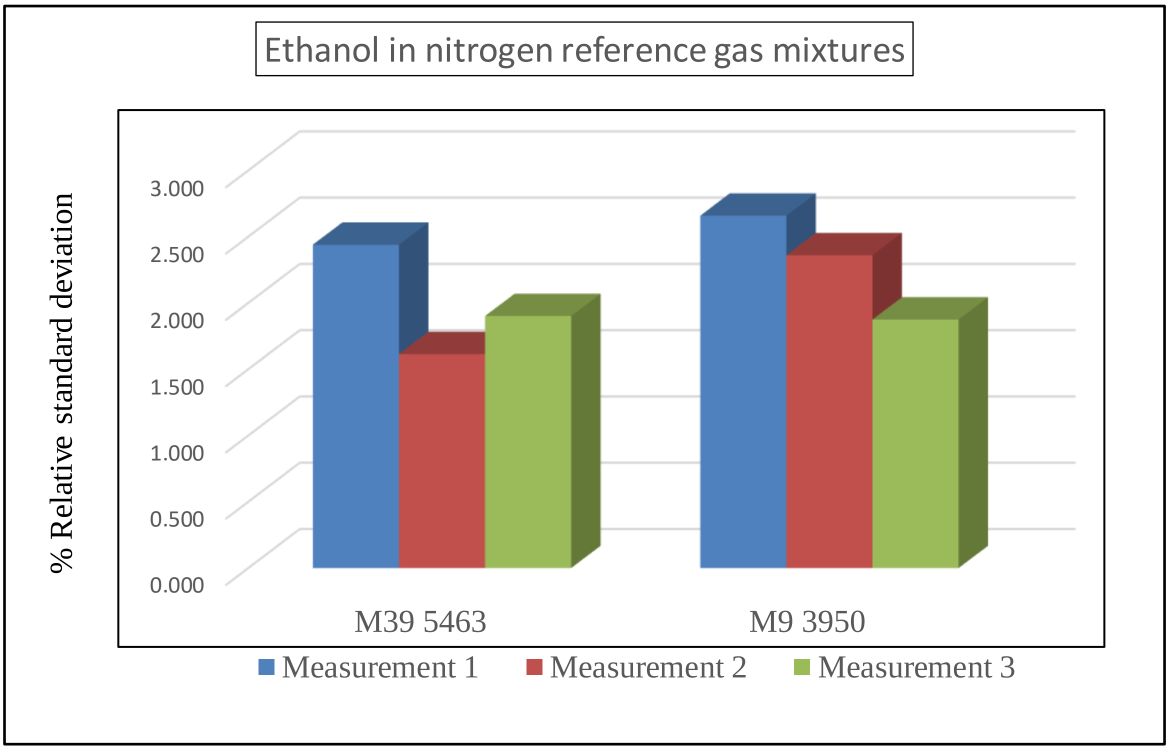


Figure 4.17: Repeatability measurements for 5 µmol/mol ethanol reference gas mixtures using M39 5463 as reference

4.6.3 Validation of ethanol in nitrogen reference gas mixtures

To verify the consistency, reliability, and accuracy of the prepared reference gas mixtures with their gravimetric mole fractions, the reference gas mixtures were validated against other independently prepared reference gas mixtures. The ethanol reference gas mixtures were validated with the gas chromatography coupled with flame ionisation detector. One gas mixture was chosen as a reference to validate other prepared gas mixtures of ethanol with similar mole fraction. Using the single- or one-point calibration method, verification mole fraction was determined using equation 3.4. The uncertainty contribution of each sample was calculated from the repeatability measurements of the reference used and the sample together with the gravimetric uncertainty of the reference mixture. The gravimetric and verification mole fractions' comparison of ethanol are shown in Table 4.42.

The validation results in Table 4.42 show a % difference of less than 0.56 % absolute values for prepared ethanol reference gas mixtures with an overall uncertainty less than 0.15 µmol/mol. The percentage relative expanded uncertainty gave values between 2.43 to 2.99 % for ethanol reference gas mixtures. Therefore there was no deviation between the gravimetric and the verification values of ethanol in nitrogen reference gas mixtures and these mixtures met the validation criteria as set in Table 3.4 and can be further used for either preparation or as a reference.

Table 4.42: Validation data for ethanol in nitrogen primary standard gas mixtures using gas chromatography

Cylinder Number	Gravimetric mole fraction (µmol/mol)[1]	Gravimetric uncertainty (µmol/mol)[2]	Average verification mole fraction (µmol/mol)[3]	Verification uncertainty (µmol/mol)[4]	% Difference[5]	Combined Expanded uncertainty (U) (k=2)[6]	% Relative expanded uncertainty (%REU)[7]
M9 3950	5.00	0.01	5.02	0.07	-0.56	0.14	2.73
M9 3944	5.00	0.01	5.01	0.07	-0.18	0.14	2.85
M9 3862	4.98	0.01	5.01	0.06	-0.43	0.12	2.43
M39 5463	4.99	0.01	4.99	0.07	0.02	0.15	2.99

[1] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7 and represented by $\boldsymbol{x_g}$. [2] Associated standard uncertainty determined using the GRAVCALC software (Brown, 2009) and represented by $\boldsymbol{u_{xg}}$. [3] Verification mole fraction obtained from the verification results calculated using equation 3.4 and represented by $\boldsymbol{x_a}$. [4] Associated verification standard uncertainty obtained from the measurement repeatability and represented by $\boldsymbol{u_{xa}}$. [5] Percentage difference between the gravimetric and analytical value calculated using equation 3.13. [6] Combined expanded uncertainty from the gravimetric and analytical uncertainties calculated as $(\sqrt{\boldsymbol{2(u(x_g)^2 + u(x_a)^2}})$ using equation 2.19 and equation 3.14. [7] Percentage relative expanded uncertainty calculated using equation 3.16.

4.6.4 Internal consistency results of ethanol in nitrogen reference gas mixtures

The consistency of the ethanol in nitrogen reference gas mixtures with similar mole fraction was determined through an internal consistency study. Cylinder M9 3944 and M39 5463 with mole fraction of 5 µmol/mol ethanol in nitrogen were used as reference to carry out the internal consistency study. Table 4.43 and Table 4.44 show results of the consistency of ethanol in nitrogen reference mixtures. Figure 4.18 to 4.19 illustrates graphically the calculated sensitivity and sensitivity ratios for each sample and the reference when M9 3944 and M39 5463 were used as references, respectively.

The percentage deviation of the sensitivity ratios between the mixture samples and the reference mixture was between 0.63 to 7.19 % absolute values for reference gas mixtures of M9 3862, M9 3950 and M39 5463 when M9 3944 was used as a reference. When M39 5463 was used as a reference, percentage deviation in the sensitivity ratios between the mixture samples and the reference mixture was between 0.59 to 5.14 % absolute value for reference gas mixture of 5 µmol/mol ethanol in nitrogen. The prepared ethanol in nitrogen reference gas mixtures showed poor internal consistency amongst each other with significant difference from the gravimetric value.

Table 4.43: Internal consistency results of the analysis of ethanol in nitrogen using M9 3944 as a reference mixture

Cylinder number	Gravimetric mole fraction (µmol/mol)[1]	Average Response[2]	Sensitivity[3]	Sensitivity ratio[4]	% Difference[5]
M9 3944	5.001	22.268	4.453	1.000	Reference
M9 3862	4.984	20.704	4.154	0.991	7.192
M9 3950	4.997	22.392	4.481	1.030	-0.632
M39 5463	4.994	20.920	4.189	0.974	6.304

[1] Gravimetric value from the gravimetric preparation in accordance to ISO 6142 calculated using equation 2.7. [2] instrument response from the verification measurements represented by peak area. [3] Sensitivity is calculated by considering the peak area divide it by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [4] Sensitivity ratio is calculated by dividing the sensitivity of the sample by sensitivity of the reference calculated using equation 3.7. [5] Percentage difference between the sensitivity ratios of the reference and the sample.

Table 4.44: Internal consistency results of the analysis of ethanol in nitrogen using M39 5463 as a reference mixture

Cylinder number	Gravimetric mole fraction (μmol/mol)[1]	Average Response[2]	Sensitivity[3]	Sensitivity ratio[4]	% Difference[5]
M39 5463	4.994	20.943	4.194	1.000	Reference
M9 3862	4.984	21.024	4.218	1.026	-0.590
M9 3950	4.997	21.469	4.297	1.035	-2.397
M9 3944	5.001	22.107	4.421	1.018	-5.138

[1] Gravimetric value from the gravimetric preparation in accordance with ISO 6142 calculated using equation 2.7. [2] instrument response from the verification measurements represented by peak area. [3] Sensitivity is calculated by considering the peak area divide it by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [4] Sensitivity ratio is calculated by dividing the sensitivity of the sample by sensitivity of the reference calculated using equation 3.7. [5] Percentage difference between the sensitivity ratios of the reference and the sample.

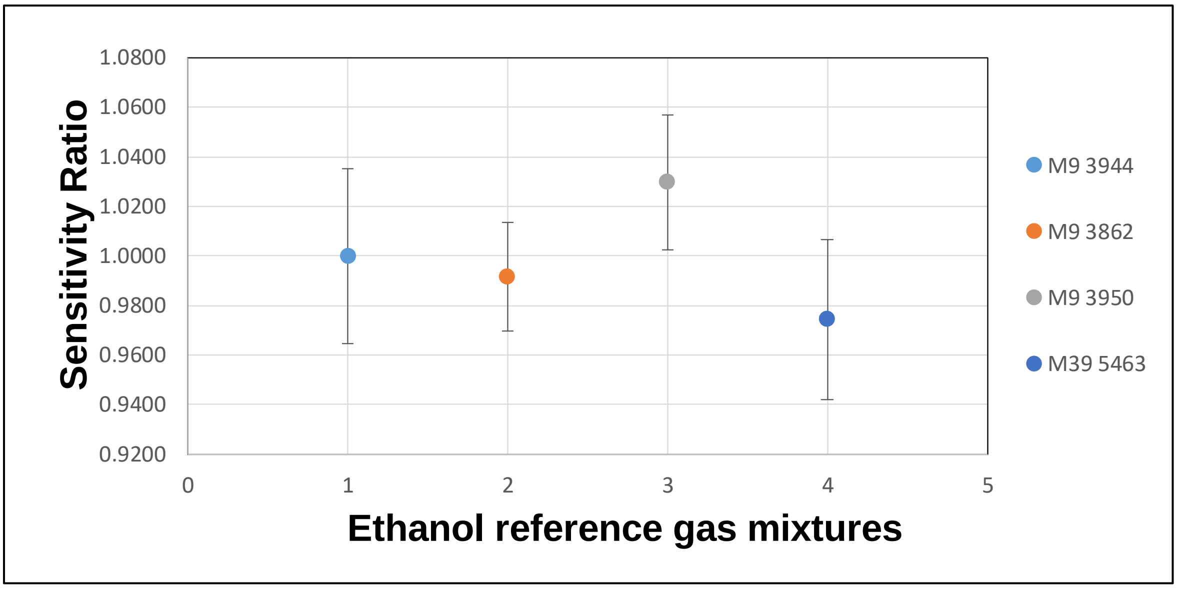


Figure 4.18: Internal consistency graph for ethanol in nitrogen reference gas mixtures using M9 3944 as a reference

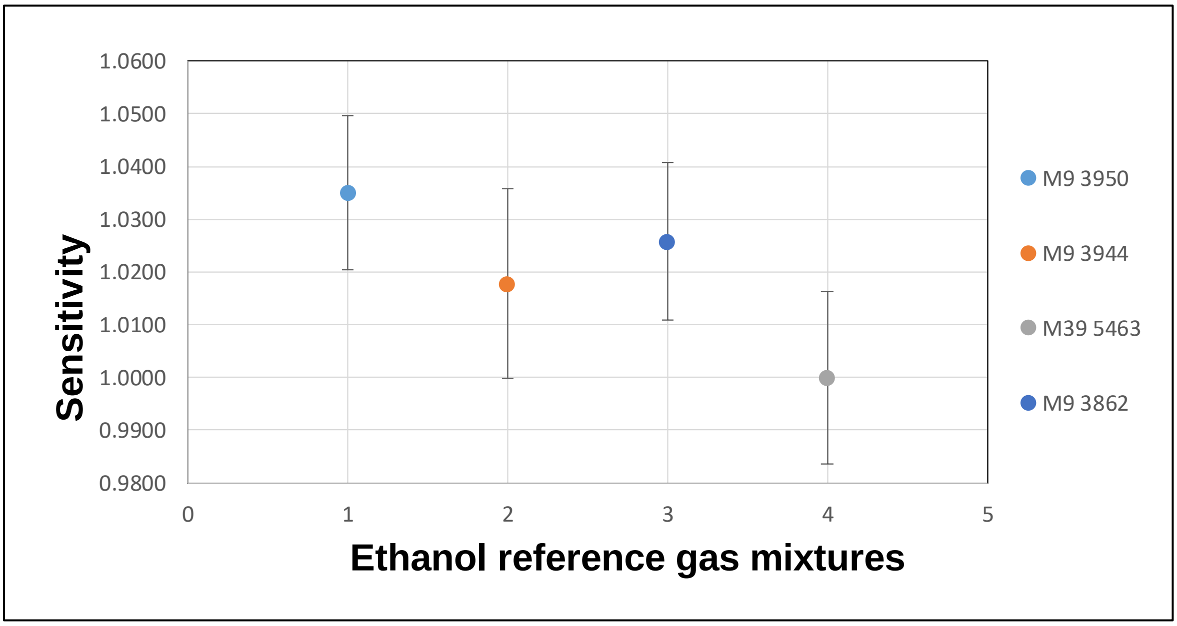


Figure 4.19: Internal consistency graph for ethanol in nitrogen reference gas mixtures using M39 5463 as a reference

4.7 MULTI-COMPONENT OF OVOCs IN NITROGEN REFERENCE GAS MIXTURES RESULTS

4.7.1 Gravimetric preparation of multi-component OVOCs reference gas mixtures

The multi-component of Oxygenated VOCs was gravimetrically prepared in a one-step dilution. Four OVOCs multi-component reference gas mixtures containing ($C_3H_6O/CH_3OH/C_2H_5OH/C_4H_9OH$) were prepared. Vapour pressures for these components are shown in Table 3.2 in chapter 3. The mole fraction for these gas mixtures was 5 µmol/mol of acetone, methanol ethanol and n-butanol in nitrogen reference gas mixtures. The gravimetric mole fraction and their associated gravimetric uncertainties for each multi-component mixture are shown in Table 4.45. The % REU for the prepared OVOCs gas mixtures was above 2.40 %.

