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Development of primary reference gas mixtures for volatile organic compound monitoring in South Africa

by

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Dedication

I dedicate this dissertation to my family, my wife, Pulane Dinah Ntsasa, my daughter Lerekolahae Reratilwe Ntsasa and my son Thoriso Ea Rona Ntsasa. You are the motivation to my success.

To my friends who have always pushed me to finish the project.

Declaration

I, Napo Godwill Ntsasa, declare that the dissertation, which I hereby submit for the degree Master of Chemistry at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.



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Summary

Direct monitoring of volatile organic compounds (VOCs) emitted from industrial sources and the monitoring of ambient levels thereof in the atmosphere, play an essential role in providing data for various legislative requirements. Many volatile organic compounds are emitted into the atmosphere from biomass burning, power stations, and many other sources. Once in the atmosphere, the volatile organic compounds are known to play a role in the generation of ozone by reaction with other constituents of air. There are many observed adverse effects on the environment due to air pollutants and their reaction products, such as reduced visibility due to heavy fog, which includes emitted particles, photochemical smog, acid rain due to the emissions of nitrogen and sulphur oxides, and ozone depletion.

Gas reference standards are used for the calibration of equipment used to measure the VOC pollutants. The gas reference standards are also a source of traceability, linked directly to the international system of units (SI) due to the realisation of measurement capabilities through primary methods such as gravimetry and coulometry.

In this study, reference gas mixtures containing benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene (BTEX), were prepared by gravimetric methods at mole fractions of between 5 nmol/mol to 30 μ mol/mol in this study. The preparation was performed using three different techniques: the micro-gravimetric method using small glass capillary tubes, developed at the National Institute of Standards and Technology (NIST), the stainless steel (loop) method with the dedicated minimum dead volume connector developed at National Physical Laboratory (NPL) and the direct liquid injection method using a dedicated heated syringe heater to volatilise components and flushed with small amounts of nitrogen developed at Korean Research Institute of Standards and Science (KRISS). After the preparation, a comparison was achieved by analysis of the BTEX gas mixtures using gas chromatography with flame ionisation detection (GC-FID).

The NIST method was used to directly prepare 500 nmol/mol, which showed large uncertainty values due to poor weighing repeatability. With the NPL method, the 30 μ mol/mol [BTX (benzene, toluene and p-xylene)], and the 10 μ mol/mol BTEX were achieved. The KRISS method was used to prepare 10 μ mol/mol of BTEX. The NPL and the KRISS methods were compared by GC-FID analysis and showed comparability to within 2% of the gravimetric values.

Stability studies on 30 $\mu\text{mol/mol}$ (BTX) gas mixtures showed minimal loss of benzene, toluene and p-xylene over 24 months. However, the long-term stability analysis was affected by the demand for cylinders for other vital projects. Unfortunately, many of the gas mixtures were discarded to allow the cylinders to be used in other projects.

The reference gas standards were internationally benchmarked through the National Metrology Institute of South Africa (NMISA) participation in key comparisons Asia Pacific Metrology Programme (APMP.QM-S12, APMP.QM-S14) and Consultative Committee for Amount of Substance (CCQM-K10). In the two APMP comparisons, the NMISA results had large deviations from the comparison reference values, mainly from the poor analysis methods due to the inefficiency of trapping of components using pre-concentrators. However, in the CCQM-K10, NMISA showed improved results, with most values within 0,7 nmol/mol at 5 nmol/mol nominal mole fraction, compared to 30 nmol/mol obtained in APMP.QM-S12 and 10 nmol/mol were obtained in APMP.QM-S14, both at 100 nmol/mol. This improvement in CCQM-K10 was attributed to the improved analysis of BTEX at nmol/mol by optimizing the pre-concentrator conditions, which improved both the repeatability and the accuracy of BTEX standards used to analyse the comparison gas mixture.

The contributions to the uncertainty of measurement were from the weighing of capillary tubes, weighing of stainless steel loops, weighing of syringes, purity data, and GC-FID verification data.

The BTEX reference gas mixtures prepared in this study will be used as a source of traceability in South Africa for air pollution monitoring.

List of abbreviations and acronyms

APMP	Asia Pacific Metrology Programme
AWD	Automated Weighing Device
BIPM	International Bureau for Weights and Measures
BTEX	Benzene, Toluene, Ethylbenzene, o-xylene, m-xylene, p-xylene
BTX	Benzene, Toluene, Xylenes
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
CoA	Certificate of Analysis
DEA	Department of Environmental Affairs
DFFE	Department of Forestry, Fishery and the Environment
DoE	Degree of Equivalence
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 Spectrometry
ISO	International Organization for Standardisation
IUPAC	International Union of Pure and Applied Chemistry
KCRV	Key Comparison Reference Value
KRISS	Korea Research Institute of Standards and Science
LOD	Limit of Detection
LOQ	Limit of Quantification
NACA	National Association of Clean Air
NIST	National Institute of Standard and Technology
NMI	National Metrology Institute
NMISA	National Metrology Institute of South Africa
NPL	National Physical Laboratory

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
SDS	Safety Data Sheet
SSV	Stream Selection Valve
TCD	Thermal Conductivity Detector
VIM	International Vocabulary of Metrology
VOC	Volatile Organic Compound
VSL	Van Swinden Laboratory (Dutch Metrology Institute)
WMO-GAW	World Meteorological Organization-Global Atmosphere Watch

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1. Introduction

This chapter introduces the impact of the volatile organic compounds in the atmosphere, provides the significance of the study, problem statement, aims and objectives are discussed. It also introduces the importance of the primary reference gas mixtures as a source of traceability in air pollution measurement in the legislative framework. Finally, the dissertation outline is presented.

1.1 Problem statement

Air pollution (both household and ambient air) has been recognized as a threat to human health long before industrialisation (Mosley, 2014). The industrial revolution transformed the world's economic activities, with the manufacturing of various products for different applications and uses. Activities such as electricity generation from coal, and the development of modes of transport such as vehicles, ships, and aircraft, have contributed positively to the world's economy. However, the downside of such activities have resulted in a reduction in environmental health due to air pollution caused by the emission of dangerous compounds into the atmosphere.

The sources of air pollutants are natural and anthropogenic. Natural sources include volcanic eruptions, biogenic and forest fires (biomass burning), while anthropogenic sources include power plants, chemical plants, transport vessels, mining activities, and many more. Once in the atmosphere, pollutants undergo many photochemical reactions with other constituents, in which some may form secondary pollutants, such as ground-level ozone (Grenfell et al., 2010; Rhoderick et al., 2018) and aerosols (Englert et al., 2017). There are many observed adverse effects on the environment due to air pollutants and their reaction products, such as, reduced visibility, photochemical smog, acid rain due to the emissions of nitrogen and sulphur oxides, and ozone depletion.

There are many types of pollutants in the atmosphere; those of interest in this study are volatile organic compounds (VOCs). The VOCs are widely known to contribute to the formation of tropospheric ozone (Derwent et al., 2007; Jaars et al., 2014).

The VOCs of interest in this study are benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene (BTEX), which are similar in structure and present similar

characteristics with a distinctive odour. The BTEX compounds are used in manufacturing chemical products, such as additives to fuel, paint, and as solvents for many other applications.

The human health effects associated with VOCs are respiratory, carcinogenic and neurotoxic (U.S. EPA, 2017). They enter the human body through direct skin contact and breathing in polluted air. BTEX are listed in the original list of 187 toxic air pollutants (U.S. EPA, 1990).

The VOCs are known to be present in the atmosphere at nmol/mol down to pmol/mol amount of fraction (Grenfell et al., 2010). VOC measurements reported for legislative purposes are often reported in micro-gram per cubic metre ($\mu\text{g}/\text{m}^3$), as shown in Table 1-1. The format of the units used represents the values of the VOCs calculated from the analytical technique calibrated using the known composition of references gas standards linked to the mole, which is the base unit of the amount of substance in the International System of Units (SI). The formats can be linked using accepted equations as documented in the ISO standards (ISO 14912:2003, 2003).

The legislative framework in different countries controls the monitoring of BTEX at ambient levels. Table 1-1 contains a list of selected countries with national air quality standards for benzene, with annual average limit values.

Table 1-1: Benzene air quality standards in selected countries with annual average limit values

Country	Limit (ug/m ³)
Australia	3
France	2
India	5
Japan	3
Peru	4
Scotland	3,25
South Africa	5
South Korea	5

**Source: (Sekar et al., 2019)*

The monitoring of BTEX at background levels is done by the World Meteorological Organisation - Global Atmospheric Watch programme (WMO-GAW) as non-methane hydrocarbons (NMHCs) (WMO-GAW, 2001). The WMO-GAW programme is part of the Global Climate Observing System (GCOS) established by the WMO, United Nations Educational, Scientific and Cultural Organization (UNESCO), United Nations Environment Programme (UNEP), and International Science Council (ICSU). The objective of GAW is to investigate the change in the chemical composition and related physical characteristics of the atmosphere. There were 30 VOC components initially listed to be monitored, namely ethane, ethene, ethyne, propane, propene, propyne, n-butane, 2-methyl propane, 2-methyl propene, trans-2- butene, cis-2-butene, 1-butene,1-butadiene, n-pentane, 2-methyl butane, trans-2-pentene, cis-2-pentene, cyclohexane, 2-methyl pentane, 3-methyl pentane, isoprene, n-heptane, benzene, ethylbenzene, 1,2 xylene, 1,3-xylene, 1,3,5-trimethyl benzene and 1,2,4 benzene (WMO-GAW, 1995).

Air pollution measurements are performed to record the emitted values of listed components for law enforcement, such as the primary air pollutants, which are also monitored routinely in the ambient atmosphere. In addition, for research purposes, data on VOCs, monoterpenes and greenhouse gases are reported to monitor the contribution of various sources that contribute towards ozone depletion and global warming. Such

measurements require quality protocols to ensure that data is credible. This is achieved in air pollution measurements through the use of gas calibration standards containing the components of interest. The gas calibration standards are manufactured following internationally recognised guidelines set by ISO. Air pollution measurements also require traceability to the International System of Units (SI), which is achieved through the unbroken chain of calibration of instrumentation by a set of standards having specified values and stated measurement uncertainty (Brown & Milton, 2007; Grenfell et al., 2010; Milton & Quinn, 2001; Murugan & Brown, 2015).

Figure 1-1 represents traceability hierarchy, with the primary standard representing the SI unit, as the standard with the highest metrological capability, disseminating to a field measurement through secondary and working standards, respectively (Lopardo et al., 2012). The pyramid shape also expresses the associated measurement uncertainty at each level, with the primary standard having the smallest value, increasing with the chain through to the field measurement (instrumentation calibration). Primary standards are developed and maintained at National Metrology Institutes (NMIs) and serve as national measurement standards in different countries. The National Metrology Institute of South Africa (NMISA) is designated for such activities under the Measurement Units and Measurement Standard Act 18 of 2006 (Government Gazette no 27318, 2005). Calibration gas standards of high metrological quality are manufactured at NMISA and serve as primary standards of gas measurements in South Africa and are named Primary Reference Gas Mixtures (PRGMs).

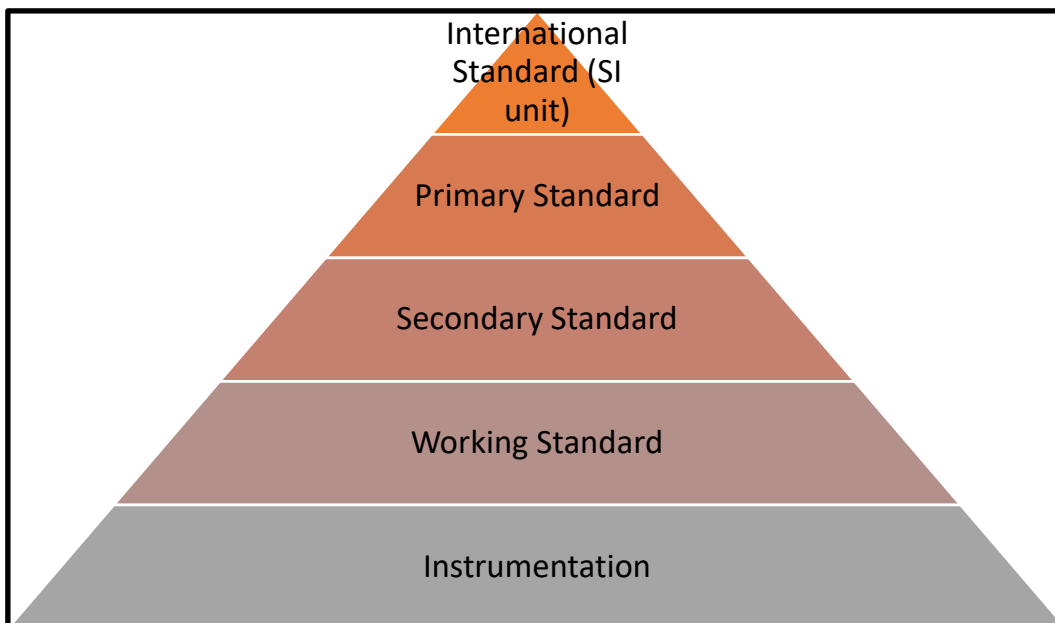


Figure 1-1: Basic measurement traceability chain

(*Source: *Lopardo et al., 2012*)

The PRGMs are manufactured by the gravimetric method and verified by analysis by comparing them to PRGMs from other NMIs. This exercise is documented in the Mutual Recognition Arrangement (MRA) document (MRA CIPM, 1999), which is the framework in which the NMIs demonstrate the international equivalence of their measurement standards through participating in the key comparisons. The International Bureau of Weights and Measurements (BIPM), comprised of member states (countries of the world), including South Africa, aims to harmonise the global measurement system to break trade barriers, and govern the MRA.

1.2 The aim and objectives of this study

The study aimed to develop primary reference gas standards containing multiple components of volatile organic compounds (VOCs) in gas cylinders using the gravimetric method based on ISO 6142. The volatile organic compounds of interest were benzene, toluene, ethylbenzene, ortho, meta, and para-xylene (BTEX).

To achieve this aim, the objectives of the study were to:

1. Use three different gravimetric preparation methods previously employed in the preparation of VOCs at the National Institute of Standards and Technology

(NIST), the National Physical Laboratory (NPL), and the Korea Research Institute of Standards and Science (KRISS), respectively.

2. Develop and optimise a GC-FID-based method for the analysis of BTEX.
3. Monitor the stability of these reference standards over time to determine their shelf life.
4. Compare the standards with those prepared by other NMIs through participation in international key comparison studies.

After establishing international equivalence, the reference standards will be disseminated to those conducting air pollution monitoring activities in South Africa.

1.3 Justification of the study

Benzene is on the list of National Ambient Air Quality Standards with other priority air pollutants such as sulphur dioxide (SO₂), nitrogen dioxide (NO₂), particulate matter (PM₁₀), ozone (O₃), lead (Pb) and carbon monoxide (CO) (Government Gazette No. 32816, 2009). These pollutants are monitored in the ambient atmosphere across South Africa, reported in the South African Air Quality Information System (SAAQIS), and serve as indicators of air pollution. Measurements of these criteria air pollutants require accurate reference standards that fulfil the requirement of metrological traceability. Among other reasons, measurements of benzene in the ambient atmosphere have been limited due to the unavailability of quality reference gas mixtures in South Africa. Benzene, together with other pollutants such as greenhouse gases and aerosols, are monitored in background atmospheric air (air that is considered to have minimal pollution due to human activity) by the South African Weather Service (SAWS) under a World Meteorological Organization-Global Atmospheric Watch Program (WMO). There are no measurements of benzene and other VOCs at the Cape Point (WMO-GAW) station due to a lack of gas reference standards.

While reference gas standards for VOCs are readily available internationally, the drawback is cost and limited shelf life. Most of the BTEX reference gas mixtures have a limited shelf life of one year, which reduces the use thereof in the field when transportation to South Africa is included, which could take between two to four months. During the government's annual air quality Lekgotla in 2010, the risks to effective air pollution monitoring in South Africa were discussed. The risks included the availability of reference gas mixtures locally to support these activities. NMISA, a key stakeholder with

the then Department of Environmental Affairs (DEA), now the Department of Forestry, Fisheries and the Environmental Affairs (DFFE), embarked on developing reference gas mixtures to support air pollution monitoring, including BTEX.

1.4 Dissertation outline

This dissertation discusses the development of accurate reference gas mixtures containing BTEX for air pollution monitoring in South Africa. Chapter 2 discusses the work done on BTEX over four decades, mainly on the preparation and analysis of these gas reference mixtures and the importance of measuring BTEX in the ambient atmosphere due to their negative contribution to air quality. In Chapter 3, the methodology involved comparing three different gravimetric preparation methods to select the most economical choice that would satisfy the metrological requirements for reference standards, are presented. Chapter 4 discusses the results in detail, followed by Chapter 5, which encompasses the conclusion and recommendations.

2. Literature review

This chapter reviews the preparation and analysis methods for gas standards, focussing on BTEX. First, the science of chemical metrology conducted worldwide, which focuses on ensuring traceability to the mole, the SI base unit of chemistry, is explained. Then, the process followed to achieve primary reference gas standards and the establishment of measurement equivalence is discussed. Finally, the methods used in the monitoring work are discussed.

2.1 Gas reference standards

There are many prescribed ways of preparing gas reference standards for measurements, as there has been a continuous improvement in the preparation of accurate reference gases. Barrat, in his review mentioned that such reference gases are prepared by either static or dynamic methods (Barratt R S, 1981). Static methods involve the preparation of reference gases using containers such as stainless steel or aluminium cylinders, glass vessels, Tedlar bags, and other containers. The containers are available in various sizes, holding reasonably large quantities of gas, such as 5 L, 10 L, 30 L and 50 L in water. The advantages of preparing gas standards in containers include the following:

- Gas cylinders generally tend to have long shelf life for most components, including VOCs,
- Gas cylinders can be safely transported across the world,
- Gas cylinders are the most effective way of performing comparisons or proficiency testing schemes,
- Low measurement uncertainties can be achieved when high precision balances are used in the weighing process during the preparation of the gas standards.

The drawback of cylinders is the considerable preparation effort required before use, such as passivation of the inner walls and removal of residual gas. Gas cylinders are generally expensive.

The other method used for preparing gas mixtures is the dynamic system, which involves mixing two streams of gas that flow continuously to generate the target mole fraction under controlled environmental conditions. The preparation of gas mixtures by the

dynamic method is prescribed in the ISO 6145 series of guidelines (ISO 6145-10, 2002). This method is useful for components which are not stable in gas cylinders, such as nitrogen dioxide (Flores et al., 2012). The method has become common in the last decade and a half, where technology has been developed to facilitate the preparation of traceable reference gas mixtures (Słomińska et al., 2014). Several dynamic methods have been developed with highly accurate results (Brewer et al., 2014; Haerri et al., 2017).

A permeation system consists of a commercial device containing the component of interest as a liquid. The permeation device is designed to allow the liquid inside to continuously permeate through a membrane at a particular rate under controlled conditions. The parameters requiring control, such as pressure, temperature, and humidity, can be monitored by equipment with traceable calibration, rendering the generation of accurate reference standards. An example of a glass U-shaped commercial device, with a permeation device containing a liquid component of interest, is shown in Figure 2-1. The carrier inlet allows a diluent gas such as nitrogen or air at a controlled flow rate to pass through the glass beads into the chamber containing vapours of liquid permeated from the device, generating a calculated gas composition that can be measured on the analytical system. The system's temperature is monitored by a calibrated thermometer in the water bath. The amount of liquid in the permeation device can be weighed at regular intervals to measure the mass loss, which is used to calculate the permeation rate at a particular temperature.

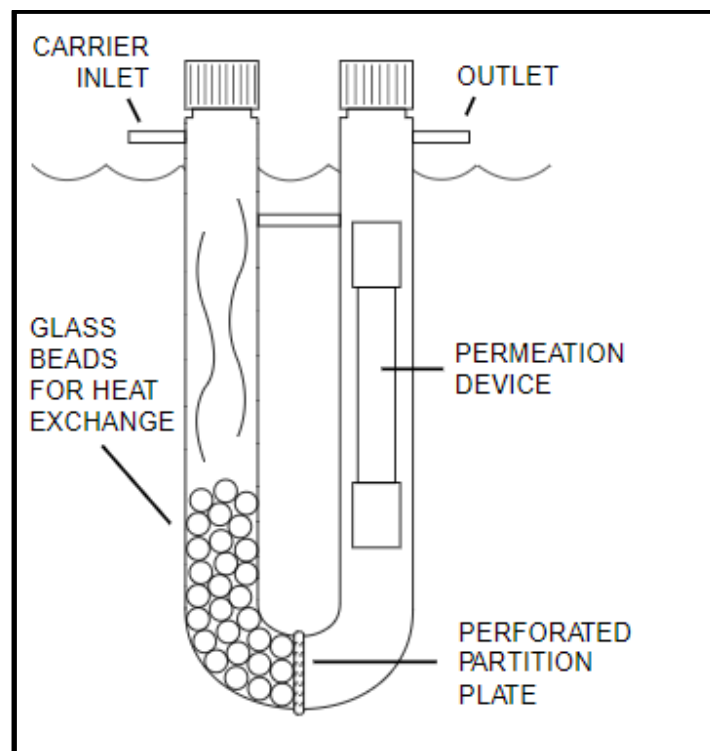


Figure 2-1: A “U” shaped glass permeation device.

(*Source: VICI Technical note 1001)

Halogenated greenhouse gases have been developed using permeation systems, for example (Guillevic et al., 2018), which are used as calibration standards for monitoring these gases. Nitrogen dioxide gas standards have been developed using permeation devices as a reference measurement in international key comparisons (Flores et al., 2012 and 2021).

2.2 Background to BTEX reference gases

Volatile organic compounds are classified according to their boiling points (Jantunen et al., 1997), ranging from 50 to 240 °C. The compounds with low boiling points are extremely volatile, and those with high boiling points above 240 °C are semi-volatile. Reference gas mixtures containing BTEX, or at least one of the components thereof, have been prepared and verified by GC-FID or GC-MS. Reference gas mixtures containing benzene and tetrachloroethylene were originally prepared by the micro-gravimetric technique (Schmidt & Rook, 1983). Since then, many reference gases traceable to the SI have been prepared, monitored for stability, and used in various

applications. The micro-gravimetric technique was further developed by preparing toxic volatile organic compounds in groups (Rhoderick & Zielinski, 1988). In these gas mixtures, the combination was chlorinated VOCs and at least one of either benzene, toluene, or xylene.

The establishment of the WMO-GAW project for monitoring reactive gases, which included the VOCs, prompted further development of VOC standards for quality control purposes (WMO-GAW, 1995). After the World Meteorological Organisation Bundesministerium für Bildung Wissenschaft, Forschung und Technologie (BMBF) workshop on “the establishment of a world calibration/ instrument intercomparison facility for VOC” in 1995, reference standards of VOCs prepared mainly were to support the WMO-GAW initiative. First, a VOC reference gas mixture containing fifteen components was prepared (Rhoderick, 1997). This was followed by the thirty-component mixture in 2006 (Rhoderick & Yen, 2006) and 2010 (Grenfell et al., 2010), using the stainless steel loop method. A diffusion technique was used to prepare two groups of VOC gas standards, a halogenated hydrocarbon group and the hydrocarbon group, which contained benzene, toluene and other hydrocarbons (Gautrois & Koppmann, 1999). Due to many available applications of traceable reference standards, both static and dynamic methods are routinely used as a source of traceability for measurements in monitoring VOCs and research.

2.3 Gravimetric preparation of BTEX

The gravimetric preparation method is the most commonly used for preparing primary reference gas mixtures (ISO 6142-1, 2015). Compounds that are liquid at room temperature are introduced into the cylinder by vacuum of the cylinder or flow assisted by a gas stream, followed by the addition of the diluent gas to obtain the desired mole fraction of components. The VOC of choice must be able to vaporise completely when introduced into the cylinder. The principle of VOC gas mixture preparation is based on the vapour pressures of the pure compounds under normal conditions. The vapour pressures of the BTEX compounds relevant to this study are listed in Table 2-1.

Table 2-1: Calculated vapour pressure of BTEX components at 20 °C

Component	Temperature (°C)	Vapour pressure (kPa)
Benzene	20	9,94
Toluene	20	2,93
Ethylbenzene	20	0,93
o-xylene	20	0,93
m-xylene	20	0,87
p-xylene	20	1,19

Source (NIST Chemistry Webbook). Vapour pressure values were obtained from the Antoine plot curve on the NIST Chemistry Webbook and calculated to SI units as shown in the table.

Data in Table 2-1 was obtained from the Antoine equation (National Institute of Standards and Technology, 2018), which relates the vapour pressures of pure compounds at different temperatures.

The Antoine equation is given in equation 2.1:

$$\log_{10} P = A - \left(\frac{B}{T+C}\right) \quad 2.1$$

Where P is the vapour pressure (bar), T is the temperature (K), and A, B, and C are compound-specific constants (Cox & Pilcher, 1970; Pedley et al., 1986; Stull et al., 1969). Alternatively, the vapour pressure of pure components is available from the safety data sheets (SDS) of the chemical supplier. The vapour pressures of compounds at specific temperatures are used to calculate the highest mole fraction allowed to prevent condensation to liquid during preparation, use, and storage during the lifetime of the gas mixture. The mass of a component allowed to vaporise in the cylinder at a specific temperature is given by the ideal gas law equation:

$$PV = nRT \quad 2.2$$

Equation 2.2 can be re-arranged to equation 2.3 below when the number of moles (n) is replaced by the molar mass of the component (MM) and the mass (m).

$$m = \frac{PVMM}{RT} \quad 2.3$$

Where P is the pure component's vapour pressure, V is a cylinder's volume, R is the ideal gas constant, and T is the temperature corresponding to the vapour pressure. It follows from equation 2.3 that for a given mole fraction, the required mass of that component should not exceed the value calculated to avoid condensation. Using the ideal gas law equation, the target mass m_i from a parent, gas can be calculated as shown in equation 2.4 (ISO 6142-1, 2015).

$$m_i = \frac{x_i P_{cyl} V_{cyl} M_i}{RT Z_f} \quad 2.4$$

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

Equation 2.4 above calculates the mass of all components required to prepare a gas mixture, including a diluent gas. When the preparation is a multi-component gas mixture of BTEX, the desired mole fraction is calculated based on the component with the lowest vapour pressure (Grenfell et al., 2010).

The steps involved in preparing a reference gas mixture by the gravimetric method are shown in Figure 2-2. The cylinder type is selected according to the availability and affordability. Gas cylinders are mainly made of stainless steel or aluminium material. The cylinder pre-treatment involves passivation of the inner surface of the cylinders with the proprietary treatment to minimise adsorption of gas molecules. This step includes leak testing by pressurising the cylinder with helium gas and using a calibrated helium gas leak tester. Following the leak testing is the actual gas mixture preparation, which is completed by firstly evacuating the cylinder to remove residual gas, then secondly to weigh the cylinder empty to obtain the mass before the addition of gas components. Thirdly, the cylinder is filled with gas components of interest, of which each component mass is weighed accurately after addition. After the addition of all gas components, including the balance gas, the cylinder is homogenised by rolling on the roller bench. The next step is verification of gravimetric concentration by analysis with the applicable method. Lastly, the international equivalence is done by participation in the international

comparison with other metrology institutes. The selection of the starting material in the second column is determined from research of interest, which is driven by the priorities of the country or market requirements. Once the starting materials have been selected, the procedure requires that purity analysis must be conducted to confirm the specification provided by the manufacturer and to fulfil the requirement of measurement traceability of primary reference material. The selection of the starting material is completely independent from the cylinder type, since any cylinder material may be tested for any combination of gas molecules, provided that there will be no reaction between the cylinder inner surface and the gas components.

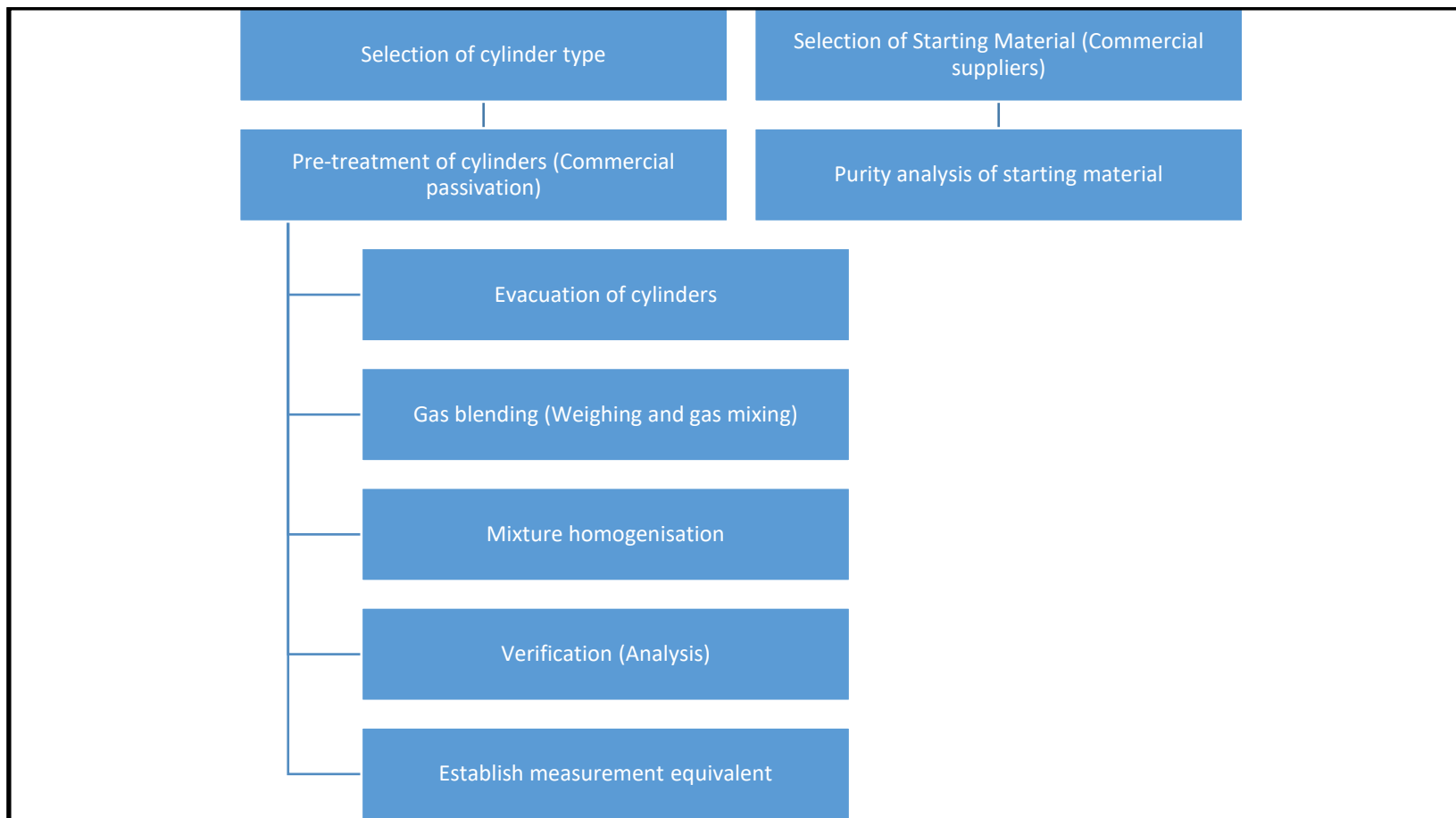


Figure 2-2: Preparation diagram of primary reference gas mixture

2.4 Purity analysis

The scope of purity analysis of the starting materials used in preparing reference gas mixtures is stipulated by the international standard (ISO 19229:2019, 2019). Therefore, the accuracy of reference gas mixtures depends on the complete assessment of the high-purity starting material. Such starting materials are gases or liquids sourced from commercial suppliers. High-purity starting materials have impurities, which result from the following processes:

- Unreacted reagents in the production of chemicals,
- Isomers of compounds under production,
- Chemicals that were introduced during the purification process.

Impurities are classified as critical, suspected, and contaminants (Duewer et al., 2004). Critical impurities present in material with a higher mole fraction than expected could render the material unfit for purpose. For example, a diluent nitrogen gas containing 10 $\mu\text{mol/mol}$ oxygen impurity cannot be used to manufacture a gas mixture containing oxygen below 10 $\mu\text{mol/mol}$. Suspected impurities are present due to material histories, such as preparation and purification. Contaminants are impurities not expected in the material, which could mean that the correct history may not be wholly known. The assessment of the purity of starting materials is also done to confirm the parent component. Impurities can render a material fit-for-purpose, depending on their level and classification. The analysis of impurities becomes significant if a reference material is directly linked to the International System of Units, i.e. if it is to be recognized as a primary reference material. This requirement is fulfilled by using methods with high metrological capabilities, such as the gravimetric method (Milton & Quinn, 2001) for purity assessment. Other methods include analysis techniques of reference material with metrological traceability (ISO 19229:2019, 2019). The technique used for quantifying impurities is gas chromatography with flame ionization detection for hydrocarbons (Duewer et al., 2004)(King & Westwood, 2001). Cavity ring-down spectroscopy is also used for gases with unique light emission characteristics (specific wavelength with no interfering species) (Persijn, 2018).

Organic chemicals are identified using a wide range of analytical techniques. Each technique has both advantages and disadvantages, depending on the application. The challenges may be overcome by combining analytical techniques to complement each other in confirming the identity of the organic chemicals. There are different approaches to ensuring that purity assessment is performed adequately which are (Westwood et. al, 2013):

- The direct analysis of the parent component,
- The analysis of total impurities and subtraction from unity.

The choice of the method used depends on the availability of analytical techniques and the level of uncertainty to be achieved.

2.5 Methods of gravimetric preparation

2.5.1 Syringe liquid method

This method employs a gas-tight syringe filled with the pre-calculated amount of a liquid component to be introduced into an evacuated cylinder. The syringe is accurately weighed with a liquid component before and after transferring into the evacuated cylinder. The difference between these two weighing cycles amounts to the mass of the liquid component introduced to the cylinder (ISO 6142-1, 2015). Figure 2-3 shows the introduction of liquid into the cylinder using the syringe.



Figure 2-3: Introduction of liquid using the syringe method

(*Source: ISO 6142-1:2015)

2.5.2 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 weighing it again (Rhoderick & Miller, 1990; Rhoderick & Yen, 2006; Rhoderick & Zielinski, 1988). The mass of the liquid introduced corresponds to the mass difference between the empty and filled glass tube. The glass tube is then connected to the filling line and transferred into the cylinder after the glass tube has been broken by high-pressure matrix gas. Some vaporisation of the liquid may occur during the sealing of the glass tube, especially with

volatile components, therefore, it is recommended to cool the tube before sealing it (Rhoderick, 1997).

2.5.3 Loop injection method

Tubing constructed from stainless steel with known volume is used to transfer liquid to the cylinder (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. A highly sensitive semi-micro comparator balance weighs the loop. In this preparation, a reference loop is required for the comparison method used as the loop is weighed 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 the difference of two weighing cycles of the loop before and after addition into the cylinder.

2.5.4 The U-tube method

Figure 2-4 shows a schematic diagram of the U-tube (6) connected to a gas manifold, with a vacuum (5), a cylinder to be filled and a diluent gas, with the direction of flow being from T-type connector 1 to the opposite side (ISO 6142-1, 2015). The side at T-type connector 1 is high-pressure diluent gas such as nitrogen, and the opposite side is the cylinder to be filled. The shut-off valves control the gas stream to evacuate, fill, and allow the U-tube to be connected and disconnected for liquid filling and weighing.

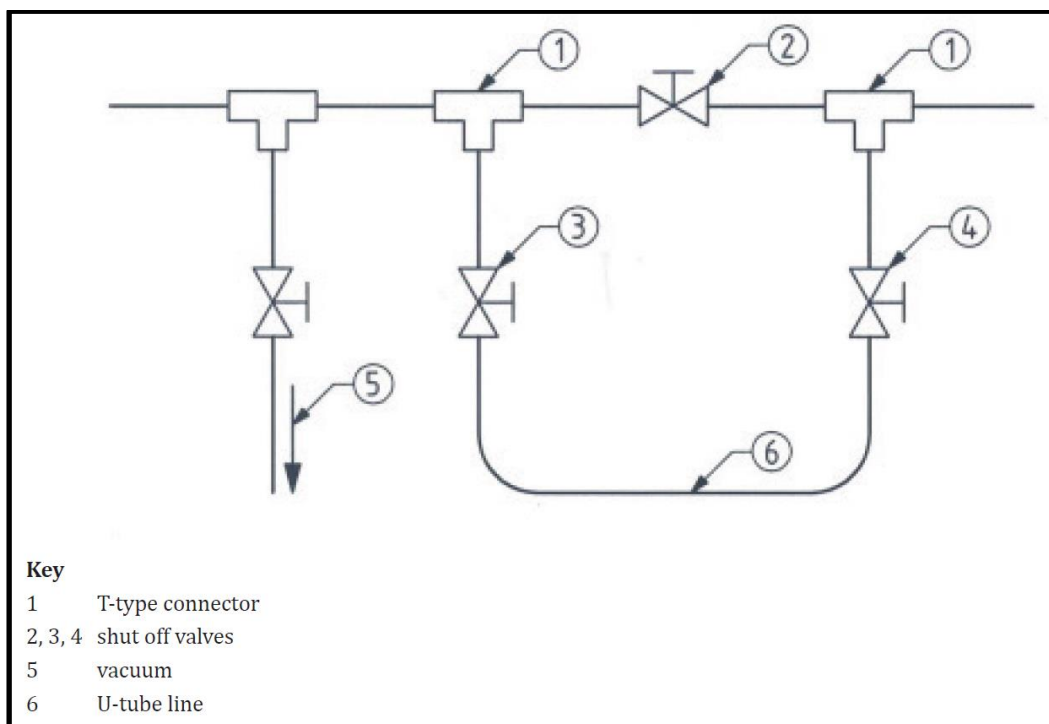


Figure 2-4: The U-tube method

(*Source ISO 6142-2015)

2.6 Analysis techniques for hydrocarbons

2.6.1 Gas chromatography with flame ionization detector

Gas chromatography flame ionization detection is the most widely used technique for analysing hydrocarbons (King & Westwood, 2001). It is a technique that separates hydrocarbon components according to their interaction with the column's stationary phase. There are many commercially available analytical columns with various stationary phases, such as the following:

- Porous layer opens tubular columns containing particles of different sizes, and the separation of components is based on the molecular size (Rhoderick et al., 2018)(Janse van Rensburg et al., 2007).
- Wall-coated open tubular columns with walls coated with liquid stationary phase, separating components by solvation (Liu et al., 1997).