Table 4.45: Gravimetric mole fraction and expanded uncertainty results of prepared OVOCs reference gas mixtures

Cylinder Number	Component	Gravimetric mole fraction (µmol/mol)[1]	Expanded uncertainty (µmol/mol)[2], k=2	Relative Expanded Uncertainty (% REU)[3]
D62 6448	Acetone	5.081	0.154	3.041
	Methanol	5.112	0.280	5.479
	Ethanol	5.635	0.195	3.457
	n-butanol	5.038	0.121	2.403
D62 6534	Acetone	7.194	0.199	2.766
	Methanol	5.564	0.361	6.483
	Ethanol	4.635	0.251	5.413
	n-butanol	4.842	0.156	3.218
D62 6567	Acetone	5.059	0.161	3.178
	Methanol	4.679	0.292	6.231
	Ethanol	4.998	0.203	4.057
	n-butanol	4.706	0.126	2.676
D62 6597	Acetone	4.302	0.150	3.476
	Methanol	4.179	0.271	6.488
	Ethanol	5.007	0.189	3.766
	n-butanol	4.747	0.117	2.468

[1] Gravimetrically prepared mole fraction of OVOCs was calculated using equation 2.7 in accordance with ISO 6142-1:2015. [2] Gravcalc software was used to determine the expanded uncertainty of the gravimetrically OVOCs in nitrogen reference gas mixtures at 95 % confidence level with coverage

factor of $k = 2$. [3]Equation 3.16 was used to determine the percentage relative expanded uncertainty (%REU) expressed as relative value of gravimetric uncertainty to the gravimetric mole fraction.

4.7.2 Method Optimisation for the verification of multi-component OVOCs on gas chromatography

The verification of the OVOCs was done on the gas chromatography coupled with flame ionisation detector (GC-FID). The elution order for the OVOCs gas mixture using GC-FID was according to increasing polarity of the substances and the size of the molecules with the alcohols with lower boiling points eluting first and higher boiling point alcohols eluting later (Lin *et al.*, 2014). Therefore for these OVOCs, acetone will elute first, and n-butanol elute last. Table 4.46 shows the boiling points of the selected OVOCs for this study.

Table 4.46: Boiling points for multi-component OVOCs (Source:[a]PubChem website)

Component	Boiling point in degrees Celsius (°C)
Acetone	56.1 °C
Methanol	64.7 °C
Ethanol	78.2 °C
n-Butanol	117.6 °C

[a]https://pubchem.ncbi.nlm.nih.gov/compound, assessed date 18 May 2020)

The OVOCs were run on temperature programming with 75 °C as initial temperature for 2.0 minutes and ramped at 20 °C/min to 100 °C for 1 minute to enhance better separation between acetone, methanol, and ethanol. Separation was achieved as illustrated in the chromatogram in figure 4.19.

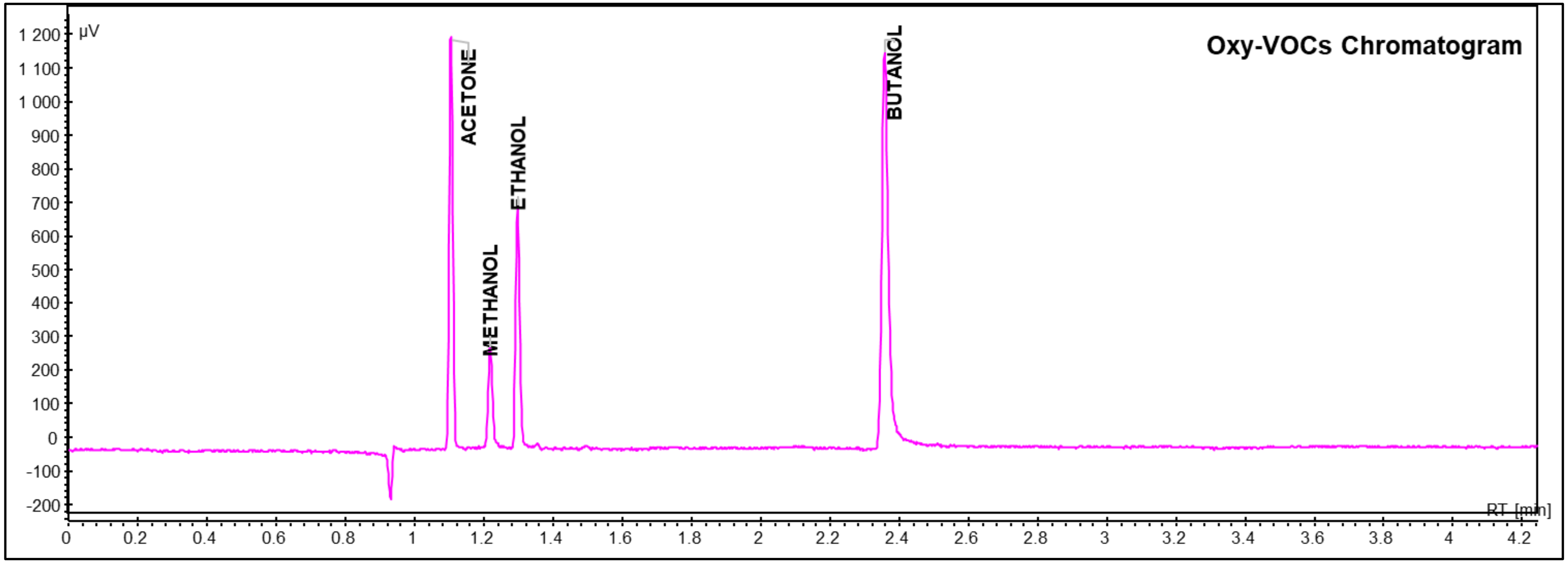


Figure 4.19: Chromatogram for the Oxygenated Volatile Organic Compounds in nitrogen verified on the GC-FID

4.7.3 Verification of multi-components OVOCs reference gas mixtures using gas chromatography

The OVOCs reference gas mixtures were analysed with gas chromatography coupled with flame ionisation detector with the substitution method where ‘A’ and ‘B’ represent the reference and sample, respectively. Thus the verification was done using one or single -point calibration method, where the reference mixture was analysed before and after the sample mixture. One of OVOCs reference gas mixture was used as a reference to monitor the changes during the verification and to monitor the drift of the instrument during the analysis. The comparison method was used to measure the consistency of the prepared reference gas mixture with similar mole fractions. The prepared OVOCs have similar mole fractions which differ by less than 1 % relative to one another. This is an important aspect when doing analysis with non-linear instruments because the uncertainty contribution from any deviation from linearity of the instrument response can then be ignored and considered insignificant. Data calculations included average response, verification mole fraction, % RSD, sensitivity and % deviation. Table 4.47 to Table 4.50 show the measurement results of different reference used for verification.

The % RSD was found to be higher than 1.21 % absolute value for all the mixtures of Oxy-VOC gas mixtures especially for the ethanol component in the multi-component mixture of acetone, methanol, ethanol, and n-butanol. Therefore the overall measurements show poor repeatability. Ethanol shows a deviation of more than 24 % absolute value from all the mixtures. This could be that ethanol is more hygroscopic and might have attracted some water from the air during gravimetric preparation. The deviation of acetone was observed to be between 0.65 to 13.74 % which still shows significant difference between the gravimetric mole fraction and verification mole fraction. Methanol also gave a larger deviation between the gas mixtures which ranged between 0.84 to 22.24 % absolute value. N-Butanol deviated from 0.28 to 4.99 % absolute value through the overall measurements showing significant difference between the gravimetric mole fraction and verification mole fraction. Thus the larger deviation in the measurements could be caused by the inconsistency in the gravimetric mole fraction during the preparation which affected the value assignment of the samples. Negative bias was observed when gas mixtures cylinder D62 6534 was used as reference, where most readings were lower than expected.

Table 4.47: Verification measurement results of the multi-component of OVOCs in nitrogen gas mixtures using D62 6567 as the reference

Cylinder Number	Component	Gravimetric mole fraction (μmol/mol)[1]	Instrument Average response[2]	% RSD[3]	Sensitivity[4]	Verification mole fraction (μmol/mol)[5]	% Difference[6]
D62 6567	Acetone	5.06	10.96	0.78	2.06	**Reference**	
	Methanol	4.68	3.43	1.54	0.66		
	Ethanol	5.00	8.17	1.03	1.53		
	n-butanol	4.71	25.33	1.71	4.98		
D62 6534	Acetone	7.19	15.26	0.52	2.12	7.06	1.93
	Methanol	5.56	4.17	1.18	0.75	5.68	-2.11
	Ethanol	4.63	10.01	0.62	2.16	6.15	-24.60
	n-butanol	4.84	25.93	1.37	5.35	4.87	-0.51
D62 6448	Acetone	5.08	10.87	0.70	2.14	5.05	0.65
	Methanol	5.11	3.79	1.67	0.74	5.38	-5.06
	Ethanol	5.63	8.83	1.10	1.57	5.74	-1.85
	n-butanol	5.04	27.60	1.66	5.48	5.30	-4.99
D62 6597	Acetone	4.30	8.88	0.78	2.07	4.09	5.16
	Methanol	4.18	3.49	1.62	0.84	4.81	-13.04
	Ethanol	5.01	8.15	0.90	1.63	4.98	0.56
	n-butanol	4.75	26.18	1.88	5.52	4.82	-1.49

[1]Mole fraction of the prepared multi- component of acetone, methanol, ethanol, and n-butanol gas mixtures was determined using equation 2.7 according to ISO 6142-1:2015. [2]instrument response from the analytical measurements represented by peak area. [3]Percentage relative standard deviation (%RSD) calculated using equation 3.9 as a measure of the measurement repeatability. [4]Sensitivity is calculated by considering the peak area divided by the mole

fraction using equation 3.5 and 3.6 for the reference and sample, respectively.[5]Analytical value obtained from the analytical results calculated using equation 3.4. [6]Percentage difference between the gravimetric and analytical value calculated using equation 3.11 to monitor the changes during analysis.

Table 4.48: Verification measurement results of the multi-component of OVOCs in nitrogen gas mixtures using D62 6448 as the reference

Cylinder Number	Component	Gravimetric mole fraction (μmol/mol)[1]	Instrument Average response	% RSD	Sensitivity	Verification mole fraction (μmol/mol)	% Difference
D62 6448	Acetone	5.08	10.91	0.99	2.21	**Reference**	
	Methanol	5.11	3.72	1.42	0.75		
	Ethanol	5.63	8.78	1.15	1.59		
	n-butanol	5.04	27.93	1.77	5.60		
D62 6534	Acetone	7.19	15.24	0.87	2.12	7.08	1.68
	Methanol	5.56	4.12	1.13	0.74	5.61	-0.84
	Ethanol	4.63	10.00	0.96	2.16	6.37	-27.25
	n-butanol	4.84	26.67	1.90	5.51	4.78	1.21
D62 6567	Acetone	5.06	10.89	0.62	2.15	5.08	-0.47
	Methanol	4.68	3.28	1.88	0.70	4.51	3.72
	Ethanol	5.00	7.92	1.78	1.59	5.13	-2.58
	n-butanol	4.71	25.12	2.86	5.34	4.52	4.14
D62 6597	Acetone	4.30	8.78	0.65	2.04	3.78	13.74
	Methanol	4.18	3.50	1.67	0.84	4.40	-5.07
	Ethanol	5.01	8.10	0.91	1.62	4.91	1.94
	n-butanol	4.75	26.26	1.44	5.53	4.65	2.18

[1]Mole fraction of the prepared multi- component of acetone, methanol, ethanol, and n-butanol gas mixtures was determined using equation 2.7 according to ISO 6142-1:2015. [2]instrument response from the analytical measurements represented by peak area. [3]Percentage relative standard deviation (%RSD)

calculated using equation 3.9 as a measure of the measurement repeatability. [4]Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively.[5]Analytical value obtained from the analytical results calculated using equation 3.4. [6]Percentage difference between the gravimetric and analytical value calculated using equation 3.11 to monitor the changes during analysis.

Table 4.49: Verification measurement results of the multi-component of OVOCs in nitrogen gas mixtures using D62 6597 as the reference

Cylinder Number	Component	Gravimetric mole fraction (µmol/mol)[1]	Instrument Average response	% RSD	Sensitivity	Verification mole fraction (µmol/mol)	% Difference
D62 6597	Acetone	4.30	8.72	0.68	2.03	**Reference**	
	Methanol	4.18	3.33	2.14	0.80		
	Ethanol	5.01	7.87	1.17	1.57		
	n-butanol	4.75	25.74	2.39	5.42		
D62 6534	Acetone	7.19	15.15	0.47	2.11	7.45	-3.47
	Methanol	5.56	4.06	1.47	0.74	5.13	8.39
	Ethanol	4.63	9.84	2.02	2.15	6.32	-26.71
	n-butanol	4.84	26.47	2.80	5.54	5.09	-4.84
D62 6448	Acetone	5.08	10.80	0.80	2.13	5.34	-4.77
	Methanol	5.11	3.40	3.02	0.67	4.18	22.24
	Ethanol	5.63	8.36	2.10	1.48	5.34	5.44
	n-butanol	5.04	27.83	1.51	5.52	4.95	1.78

[1]Mole fraction of the prepared multi- component of acetone, methanol, ethanol, and n-butanol gas mixtures was determined using equation 2.7 according to ISO 6142-1:2015. [2]instrument response from the analytical measurements represented by peak area. [3]Percentage relative standard deviation (%RSD) calculated using equation 3.9 as a measure of the measurement repeatability. [4]Sensitivity is calculated by considering the peak area divided by the mole

fraction using equation 3.5 and 3.6 for the reference and sample, respectively.[5]Analytical value obtained from the analytical results calculated using equation 3.4. [6]Percentage difference between the gravimetric and analytical value calculated using equation 3.11 to monitor the changes during analysis.