The flame ionization detector is sensitive to hydrocarbons and has a dynamic linear range spanning from milli-mole (mmol/mol) to nano-mole (nmol/mol) (Rhoderick, 1991).

GC-FID analyses carbon dioxide (CO₂) and carbon monoxide (CO) at ambient and background levels by first converting them to methane through a reaction with hydrogen at 400 °C (methaniser) using nickel catalyst, due to its wide dynamic range. This method has lower uncertainties than spectroscopic methods (Flores et al., 2019; Janse van Rensburg et al., 2007; Rhoderick & Dorko, 2004). It has been demonstrated that the flame ionisation detector is less sensitive to the chlorinated hydrocarbons by comparison of data using the electron capture detector (ECD), which is more sensitive to the chlorinated hydrocarbons (Rhoderick, 1991).

2.6.2 Gas chromatography with mass spectrometry

Mass spectrometry provides unique features to qualitatively identifying many hydrocarbons in samples when used as a detector for gas chromatography. The principle of mass spectrometry is the ionisation and fragmentation of molecules by high energy impact. The fragmented ions are further separated according to their mass-to-charge ratio (m/z). The separation is achieved through a mass analyzer; the most commonly used mass spectrometer for volatile hydrocarbons is a mass selective detector (MSD) (Wylie, 2001). The mass spectrometer can detect compounds at the pico-mole level (Yan et al., 2017). This is particularly useful for analysing hydrocarbons in the atmosphere since many hydrocarbons are present at ultra-trace levels (Yoon et al., 2019).

2.7 Measurement equivalence

The measurement equivalence is established through coordinating international key comparisons conducted by the International Bureau of Weights and Measurements (BIPM). The key comparisons confirm the measurement capabilities of the NMIs and Designated Institutes (DIs) in producing reliable and accurate national measurement standards (MRA CIPM, 1999).

The role of the National Metrology Institutes is to realise the International System of Units (SI units), by preserving well-known artefacts (the kilogram) used as reference standards and to underpin new measurement capabilities. In addition, reference standards are used as a source of traceability for many measurements worldwide, thus breaking barriers to trade and promoting the harmonisation of scientific measurements.

The measurement capabilities of the international key comparisons in the gas analysis field are achieved by comparison of components measured at similar mole fractions of the same components (Van der Veen & Cox, 2003). The nominated NMI coordinates gas cylinders containing components of interest. The NMI coordinating the comparison usually prepares and analyses the samples before and after shipping to the participants (participating NMIs), where homogeneity and stability are computed. The equation governing the degree of equivalence between the coordinating laboratory and the participating laboratory is headed by equation 2.5 (Van der Veen & Cox, 2003).

$$D_i = (x_i - x_{igrav}) \quad 2.5$$

where D_i is the degree of equivalence of component i , x_i is the analytical result reported for component i and x_{igrav} is the gravimetric value of component i . The degree of equivalence is expressed with expanded uncertainty, which is calculated by equation 2.6.

$$U_i = k \sqrt{(u_i^2 + u_{igrav}^2)} \quad 2.6$$

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.

Many international key comparisons are conducted across the SI system to achieve the required measurement capability. The measurement capability that supports the volatile organic compounds has been previously shown, in 2002 by the Consultative Committee for the Amount of Substance- key comparison (CCQM-K7) for the measurement of BTEX gas standards at 50-100 nmol/mol (Guenther et al., 2002). Figure 2-5 shows the graphical representation of the results of degrees of equivalence of benzene at 50 nmol/mol. Blue squares represent the value for each participant, the zero line represents the reference value of each sample, and the error bars represent combined expanded uncertainty calculated according equation 2.6.

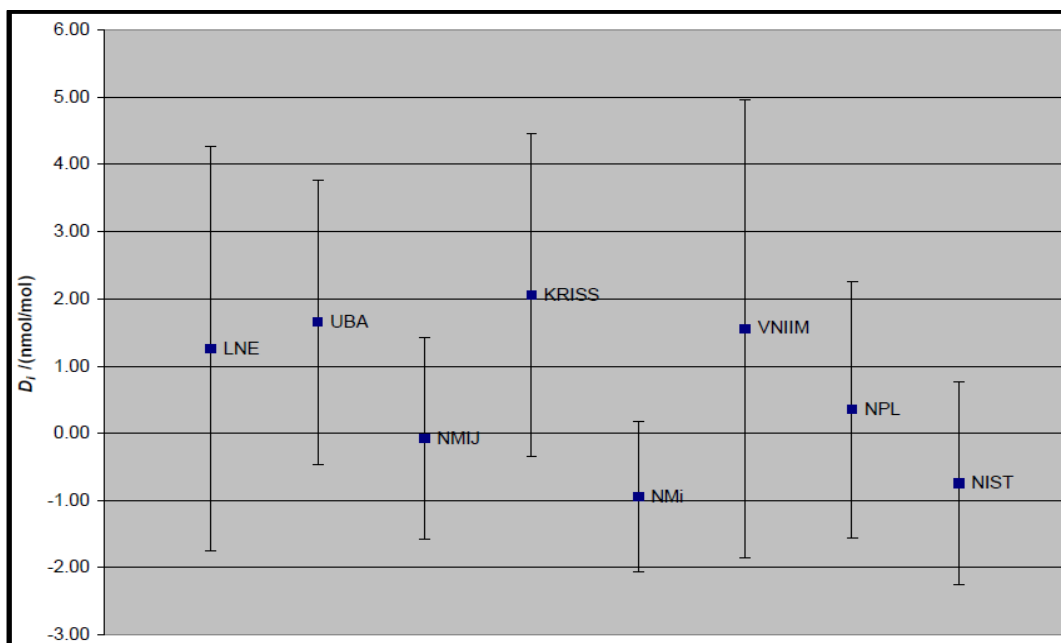


Figure 2-5: Degrees of equivalence for benzene at nominal 50 nmol/mol

(*Source: CCQM-K7)

It is observed that all participants (abbreviated names on the graphs) are equivalent to one another; their reported values are consistent with the respective reference values since the corresponding uncertainty covers the reference value. For example, the results of the degree of equivalence of toluene are shown in Figure 2-6, where the values of UBA, LNE, VNIIM and NIST are inconsistent with the reference values. A similar analogy is used for ethyl benzene, m-xylene and o-xylene, which are not shown.

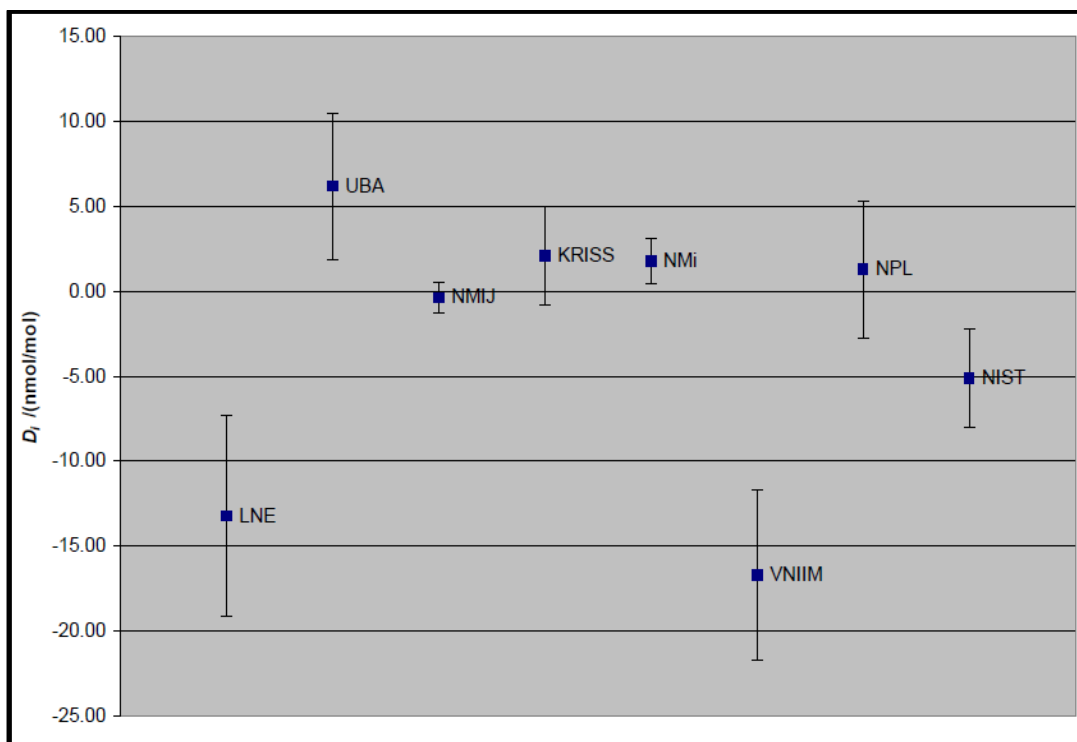


Figure 2-6: Degrees of equivalence for toluene at nominal 80 nmol/mol

(*Source: CCQM-K7)

In another study, the measurement capability of BTEX gas standards at a mole fraction of 5-10 nmol/mol was completed, the CCQM-K10 (Guenther et al., 2002). Figure 2-7 shows that the results of the degree of equivalence of benzene for all the participants are consistent with the reference value, except the results of NPL.

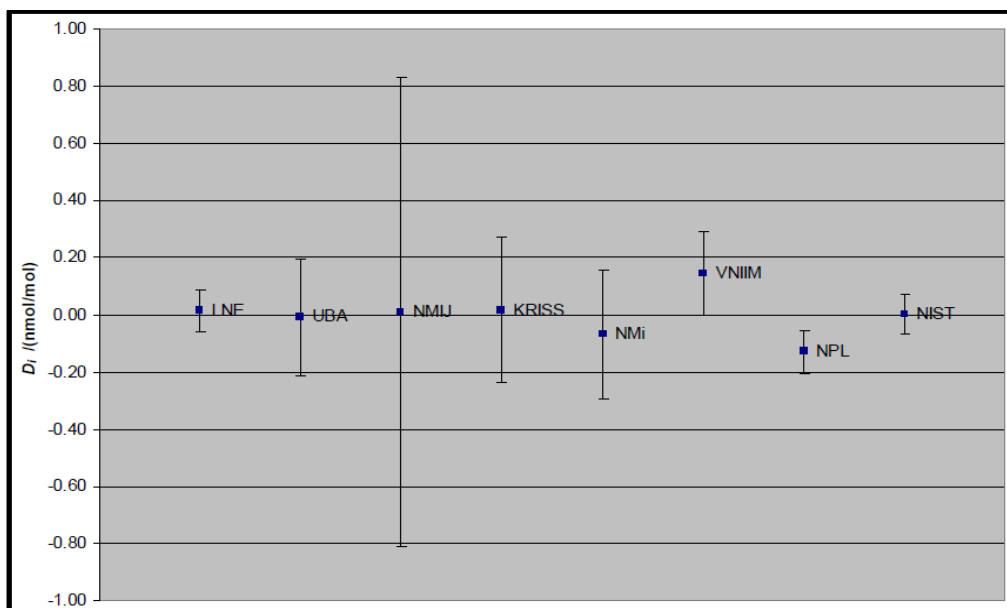


Figure 2-7: Degrees of equivalence for benzene at nominal 5 nmol/mol

(*Source: CCQM-K10)

In Figures 2-8 and 2-9, the inconsistent results for the degree of equivalence for toluene at 8 nmol/mol and o-xylene at 8 nmol/mol are that of VNIIM and NPL.

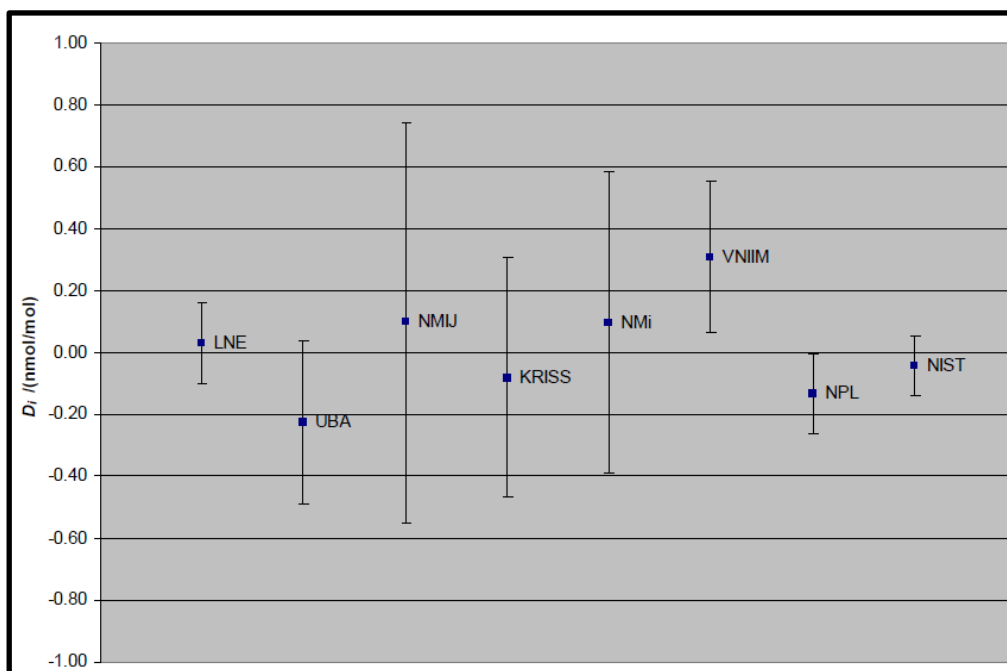


Figure 2-8: Degrees of equivalence for toluene at nominal 8 nmol/mol

(*Source: CCQM-K10)

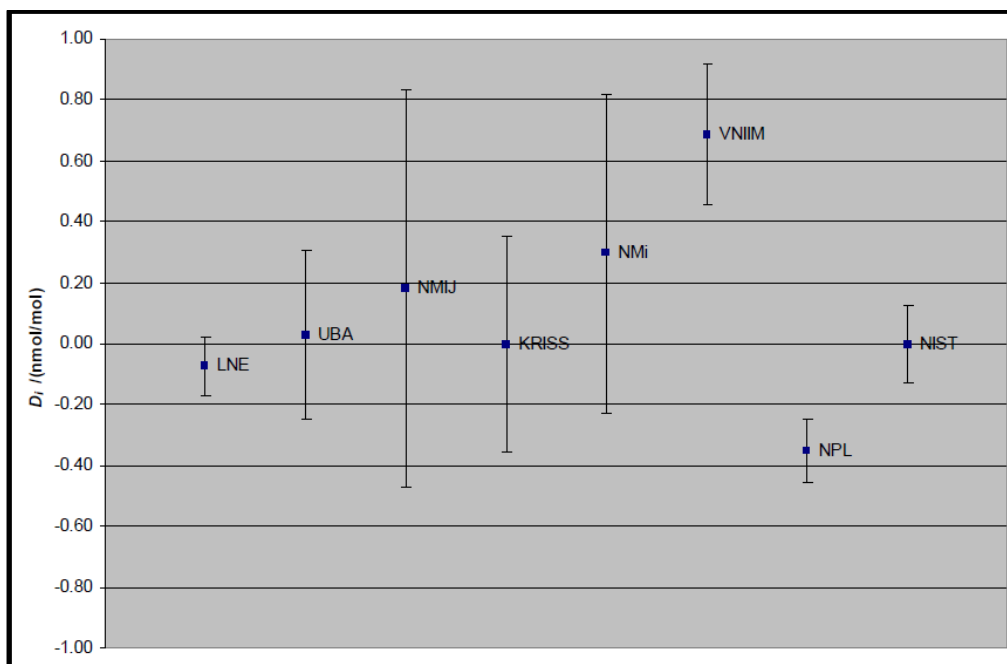


Figure 2-9: Degrees of equivalence for ortho-xylene at nominal 8 nmol/mol

(*Source: CCQM-K10)

The European Association of National Metrology Institutes (EURAMET) conducts regional comparisons that underpin measurement capabilities for VOCs. Figure 2-11 compares extracted data for BTEX from the EURAMET 886 report (Grenfell et al., 2010). In a study that the NPL coordinated, the results indicate better comparability among the five participants, an improvement from the CCQM-K10 in 2002, except FMI; the reported reason was that their calibration system used was BTEX solutions, which resulted in bias in their results.

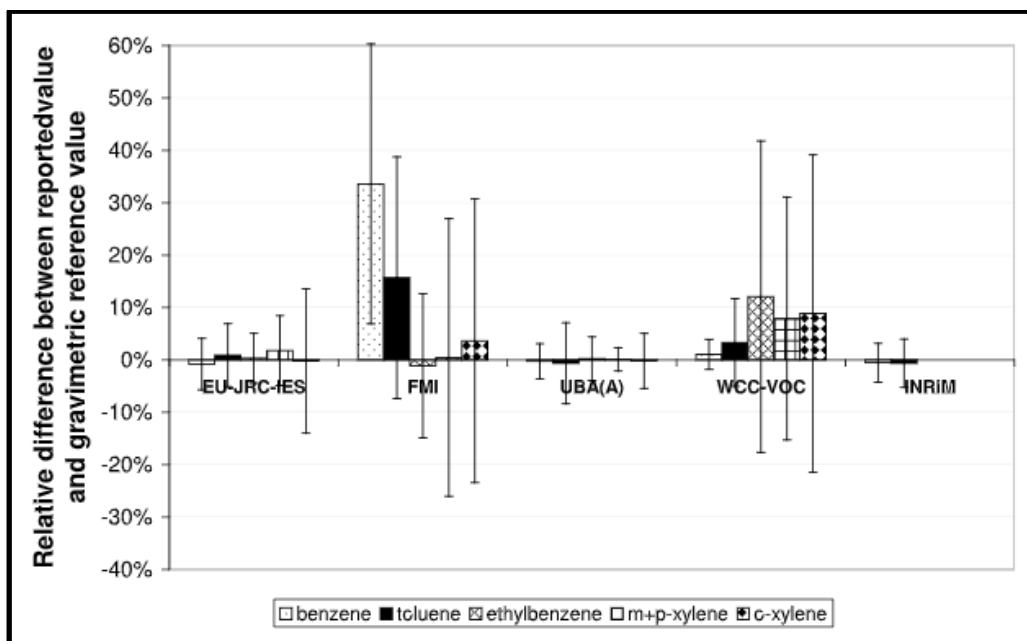


Figure 2-10: The results of BTEX at 3-4 nmol/mol extracted from the EURAMET 886 VOC comparison

(*Source: Grenfell et.al, 2010)

3. Experimental

This chapter details experiments followed to prepare BTEX gas mixtures by the gravimetric method. First, sources of high-purity starting materials and apparatus used are discussed. Then, methods of preparation and analysis are explained. Finally, the equipment used at various stages of the study is discussed.

3.1 High-purity starting materials

High-purity starting materials of benzene, toluene, ethylbenzene, o-xylene, m-xylene, and p-xylene, were sourced from Sigma Aldrich as shown in Table 3-1, which includes specification values and LOT numbers.

Table 3-1: Volatile organic compounds specification

Component	Specification from Manufacturer (%)	Lot number
Benzene	99,95	STBB0083
Toluene	99,9	SZBA0940
Ethylbenzene	99,9	00496PK
Ortho-xylene	99,1	1421425
Meta-xylene	99,7	BCBC1553
Para-xylene	99,7	1432941
Styrene	99,0	STBF9580V

Nitrogen BIP (Built-in-Purifier, BIP TM) gas was used as a diluent gas sourced from Air Products Southern Africa, with the minimum specification of 99, 9999%, excluding the impurity of argon, as specified by the manufacturer.

3.2 Instrumentation and materials

The gas cylinders used were made of aluminium sourced from Luxfer in the United Kingdom with a water capacity of 5 dm³ and 10 dm³, respectively. The cylinders were fitted with stainless steel valves with a Hastelloy® diaphragm sourced from Rotarex in

Luxemburg. For the evacuation of the cylinders, a Pfeiffer turbo molecular pump (HiCube 400 series, Germany) was used, shown in Figure 3-1.



Figure 3-1: Cylinders connected in the evacuation station

The syringes, glass vials, and stainless-steel transfer vessels were weighed using a Sartorius semi-microbalance (Model MC 210S) with a capacity of 210 g and readability of 0,01 mg, as shown in Figure 3-2.

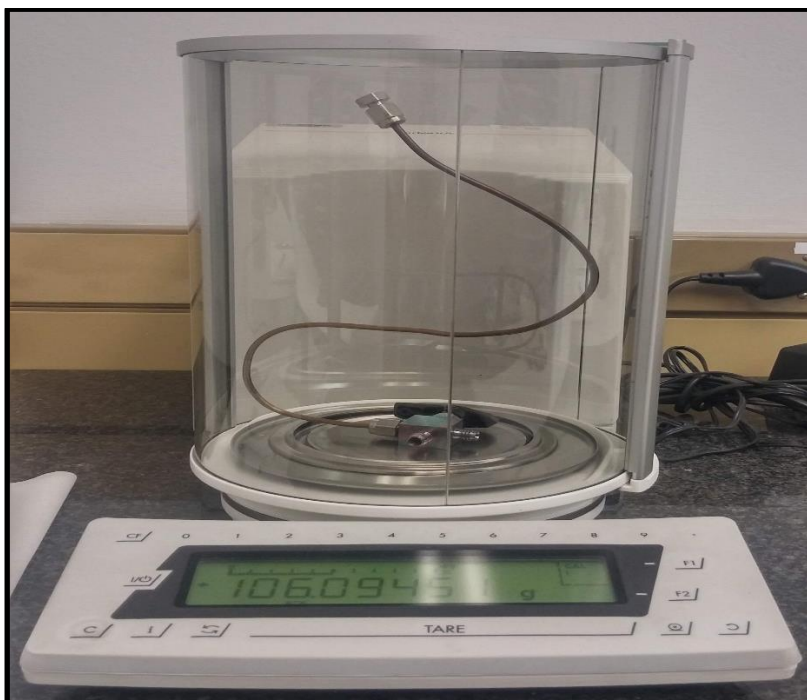


Figure 3-2: Sartorius semi-microbalance weighing transfer vessel

The syringes used were gas-tight (Hamilton 81056 series) sourced from Sigma Aldrich (Germany). The stainless-steel transfer vessels were made of 316 stainless steel tubing, sealed with a stainless steel cap at one end and a stainless steel 3-way valve at the other, sourced from Swagelok® (United States of America). The tubing diameter was 3,175 mm and was approximately 280 mm in length. Sulfinert® treated stainless steel transfer vessels with similar materials and dimensions were used. The two transfer vessels were used to determine the adsorption of BTEX in the tubing during preparation. The tubes were shaped as shown in Figure 3-2 to allow them to fit into the balance and determine the correct weight.

The glass capillary tubes were made of borosilicate glass of 100 mm length and 1 mm diameter (Sigma Aldrich, USA), an example shown in Figure 3-3.



Figure 3-3: Borosilicate glass capillary tube

(*Source: Eisco website, <https://www.eiscolabs.com/products/ch0882>)

The glass capillary tubes were weighed using a Mettler Toledo ultra-micro balance (Model UM 3) with a capacity of 3 g and a readability of 0,1 μg , shown in Figure 3-4. To prepare the gas mixtures at a nominal mole ratio of 500 nmol/mol or less, the capillary tubes are broken to a correct size by heating on the open flame, to which the tube heats up and melts. Then, the soft, heated capillary tube was pulled apart at both ends, creating a smaller size.



Figure 3-4: Weighing of capillary tubes on Mettler Toledo ultra-micro balance.

The weighing of cylinders was completed using the mass comparator balances. Before March 2017, all cylinders were weighed using the mass comparator balance (Mettler Toledo PR 10003) with a capacity of 10 kg and readability of 1 mg. The balance weighed only cylinders with an internal volume of 5 dm³, as shown in Figure 3-5.



Figure 3-5: Mass comparator with suspension pan for 5 dm³ cylinders

From April 2017, all cylinders were weighed using the Automated Weighing Device (AWD) procured from the Korean Institution of Standard and Science (KRISS). A motor controls the AWD to rotate the cylinders by interchangeably placing them on the mass comparator balance (Mettler Toledo Model XP26003L with a capacity of 26,1 kg and 1 mg readability). The automation and data capturing were programmed using LabVIEW software programmed at NMISA. Figure 3-6 shows the AWD weighing cylinders.



Figure 3-6: AWD for weighing of cylinders

The filling of gas (nitrogen diluent gas) was done on a gas manifold (Filling Station) shown in Figure 3-7. The gas manifold was constructed from 316 stainless steel tubing, nuts, shut-off valves and flow control valves. The stainless steel parts were sourced from Swagelok in the USA. Gas manifolds are designed and assembled by the gas manufacturers; the one shown in Figure 3-6 was sourced from KRISS. In addition, NMISA has their own assembled gas manifold.



Figure 3-7: Gas Filling Station or Manifold

The gas filling station was constructed of 316 stainless steel tubing, configured with shut-off valves to isolate the nitrogen gas side, the filling side, and the evacuation pump. The evacuation pump was used to remove the residual gas from the filling station. For evacuation purposes, a Pfeiffer turbopump (HiCube 80, Germany) was used with the capability of a vacuum of 1×10^{-7} hPa. Alternatively, a dry scroll vacuum pump (Scroll Meister ISP 250 series, Anest Iwata in the USA) with the capability of vacuum $1,2 \times 10^{-4}$ hPa was used. After adding all gas components (the components of interest and the diluent gas), and the final weighing, the cylinder was homogenised on a roller bench (Figure 3-8) for a minimum of two hours. The roller bench was designed and assembled at NMISA based on the cylinder's dimensions.



Figure 3-8: Roller bench for homogenisation

The analysis was completed using gas chromatography coupled with a flame ionisation detector. For the analysis of BTEX gas reference standards at a micro-mole fraction amount ($\mu\text{mol/mol}$), the Varian 3800 (USA) series and the Agilent 7890 (USA) were used. The analysis of nano-mole fraction amounts (nmol/mol) gas reference standards was completed by using the Entech 7200 (Entechinst, USA) and Nutech 8900 (Nutechinst, USA) pre-concentrators. The pre-concentrator systems were used to trap the BTEX components and remove carbon dioxide and residual moisture. The pre-concentrator consists of a series of commercially available adsorbent materials trapping volatile organic compounds under cold conditioning using liquid nitrogen.

3.3 Gravimetric preparation of BTEX standards in cylinders

The preparation of reference gas mixtures was completed following the guidelines of ISO 6142. Gas mixtures with components at a nominal mole fraction of 30, 10, and 2 $\mu\text{mol/mol}$ were prepared directly from pure starting material, followed by the addition of

nitrogen gas to a pre-calculated mole fraction. A minimum of four gas mixtures were prepared at a chosen mole fraction, enabling verification using a one-point calibration method for similar mole fraction components. For gas standards at a mole fraction of 30 $\mu\text{mol/mol}$, three components (i.e. benzene, toluene, and one of the xylene isomers) were prepared. This was done because of industry demands to calibrate field instruments for air pollution monitoring in South Africa. BTEX standards at nominal mole fractions of 500, 100, and 5 nmol/mol were prepared by dilution from high mole fraction gas mixtures.

3.4 Preparation of BTEX gas reference mixtures

The gas reference mixtures contained in gas cylinders (static method) were prepared by the gravimetric method following the ISO 6142 guidelines (ISO 6142-1, 2015), involving steps detailed in the following section. The production diagram is shown in Figure 3-9

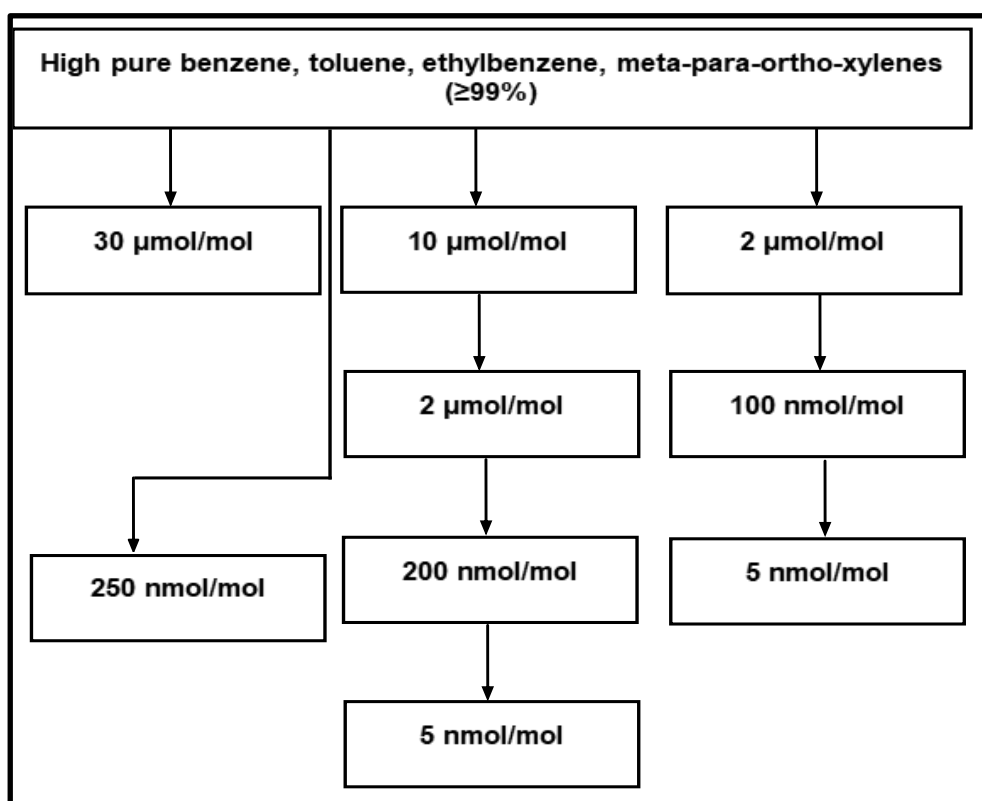


Figure 3-9: The production diagram of BTEX gas reference mixtures

3.3.1 Cylinder treatment

Before using the cylinders, they were fitted to the valves and tested for leaks using helium gas (5.0 purity, Air Products Southern Africa). Although expensive, helium is of low density and will escape the cylinder through the tiniest opening. The cylinders were filled with helium to about 2 MPa and tested for leaks by a calibrated helium leak tester at Air Products. The passivation process followed the leak testing by treating the internal walls of the cylinders with a patented fluorination process at Pelchem in South Africa. The cylinders were treated with hydrogen fluoride polymer to passivate active sites on cylinder walls, thereby protecting the cylinder from corrosion and minimising adsorption of components onto the walls of the cylinder.

3.3.2 Addition of BTEX components into the cylinder

3.3.2.1 Method 1 (NIST method)

For this procedure, the micro-gravimetric method was used. The capillary tubes (100 mm in length) were reduced to a smaller size to enable sampling of a small amount of liquid (approximately 50 μL is required to prepare 500 nmol/mol of standard). The capillary tubes were reduced by placing them in an open flame; the heat caused the glass to soften, which was then pulled apart at both ends with tweezers, creating a thin-walled diameter on the heated ends. When the capillary tube was removed from the flame, it cooled rapidly and broke off. One side was re-sealed in the flame, and the other was left open to allow the organic liquid to be drawn into the capillary tube. The reduced capillary tubes were weighed empty to obtain the mass of the tube. Figure 3-9 shows the schematic diagram of liquid addition into the capillary tube. The organic liquid (benzene for example) was added into the test tube. The capillary tube was placed in the test tube with the opened side exposed to the organic liquid. The empty syringe was fitted on the test tube with a seal. When the syringe was pushed in, it displaced the air out of the capillary tube. When the syringe was pulled, it created a vacuum in the capillary tube and the BTEX component filled into the capillary tube. The capillary tube was weighed before sealing to observe that the pre-calculated required mass of the particular component was achieved. When the required mass of the organic liquid was achieved, the capillary tube was sealed in the flame and allowed to cool before weighing.

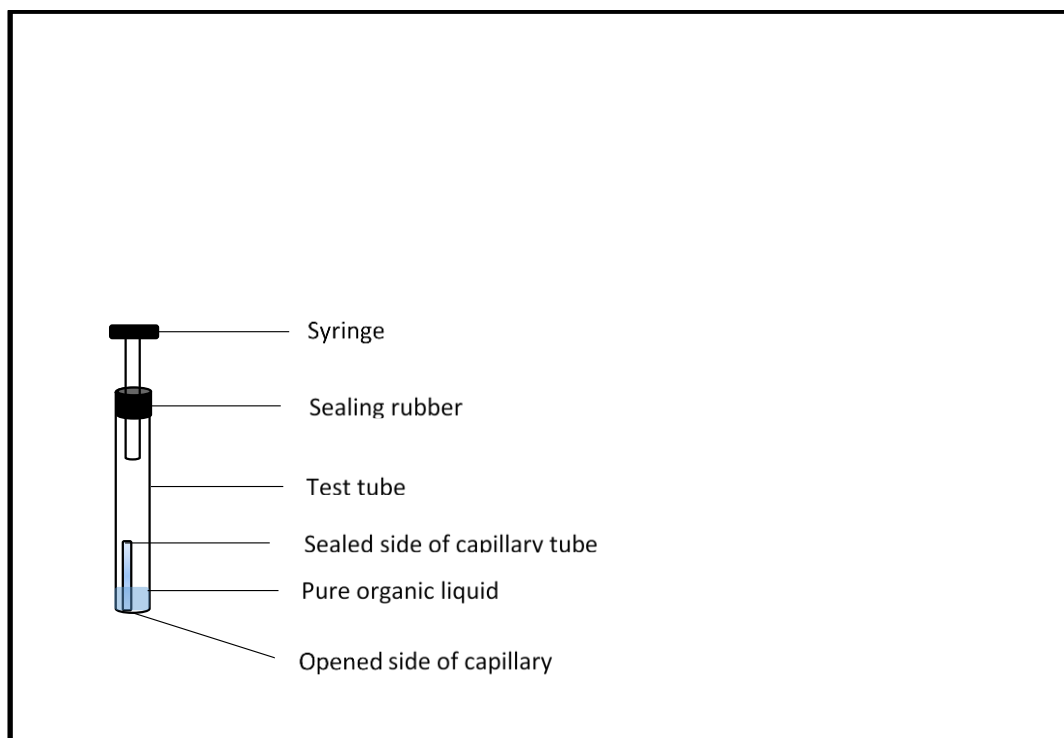


Figure 3-10: A schematic diagram of organic liquid addition into the capillary tube

The sealing of highly flammable organic liquid was achieved by placing the capillary tube in ice to prevent the loss, as shown in Figure 3-11.



Figure 3-11: Sealing of a capillary tube containing a highly volatile component using dry ice

Before adding components into the cylinder, the capillary tubes containing organic liquid components were each weighed at least three on the microbalance. Then, the organic liquid in the capillary tube was transferred into the evacuated cylinder, as shown in Figure 3-12.