Table 4.50: Verification measurement results of the multi-component of OVOCs in nitrogen gas mixtures using D62 6534 as the reference

Cylinder Number	Component	Gravimetric mole fraction (µmol/mol)[1]	Instrument Average response	% RSD	Sensitivity	Verification mole fraction (µmol/mol)	% Difference
D62 6534	Acetone	7.19	15.17	0.52	2.11	**Reference**	
	Methanol	5.56	4.13	1.24	0.74		
	Ethanol	4.63	9.98	0.70	2.15		
	n-butanol	4.84	26.93	1.70	5.56		
D62 6448	Acetone	5.08	10.82	0.63	2.13	5.15	-1.39
	Methanol	5.11	3.65	1.77	0.71	4.96	3.12
	Ethanol	5.63	8.78	0.97	1.56	4.10	37.55
	n-butanol	5.04	28.00	2.28	5.56	5.02	0.28
D62 6567	Acetone	5.06	10.97	0.66	2.17	5.18	-2.30
	Methanol	4.68	3.37	0.44	0.72	4.53	3.38
	Ethanol	5.00	8.11	1.33	1.62	3.76	32.98
	n-butanol	4.71	25.75	2.11	5.47	4.62	1.89
D62 6597	Acetone	4.30	8.71	0.97	2.03	4.14	3.97
	Methanol	4.18	3.49	1.99	0.84	4.69	-10.85
	Ethanol	5.01	8.08	0.53	1.61	3.76	33.26
	n-butanol	4.75	26.58	1.69	5.60	4.83	-1.77

[1] Mole fraction of the prepared multi- component of acetone, methanol, ethanol, and n-butanol gas mixtures was determined using equation 2.7 according to ISO 6142-1:2015. [2] instrument response from the analytical measurements represented by peak area. [3] Percentage relative standard deviation (%RSD)

calculated using equation 3.9 as a measure of the measurement repeatability. [4] Sensitivity is calculated by considering the peak area divided by the mole fraction using equation 3.5 and 3.6 for the reference and sample, respectively. [5] Analytical value obtained from the analytical results calculated using equation 3.4. [6] Percentage difference between the gravimetric and analytical value calculated using equation 3.11 to monitor the changes during analysis

4.7.4 Validation of multi-components of OVOCs in nitrogen reference gas mixtures

To check the consistency, reliability, and accuracy of the prepared 5 µmol/mol OVOCs reference gas mixtures with their gravimetric mole fractions, the reference gas mixtures were validated against an independently prepared reference gas mixture of 5 µmol/mol. One gas mixture was chosen as a reference to validate the other prepared gas mixtures. Using the single- or one-point calibration method, verification mole fraction was determined using equation 3.4. The uncertainty contribution of each sample was calculated from the repeatability measurements of the reference used and the sample together with the gravimetric uncertainty of the reference mixture. The gravimetric and verification mole fractions' comparison of OVOCs are shown in Table 4.51. The percentage difference between gravimetric and verification mole fraction was calculated by (x_g - x_a) and found to be more than the calculated combined uncertainties form gravimetric preparation and verification measurements as illustrated in Table 4.51. Therefore the validation criteria as per Table 3.4 for the verified mixtures of OVOCs against a chosen reference were not met.

The final uncertainty which is the percentage relative expanded uncertainty from gravimetric uncertainty and verification uncertainty was calculated for all components of OVOCs in the gas mixtures. The % REU for acetone in the multi-component was between 3.0 to 9.3 %, n-butanol was between 4.5 to 7.1 %. Methanol and ethanol gave the highest overall uncertainty which ranged from 7.6 to 12.1 %. Large % REU were observed for methanol and ethanol in all the multi-component mixtures of OVOCs, which could be due to higher gravimetric uncertainties and hence deviation from the gravimetric mole fraction of these components were highest with ethanol at 29 to 38 % absolute values and methanol 2.4 to 8.8 % absolute values. The unaccounted losses of ethanol and methanol during the transfer of liquids into the cylinder resulted in large deviation and led to incorrect gravimetric mole fraction (Rappenglück *et al.*, 2006); (Rhoderick and Zielinski, 1988). The overall results show significant differences between gravimetric mole fraction and verification mole fraction of the components of OVOCs

Table 4.51: Validation results of 5 µmol/mol multi-component OVOCs in nitrogen primary standard gas mixtures using gas chromatography

Cylinder Number	Component	Gravimetric mole fraction (µmol/mol)[1]	Gravimetric uncertainty (µmol/mol)[2]	Verification mole fraction (µmol/mol)[3]	Verification uncertainty (µmol/mol)[4]	% Difference[5]	Combined Expanded uncertainty (U) (k=2)[6]	% Relative expanded uncertainty (%REU)[7]
D62 6448	Acetone	5.08	0.08	5.127	0.164	-0.90	0.33	6.38
	Methanol	5.11	0.14	4.994	0.252	2.37	0.50	10.07
	Ethanol	5.63	0.10	4.072	0.176	38.37	0.35	8.64
	n-butanol	5.04	0.06	5.031	0.113	0.13	0.23	4.51
D62 6567	Acetone	5.06	0.08	5.154	0.162	-1.84	0.32	6.30
	Methanol	4.68	0.15	4.488	0.271	4.25	0.54	12.07
	Ethanol	5.00	0.10	3.762	0.189	32.85	0.38	10.04
	n-butanol	4.71	0.06	4.583	0.115	2.69	0.23	5.04
D62 6534	Acetone	7.19	0.10	7.666	0.118	-6.16	0.24	3.08
	Methanol	5.56	0.18	5.875	0.224	-5.30	0.45	7.64
	Ethanol	4.63	0.13	6.528	0.161	-29.01	0.32	4.93
	n-butanol	4.84	0.08	4.985	0.125	-2.86	0.25	5.03
D62 6597	Acetone	4.30	0.07	4.144	0.192	3.80	0.38	9.25
	Methanol	4.18	0.14	4.581	0.271	-8.79	0.54	11.82
	Ethanol	5.01	0.09	3.697	0.188	35.44	0.38	10.17
	n-butanol	4.75	0.06	4.744	0.168	0.05	0.34	7.09

[1] Gravimetric value from the gravimetric preparation according to ISO 6142 calculated using equation 2.7 and represented by $\boldsymbol{x_g}$. [2] Associated standard uncertainty determined using the GRAVCALC software (Brown, 2009) and represented by $\boldsymbol{u_{xg}}$. [3] Verification mole fraction obtained from the verification results calculated using equation 3.4 and represented by $\boldsymbol{x_a}$. [4] Associated verification standard uncertainty obtained from the measurement repeatability and represented by $\boldsymbol{u_{xa}}$. [5] Percentage difference between the gravimetric and analytical value calculated using equation 3.13. [6] Combined expanded uncertainty

from the gravimetric and analytical uncertainties calculated as $(\sqrt{\boldsymbol{2(u(x_g)^2 + u(x_a)^2}})$ using equation 2.19 and equation 3.14. [7]Percentage relative expanded uncertainty calculated using equation 3.16.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

This chapter will provide a summary, conclusion of this dissertation in relation to the development of primary standard gas mixtures of the selected sulphur compounds and oxygenated volatile organic compounds gas mixtures. Because of the fast-growing technology, this chapter will give some recommendations and also future improvements.

5.1 CONCLUSION

The air quality monitoring industry in South Africa requires accurate and traceable reference gas mixtures for reliable measurements of selected sulphur compounds and oxygenated volatile organic compounds. This study aimed to develop primary reference gas mixtures of selected sulphur compounds and OVOCs. The selected components were hydrogen sulphide, sulphur dioxide, acetone, methanol, ethanol, isopropanol, and n-butanol at 10 µmol/mol for sulphur compounds, 5 µmol/mol for OVOCs except for isopropanol which was produced at 200 µmol/mol. Qualitative and quantitative measurements methods of reference gas mixtures are continuously developed to ensure the quality of measurement results. The sulphur compounds of hydrogen sulphide and sulphur dioxide and oxygenated volatile organic compounds of acetone, methanol, ethanol, isopropanol, and n-butanol in nitrogen were successfully produced gravimetrically in accordance with International Organization for Standardization ISO 6142-1:2015. The first step in producing the reference gas mixtures of sulphur compounds and OVOCs included the purity assessment of the high purity gases and chemicals using gas chromatograph coupled with different detectors and the coulometric method for analysis of moisture content.

The purity assessment results for high purity Built-in-purifier (BIP^{TM}) nitrogen used as diluent gas was above 99.99 % mol/mol. For high purity sulphur dioxide and hydrogen sulphide results were 94.7 % mol/mol and 99.7 % mol/mol, respectively. The purity assessment results for ethanol were 99.9 % mol/mol with only moisture content analysed and for the other impurities were calculated using manufacturer’s specification. The other high purity chemicals were calculated using rectangular distribution because manufacture’s specification was used with mostly water reported as the major impurity for the OVOCs. The gravimetric preparation of 10 and 5 µmol/mol for sulphur compounds and ethanol respectively was done using multiple - steps dilution to achieve the final target mole fraction being prepared. The single – step dilution method was used for the preparation of binary and multi-components gas mixtures of OVOCs from liquid chemicals.

The primary standard gas mixtures of sulphur compounds at mole fraction of 10 µmol/mol were successfully prepared with percentage relative expanded uncertainty of less than 0.12 % REU for sulphur dioxide, less than 0.041 % REU for newly prepared hydrogen sulphide and less than 2.1 % REU for previously prepared hydrogen sulphide. The primary standard gas mixtures of oxygenated volatile organic compounds at mole fraction of 5 µmol/mol were successfully produced with a relative expanded uncertainty of less than 0.068 % REU for isopropanol, less than 0.35 % for ethanol and more than 2.4 % REU for multi-component of OVOCs. The OVOCs were analysed by gas chromatography coupled with flame ionisation detector using a single-point calibration method. The analysis of sulphur compounds was done using a gas chromatography coupled with pulsed discharge helium ionisation detector (GC-PDHID), Non-dispersive ultraviolet (NDUV) analyser and Ultraviolet (UV) fluorescence analysers. The analytical method on the GC-PDHID and UV Fluorescence used was a one-point calibration method and multi-point calibration was used for NDUV.

In order to determine the agreement between the gravimetric value and analytical value, internal consistency of the sulphur compounds and OVOCs was performed. Thus the final percentage relative expanded uncertainty for both gravimetric and analytical uncertainty was calculated to be 1.2 % REU for H_2S, 0.49 to 0.52 % REU SO_2 on NDUV and 0.16 to 0.26 % SO_2 on UV fluorescence. The final percentage relative expanded uncertainty for OVOCs were in the range of 0.37 to 0.50 % REU for isopropanol, 2.4 to 3.0 % REU for ethanol and 3.1 to 12 % REU for the multi-component of OVOCs. The larger uncertainties from ethanol and methanol are ascribed to the challenges encountered during the gravimetric preparation process with losses during transferring of liquid chemicals to the gas cylinder and thus led to incorrect gravimetric mole fractions. This resulted in a huge difference for ethanol and methanol during the analytical measurements. It was observed that the % REU for ethanol binary were less than 3.0% compared to the measurements of ethanol in the multi-components of OVOCs. This could be the different gravimetric preparation methods used. For ethanol binary the multi-steps dilution method was used and hence for the multi-components of OVOCs, single-step dilution method was used for the lower mole fraction targeted. This resulted in some major errors during preparation of the OVOCs. Therefore single-step dilution for lower mole fraction of OVOCs is not recommended.

Stability assessment was done to monitor the behaviour of gravimetrically prepared reference gas mixtures. In this study, only hydrogen sulphide reference gas mixture was monitored for stability and the results showed that H_2S gas mixtures can be stable over a period of 2 years within the measurement uncertainty of 1 %. The adsorption/desorption study was conducted to assess the effect of adsorption/desorption of hydrogen sulphide on the inner surfaces of the aluminium cylinder. In this study, a mole fraction of 10 µmol/mol hydrogen sulphide was used for the assessment and results showed that uncertainty measurement of adsorption/desorption was calculated to be 0.039 %. Thus concluding no adsorption of hydrogen sulphide on the inner surface of the aluminium cylinder. Therefore a proper understanding of the behaviour of sulphur compounds and OVOCs is needed when preparing these components. The development of selected sulphur compounds and oxygenated volatile organic compounds was successfully achieved.

5.2 RECOMMENDATION AND FUTURE WORK

The sulphur compounds reference gas mixtures have been developed by different national metrology institutes especially at lower mole fractions of parts per billion (ppb) level. Therefore further work needs to be done to prepare sulphur compounds at ppb level in South Africa in support of the ambient air quality monitoring measurements. Also further work on sulphur compounds should include adsorption and stability studies for all the developed sulphur compounds. The developed reference gas mixtures of OVOCs supports the law enforcement industry and also field of gas sensing. Future work on OVOCs should include stability and adsorption studies of these components.

It is recommended that other selected sulphur compounds reference gas mixtures such as dimethyl sulphide (DMS) and ethyl mercaptans be developed in support of air quality monitoring industry. A recommendation is made that development of low mole fraction of OVOCs reference gas mixtures be done with multi-steps dilution to avoid losses during preparation process.

CHAPTER 6: REFERENCES

In this chapter, it will detail all the references/sources used to compile and complete this research study.

6.1 REFERENCE LIST

Abdelhalim, M. A. K., Moussa, S. A. A. and Al-Mohy, Y. H. (2013) ‘Ultraviolet-visible and fluorescence spectroscopy techniques are important diagnostic tools during the progression of atherosclerosis: Diet Zinc Supplementation Retarded or Delayed Atherosclerosis’, *BioMed Research International*, 2013, pp 1-8

Alink, A. and Van Der Veen, A. M. H. (2000) Uncertainty calculations for the preparation of primary gas mixtures Part 1: Gravimetry, *Metrologia*, 37, pp 641-650.

ASTM Standard, E1064-16, (2016), 'Standard test method for water in Organic Liquids by Coulometric Karl Fischer Titration', *ASTM International*, (West Conshohocken),

BIPM, IEC, ILAC IFCC, IUPAC, ISO, OIML and IUPAP (2012) International vocabulary of metrology-Basic and general concepts and associated terms (VIM) (Sèvres: JCGM 200:2012).

BIPM, IEC, ILAC IFCC, IUPAC, ISO, OIML and IUPAP 2008 Evaluation of measurement data- Guide to the expression of uncertainty in measurement (JCGM 100:2008).

BIPM, IEC, IFCC, IUPAC, IUPAP and OIML (1995) Guide to the Expression of Uncertainty in Measurement, 2nd Ed.

Bose, A., Thomas, I, Kavitha G. and Abraham, E. (2018) ‘Fluorescence spectroscopy and its applications: A Review', *International Journal of Advances in Pharmaceutical Analysis*, 08, pp 01-08.

Brewer, P. J., Miñarro, M. D., Di Meane, E. A. and Brown, R. J. C. (2014) ‘A high accuracy dilution system for generating low concentration reference standards of reactive gases’, *Measurement: Journal of the International Measurement Confederation*, 47(1), pp 607–612.

Brown, A. (2009) *NPL REPORT AS 42 GravCalc2 (version 2.3.0) User Guide*.

Brown, A. S, Brookes, C, Downey, M.L, Augusto, C.R, Sobrinho, D.G, Woo, J.C, Kim, J.S, Fűkő, J.T, Guenther, F, Gameson, L, Tshilongo, J, Val'ková, M, Kustikov, Y, Fatina, O, Milton, M.J.T, Vargha, G.M, Uehara, S, De Lima Fioravante, A, Dias, F, Kim, B.M, Mace, T, Qiao, H, Rhoderick, J, Botha, A, Ntsasa, N.G, Durisova, Z, Konopelko, L and Wessel, R.. (2013) 'Final report on CCQM-K93: Preparative comparison of ethanol in nitrogen', *Metrologia Technical Supplement*, 50, 08025

Brown, A. S., Van Der Veen, A. M. H., Arrhenius, K., Downey, M. L., Kühnemuth, D., Li, J., Ent, H. and Culleton, L. P. (2014) ‘Traceable reference gas mixtures for sulfur-free natural gas odorants’, *Analytical Chemistry*. American Chemical Society, 86(13), pp. 6695–6702. doi: 10.1021/ac501525d.

Brown, A. S., van der Veen, A. M. H., Arrhenius, K., Murugan, A., Culleton, L. P., Ziel, P. R. and Li, J. (2015) ‘Sampling of gaseous sulfur-containing compounds at low concentrations with a review of best-practice methods for biogas and natural gas applications’, *TrAC - Trends in Analytical Chemistry*, 64, pp. 42–52. doi: 10.1016/j.trac.2014.08.012.

Brown, R. J. C., Brewer, P. J., Harris, P. M., Davidson, S., Van Der Veen, A. M. H. and Ent, H. (2017) ‘On the traceability of gaseous reference materials’, *Metrologia*, 54(3), pp. L11–L18. doi: 10.1088/1681-7575/aa6ede.

Davenport, J. J., Hodgkinson, J., Saffell, J. R. and Tatam, R. P. (2018) ‘Non-Dispersive Ultra-Violet Spectroscopic Detection of Formaldehyde Gas for Indoor Environments’, *IEEE Sensors Journal*, 18(6), pp. 2218–2228. doi: 10.1109/JSEN.2018.2795042.

Demirbas, A. (2008) ‘Biofuels sources, biofuel policy, biofuel economy and global biofuel projections’, *Energy Conversion and Management*, 49(8), pp. 2106–2116. doi: 10.1016/j.enconman.2008.02.020.

Eurachem/CITAC Working Group., Ellison, S. L. R., Rosslein, M. and Williams, A., Eurachem. and Co-operation on International Traceability in Analytical Chemistry. (2000) *Quantifying uncertainty in analytical measurement.* Eurachem.

Grenfell, R. J. P., Milton, M. J. T., Harling, A. M., Vargha, G. M., Brookes, C., Quincey, P. G. and Woods, P. T. (2010) ‘Standard mixtures of ambient volatile organic compounds in synthetic and whole air with stable reference values’, *Journal of Geophysical Research Atmospheres*, 115(14), D14302, doi: 10.1029/2009JD012933.

Guenther, F. R., Kelley, M. E., Mitchell, G.D., De Jesus Avila Salas, M., Delgado, K., Murillo, F.R., Caballero, V.M.S., Castorena, A.P., Shinji, U., Ciecior, D., Da Cunha, V.S., Augusto, C.R., Ribeiro, C.C., De Lima Fioravante, A., Dias, F., Sang-Hyub, O., Mace, T., Sutour, C., Bűki, T., Qiao, H., Botha, A., Mogale, D.M., Tshilongo, J., Ntsasa, N., Mphamo, T., Uprichard, I., Milton, M., Vargha, G., Brookes, C., Johri, P., Valkova, I.M., Konopelko, L., Kustikov, Y., Pankratov, V.V., Rumyantsev, D.V., Pavlov, M.V., Gromova, E.V., Van der Veen, A., Van Otterloo, P. and Wessel, R.M. (2011) 'International Comparison CCQM-K76: Sulfur Dioxide in Nitrogen', *Metrlogia Technical Supplement*, 48, 08015.

Guenther, F. R., Miller, W. R., Duewer, D. L., Heo, G. S., Kim, Y.-D., Van Der Veen, A. M. H., Konopelko, L., Kustikov, Y., Shor, N., Brookes, C., Milton, M., Dias, F. and Qiao, H. (2007) 'International Comparison CCQM-K41: Hydrogen sulfide in nitrogen', *Metrologia Technical Supplement*, 44,08004.

Hindayani, A., Zuas, O., Mulyana, M. R., Budiman, H., Styarini, D., Herwahyu Krismastuti, F. S. and Sirenden, B. H. (2019) ‘Validated method for trace impurities analysis in bulk gas using Gas Chromatography with Pulse Discharge Helium Ionization Detection’, *Journal of Physics: Conference Series*, 1153, doi: 10.1088/1742-6596/1153/1/012033.

Holland, P. E., Woods, P. T., Brookes, C., Uprichard, I., Quincey, P., Robinson, R., D’Souza, H., Milton, M., Goody, B., Bell, W. and Alphonso, D. (2005) ‘The development of gas standards and calibration techniques for measurements of vehicle, aircraft and industrial emissions, natural gas, occupational exposure and air quality’, *Traceability in Chemical Measurement*, 6, pp. 212–221. doi: 10.1007/3-540-27093-0_35.

Hu, S., Wu, H., Wang, D. and Li, J. (2013) ‘A transfer technique of small amount of gas for the preparation of standard gas mixtures’, *Measurement: Journal of the International Measurement Confederation*.., 46(3), pp. 1084–1088. doi: 10.1016/j.measurement.2012.11.002.

International Organization for Standardization, ISO 6145-1: 2003 – Gas Analysis-Preparation of calibration gas mixtures using dynamic volumetric methods-Part 1: Methods of calibration (Geneva: ISO).

International Organization for Standardization, ISO GUIDE 98-3: 2008 – Uncertainty of measurement-Part 3: Guide to the expression of uncertainty in measurement (GUM:1995) (Geneva:ISO).

International Organization for Standardization, ISO 6143:2001 Gas Analysis – Comparison Methods for Determining and Checking the Composition of Calibration Gas Mixtures (Geneva: ISO).

International Standard, ISO 17034: 2016 General requirements for the competence of reference material producers (Geneva: ISO).

International Organization for Standardization, ISO 19229-1: 2015 Gas Analysis – Purity analysis and the treatment of purity data (Geneva: ISO).

International Organization for Standardization, ISO 6142-1: 2015 Gas Analysis – Preparation of Calibration Gas Mixtures – Part 1: Gravimetric Method for Class I Mixtures (Geneva: ISO).

International Organization for Standardization, ISO 17034: 2016 General requirements for the competence of reference material producers (Geneva: ISO).

International Organization for Standardization, ISO 12963: 2017 – Gas Analysis-Comparison methods for the determination of the composition of gas mixtures based on one- and two-point calibration (Geneva: ISO).

Janse van Rensburg, M., Botha, A. and Rohwer, E. (2007) ‘Analysis of trace amounts of carbon dioxide, oxygen and carbon monoxide in nitrogen using dual capillary columns and a pulsed discharge helium ionisation detector’, *Journal of Chromatography A*, 1167(1), pp. 102–108. doi: 10.1016/j.chroma.2007.07.055.

Kampa, M. and Castanas, E. (2008) ‘Human health effects of air pollution’, *Environmental Pollution*, 151, pp. 362–367. doi: 10.1016/j.envpol.2007.06.012.

Kim, Y. D., Heo, G. S., Lee, S., Han, Q., Wu, H., Konopelko, L.A., Kustikov, Y.A, Malginov, A.V., Gromova, E.V., Pankratov, V.V., Pavlov, M.V and Botha, A (2014), 'Final report on international key comparison APMP.QM-K41: 10 µmol/mol hydrogen sulfide in nitrogen', *Metrologia Technical Supplement*, 51, 08012.

Kim D, Kim YD, Lee S, Smeulders D, Wu H, Fuko J, van Wijk JIT, va der Veen AMH, Tshilongo J, Dias F, Costa C, Konopelko L, Efremova O & Bartlett S 2017: International Comparison CCQM-K41.2017- Hydrogen sulphide in nitrogen, Draft A Report. Republic of Korea: Korea Research Institute of Standards and Science.

Kovalevsky, Jean and Kovalevsky, J (2000) 'The consequences of the mutual recognition of measurement standards for international metrology', *Accreditation and Quality Assurance*, 5, pp 409-413.

Lee, J. Y., Marti, K., Severinghaus, J. P., Kawamura, K., Yoo, H. S., Lee, J. B. and Kim, J. S. (2006) ‘A redetermination of the isotopic abundances of atmospheric Ar’, *Geochimica et Cosmochimica Acta*, 70(17), pp. 4507–4512. doi: 10.1016/j.gca.2006.06.1563.

Lee, S., Kim, M. E., Oh, S. H. and Kim, J. S. (2017) ‘Determination of physical adsorption loss of primary standard gas mixtures in cylinders using cylinder-to-cylinder division’, *Metrologia*, 54(6): pp. L26–L33. doi: 10.1088/1681-7575/aa87b8.

Legreid, G., Lööv, J. B., Staehelin, J., Hueglin, C., Hill, M., Buchmann, B., Prevot, A. S. H. and Reimann, S. (2007) ‘Oxygenated volatile organic compounds (OVOCs) at an urban background site in Zürich (Europe): Seasonal variation and source allocation’, *Atmospheric Environment*, 41(38), pp. 8409–8423. doi: 10.1016/j.atmosenv.2007.07.026.

Leuenberger, M. C., Schibig, M. F. and Nyfeler, P. (2015) ‘Gas adsorption and desorption effects on cylinders and their importance for long-term gas records’, *Atmospheric Measurement Techniques Discussion*, 8(8), pp. 8083–8112. doi: 10.5194/amtd-8-8083-2015.

Lewtas, J. (2007) ‘Air pollution combustion emissions: Characterization of causative agents and mechanisms associated with cancer, reproductive, and cardiovascular effects’, *Mutation Research - Reviews in Mutation Research*, 63,: pp. 95–133. doi: 10.1016/j.mrrev.2007.08.003.

Lin, X., Fan, J., Wen, Q., Li, R., Jin, X., Wu, J., Qian, W., Liu, D., Xie, J., Bai, J. and Ying, H. (2014) ‘Optimization and validation of a GCFID method for the determination of acetone-butanol-ethanol fermentation products’, *Journal of Chromatographic Science*, 52(3), pp. 264–270. doi: 10.1093/chromsci/bmt022.

Makoś, P., Przyjazny, A. and Boczkaj, G. (2019) ‘Methods of assaying volatile oxygenated organic compounds in effluent samples by gas chromatography—A review’, *Journal of Chromatography.*, 1592: pp.143–160. doi: 10.1016/j.chroma.2019.01.045.

Marić, I. (2005) ‘The Joule-Thomson effect in natural gas flow-rate measurements’, *Flow Measurement and Instrumentation*, 16(6), pp. 387–395. doi: 10.1016/j.flowmeasinst.2005.04.006.

Martinez, S., Chemist, I. and Pijpelink, J. (2012) *Protect Natural Gas Sample Integrity and Prevent Sulfur Loss with Sulfinert® Sample Cylinders Innovative*

Chromatography Solutions. Available at: www.restek.com.

Matsumoto, N., Watanabe, T., Maruyama, M., Horimoto, Y., Maeda, T. and Kato, K. (2004) ‘Development of mass measurement equipment using an electronic mass-comparator for gravimetric preparation of reference gas mixtures’, *Metrologia*, 41(3), pp. 178–188. doi: 10.1088/0026-1394/41/3/011.

Mellouki, A., Wallington, T, Chen, J. and Wallington, TJ (2015) ‘Atmospheric Chemistry of Oxygenated Volatile Organic Com-pounds (OVOCs): Impacts on Air Quality and Climate’, *Chemical Reviews*, 115(10), pp 3984-4014,. doi: 10.1021/cr500549nï.

Miller, W. R. and Guenther, F. R. (2007) ‘The certification of a nominal 20 µmol/mol H2S/N2 standard reference material using two independent methods’, in *Analytical and Bioanalytical Chemistry*, 387(7), pp. 2433–2439. doi: 10.1007/s00216-006-1056-3.