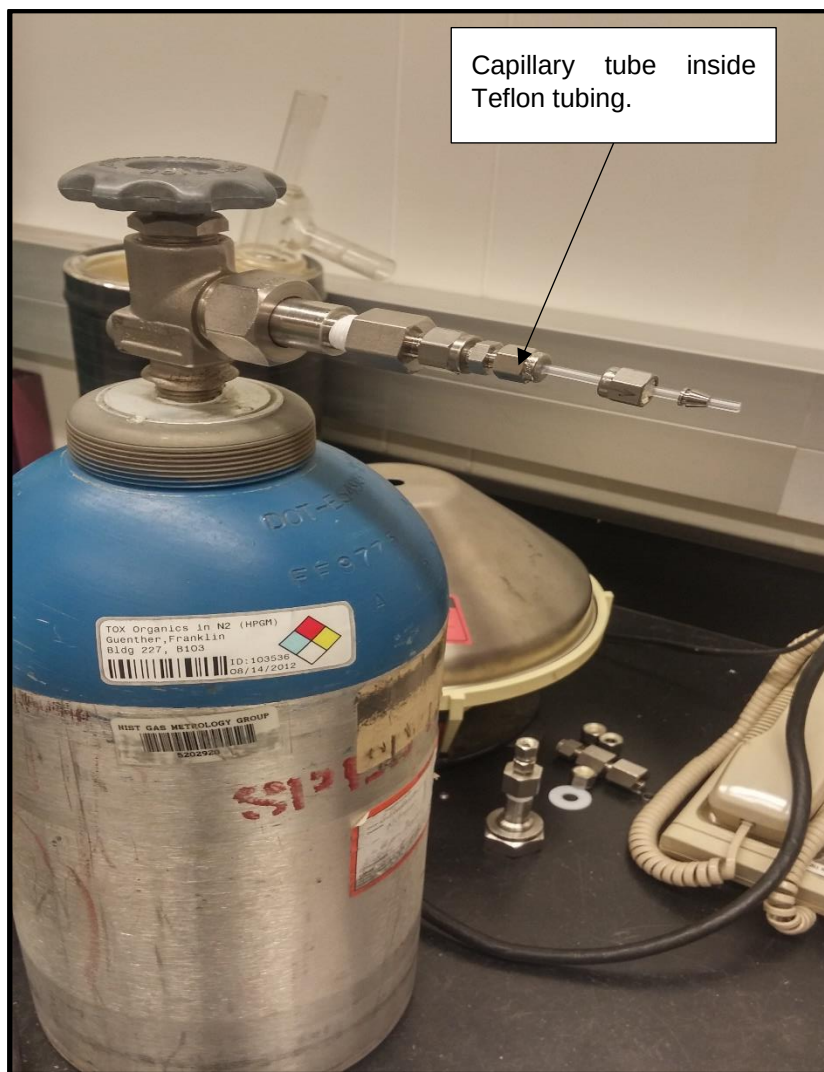


Figure 3-12: Addition of organic liquid into the cylinder

The capillary tube was placed inside the Teflon tubing. The capillary tube creates a seal on the side of the Teflon tubing exposed to the atmosphere. The side of the capillary tube connected to the cylinder was broken off by pinching the Teflon tubing with pliers, forcing the liquid into the cylinder by vacuum when the cylinder valve was opened. An electric heat gun was used to vaporise the less volatile components to be transferred via gentle heating of the Teflon tubing. To aid the transfer of organic components into the cylinder, a small amount of nitrogen gas was purged through the Teflon tube, connected

to the side exposed to the atmosphere, after the initial organic liquid was drawn into the cylinder by vacuum. Organic components were added sequentially following the steps explained above, starting with the least volatile to the most volatile component. The amount of liquid transferred into the cylinders was calculated by the mass difference of empty and filled capillary tubes. Next, pre-calculated diluent gas was added to the gas cylinders at the filling station, followed by weighing using the mass comparator balance.

3.3.2.2 Method 2 (The NPL method)

This method mixed organic components into a glass vial (15 ml) sealed with a septum (PTFE). The amount of each organic component required was pre-calculated based on the required mole fraction to be prepared (e.g. 10 $\mu\text{mol/mol}$). An empty vial was weighed accurately on the semi-micro balance. Each organic component was added to the vial, by injecting the required volume measured by the gas-tight syringe (Hamilton) through the septum, followed by the accurate weighing of the glass vial. The organic components were added sequentially, starting with the component that was least volatile. The total weight of the solution was calculated. The gas-tight syringe drew an aliquot of the total solution from the vial and added it to the evacuated stainless-steel transfer vessel. The transfer vessel was evacuated to a vacuum of $1,6 \times 10^{-6}$ mbar at the gas manifold. The transfer vessel was weighed with liquid, followed by the transfer of liquid into the cylinder by vacuum obtained during the evacuation process. The transfer vessel was connected to the cylinder valve via a special connection called the Minimal Dead Volume (MDV) connector (item iii in the picture a of Figure 3-13). The MDV connector has a small internal volume compared to the volume of the normal cylinder bullnose, resulting in insignificant losses of organic liquid by adsorption during transfer. The mass of the solution added into the cylinders was calculated by the difference between the weight of the transfer vessel with liquid and the weight after the liquid transfer into the cylinder.

The apparatus used for the NPL method are shown in Figure 3-12. In the picture the following apparatus is shown;

- i. Valve nut for CGA-330 cylinder (left turn)- specially made by Rotarex for NMISA
- ii. NPL MDV valve nut for DIN 14 valve- NPL patent
- iii. NPL MDV bullnose-NPL patent
- iv. NPL MDV connector with 3,175 mm diameter brass nut
- v. Valve nut for CGA-330 cylinder (right turn)- specially made by Rotarex for NMISA

In picture b, the following apparatus is shown;

- i. Sulfinert-treated stainless steel vessel with end cap and three-way valve
- ii. 1 ml Hamilton gas-tight syringe
- iii. 316 stainless steel vessel without end cap and three-way valve

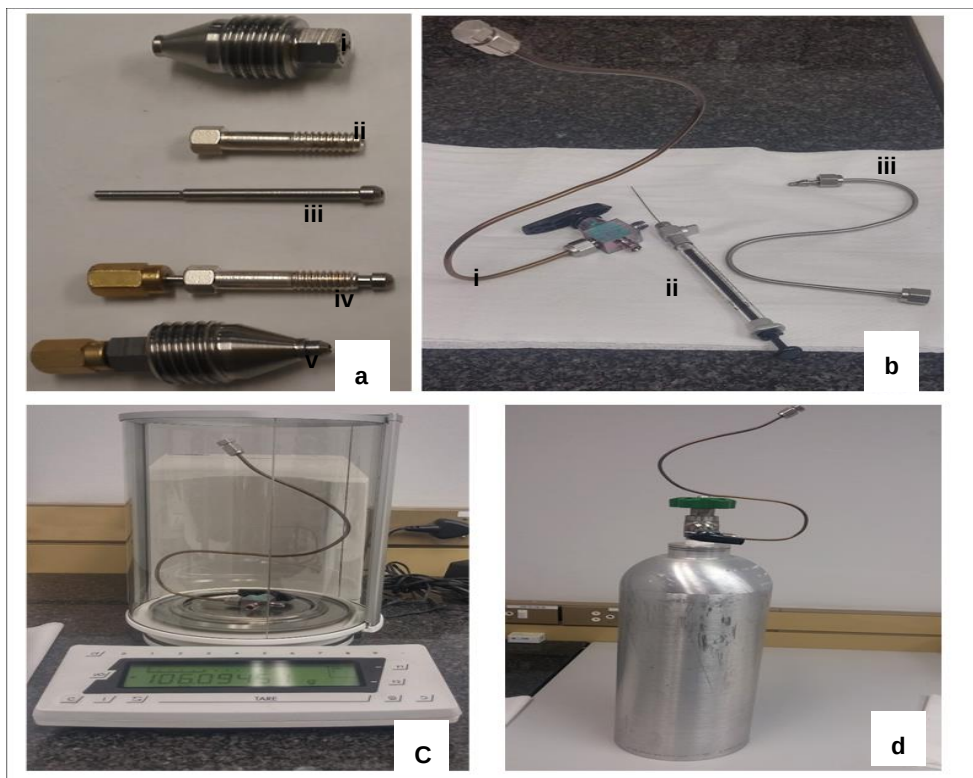


Figure 3-13: Apparatus used for NPL method. a) MDV connector, b) stainless steel vessel, c) Weighing of a vessel, d) Connection of vessel to a cylinder

The cylinder valve is pre-drilled to fit the MDV connector (NPL patent), Figure 3-14



Figure 3-14: NPL cylinder valve pre-drilled to fit MDV connector

(Sourced from NPL)

3.3.2.3 Method 3 (The KRISS method)

A stock solution containing all required components was used to prepare the multi-component mixture. Components of BTEX were added into a pre-weighed empty vial (15 ml with PTFE septum) according to their vapour pressure, starting with the component with the lowest vapour pressure. Each component was added into the vial by injection of a known volume with a gas-tight syringe. The vial was accurately weighed on the semi-micro balance after each addition of the component. The mass of each added component was calculated by the difference between the two successive weighings. The mixed components were added into the cylinder by drawing the known volume into the gas tight syringe, followed by accurate weighing. After weighing the syringe with stock solution, it was transferred into the cylinder through a dedicated heated syringe connector, as shown in Figure 3-15. The syringe connector was heated to a temperature between 50

and 60 °C by a dedicated heating block controlled by electronic setting with a thermocouple. The stock solution in the syringe connector is vapourised and swept into the cylinder by purging with about 0,35 MPa of nitrogen. The mass of stock solution added into the cylinder was obtained by difference of the mass of syringe with solution and the mass of empty syringe after transferring into the cylinder. The cylinder was weighed roughly on the mass comparator balance to determine the mass of nitrogen used to sweep the stock solution into the cylinder. The final mass of nitrogen required was calculated, considering the nitrogen already in the cylinder. The required mass of nitrogen was added into the cylinder using the gas filling station in Figure 3-7.



Figure 3-15: Addition of BTEX into the cylinder using KRIS heating syringe block

After the final weighing, all gas mixtures were homogenised by placing them on the roller bench in Figure 3-7 for a minimum of two hours before analysis.

3.5 Purity analysis of starting materials

The purity analysis of the starting material was done using gas chromatography with a flame ionisation detector (FID), mass selective detector (MSD), pulsed discharged helium ionisation detector (PDHID) and methaniser FID. The purity analysis of BTEX was done using the Agilent 7890B GC-FID-MSD. Approximately 0,5 ml of pure

component was placed in the 15 ml GC vial (gas tight) and allowed to equilibrate between liquid and vapour. One (1 μ L) of each pure component was injected individually onto the HP-INNOWax column (60 m x 0,32 mm id x 0,5 μ m df). The method parameters are shown in Table 3-2. The effluent from the analytical column was split to FID and MSD via capillary flow technology (CPT). The CPT is designed to configure the GC with multiple detectors using capillary columns to provide various signals of the same sample. In this case, the sample was split to the FID for quantitative analysis and to the MSD for qualitative analysis.

Table 3-2: Method parameters for purity analysis using Agilent 7890B GC-FID-MSD

Parameter	Condition
Injector source	GC ALS (10 μ L syringe)
Injection volume	1 μ L
Wash Solvent	Methanol
Split ratio	2:1
Injector temperature	250 $^{\circ}$ C
Carrier gas	Helium
Column type	HP INNOWAX (60 m x 320 μ m id x 0,5 μ m df)
Column flow	1,5 ml/min
Oven temperature programming	Initial temperature at 40 $^{\circ}$ C held for 5 minute, ramp at 4 $^{\circ}$ C/min to 60 $^{\circ}$ C (hold 3 minutes), ramp at 10 $^{\circ}$ C/min to 120 $^{\circ}$ C (hold 15 minutes).
Detector temperature (FID)	300 $^{\circ}$ C
MS transfer line temperature	250 $^{\circ}$ C
MSD acquisition mode	Scan
Solvent delay	3 minutes
Splitter column to FID pressure	0,5 psi
Splitter column to MSD pressure	0,5 psi

Impurities of high-purity nitrogen were quantified according to the following;

- CH₄, CO and CO₂ were analysed using a GC-FID with methaniser on a combination of Restek shin carbon 2 m,100/120 mesh, 1/8 inch od, 2.0 mm id and molesieve 5A 2m, 80/100 mesh, 1/8 inch od, 2.0 mm id columns.
- Ar, O₂ and H₂ were analysed using a GC-PDHID on a CP-molesieve 5A plot column (50 m x 0.53 mm id x 50 μ m df).

The analytical conditions for the analysis of Ar, O₂ and H₂ are shown in Table 3-3.

Table 3-3: Analysis of Ar, O₂, and H₂ in N₂ using Agilent 7890 GC-PDHID.

Parameter	Experimental conditions
Column	CP-molesieve 5A plot column (50 m x 0.53 mm x 50 µm)
Column pressure	250 kPa
Detector	PDHID
Oven temperature	30 °C isothermal for 8 minutes
Detector temperature	300 °C
Sample flow	100 mL/min
Sample loop	500 µL
Total run time	8 minutes

The analytical conditions for CH₄, CO and CO₂ analysis are shown in Table 3-4.

Table 3-4: Analytical conditions for CH₄, CO and CO₂ in N₂ BIP on Agilent GC-FID 7890B

Parameter	Experimental conditions
Column 1	Restek shin carbon 2 m,100/120 mesh, 1/8 inch od, 2.0 mm id
Column 2	Molesieve 5A 2m, 80/100 mesh, 1/8 inch od, 2.0 mm id.
Column pressure	250 kPa for both columns
Oven temperature programming	60 °C for 3.2 minutes, ramp to 90 °C for 3.8 minutes
Detector temperatures	FID – 300 °C and methaniser at 400 °C
Sample flow	100 mL/min
Sample loop	2 mL
Total run time	9 minutes

3.6 Analysis of BTEX gas mixtures

The gas mixtures were analysed using gas chromatography with a flame ionization detector. The samples were connected to a multipoint stream selection valve (VICI valve) for the selection of samples. The stream selection valve was connected to the gas sampling valve of the GC. The gas sampling valve is usually a six-port valve used to sample the gas and inject it into the inlet of the GC. A typical configuration of a six-port valve is shown in Figure 3-16.

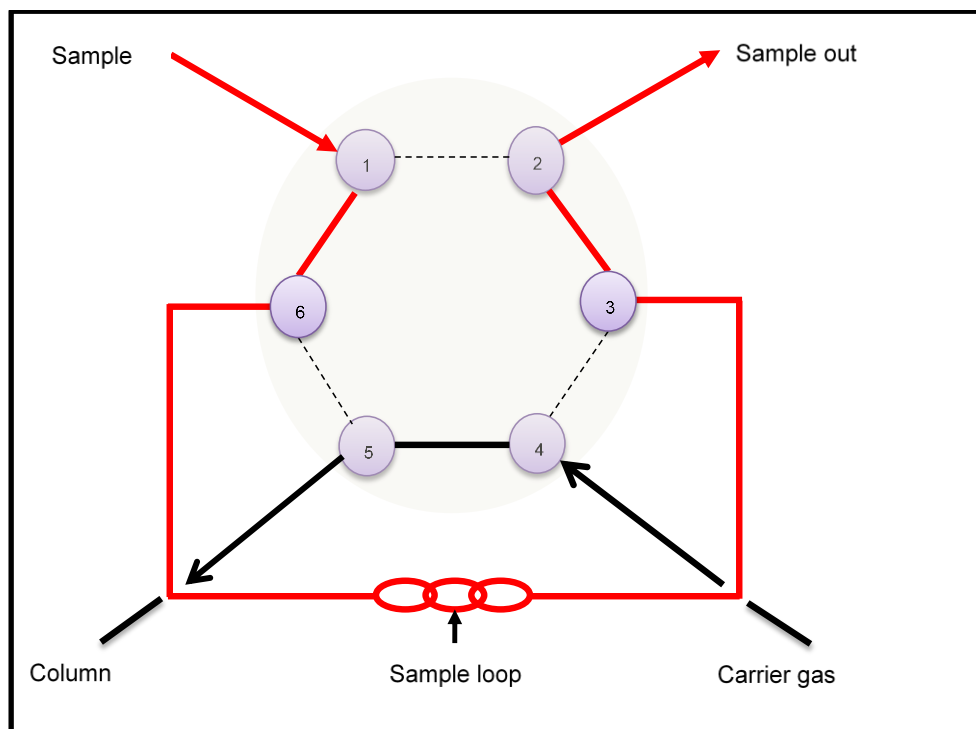


Figure 3-16: A typical six-port sampling valve

In the configuration (sampling or filling mode), the valve is in the filling position where the sample is entering position 1, connects to position 6, fills the sample loop, and goes out to vent via position 3, as shown by the red lines. The carrier gas enters from position 4 to position 5 into the GC. When the valve switches to inject, positions 3 and 4 connect, positions 5 and 6 connect to introduce the sample into the GC column. Then position 1 and position 2 connect, and the system is vented. For the analysis of mole fraction higher than $1 \mu\text{mol/mol}$, a 0.05 ml to 1 ml sample loops were used. For low mole fraction analysis of less than $1 \mu\text{mol/mol}$, a 2 ml to 10 ml sample loop was used.

The gas mixtures containing 2 to $30 \mu\text{mol/mol}$ of BTEX were analysed using a GC-FID (Varian 3800 and the Agilent 7890B). The analysis set-up was done as shown in Figure 3-17. The diagram has four cylinders under analysis, the sixteen black dots with white holes representing the positions connected to the multi-position stream selection valve. The exit position of the stream selection valve is connected to a mass flow controller. The gas stream enters the sample loop connected to a gas sampling valve in the filling position. In the injection position, the sampling valve switched, allowing the carrier gas to sweep the sample into the GC-FID. A valve switching to the inject position triggers the GC software (Agilent open Lab) to acquire the analysis run.

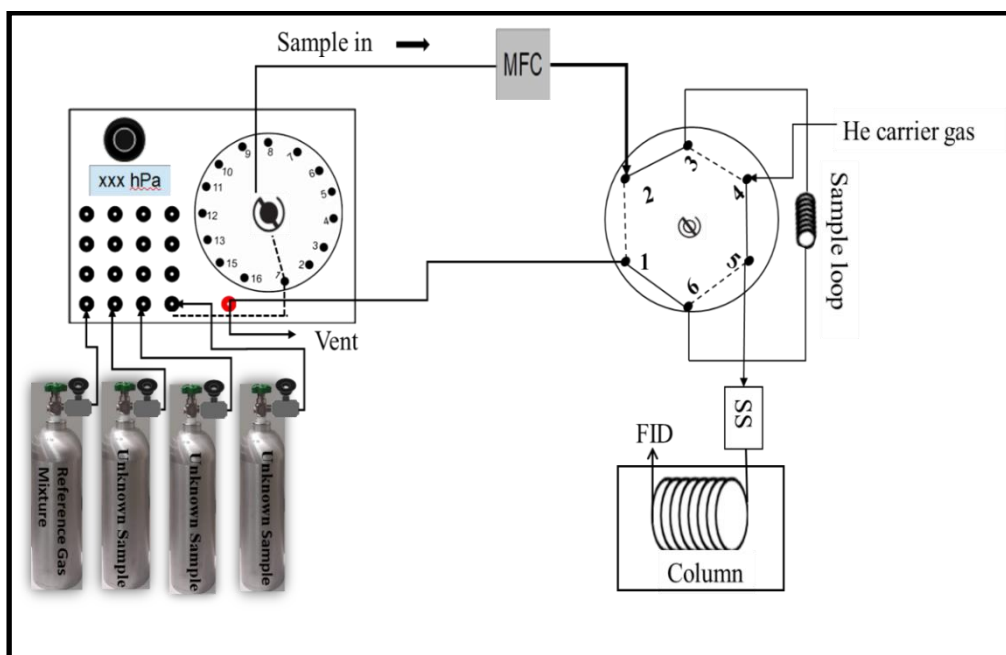


Figure 3-17: A schematic diagram of sample-path from sample to GC-FID

The gas mixtures were connected to a sampler box containing a multi-position stainless steel valve (VICI valves, USA), the pressure transducer (WIKA), with readout to monitor the pressure of cylinders, the mass flow controller (Bronkhorst) was used to maintain flow from the cylinders to the gas sampling valve. The gas lines were made of 1,59 mm diameter Sulfinert-treated tubing. The gas mixtures were injected into the GC inlet by the 6-port sampling valve.