Milton, M. J. T. and Quinn, T. J. (2001) *Primary methods for the measurement of amount of substance*. *Metrologia*, 38(4), pp. 289–296. doi:10.1088/0026-1394/38/4/1

Milton, M. J. T., Vargha, G. M. and Brown, A. S. (2011) ‘Gravimetric methods for the preparation of standard gas mixtures’, *Metrologia*, 48(5). pp. R1-R5. doi: 10.1088/0026-1394/48/5/R01.

Mokhatab, S. and Mak, J. Y. (2015) Handbook of Natural Gas Transmission and Processing., *Nitrogen Content Basic Concepts of Natural Gas Process-ing.* 3rd Edition., Elsevier Inc., *pp.* 123-135.doi.org/10.1016/B978-0-12-801499-8.00003-1.

Naidoo, S., Piketh, S. and Curtis, C. (2015) *Domestic Fuel Combustion in Un-electrified Low-income Settlements in South Africa*.

National Environmental Management 2004: Air Quality Act (Act No. 39 of 2004). South Africa: Government Notice.

Park, S. Y., Kim, J. S., Lee, J. B., Esler, M. B., Davis, R. S. and Wielgosz, R. I. (2004) ‘A redetermination of the argon content of air for buoyancy corrections in mass standard comparisons’, *Metrologia*, 41(6), pp. 387–395. doi: 10.1088/0026-1394/41/6/005.

Persijn, S. (2018) ‘Purity Analysis of Gases Used in the Preparation of Reference Gas Standards Using a Versatile OPO-Based CRDS Spectrometer’, *Journal of Spectroscopy*. Hindawi Limited, 2018. doi: 10.1155/2018/9845608.

Poole, C. F. (2015) ‘Ionization-based detectors for gas chromatography’, *Journal of Chromatography A*. Elsevier B.V., pp.137–153. doi: 10.1016/j.chroma.2015.02.061.

Preece SLM, Casey KD & Auvermann BW 2012: Hydrogen sulphide emissions from open/dry-lot cattle-feeding operations. Air quality education in animal agriculture. United State of America: Texas.

Radzi Bin Abas, M., Oros, D. R. and Simoneit, B. R. T. (2004) ‘Biomass burning as the main source of organic aerosol particulate matter in Malaysia during haze episodes’, *Chemosphere*, 55(8), pp.1089-1095. doi: 10.1016/j.chemosphere.2004.02.002.

Rappenglück, B., Apel, E., Bauerfeind, M., Bottenheim, J., Brickell, P., Čavolka, P., Cech, J., Gatti, L., Hakola, H., Honzak, J., Junek, R., Martin, D., Noone, C., Plass-Dülmer, C., Travers, D. and Wang, D. (2006) ‘The first VOC intercomparison exercise within the Global Atmosphere Watch (GAW)’, *Atmospheric Environment*, 40(39), pp. 7508–7527. doi: 10.1016/j.atmosenv.2006.07.016.

Rhoderick, G. C., Cecelski, C. E., Miller, W. R., Worton, D. R., Moreno, S., Brewer, P. J., Viallon, J., Idrees, F., Moussay, P., Kim, Y. D., Kim, D., Lee, S., Baldan, A. and Li, J. (2019) ‘Stability of gaseous volatile organic compounds contained in gas cylinders with different internal wall treatments’, *Elementa*. University of California Press, 7(1). doi: 10.1525/elementa.366.

Rhoderick, G. C. and Zielinski, W. L. (1988) ‘Preparation of Accurate Multicomponent Gas Standards of Volatile Toxic Organic Compounds in the Low-Parts-per-Billion Range’, *Analytical Chemistry*, 60(22), pp. 2454–2460. doi: 10.1021/ac00173a004.

Robinson, E. and Robbins, R. C. (1970) ‘Gaseous sulfur pollutants from urban and natural sources’, *Journal of the Air Pollution Control Association*, 20(4), pp. 233–235. doi: 10.1080/00022470.1970.10469396.

Schultz, M. G., Akimoto, H., Bottenheim, J., Buchmann, B., Galbally, I. E., Gilge, S., Helmig, D., Koide, H., Lewis, A. C., Novelli, P. C., Plass-Dölmer, C., Ryerson, T. B., Steinbacher, M., Steinbrecher, R., Tarasova, O., Tørseth, K., Thouret, V. and Zellweger, C. (2015) ‘The global atmosphere watch reactive gases measurement network', *Elementa*. BioOne, 3, pp. 1–23. doi: 10.12952/journal.elementa.000067.

Słomińska, M., Konieczka, P. and Namieśnik, J. (2014) 'New developments in preparation and use of standard gas mixtures', *TrAC - Trends in Analytical Chemistry*., 62., pp. 135–143. doi: 10.1016/j.trac.2014.07.013.

Skoog, D.A., Holler, F.J. and Crouch, S.R. (2007) '*Principles of Instrumental Analysis,* 6th edition, Belmont, Harris

Smith, I. M. and Onakunle, F. O. (2007) *XLGENLINE Version 1.0-Software Documentation*.

Tirpitz, J. L., Pöhler, D., Bobrowski, N., Christenson, B., Rüdiger, J., Schmitt, S. and Platt, U. (2019) 'Non-dispersive uv absorption spectroscopy: A promising new approach for In-situ detection of sulfur dioxide', *Frontiers in Earth Science*, 7(March), pp. 1–15. doi: 10.3389/feart.2019.00026.

Trapmann, S., Botha, A., Linsinger, T. P. J., Mac Curtain, S. and Emons, H. (2017) 'The new International Standard ISO 17034: general requirements for the competence of reference material producers', *Accreditation and Quality Assurance*. Springer New York LLC, 22(6), pp. 381–387. doi: 10.1007/s00769-017-1285-5.

Vögtlin Instruments AG. (2013), Get red-y 5 software (version:get_redy_E1_5) operating instructions.

Yang, I., Lee, J. B., Moon, D. M. and Kim, J. S. (2017) 'Preparation of primary reference material of argon in oxygen by the gravimetric method for application to thermometry', *Metrologia*. Institute of Physics Publishing, 54(2), pp. 184–192. doi: 10.1088/1681-7575/aa5894.

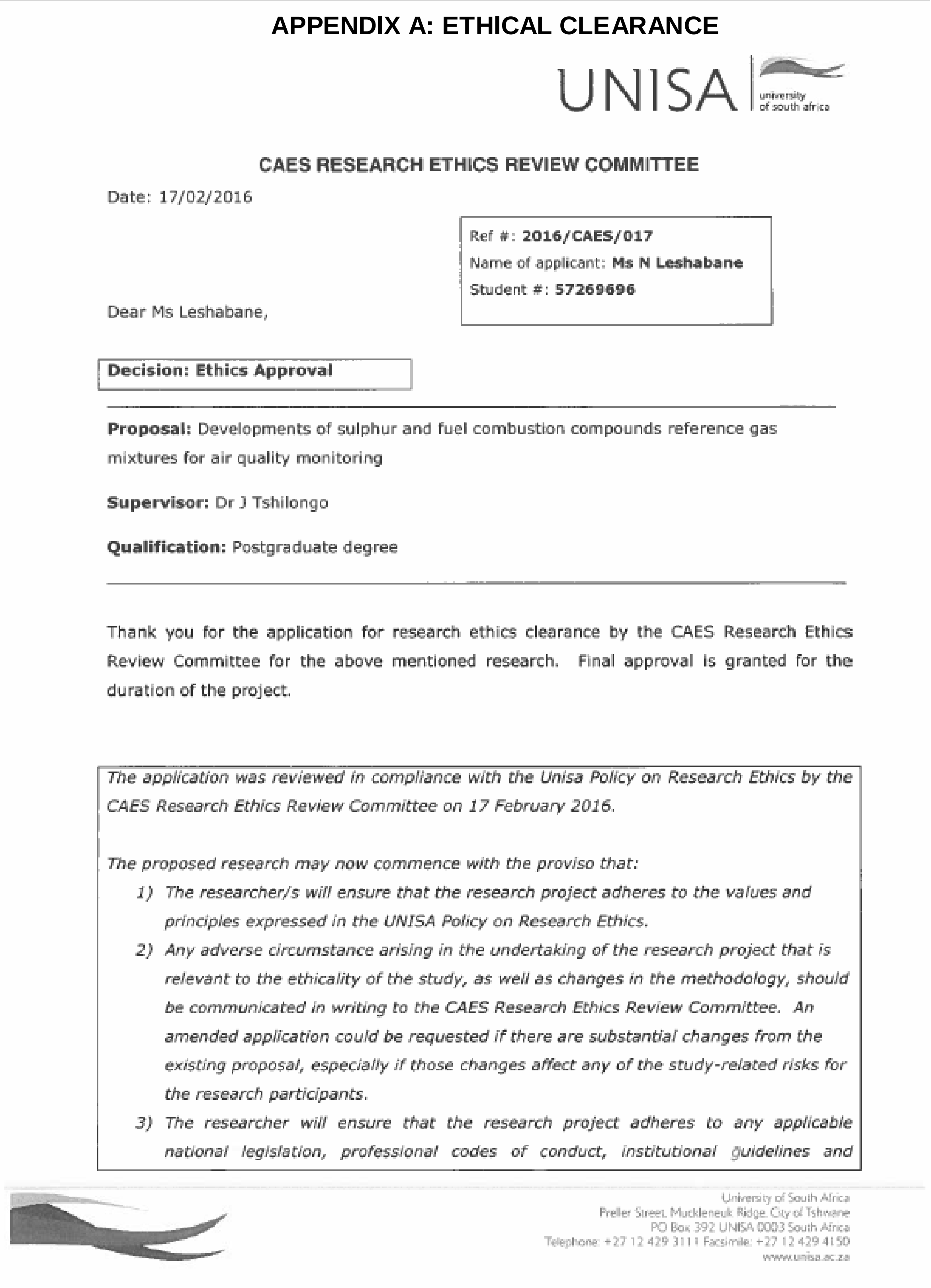
Zheng, F., Xin, Z., Zhi'ang, L., Fanfeng, D., Liaoyu, D. and Liwen, Z. (2019) 'Application of the loop method to the preparation of gas reference material, NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/)'. doi: 10.3787/j.issn.

Zuas, O. and Budiman, H. (2016) 'Procenjivanje perciznosti i tačnosti GC-TCD metode za odredjivanje ugljen-dioksida, propana i ugljen-monoksida pri različitim protocima gasnog nosača', *Hemijska Industrija*. Association of Chemists and Chemical Engineers of Serbia, 70(4), pp. 451–459. doi: 10.2298/HEMIND150315051Z

APPENDICES

This chapter will detail all relevant information or supporting information which has been considered or deemed important for this study. More important, the Turn-it-in, the ethical clearance and the intention to submit.

APPENDIX A: ETHICAL CLEARANCE



UNISA university of south africa

CAES RESEARCH ETHICS REVIEW COMMITTEE

Date: 17/02/2016

Ref #: **2016/CAES/017**
Name of applicant: **Ms N Leshabane**
Student #: **57269696**

Dear Ms Leshabane,

Decision: Ethics Approval

Proposal: Developments of sulphur and fuel combustion compounds reference gas mixtures for air quality monitoring

Supervisor: Dr J Tshilongo

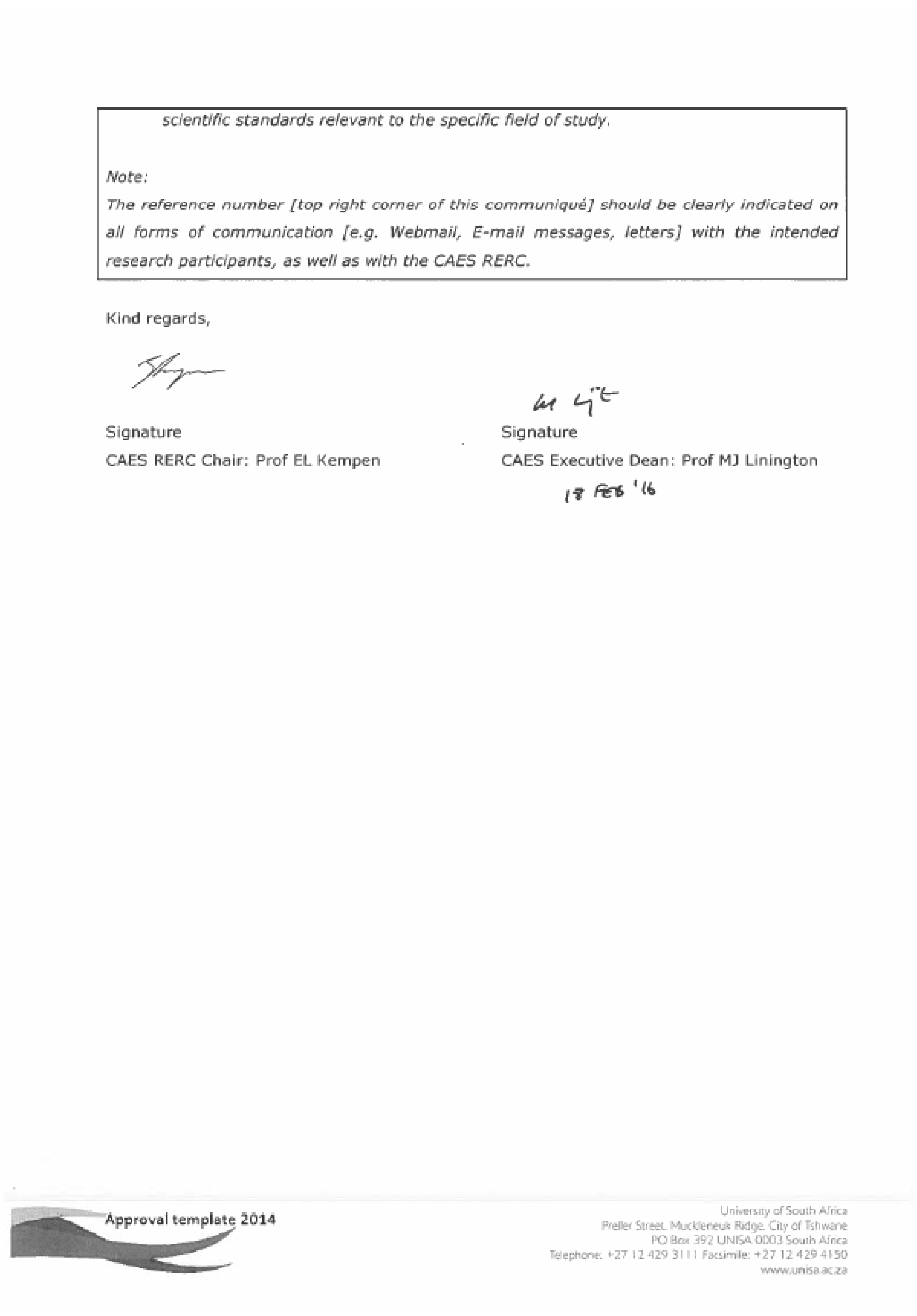
Qualification: Postgraduate degree

Thank you for the application for research ethics clearance by the CAES Research Ethics Review Committee for the above mentioned research. Final approval is granted for the duration of the project.

The application was reviewed in compliance with the Unisa Policy on Research Ethics by the CAES Research Ethics Review Committee on 17 February 2016.

The proposed research may now commence with the proviso that:

1) *The researcher/s will ensure that the research project adheres to the values and principles expressed in the UNISA Policy on Research Ethics.*
2) *Any adverse circumstance arising in the undertaking of the research project that is relevant to the ethicality of the study, as well as changes in the methodology, should be communicated in writing to the CAES Research Ethics Review Committee. An amended application could be requested if there are substantial changes from the existing proposal, especially if those changes affect any of the study-related risks for the research participants.*
3) *The researcher will ensure that the research project adheres to any applicable national legislation, professional codes of conduct, institutional guidelines and*



scientific standards relevant to the specific field of study.

Note:

The reference number [top right corner of this communiqué] should be clearly indicated on all forms of communication [e.g. Webmail, E-mail messages, letters] with the intended research participants, as well as with the CAES RERC.

Kind regards,

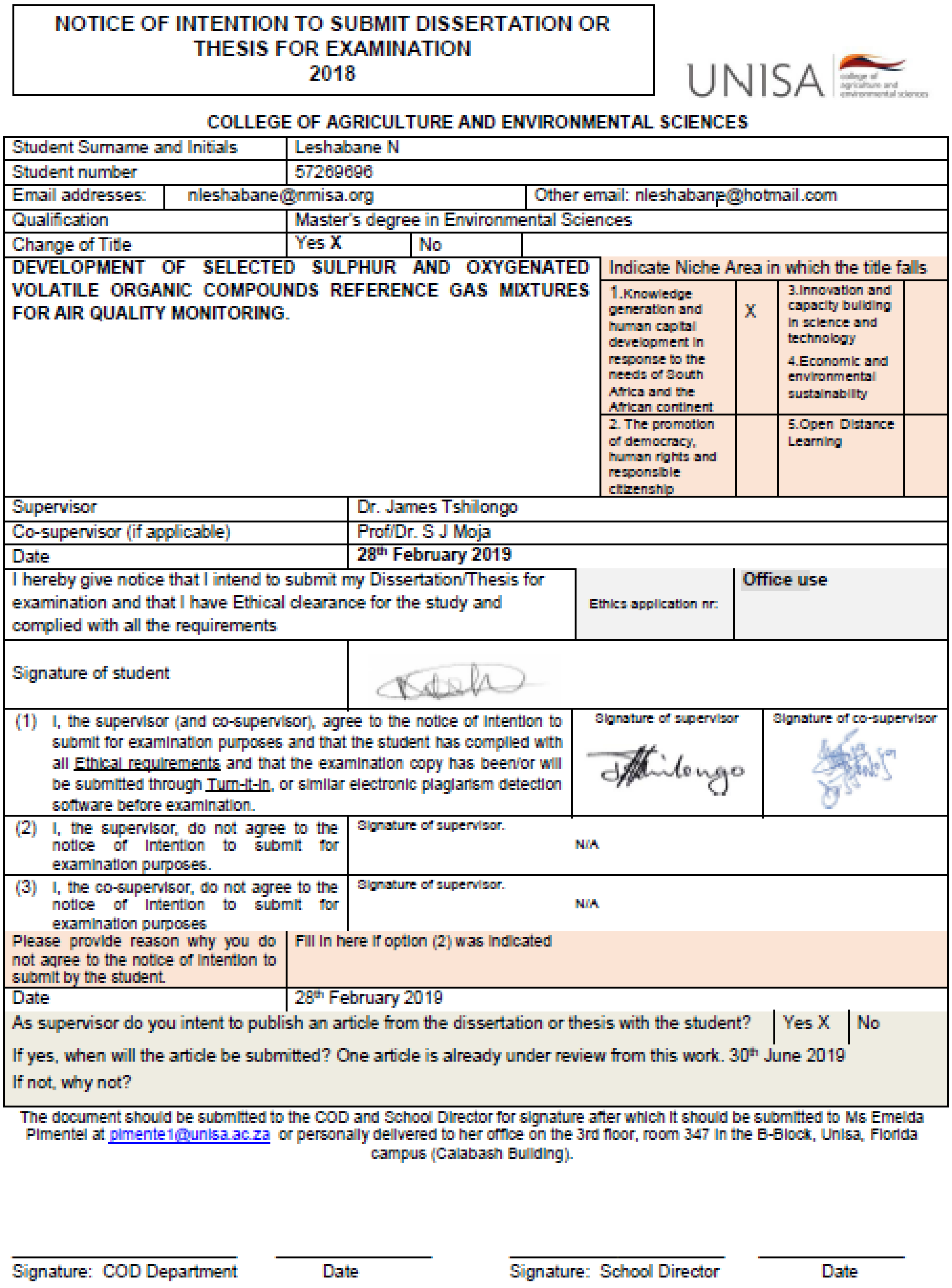
Signature
CAES RERC Chair: Prof EL Kempen

Signature
CAES Executive Dean: Prof MJ Linington
18 Feb '16

Approval template 2014

University of South Africa
Preller Street, Muckleneuk Ridge, City of Tshwane
PO Box 392 UNISA 0003 South Africa
Telephone: +27 12 429 3111 Facsimile: +27 12 429 4150
www.unisa.ac.za

APPENDIX B: INTENTION TO SUBMIT



NOTICE OF INTENTION TO SUBMIT DISSERTATION OR THESIS FOR EXAMINATION
2018

UNISA college of agriculture and environmental sciences

COLLEGE OF AGRICULTURE AND ENVIRONMENTAL SCIENCES

Student Surname and Initials	Leshabane N	
Student number	57269696	
Email addresses:	nleshabane@nmisa.org	Other email: nleshabane@hotmail.com
Qualification	Master's degree in Environmental Sciences	
Change of Title	Yes X	No

DEVELOPMENT OF SELECTED SULPHUR AND OXYGENATED VOLATILE ORGANIC COMPOUNDS REFERENCE GAS MIXTURES FOR AIR QUALITY MONITORING.

Indicate Niche Area in which the title falls

1.Knowledge generation and human capital development in response to the needs of South Africa and the African continent	X	3.Innovation and capacity building in science and technology 4.Economic and environmental sustainability	
2. The promotion of democracy, human rights and responsible citizenship		5.Open Distance Learning	

Supervisor	Dr. James Tshilongo
Co-supervisor (if applicable)	Prof/Dr. S J Moja
Date	**28th February 2019**

I hereby give notice that I intend to submit my Dissertation/Thesis for examination and that I have Ethical clearance for the study and complied with all the requirements	Ethics application nr:	**Office use**
Signature of student		

(1) I, the supervisor (and co-supervisor), agree to the notice of intention to submit for examination purposes and that the student has complied with all Ethical requirements and that the examination copy has been/or will be submitted through Turn-it-in, or similar electronic plagiarism detection software before examination.	Signature of supervisor	Signature of co-supervisor
(2) I, the supervisor, do not agree to the notice of intention to submit for examination purposes.	Signature of supervisor. N/A	
(3) I, the co-supervisor, do not agree to the notice of intention to submit for examination purposes	Signature of supervisor. N/A	
Please provide reason why you do not agree to the notice of intention to submit by the student.	Fill in here if option (2) was indicated	
Date	28th February 2019	

As supervisor do you intent to publish an article from the dissertation or thesis with the student?	Yes X	No

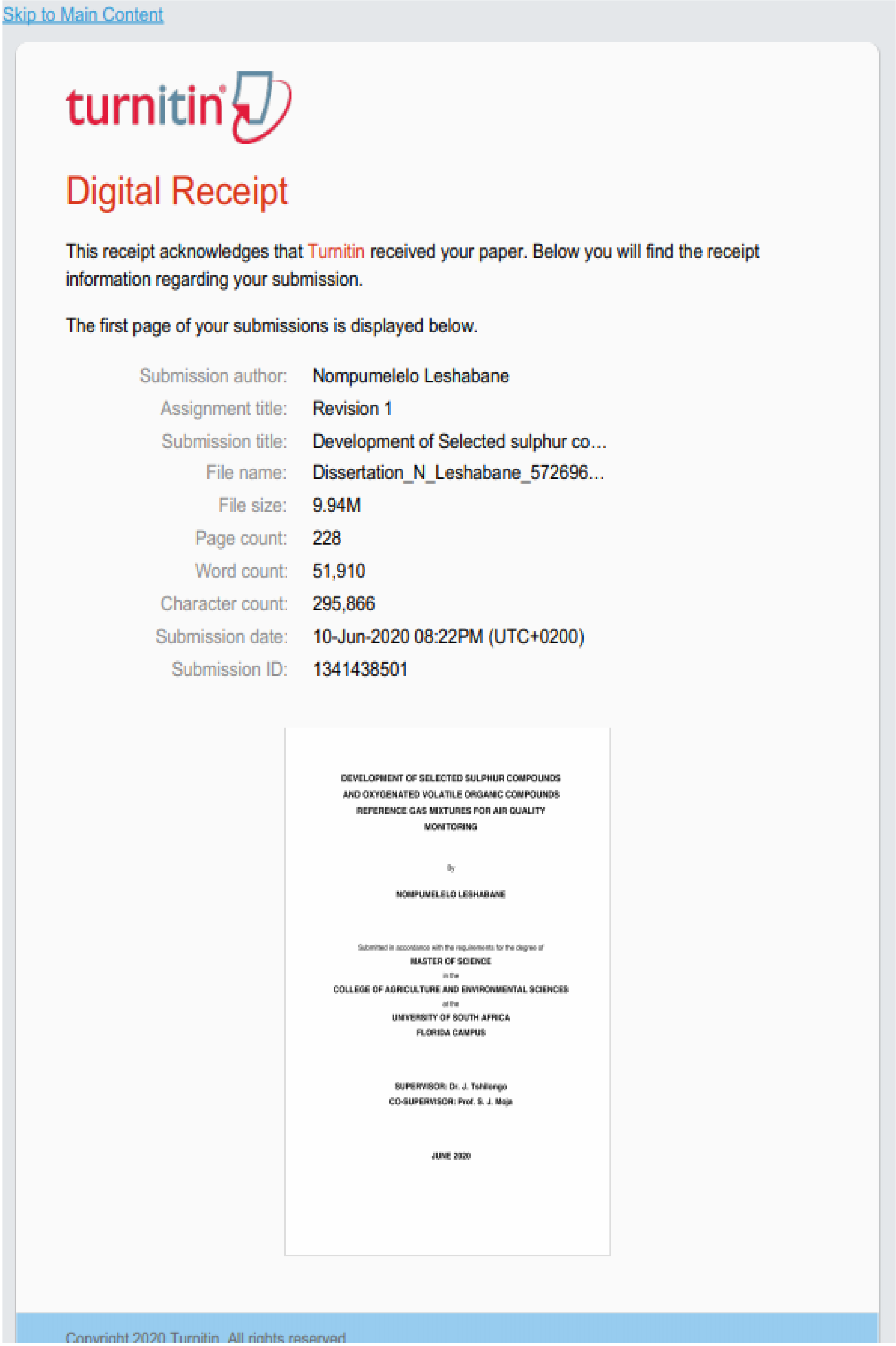
If yes, when will the article be submitted? One article is already under review from this work. 30th June 2019

If not, why not?

The document should be submitted to the COD and School Director for signature after which it should be submitted to Ms Emelda Pimentel at pimente1@unisa.ac.za or personally delivered to her office on the 3rd floor, room 347 in the B-Block, Unisa, Florida campus (Calabash Building).

Signature: COD Department
Date
Signature: School Director
Date

APPENDIX C: TURN IT IN ORIGINALITY REPORT



Skip to Main Content

turnitin

Digital Receipt

This receipt acknowledges that Turnitin received your paper. Below you will find the receipt information regarding your submission.

The first page of your submissions is displayed below.