The samples with a mole fraction of 500 nmol/mol and below were analysed by introduction into the pre-concentrating unit followed by injection into the GC-FID. Two pre-concentrating units were used, the Entech 7200 and the Nutech 8900 DS, operated under cryogenic conditions.

The flow diagram of the ENTECH 7200 pre-concentrator is shown in Figure 3-18, showing the system's main parts, the valves for the flow path, the three pre-concentration modules, the hydrocarbon trap, the volume determination reservoir, the flow devices and pressure gauges for different purposes. Figure 3-18 also shows event three of twenty-one, where the following happens;

- Helium gas flows through module 3 cryo-focuser into the GC-FID column,

- Module 1 and 2 are cooled to below -10 °C to dehydrate the sample, followed by trapping at -150 °C

The conditions for the analysis of the samples are stipulated in the methods used for gas mixtures containing nmol/mol mole fraction.

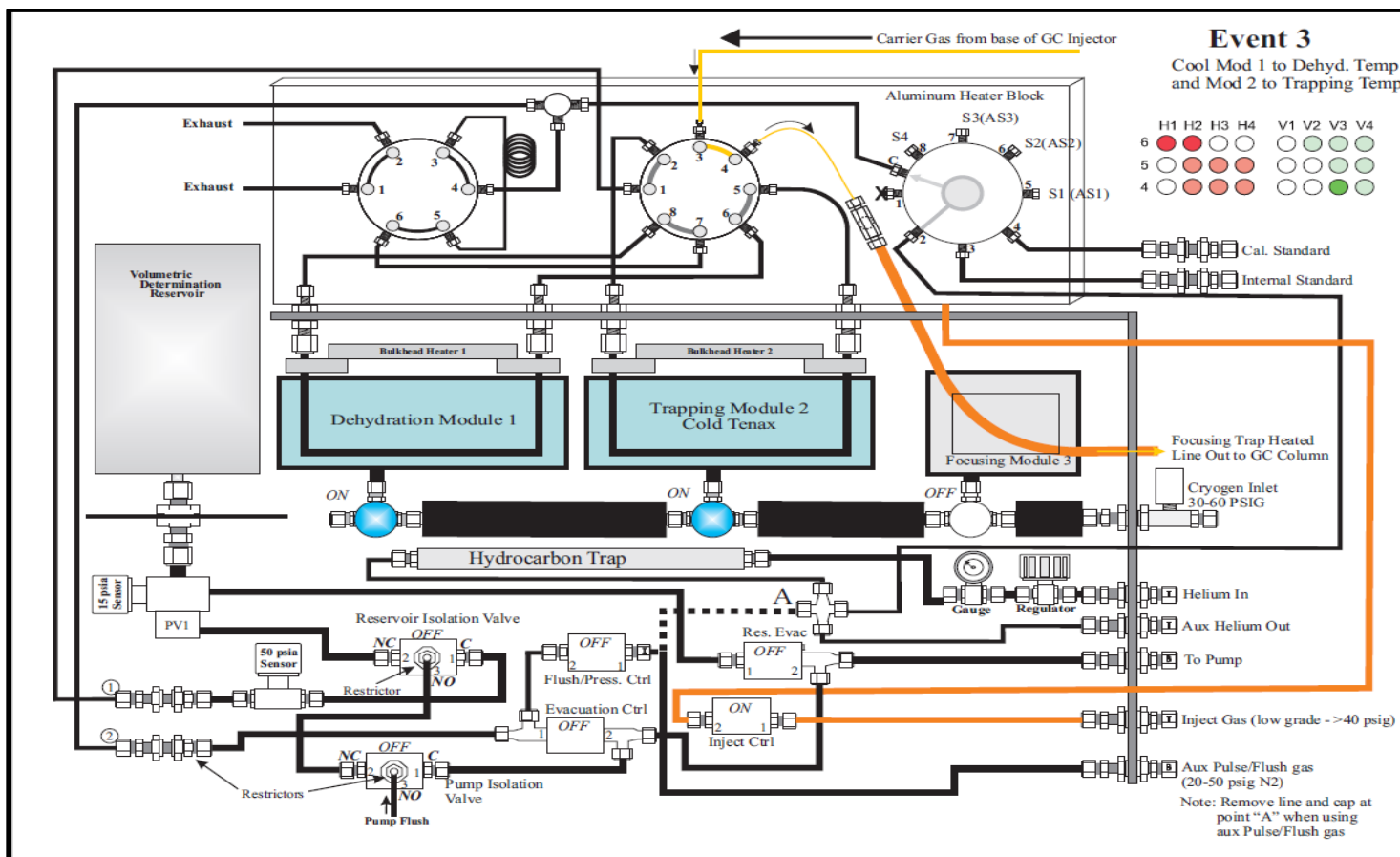


Figure 3-18: Entech 7200 flow path

(*Source: Entech Instruments, 2016)

Figure 3-19 shows the flow path of the NUTECH 8900 DS pre-concentrator. It has three modules, module one with TENAX trapping the VOCs, and allowing water and carbon dioxide to pass, module two with glass beads for the trapping of light carbon molecules and water removal, followed by module three which is a focusing step before injection into the GC. The simple design of the NUTECH system offers some advantages such as easy operation and fewer parameters to be controlled.

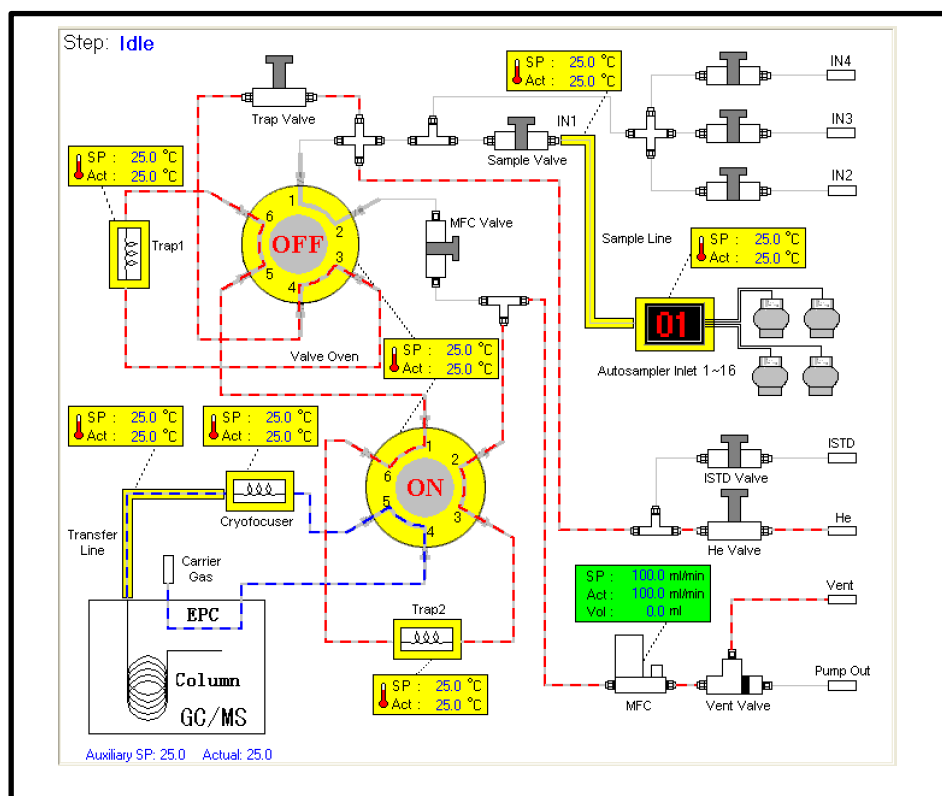


Figure 3-19: Nutech 8900 DS flow path

(*Source: Nutech/GD Environmental Supplies, Inc., 2016)

3.6.1 Method development

The analysis of components was done using two different columns. The choice of columns was based on the literature survey. The DB-624 and DB-WAX columns were used. The literature elution order of both columns was verified by the analysis of BTEX-certified reference material obtained from the Organic Laboratory of NMISA. Each component was analysed, followed by the analysis of all components in the methanol matrix. The method was optimised by changing the mobile phase flow rate, especially for the DB-WAX column, to separate m- and p-xylene. The following section details the method use for the analysis of BTEX.

3.6.2 Analysis of 30 µmol/mol of BTX prepared by NPL method.

After the gravimetric preparation of 30 µmol/mol, the analysis was done using a Varian-3800 GC-FID. The analysis method is shown in Table 3-5.

Table 3-5: Method parameters for analysis of 30 µmol/mol BTEX using Varian CP-3800 GC-FID.

Parameter	Condition
Injector source	Gas valve
Injection volume	100 µL
Split ratio	2:1
Injector temperature	220 °C
Carrier gas	Helium
Column type	Restek-DB-624 Sil (60 m x 0.25 mm id x 0.5 µm df)
Column flow	3,4 ml/min
Oven temperature programming	Isothermal at 60 °C
Detector temperature (FID)	225 °C
Total run time	3 minutes

3.6.3 Analysis of 10 µmol/mol of BTEX prepared by the NPL method

After the gravimetric preparation of 10 µmol/mol, the analysis was done using a Varian-3800 GC-FID. The analysis method is shown in Table 3-6.

Table 3-6: Method parameters for analysis of 10 µmol/mol BTEX using Varian CP-3800 GC-FID.

Parameter	Condition
Injector source	Gas valve
Injection volume	250 µL
Split ratio	No split (on-column injection)
Injector temperature	220 °C
Carrier gas	Helium
Column type	Restek Rxi-624SilMS (60 m x 0,32 mm id x 1,8 µm df)
Column flow	5 ml/min
Oven temperature programming	Initial temperature at 45 °C held for 1 minute, ramp at 5 °C/min to 120 °C , ramp at 50 °C/min to 220 °C (hold 1 minute).
Detector temperature (FID)	250 °C
Total run time	19 minutes

3.6.4 Analysis of 10 µmol/mol of BTEX prepared by KRISS method

After the gravimetric preparation of 10 µmol/mol, the analysis was done using an Agilent 7890B GC-FID. The analysis method is shown in Table 3-7.

Table 3-7: Method parameters for analysis of 10 µmol/mol BTEX using Agilent 7890B GC-FID.

Parameter	Condition
Injector source	Gas valve
Injection volume	250 µL
Split ratio	5:1
Injector temperature	250 °C
Carrier gas	Hydrogen
Column type	Agilent DB-624 (60 m x 0,32 mm id 1.8 µm df)
Column flow	2 ml/min
Oven temperature programming	Initial temperature at 45 °C held for 2 minute, ramp at 5 °C/min to 140 °C, (hold 1 minute).
Detector temperature (FID)	300 °C
Total run time	22 minutes

3.6.5 Analysis of 100 nmol/mol of BTEX for Asia Pacific Metrology Programme (APMP.QM-S12)

The analysis of the 100 nmol/mol BTEX gas mixture during the participation in the Asian Pacific Metrology Programme (APMP.QM-S12), was conducted using the parameters shown in Table 3-7.

Table 3-4: Method for analysing 100 nmol/mol BTEX for APMP.QM-S12 using an Agilent 7890B GC-FID coupled with ENTECH 7200 pre-concentrator.

Parameter	Condition
Carrier gas	Nitrogen Built-In-Purifier (BIP)
Split ratio	Splitless mode through the cryogenic pre-concentrator
Column type	HP-INNOWax, (60 m x 0,320 mm id x 0.5 µm df)
Column flow	3.4 ml/min
Oven program	40 °C hold for 5 min, ramp at 2 °C/min to 60 °C hold for 2 min, ramp at 4°C/min to 75°C hold for 1 min, ramp at 20°C/min to 120°C hold for 2 min.
Detector	FID at 240 °C
ENTECH CONDITIONS	
Trap 1 (Empty tube), operated at -40 °C	Removal of CO ₂ and H ₂ O
Trap 2 (Tenax TA) operated at -40 °C	Trapping of VOCs
Cry focuser operated at -150 °C	Focusing of VOCs before injection into the column

3.6.6 Analysis of 100 nmol/mol of BTEX for Asia Pacific Metrology Programme (APMP.QM-S14)

The analysis of the 100 nmol/mol BTEX gas mixture during the participation in the Asian Pacific Metrology Programme (APMP.QM-S14), was conducted using the parameters shown in Table 3-8.

Table 3-5: Analysis method of 100 nmol/mol of BTEX for APMP.QM-S14 using an Agilent 7890B GC-FID coupled with NUTECH 8900 DS pre-concentrator

Parameter	Condition
Carrier gas	Helium
Split ratio	The split-less mode through the cryogenic pre-concentrator
Column type	DB-624, (60 m x 0,32 μ m id x 1.8 μ m df)
Column flow	2 ml/min
Oven program	40 °C hold for 5 min, ramp at 2 °C/min to 60 °C hold for 2 min, ramp at 4°C/min to 75°C hold for 1 min, ramp at 20 4°C/min to 120°C hold for 2 min.
Detector	FID at 250 °C
NUTECH CONDITIONS	
Trap 1 (Tenax TA), operated at -100 °C	Trapping of VOCs
Trap 2 (Glass beads) operated at -20 °C	Tapping of CO ₂ and H ₂ O
Cry focuser operated at -165 °C	Focusing of VOCs before injection into the column

3.6.7 Quantification of the uncertainty of measurement

The uncertainty of measurement was quantified following the guide to uncertainty of measurement (GUM) guidelines. The uncertainty of measurement of gas mixtures has two components: the uncertainty of the gravimetric preparation and the uncertainty of analysis. The gravimetric uncertainty components are further discussed in Section 4.2.

The uncertainty of $x_{k,j}$, the amount-of-substance fraction of component k in parent gas or liquid j , was calculated from the purity analysis data, where mole fractions of the parent component and the impurities were computed from the GC-FID data.

The uncertainty of m_j , the mass added of parent gas or liquid j , was calculated from the weighing data of each component on the analytical balance. It follows that the NIST method has two weighing sequences of the glass capillary tubes, for each sequence, the experimental standard deviation of the mean (ESDM) was calculated and combined to estimate the weighing uncertainty, and repeatability was determined from the capability of the balance during weighing.

The tare or reference glass capillary tube is used during the weighing process. Since both the tare glass tube (reference tube) and the sample tube experience the same

weighing effect, the resolution, the linearity and the position of the glass capillary tube as uncertainty components cancel out, only the repeatability in the form of ESDM is computed. The same analogy was followed for computing of weighing uncertainty for the NPL and the KRISS methods. The uncertainty of M_i , the molar mass of component is calculated from the IUPAC molar mass data, where the mass of each compound was computed based on the elemental composition of carbon and hydrogen, including their stoichiometric values. The molar mass in the IUPAC is accompanied by the uncertainty values of each element included in the calculation. The uncertainty contributions of q , the number of components in the mixture and r , the number of parent gases or liquids, are constants and are included in the quantification. The Gravcalc software (Brown, 2009) from NPL was used to calculate the mole fraction and uncertainty of all components in the gravimetrically prepared reference gas mixtures according to ISO 6142. For gas chromatography, the uncertainty calculation was based on the peak areas obtained during the analysis of the sample and reference cylinders and the gravimetric uncertainty of the reference gas mixture used to verify the prepared gas mixtures as further described in Section 4.3.

4. Results and discussion

The results of the study are discussed in detail in Chapter 4. Data for purity analysis, gravimetric preparation, and gas mixture verification are presented and explained. The measurement uncertainty is defined. Finally, the international key comparison findings for determining the international measurement equivalence of the BTEX reference gas mixtures are thoroughly explained.

4.1 Purity analysis

Analyzing impurities in the pure starting material is a crucial step to ensure that the material is fit for its purpose. Some materials may contain an impurity at a higher than expected value, thus rendering the material unfit for purpose (ISO 6142-1, 2015). For example, the impurity of 100 $\mu\text{mol/mol}$ of oxygen in nitrogen will render the nitrogen unsuitable for preparing gas mixtures containing oxygen at 100 $\mu\text{mol/mol}$ or less.

The mole fraction of the parent component is expressed by equation 4.1 (ISO 19229:2019, 2019):

$$x_{parent} = 1 - \sum_{k=1}^n x_k \quad 4.1$$

Where, x_{parent} is the mole fraction of the parent component, x_k is the mole fraction of impurity k determined by analysis, n is the total number of impurities. The associated measurement uncertainty of the parent component is calculated by following the law of propagation of uncertainty using equation 4.2 (JCGM 100, 2008):

$$u^2(x_c) = \sum_{i=1}^n u^2(x_{ic}) \quad 4.2$$

Where $u^2(x_c)$ is the standard uncertainty of the parent component and $u^2(x_{ic})$ represents the standard uncertainty of the expected impurity i for the total number of impurities n present in the parent component.

The quantification of organic impurities is also be expressed as the weight of the components, as shown by equation 4.3 (Westwood et al., 2013):

$$w_{parent} = \frac{m_{parent}}{m_{parent} + \sum m_k} \quad 4.3$$

Where, w_{parent} is the mass fraction of the parent component in the aliquot, m_{parent} is the mass of the parent in the aliquot, $\sum m_k$ is the sum of the mass of impurities in the aliquot. This approach is fundamental when the impurities are quantified using reference standards prepared in the laboratories by diluting a known certified reference material which has an accompanying certificate with quantity values and associated measurement uncertainties.

It may not be possible to identify some impurities present in the starting material due to the unavailability of suitable analytical techniques. In such cases, when the values of such impurities are specified in the manufacturer's specification, the approach is to estimate their mole fraction by calculating the semi-range of the stated value, according to equation 4.4.

$$x_i = \frac{a_- + a_+}{2} \quad 4.4$$

Where the mole fraction of the impurity from the manufacturer's specification is x_i , a_- + a_+ are lower and upper bounds values, respectively. The associated measurement uncertainty is the rectangular distribution shown in equation 4.5 below:

$$u_{xi} = \frac{x_i}{\sqrt{3}} \quad 4.5$$

A similar approach to the estimation of impurity below the detection limit of the analytical technique is used when the mole fraction will be the semi-range of the calculated detection limit and the uncertainty calculated will be rectangular, as shown in equations 4.4 and 4.5, respectively.