Submission author:	Nompumelelo Leshabane
Assignment title:	Revision 1
Submission title:	Development of Selected sulphur co…
File name:	Dissertation_N_Leshabane_572696…
File size:	9.94M
Page count:	228
Word count:	51,910
Character count:	295,866
Submission date:	10-Jun-2020 08:22PM (UTC+0200)
Submission ID:	1341438501

DEVELOPMENT OF SELECTED SULPHUR COMPOUNDS
AND OXYGENATED VOLATILE ORGANIC COMPOUNDS
REFERENCE GAS MIXTURES FOR AIR QUALITY
MONITORING

By

NOMPUMELELO LESHABANE

Submitted in accordance with the requirements for the degree of
MASTER OF SCIENCE
in the
COLLEGE OF AGRICULTURE AND ENVIRONMENTAL SCIENCES
of the
UNIVERSITY OF SOUTH AFRICA
FLORIDA CAMPUS

SUPERVISOR: Dr. J. Tshilongo
CO-SUPERVISOR: Prof. S. J. Moja

JUNE 2020

Development of Selected sulphur compounds and oxygenated volatile organic compounds reference gas mixtures for air quality monitoring

ORIGINALITY REPORT

18%	11%	13%	8%
SIMILARITY INDEX	INTERNET SOURCES	PUBLICATIONS	STUDENT PAPERS

PRIMARY SOURCES

1	naca.org.za Internet Source	1%
2	iopscience.iop.org Internet Source	1%
3	repository.up.ac.za Internet Source	1%
4	hdl.handle.net Internet Source	<1%
5	kcdb.bipm.org Internet Source	<1%
6	Sangil Lee, Mi Eon Kim, Sang Hyub Oh, Jin Seog Kim. "Determination of physical adsorption loss of primary standard gas mixtures in cylinders using cylinder-to-cylinder division", Metrologia, 2017 Publication	<1%
7	www.bipm.info	

APPENDIX D: PUBLICATION BY NOMPUMELELO LESHABANE

Accreditation and Quality Assurance
https://doi.org/10.1007/s00769-021-01461-z

GENERAL PAPER

Quantitation of hydrogen sulfide reference gas mixtures to provide traceability for indoor air quality monitoring

Nompumelelo Leshabane[1,2] · James Tshilongo[2,3] · Shadung J. Moja[2,4] · Napo G. Ntsasa[3] · Gumani Mphaphuli[1] · Mudalo I. Jozela[1]

Received: 22 May 2020 / Accepted: 2 March 2021

Abstract

Accurate measurements for the determination of hydrogen sulfide (H_2S) are critical for the compliance with legislation in various industries, including natural gas and environmental sectors such as air pollution monitoring. H_2S measurements at ambient level are challenging because H_2S tends to adsorb on the internal surfaces of the sample collection devices such as gas cylinders and transfer lines. Prolonged exposure to H_2S has known health implications to humans, such as irritation to the nose, throat and airways that results in coughing or inflammation, wheezing and shortness of breath around the chest. H_2S is mainly monitored for occupational health and safety and indoor air quality monitoring. It is a highly reactive gas that can easily react with oxygen to form sulfur dioxide (SO_2) and with water to form sulfuric acid (H_2SO_4). The traceability of H_2S measurements is achieved through the preparation of reference gas mixtures. These gas mixtures are gravimetrically prepared in accordance with International Organization for Standardization (ISO 6142–1:2015). The H_2S reference gas mixtures were produced with the highest metrological capability; thus, the molar mass, purity assessment, and the weighing gave an overall gravimetric relative uncertainty which is less than 0.10% (k=1). One of the biggest challenges in producing a H_2S reference gas mixture is the handling of a gas cylinder from the gravimetric preparation process until the verification stage. This work will detail the improved techniques and measurements used to produce the H_2S reference gas mixtures. The internal consistency between the mixtures was verified using a non-dispersive ultraviolet (NDUV) spectroscopy analyzer, an ultraviolet fluorescence spectroscopy (UVFS) analyzer and gas chromatography coupled with a pulsed discharged helium ionization detector (GC-PDHID). Our measurement uncertainty results show that the gravimetric value, internal consistency, adsorption, homogeneity, and stability were within a relative uncertainty of 1.2% as compared to our previous uncertainty of 4.4%. This is a significant improvement for the measurements of H_2S reference gas mixtures.

Keywords Improved measurements · Indoor air quality · H_2S reference gas mixtures · Measurement uncertainty

Introduction

Hydrogen sulfide (H_2S) is a colourless gas with a rotten egg odour, is highly poisonous, that can paralyze the respiratory system leading to death. It is also a flammable gas which will ignite explosively when exposed to heat, open flames, oxidizers, and it is very corrosive in wastewater applications. H_2S occurs both naturally (e.g., swamps, natural gas) and from manmade processes (e.g., pulp and paper mills, petroleum refineries and power plants). This extremely hazardous substance is mainly monitored for occupational health and safety [1]. The National Environmental Management of Air Quality Act 2004 (Act No. 39 of 2004) stipulates that all the measures to follow and comply with, for continuous measurements of H_2S in the air pollution monitoring industries in

---

✉ Nompumelelo Leshabane
nleshabane@nmisa.org

[1] National Metrology Institute of South Africa (NMISA), Private Bag X34, Lynnwood Ridge, Pretoria 0182, South Africa

[2] College of Agriculture & Environmental Sciences, University of South Africa, Florida Park, Roodepoort 1709, South Africa

[3] Analytical Service Division, MINTEK, 200 Malibongwe Drive, Randburg 2194, South Africa

[4] Council for Geoscience, Water and Environment Business Unit, Applied Geoscience Division, 280 Pretoria Street, Silverton, Pretoria 0001, South Africa

South Africa. It is also used as an odorant which is added to natural gas to enable any leaks of natural gas to be detected by the public for safety purposes [2]. To support the ambient and indoor air quality monitoring in South African, in accordance with the set regulations of the air quality act, the National Metrology Institute of South Africa (NMISA) has developed H_2S in a nitrogen (N_2) gaseous matrix as primary reference gas mixture (PRGMs). The NMISA gravimetrically prepares primary standard gas mixtures (PSGMs) which are traceable to both International System (SI) of unit of mass (kg) and amount of substance (mol).

Purity analysis is a critical step for the preparation of the primary reference gas mixtures. The accuracy of the gravimetrically prepared reference gas mixtures depends significantly on the purity of the parent gases used to prepare the primary reference gas mixtures. The uncertainty contributions from the impurities of the pure or parent gases contribute on the uncertainty of the final mixture composition. An accurate measurement of diluent gas (N_2) in high pure H_2S is critical, since errors in the measurement of N_2 gas can influence the quality of reference material produced. Therefore, the amount of N_2 in the high purity H_2S was analyzed before the preparation of reference gas mixtures [3].

H_2S is highly reactive and tends to adsorb on the inner surface of the aluminum cylinder and transfer lines. Thus, the loss increases with decreasing amount of fraction of H_2S. Passivated and pretreated aluminum cylinders will largely prevent reactions between surfaces and components [2]. According to Leuenberger et.al. [4], adsorption is an increase in mole fractions of a dissolved substance at the interface of a condensed and a liquid phase due to operation of surface forces. It can also be observed at the interface of a condensed and a gaseous phase. Adsorption is divided into physisorption and chemisorption where binding energies can either form mono- or multilayers. The effect of adsorption is very minimal on the surface of aluminum cylinders as compared to the stainless-steel surface. Adsorption tends to increase with lower pressures and hence determination of minimal end pressure of the cylinder used for calibration purposes is critical. Therefore, it is recommended to use aluminum cylinders and to minimize temperature fluctuations in order to limit desorption and thermal diffusion effects [4].

All reference material producers are to state the period of stability of the reference material they produce. The knowledge of previously determined measurements for specific gas mixtures and mole fractions will assist in establishing long-term and short-term stability periods [8]. One of the challenges in developing accurate reference gas mixtures for H_2S is the stability of the primary standard gas mixtures in the gas cylinders. In order to establish the accuracy and the reliability of the reference gas mixtures prepared, they need to be certified with the validity period [8]. The main focus of this work is to detail the improved techniques and measurements used to produce the H_2S reference gas mixtures, thereby improving measurement uncertainties in South Africa. The period of validity is determined by analysis of reference gases at regular intervals until a significant degradation (loss of homogeneity) is observed.

Experimental

In this work H_2S reference gas mixtures were produced from the high purity H_2S and high purity N_2 Built- in-Purifier (BIP™) purchased from Takachiho Chemical Industrial (Japan) and Air Products Southern Africa, respectively. The manufacturer specification for high purity H_2S was 99.99% (cylinder number: 3 K-37622) and that of high purity nitrogen Built-in-Purifier (BIP™) gas was 99.9999%. The purity assessment was done by using gas chromatography coupled with thermal conductivity detector (GC-TCD), for impurities of hydrogen (H_2), nitrogen (N_2) and oxygen (O_2). Gas chromatography coupled with flame ionization detector (GC-FID) was used for impurities of carbon monoxide (CO), methane (CH_4) as total hydrocarbons (THCs). Another Agi-lent 7890B gas chromatography coupled with pulsed dis-charge helium ionization detector (GC-PDHID) was used for the analysis of carbon dioxide (CO_2**)** and argon (Ar) impuri-ties. Sulfur-containing compound impurities such as SO_2, ethyl mercaptans (CH_3CH_2SH), carbon disulfide (CS_2) and carbonyl sulfide (COS) were assessed using gas chroma-tography coupled with sulfur chemiluminescence detector (GC-SCD).

The primary standard gas mixtures (PSGMs) were gravimetrically prepared, in accordance with ISO 6142–1:2015 using high purity H_2S as the starting material. The gravimetric preparation of primary standard gas mixtures involved a four steps dilution to the final range of 8 to 12 µmol/mol. The production scheme followed is shown in Fig. 1. The homogenization of the H_2S in N_2 gas mixtures was done immediately after addition of the final component or diluent gas. These gas mixtures were rolled for a minimum of 2 h. The H_2S reference gas mixture was analyzed using different analytical techniques such as non-dispersive ultraviolet (NDUV) spectroscopy, GC-PDHID and ultraviolet fluorescence spectroscopy (UVFS).

Gravimetrically prepared primary standard gas mix-tures of H_2S were verified using the ABB Limas 11 NDUV analyzer. The system was purged with high purity N_2 after every sample analysis using LabVIEW software to control the sampling gas system. Sample introduction was done with Teflon tubing. The LabVIEW software allows for any number of cycles, runs per sample and sampling combinations. Optimised conditions for the NDUV analyzer are shown in Table 1.

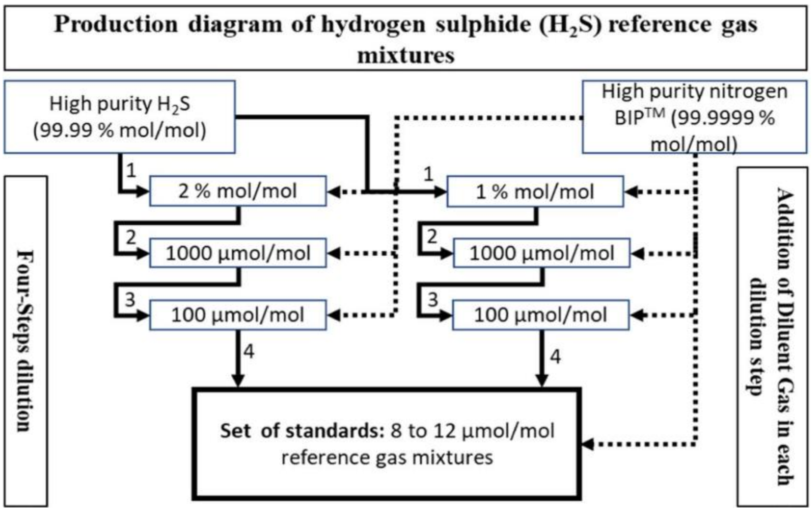


Fig. 1 Production diagram of the H_2S in nitrogen primary standard gas mixtures

Table 1 Analytical conditions for three techniques used to analyze H_2S in N_2 gas mixture

Measurement technique	Parameters	Method conditions	
GC-PDHID	Column	Hayesep Q, 80/100, 2 m, ID (2.1 mm), 1/8″	
	Oven temperature	120 ° C isothermal	
	Detector and temperature	PDHID at 150 ° C	
	Sample loop and carrier gas	1 ml and helium	
	Run time	2 min	
	Sample flow (mass flow controller)	35 ml/min	
	Number of injections	15	
		NDUV	UVFS
Analyzers	Purging time	180 s	10 min
	Sample Measurements taken	30 s	50 s
	Number of cycle repeats	4	3
	Sample flow	300	200 ml/min

The mole fraction of gravimetrically prepared H_2S refer-ence gas mixture was also analyzed with GC- PDHID. The GC-PDHID instrument was switched on for a minimum of an hour before starting the analysis to allow it to stabilize on the base line. The regulator was connected to a cylinder flushed several times then connected the cylinder with a regulator to a sulfinert-treated tubing sample line of the sampler box of the GC. The sample line was purged for few minutes before the analysis started. The GC-PDHID conditions are shown on Table 1 . The stainless-steel-treated sample loop of 1 ml was used to introduce the sample into the column through a 16-port stainless-steel-treated gas sampling valve. The prepared H_2S primary standard gas mixture of 10.3 µmol/mol was analyzed in the order of A-B-A (Reference–Sample–Reference) to correct the instrumental drift during the analysis where A and B represents the reference and sample, respectively. One of the previously prepared and analyzed H_2S gas mixture was used as a reference cylinder. The same sequence was used with repeats of a minimum of five sets. Data acquisition was done using the OpenLab software program.

Teledyne T101 UVFS analyzer was the third method used for the analysis of the gravimetrically prepared primary standard gas mixtures. The PSGMs were introduced through the sample stream of the molbloc system and mass flow controllers to control sample flow and directly to the UVFS analyzer. Data was recorded using the LabVIEW software. Optimized conditions for the UVFS analyzer are shown in Table 1.

The adsorption/desorption test for H_2S was done by using the "Equal division" method [5]. This was done in order to assess the effect of adsorption/desorption of H_2S on the inner surface of aluminum cylinder. In this method, a gas mixture cylinder with a known mole fraction of 10.01 µmol/mol and pressure of 9.0 MPa (mother cylinder) was connected to two evacuated empty cylinders (daughter cylinders). Both mother and daughter cylinders are connected to the vacuum pump through a transfer line to evacuate all the transfer lines connections. The gas mixture in the mother cylinder was transferred to the daughter cylinders until all cylinders reach equal pressure. The transferring process was done gradually to prevent the Joules–Thompson effect [6]. The mother and daughter cylinders were analyzed with the ABB Limas 11 UV analyzer to compare the mole fractions of the daughter cylinders to that of the mother cylinder.

Stability assessment was done by monitoring the primary standard gas mixtures (through analysis) at different intervals after preparation throughout this study. This investigated other factors that might lead to instability of the gas mixtures such as adsorption/desorption on the inner surface of the cylinders. To determine the short-term stability, the PSGM was analyzed immediately after gravimetric preparation. To assess the long-term stability of H_2S, newly prepared gas mixtures of mole fraction of 8 to 12 µmol/mol H_2S were used to analyze the previously prepared 10 µmol/ mol H_2S reference gas mixture. The analysis was done on the ABB Limas 11 UV analyzer. In this work, long -term stability was performed over a period of more than two years (March 2016–October 2018).

Results and discussion

Purity analysis

The results of purity analysis for high purity H_2S and high purity N $_2$ are shown in Table 2. The contribution of measurement uncertainty in the analysis of impurities comes from the repeatability of the measurement technique. The uncertainty at the limit of detection (LOD) is used when the impurity present is below LOD. Larger measurement uncertainties are associated with the best estimate when there is no technique that can analyze the impurity stated by the manufacturer. In general, source gases such as the H_2S are less pure than N-$_2$ which is used as diluent gas. Accurate measurement of diluent gas (N-$_2$) in high- purity H_2S is critical because errors in the measurement of -N_2 can be detrimental to the quality of the reference material produced.

Gravimetric preparation of H_2S in nitrogen primary standard gas mixtures

The precise gravimetric system was used to prepare H_2S in nitrogen primary standard gas mixtures. The gravimet-ric preparation measurement results are traceable to the International System of units of measurements (SI). The relative measurement uncertainties of the mole fraction of gravimetric primary standard gas mixtures of H_2S in nitrogen prepared at ambient level in this work were found to be less than 0.02%. This was also improved from previous gravimetric preparation of gas mixtures of other components in our laboratory which was ± 0.5% relative measurement uncertainty [9]

Table 2 Purity analysis for high purity for H_2S and N_2 BIP™

High-purity gas	Component	Expanded uncertainty (µmol/mol), k=2
H_2S	H_2	2800 ± 140
	N_2	2.37 ± 0.12
	Ar	61.6 ± 6.2
	H_2S	997,135.60 ± 140.16
N_2	Ar	63.6 ± 6.4
	CO	0.0050 ± 0.0050
	CO_2	0.0050 ± 0.0050
	CH_4	0.0100 ± 0.0010
	C_2H_6	0.0050 ± 0.0060
	O_2	0.00400 ± 0.00040
	H_2O	0.010 ± 0.012
	H_2	0.50 ± 0.58
	N_2	999,935.73100 ± 0.00064

Table 3 Adsorption/desorption study of 10,01 µmol/mol H_2S in the aluminum cylinder with a final pressure of 3.0 MPa

Cylinder ID	Means of analyzer response	% RSD	Response factor	% Difference
(Mother cylinder)	9.985	0.144	0.998	
NL1 (Daughter 1)	9.958	0.326	0.995	0.272
NL2 (Daughter 2)	9.999	0.049	0.999	− 0.136
NL3				

Adsorption and desorption effect (Equal division method)

The adsorption/desorption effect is expected to be larger on the lower mole fractions of H_2S [5, 7]. The pressure of the mother cylinder was at 9.0 MPa before the equal division experiment was performed. The results of the adsorption/desorption effect are shown in Table 3. There is no significant difference between the amount of fraction of 10.01 $\mu mol.mol^{-1}$ in the mother cylinder and two daughters. cylinders. Uncertainty measurement of adsorption/desorption was calculated to be 0.03%. The relative adsorption results were less than 0.5% or negligible to show no adsorption of H_2S on the inner surfaces of the aluminum cylinder [5].

Stability assessment

The results of stability assessment for the 10 μmol/ mol H_2S primary standard gas mixture over a period

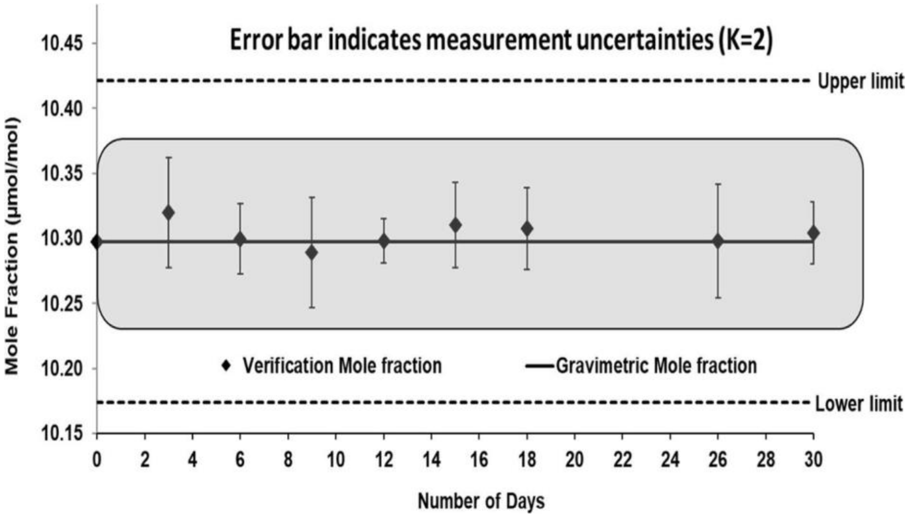


Fig. 2 Short-term stability of H_2S primary standard gas mixture

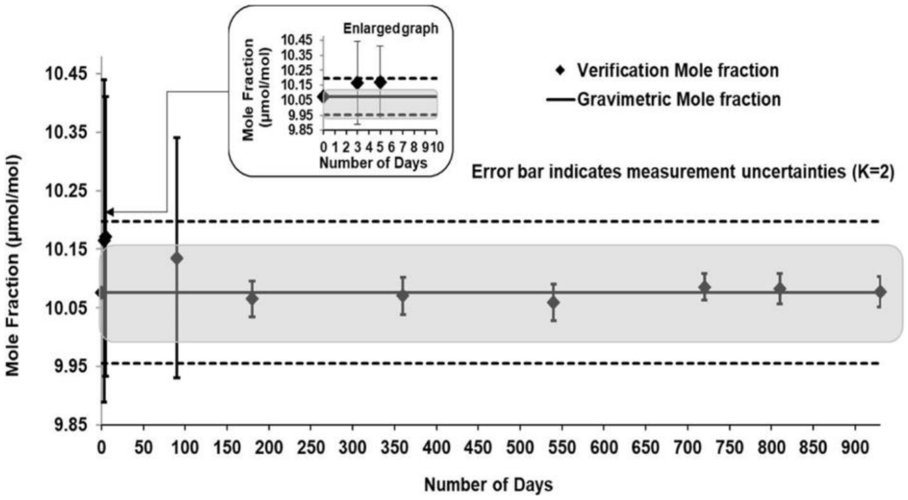


Fig. 3 Long-term stability of H_2S primary standard gas mixture

Table 4 Long-term stability of the H_2S gas mixture

Cylinder ID	Gravimetric mole fraction (μmol/mol)	Mean verification mole fractions	% RSD	% Difference	Preparation dates
NL4	9.99	9.94	0.271	− 0.501	09/10/2018
NL5	10.01	9.99	0.1465	− 0.200	09/03/2016

of 2 years. The chosen stability primary standard gas mixture was analyzed by the newly prepared PSGMs in the range of 8 to 12 µmol/mol. Figures 2 and 3 show the short-term and the long-term stability of the H_2S primary standard gas mixtures. Table 4 shows the long-term stability results with % difference of the new H_2S reference gas mixture prepared to be (-0.50%). This indicate that the gas mixture is stable for a period of 2 years within the measurement uncertainty of 1%.

Analytical methods used for analysis of H_2S gas mixture

NDUV results

The repeatability and reproducibility measurement data were done on different days. After analysis using the ABB Limas 11 UV analyzer, the data was treated by using the LabVIEW software to get the mean, standard deviation, relative standard deviation (% RSD) and the standard uncertainty. The mole fraction was computed using a set of standards on the XGENLINE Version 1.0 software based on the generalized least-square method developed by the National Physical Laboratory in UK [10]. The verification was done using the multi-point calibration method. Reference standards used for the verification ranged from 8 to 12 µmol/mol. The results obtained from the analysis of H_2S using NDUV are shown in Table 5.

Gas chromatography coupled with PDHID

The determination of H_2S in nitrogen was done using a single-point calibration with a 10 µmol/mol H_2S in nitrogen PSGM. The PSGM were connected on the multi-position sampler box to the GC. Based on the optimized analytical conditions, H_2S in N_2 gas mixture was eluted at 1.5 min. The data processed from GC-PDHID was the average of the H_2S peak area from the instrument response for both the reference and sample with standard deviation, relative standard deviation (RSD, expressed in %) to calculate the mole fraction of the PSGM. The verification was done using the single-point calibration (Reference–Sample–Reference) method, where the reference standard was analyzed before and after the sample. The results obtained from the analysis of H_2S using GC-PDHID are shown in Table 5.

UV Fluorescence

The determination of H_2S in -N_2 was done using a single-point calibration with a PSGM (10 µmol/mol H_2S in nitrogen). The PSGM and sample were connected on the same line through the molbloc system to the analyzer but analyzed alternatively following a sequence of A-B-A where A represents the standard mixture and B represents the sample mixture. Data processed from the UVFS analyzer was the average of analyzer response expressed in mole fractions with standard deviation, % RSD to calculate the mole fraction.

The verification was done using a single- point calibration (Reference–Sample–Reference) method, where the reference standard was analyzed before and after the sample. The results obtained from the analysis of H_2S using UVFS are shown in Table 5.

Conclusion

Improving the development of preparation and analysis of primary standards gas mixtures of H_2S in various matrix is critical. The highly accurate gravimetric technique has been used to produce H_2S gas mixtures with relative measurement uncertainty of less than 0.02 %. The “equal division” method was used to quantify the amount of adsorption/desorption of H_2S, used, hence the measurement uncertainty of the amount of H_2S adsorbed on the inner surface of the cylinder was accounted and it was found to be 0.03 %. The different analytical techniques used to analyze H_2S showed compara-ble results. Our measurement uncertainty results show that the gravimetric value, internal consistency, homogeneous, adsorption and stability were within relative uncertainty of 1.2% as compared to our previous uncertainty of 4.4%. Stability study showed that H_2S gas mixtures can be stable over a period of 2 years within the measurement uncertainty of 0.5%. This is a significant improvement for the meas-urements of air quality monitoring using H_2S in nitrogen primary reference gas mixtures. Therefore, the accuracy of producing H_2S primary reference gas mixtures in order to

Table 5 Measurement techniques: NDUV; UVFS; GC-PDHID used for the analysis of H_2S in N_2 with a gravimetric mole fraction of 10.3113 µmol/mol

Measurement technique	NDUV	UVFS	GC PDHID
Average verification mole fraction (µmol/mol)	10.3623	10.3110	10.2999
Standard deviation (µmol/mol)	0.0129	0.0052	0.0174
Estimated standard deviation of the mean (ESDM)	0.0053	0.0023	0.0066
Combined uncertainty	0.050	0.020	0.028
Expanded uncertainty, K= 2	0.10	0.039	0.056
Relative expanded uncertainty (%)	0.97	0.38	0.55

provide traceability for indoor air quality monitoring in this study has been successfully improved. The outcome of this work, the overall impact of improved measurement uncertainties which are traceable to SI units are critical for indoor air quality monitoring industry in South Africa., Thus this will assist in providing more accurate and reliable measurements of H_2S pollutants to South African Air Quality Information System (SAAQIS). In the near future, the improved measurement uncertainty results obtained in this work will assist NMISA in claiming for calibration measurement capability (CMC) of hydrogen sulfide primary reference gas mixtures.

Supplementary Information The online version contains supplemen-tary material available at https://doi.org/10.1007/s00769-021-01461-z.

References

1. Miller Walter R, Guenther Franklin R (2006) The certification of a nominal 20 µmol/mol H_2S /N_2 standard reference material using two independent methods. Anal Bioanal Chem 387:2433–3243. https://doi.org/10.1007/s00216-006-1056-3
2. Brown AS, Van der Veen AMH, Arrhenius K, Murugan A, Cul-leton LP, Ziel PR, Li J (2015) Sampling of gaseous sulfur-con-taining compounds at low concentrations with a review of best-practice methods for biogas and natural gas applications. Trends Anal Chem 64:42–52. https://doi.org/10.1016/j.trac.2014.08.012
3. ISO 6142–1:2015 (2015) Gas analysis - Preparation of calibration gas mixtures - Gravimetric methods, International Organization for Standardization (ISO), Geneva
4. Leuenberger MC, Schibig MF, Nyfeler P (2014) Gas adsorption and desorption effects on the cylinders and their importance for long-term gas records. Atmosph Chem Phys Discuss 14:19294–19314. https://doi.org/10.5194/acpd-14-19293-2014
5. Lee S, Kim ME, Oh SH, Kim JS (2017) Determination of physical adsorption loss of primary standard gas mixtures in cylinders using cylinder to cylinder division. Metrologia 54:L26–L33. https://doi.org/10.1088/1681-7575/aa87b8
6. Maric I (2005) The Joule – Thomson effect in natural gas flow – rate measurements. Flow Meas Instrum 16:387–395. https://doi. org/10.1016/j.flowmeasinst.2005.04.006
7. Kim ME, Kang JH, Kim YD, Lee DS, Lee S (2018) Development of accurate dimethyl sulphide primary standard gas mixtures at low nanomole per mole levels in high pressure aluminium cylinders for ambient measurements. Metrologia 55:158–166
8. ISO 17034: 2016 (2016) General requirements for the competence of reference material producers, International Organization for Standardization (ISO), Geneva
9. Tshilongo J, Botha A, Janse van Rensburg M, Leshabane N, Ntsasa NG (2009) FTIR and GC as complementary tools for analysis of corrosive gases. Accred Qual Assur 14:655–663. https:// doi.org/10.1007/s00769-009-0602-z
10. Smith IM (2010) Software for determining polynomial calibration functions by generalised least squares: user manual, NPL Report mS 11. Teddington, UK