The molecular weight of the compounds is considered a source of traceability, which must be determined and added to the purity assessment data. The molecular weight values and their associated uncertainties are obtained from the IUPAC atomic data

(Wieser et al., 2013). The molecular mass of the compound M_r is calculated according to equation 4.6 below:

$$M_r = \sum_A \varepsilon B_r(A) \quad 4.6$$

Where, where ε denotes the stoichiometric coefficient and B_r is the atomic mass of an element (A). The summation runs over all elements A present in the molecule (Van Der Veen et al., 2016). The associated uncertainty of molecular weight is calculated according to equation 4.7:

$$u^2(M_r) = \sum_A \varepsilon^2 u^2(B_r A) \quad 4.7$$

4.1.1 Purity analysis of BTEX

Purity analysis of BTEX sourced from commercial suppliers was done using gas chromatography coupled with flame ionisation detection for quantitative analysis and mass selective detection for qualitative analysis. Figure 4-1 shows the total ion chromatogram (TIC) and the flame ionisation detector (FID) chromatogram of methanol, which was used as the syringe wash solvent of the Agilent GC 7890B. The retention time of methanol on the FID is 12,703 minutes, and it does not appear on TIC due to a solvent delay of 3 minutes set up in the analysis method. Although there were no observed impurities in methanol, its retention time was recorded to ignore its presence as an impurity in the BTEX purity analysis. The methanol peak appeared in all FID chromatograms of benzene, toluene, ethylbenzene, o-xylene, m-xylene and p-xylene, as there was a considerable amount of methanol on the walls of the syringe which was used to inject headspace of each of the BTEX components into the GC. It was assumed that the headspace for each BTEX would have an adequate amount to allow for detection of the parent component and its impurities due to their volatility.

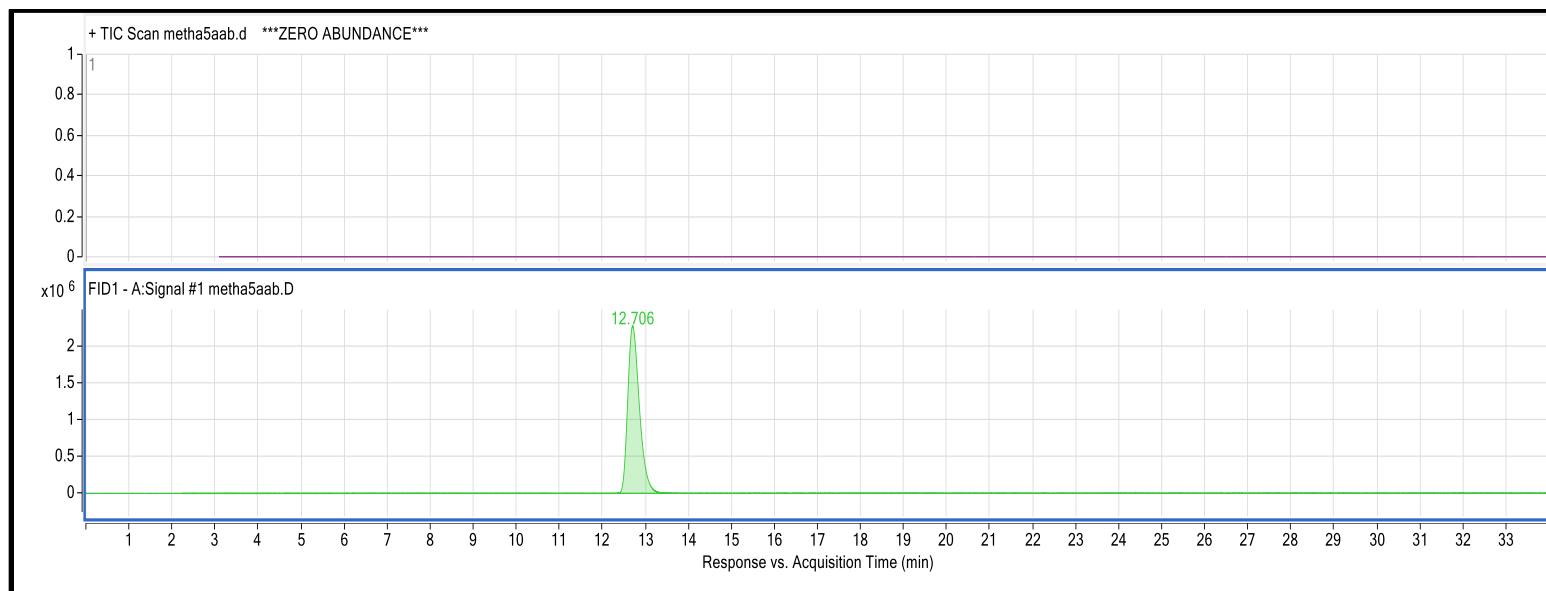


Figure 4-1: TIC and FID chromatogram of methanol

The results of the purity analysis of benzene are shown in Table 4-1. In column two of Table 4-1, the results of water and benzene from the manufacturer's certificate of analysis (CoA, LOT STBB0083) are presented. Although the amount of water in benzene was not determined experimentally, it was calculated using equation 4.4 and the semi-range to estimate its value from that provided in the certificate of analysis. The associated measurement uncertainty was assessed using equation 4.5 and assuming the triangular distribution as stipulated in the Guide to Expression of Uncertainty (JCGM 100, 2008). No other impurities were detected; the amount of benzene was calculated using equation 4.1. Figure 4-2 shows the TIC and FID chromatograms, and as shown, the methanol and benzene retention times were 12.696 and 14.484 minutes, respectively. Figure 4-3 is the corresponding mass spectrum of benzene.

Table 4-1: Purity analysis results of benzene

Components	Lot STBB0083 results from Sigma Aldrich (mol/mol).	Mole fraction (mol/mol)	Type of distribution	Standard uncertainty (mol/mol) k=1	Analytical Methods
Water	0,0002	0,0001	Rectangular	0,000058	Specification
Benzene	0,9995	0,9999	Normal	0,000058	FID/MS

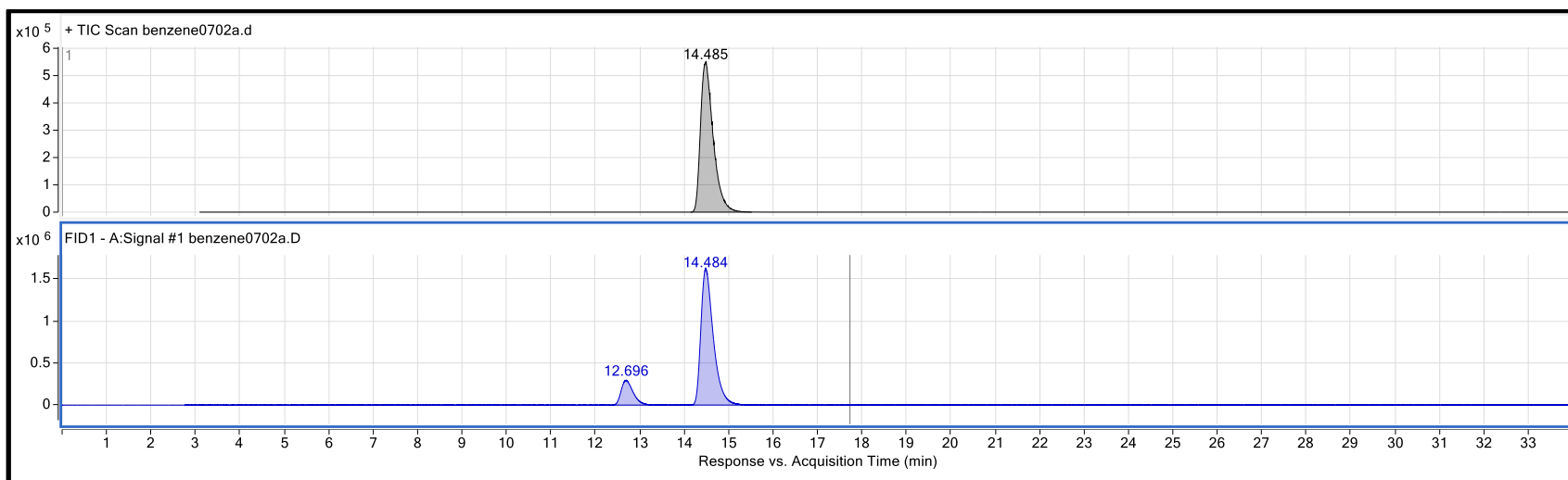


Figure 4-2: TIC and FID chromatogram of benzene

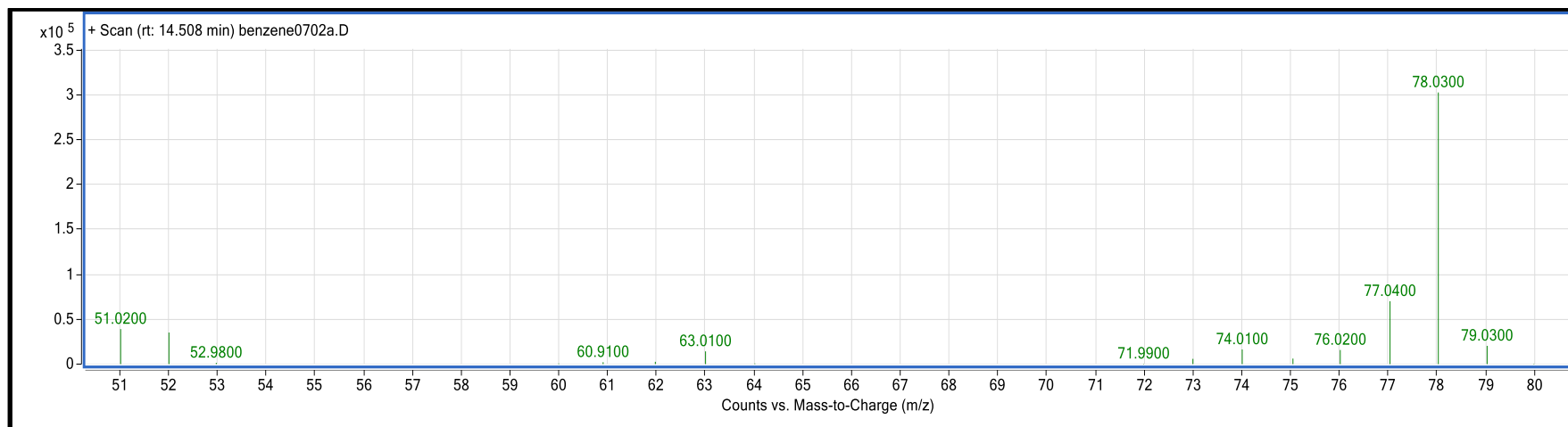


Figure 4-3: Mass spectrum (TIC) of benzene

The results of the purity analysis of toluene are shown in Table 4-2. Figure 4-4 presents the TIC and the FID chromatograms. The retention times of methanol and toluene were 12.719 and 18.064 minutes, respectively. In column two, the results of water and toluene from the manufacturer's certificate of analysis (CoA, LOT SZBA0940) are presented. The results of water were estimated similarly to that of benzene. No other impurity was detected, and the amount of toluene was calculated using equation 4.1. Figure 4-5 is the corresponding mass spectrum of toluene.

Table 4-2: Purity analysis results of toluene

Components	Lot SZBA0940 results from Sigma Aldrich (mol/mol).	Mole fraction (mol/mol)	Type of distribution	Standard Uncertainty (mol/mol) k=1	Analytical Methods
Water	0,003	0,000015	Rectangular	0,0000087	Specification
Toluene	0,999	0,999985	Normal	0,0000087	FID/MS

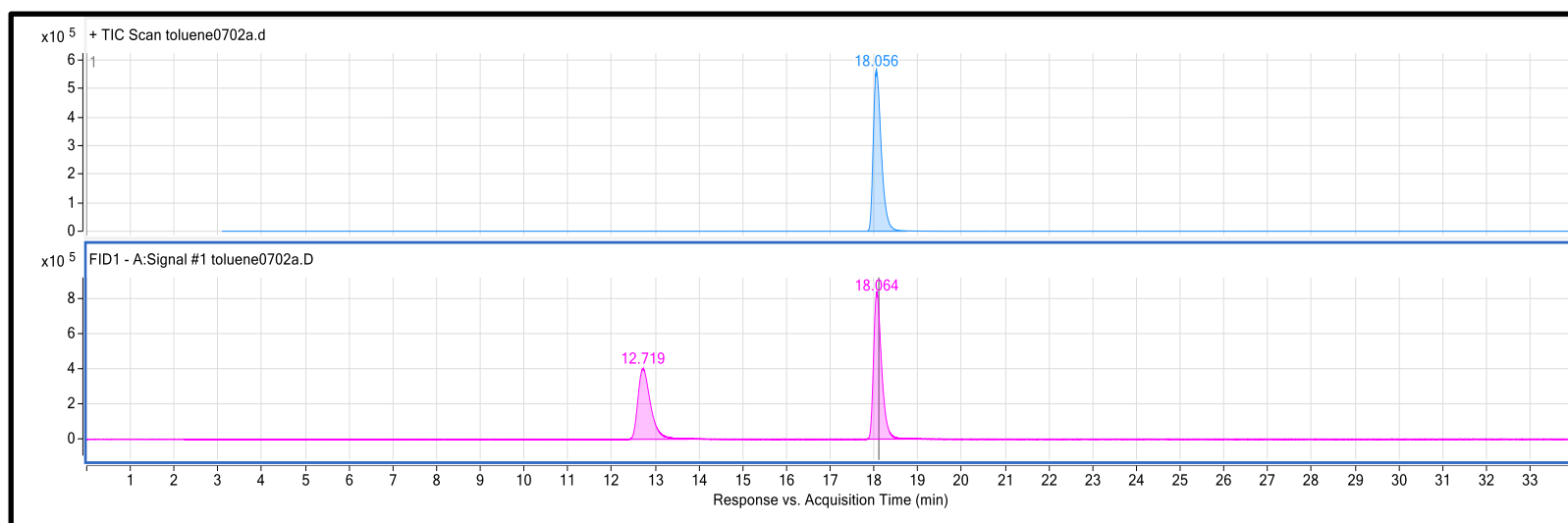


Figure 4-4: TIC and FID chromatogram of toluene

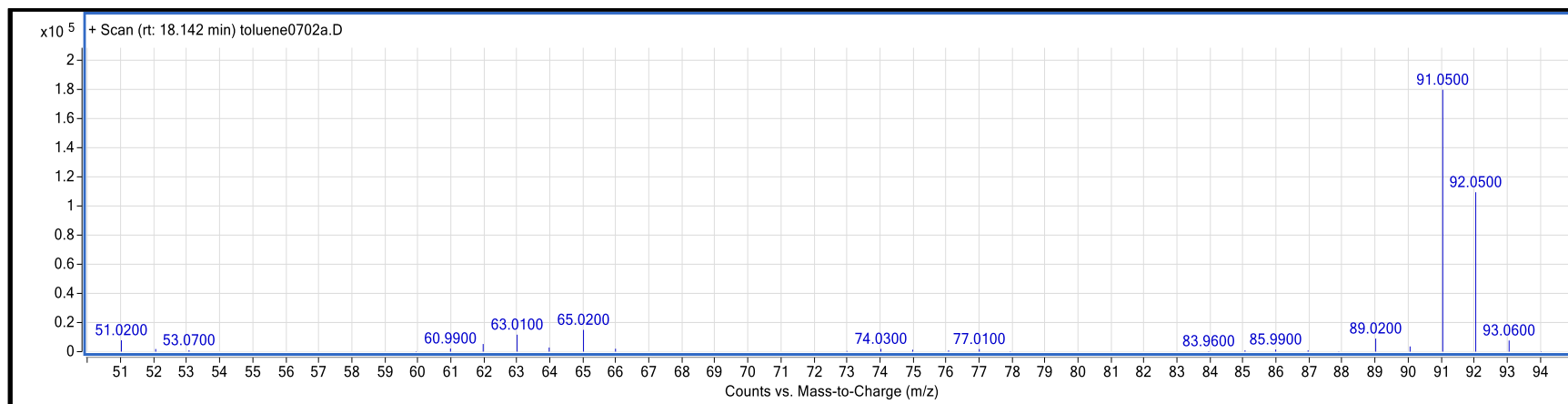


Figure 4-5: Mass spectrum of toluene

The results of the purity analysis of ethylbenzene are shown in Table 4-3. The amount of water in ethylbenzene was determined similarly to that of the previous compounds. Figure 4-6 presents the TIC and the FID chromatograms. The retention time of methanol was 12.700 minutes, and ethylbenzene was 20.664 minutes. Figure 4-7 is the corresponding mass spectrum of ethylbenzene.

Table 4-3: Purity analysis of ethylbenzene

Components	Lot 00496PK results Sigma Aldrich (mol/mol).	Mole fraction (mol/mol)	Type of distribution	Standard Uncertainty (mol/mol) k=1	Analytical Methods
Water	0,0001	0,00005	Rectangular	0,000058	Specification
Ethyl benzene	0,9990	0,999950	Normal	0,000058	FID/MS

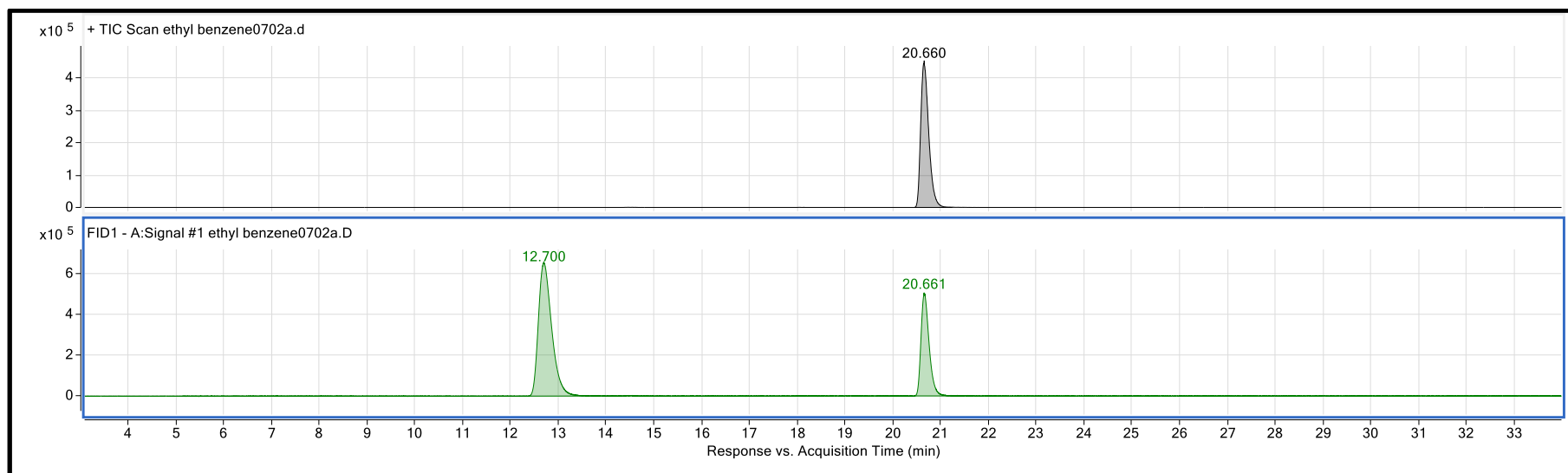


Figure 4-6: TIC and FID chromatogram of ethyl benzene

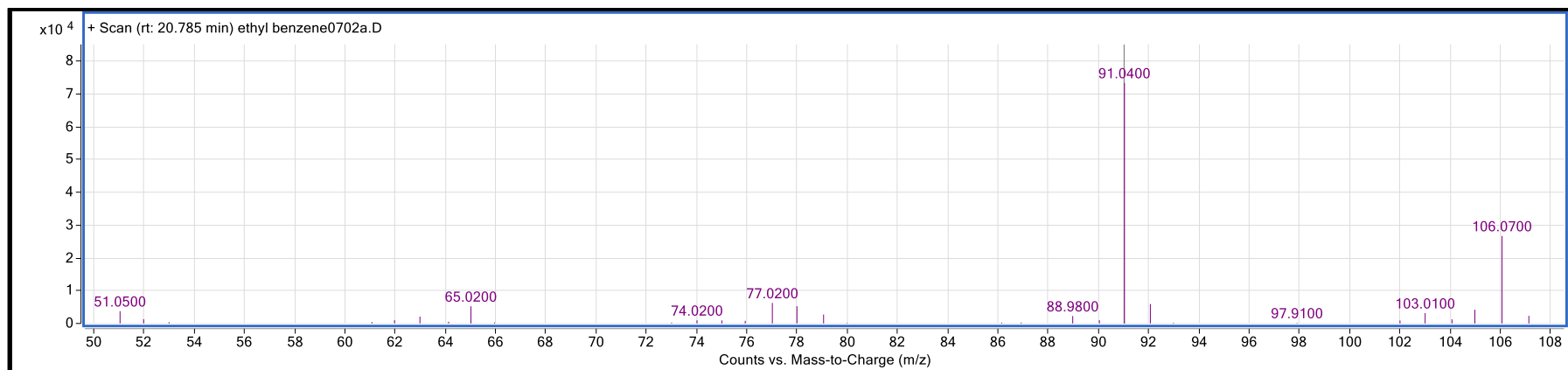


Figure 4-7: Mass spectrum of ethylbenzene

The results of the purity analysis of o-xylene are shown in Table 4-4. The values of ethylbenzene, p-xylene and m-xylene were estimated from the manufacturer's certificate of analysis by using equation 4.4 by calculating the semi-range. This was done because the initial purity data showed poor repeatability. In the initial purity experiment, 5 mg/ml of each BTEX component were prepared in methanol. The components were each injected into the GC-FID manually, using a Restek Rxi624SilMS (60 m x 0,32 mm id x 1,8 μ m df) column. The results confirmed the presence of impurities in the o-xylene, namely m-xylene and p-xylene, as shown in their respective data from the manufacturer; however, due to poor repeatability associated with manual injection and suspected carryover, the data was not used. The purity analysis approach was changed later to analyse the headspace of each of the BTEX components without dilution into methanol. In the headspace purity experiment, the solution and vapour equilibrium was assumed to be adequate since each injection run was 25 minutes, injecting the same sample 3 times. Figure 4-8 presents the TIC and the FID chromatograms. The retention time of methanol was 12.702 minutes, and o-xylene was 25.560 minutes.

Table 4-4: Purity analysis of o-xylene

Components	LOT 1421425 results Sigma Aldrich (mol/mol).	Mole fraction (mol/mol)	Type of distribution	Standard Uncertainty (mol/mol) k=1	Analytical Methods
Ethyl benzene	0,00005	0,000025	Rectangular	0,00000125	Specification
m-xylene	0,00006	0,00006	Rectangular	0,000003	Specification
p-xylene	0,006130	0,003065	Rectangular	0,000153	Specification
o-xylene		0,996850	Normal	0,000153	FID/MS

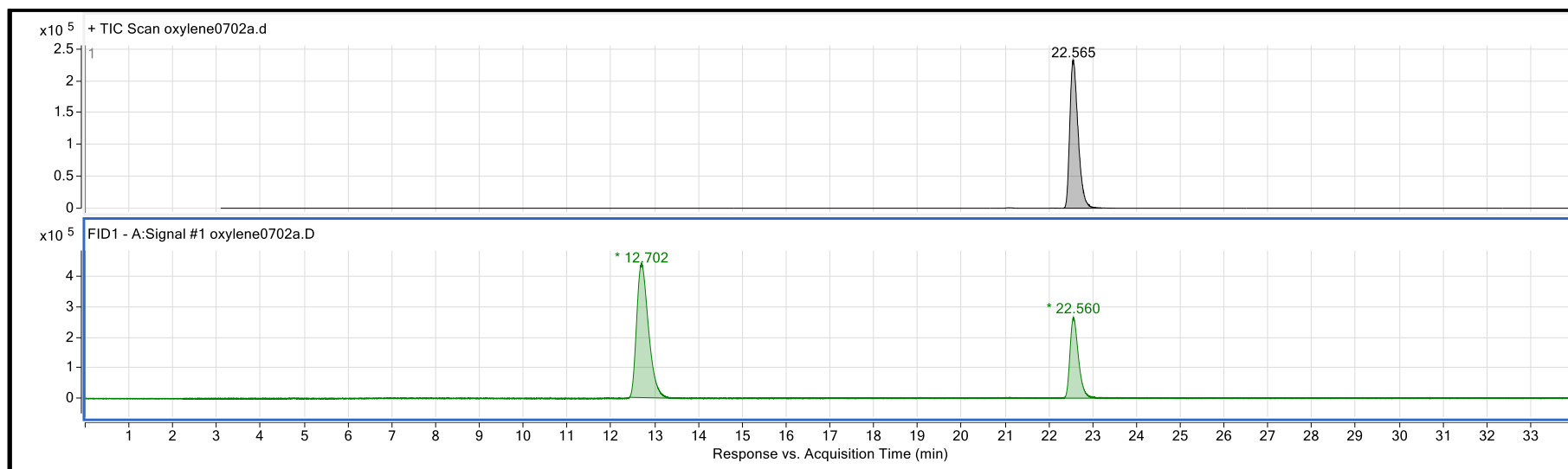


Figure 4-8: TIC and FID chromatogram of o-xylene

The results of the purity analysis of m-xylene are shown in Table 4-5. The retention time of methanol was 12.689 minutes, and that of m-xylene was 21.102 minutes. The mole fraction of impurities was estimated as explained in the purity results of o-xylene. Figure 4-9 presents the TIC and the FID chromatograms.

Table 4-5: Purity analysis of m-xylene

Components	LOT BCBC1553 form Sigma Aldrich	Mole fraction (mol/mol)	Type of distribution	Standard Uncertainty (mol/mol) k=1	Analytical Methods
o- xylene	0,00123	0,00062	Rectangular	0,00035	Specification
p- xylene	0,00116	0,00058	Rectangular	0,00034	Specification
m- xylene		0,99880	Normal	0,00018	FID/MS

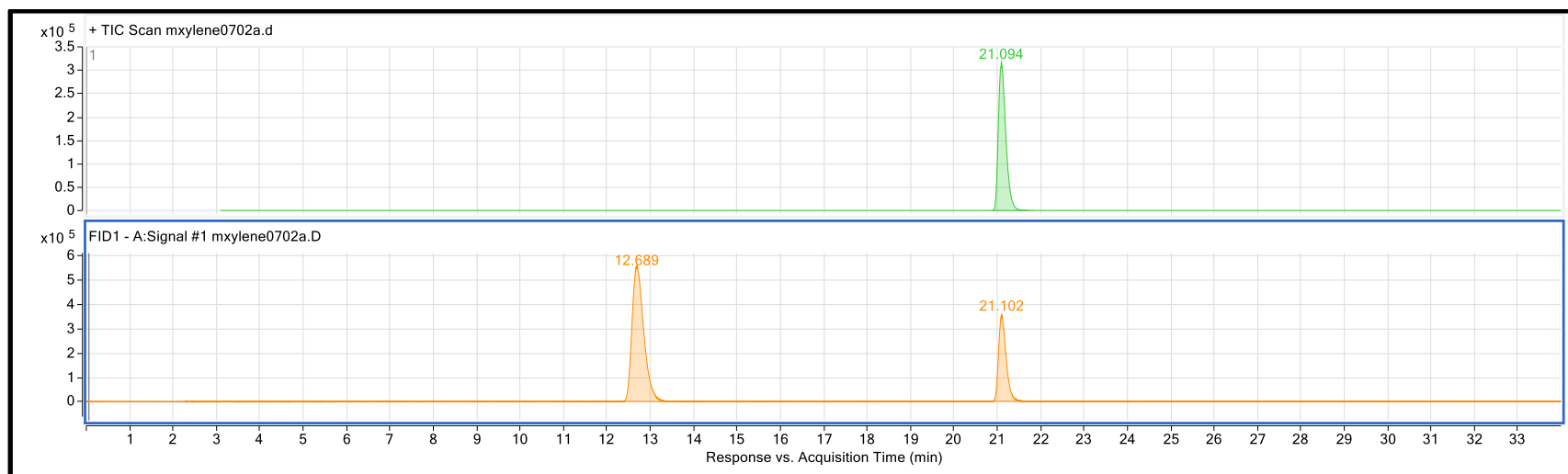


Figure 4-9: TIC and FID chromatogram of m-xylene

The results of the purity analysis of p-xylene are shown in Table 4-6. The retention time of methanol was 12.709 minutes, and that of p-xylene was 20.902 minutes. As shown in Table 4.2, the values of impurities were estimated as explained in the purity analysis of o-xylene. Figure 4-10 presents the TIC and the FID chromatograms. The TIC of xylenes was not presented since it is similar to that of ethylbenzene; therefore, FID retention time was used to distinguish between the isomers.

Table 4-6: Purity analysis of p-xylene

Components	LOT 1432941 form Sigma Aldrich	Mole fraction (mol/mol)	Type of distribution	Standard Uncertainty (mol/mol) k=1	Analytical Methods
Ethyl benzene	0,00072	0,00036	Rectangular	0,00021	Specification
Toluene	0,00070	0,000035	Rectangular	0,000021	Specification
o- xylene	0,00041	0,00021	Rectangular	0,00012	Specification
m- xylene	0,00132	0,000066	Rectangular	0,000038	Specification
p- xylene	0,9997	0,999334	Rectangular	0,00024	FID/MS

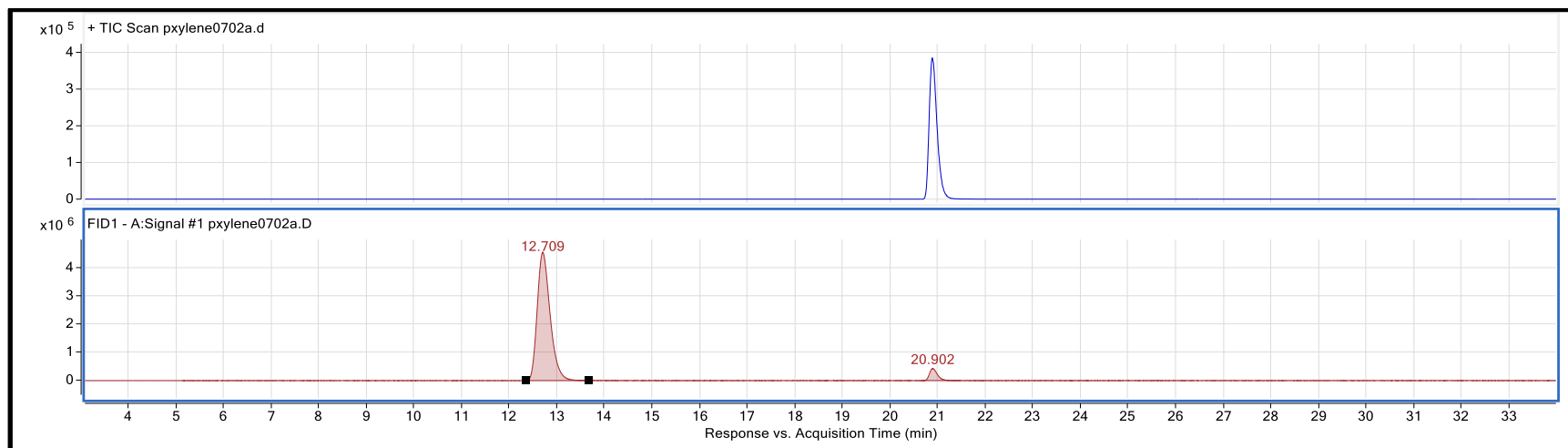


Figure 4-10: TIC and FID chromatogram of m-xylene

4.1.2 Purity analysis of nitrogen BIP

Impurities in the nitrogen gas were quantified using in-house primary reference gas mixtures (working standards) validated against other primary reference standards or through international key comparisons. Such reference gas standards are of high metrological traceability and are used for routine measurements. The results of the purity analysis of nitrogen BIP are shown in Table 4-7.

Argon, which was the significant impurity, was quantified using a 50 m x 0, 53 mm id x 50 μ m df CP-Molesieve 5A column detected by PDHID; the method parameters are stipulated in Table 3-3. For methane and carbon monoxide impurities, a Shin Carbon ST,100/120 mesh, 2 m length, 1,58 mm od, 1.0 mm id column was used. The calibration standard with the lowest mole fraction of approximately 200 nmol/mol for each compound was used; the obtained values of methane and carbon monoxide were below the lowest standard; therefore, the semi-range approach was used according to equation 4.4. It is known that the FID detection limits for hydrocarbons are lower than observed in the nitrogen; hence the semi-range approach was used as opposed to the detection limit if the values of those impurities were within the calibration range.

The carbon dioxide impurity was analysed using a Shin Carbon ST,100/120 mesh, 2 m in length, 1,58 mm od, 1,0 mm id column, eluting after both carbon monoxide and methane (Table 3-3). The column eluent was run through a methaniser (a Valco Instruments nickel catalyst tube with minimal hydrogen flow and 400 °C operation) to analyse carbon monoxide and carbon dioxide. The methane was then converted to methane, which was detected by the FID detector. It is known that the FID detector has a low response to non-hydrocarbon compounds. This method accurately analyses carbon dioxide at mole fractions less than 1000 μ mol/mol (Flores et al., 2019). It is routinely used to monitor the atmosphere's carbon monoxide and carbon dioxide levels. Hydrogen was determined in the same analysis of argon, and the estimated value was calculated using equation 4.4.

Since there was no technique for the analysis of water in the nitrogen, the manufacturer's specification was used, and the value was calculated according to equation 4.4. It was also very critical to analyse BTEX in nitrogen BIP cylinders since the final mole fraction will be at nano-mole range; thus, the analysis was done using a cryogenic pre-

concentrator method as described in Section 3.6. As a result, no BTEX compounds were found in nitrogen BIP, rendering it fit for the preparation of BTEX.

Table 4-7: Purity analysis of BIP nitrogen

Components	Mole fraction (mol/mol)	Type of distribution	Standard Uncertainty (mol/mol) k=1	Analytical Methods
Argon	0,000054	Normal	0,0000027	PDHID
Methane	0,0000000043	Rectangular	0,0000000025	FID
Carbon monoxide	0,0000000069	Rectangular	0,0000000040	FID
Carbon dioxide	0,0000000098	Normal	0,0000000011	FID
Hydrogen	0,0000000090	Rectangular	0,0000000052	PDHID
Oxygen	0,0000000050	Rectangular	0,0000000029	PDHID
Water	0,0000000100	Rectangular	0,0000000058	Specification
Nitrogen	0,99994655	Normal	0,0000027	

4.2 Gravimetric preparation of gas mixtures

The amount fraction (mole fraction) of the gas mixture was then calculated using equation 4.8 (ISO 6142-1, 2015)

$$y_k = \frac{\sum_{j=1}^r \left(\frac{x_{k,j} \times m_j}{\sum_{i=1}^q x_{i,j} \times M_i} \right)}{\sum_{j=1}^r \left(\frac{m_j}{\sum_{i=1}^q x_{i,j} \times M_i} \right)} \quad 4.8$$

Where, y_k is the amount-of-substance fraction of component k in the prepared mixture, $x_{k,j}$ is the amount-of-substance fraction of component k in parent gas or liquid j , m_j is the mass added of parent gas or liquid j , $x_{i,j}$ is the amount-of-substance fraction of component i in parent gas or liquid j , M_i is the molar mass of component i , q is the number of components in the mixture, and r is the number of parent gases or liquids.

4.2.1 Gravimetric preparation results of 500 nmol/mol BTEX gas mixture (NIST method)

A gas mixture containing BTEX at 500 nmol/mol mole fraction was prepared in October 2015. The procedure is detailed in section 3.3.2.1. For the gas mixture under discussion, the NIST (micro-gravimetric capillary tube) method was used (Guenther et al., 2002; Rhoderick & Zielinski, 1988). The results of the capillary tube weighing of cylinder FF9498 are presented in Table 4-8. First, each capillary tube was placed in the glass holder labelled with a number to trace the components. Then, each capillary was weighed empty, followed by adding components, and was then sealed in an open flame.

After sealing the capillary tubes, they were allowed to cool to room temperature and were weighed 3 times every 30 minutes. This was done to ensure that the tubes were adequately sealed and that no loss of components occurred due to improper sealing of the tubes. The last weighing measurement was used to calculate the mass of the components in the tubes. The loss of components due to leaks in the tube was observed by a continuous decrease in mass during weighing. When that happened, the affected component was repeated. The mass of each component required was pre-calculated, as shown in the last row of Table 4-8. The calculated mass of each component after

transferring into the cylinders is shown in the second last row of Table 4-8; it is the difference in mass of capillary tubes with components and the empty tubes. It is observable that the masses added are different from the pre-calculated masses, especially for benzene, toluene and p-xylene. This is due to how the components are added to the capillary tubes. The apparatus did not have measurement markings of volume added; instead, the tubes were weighed several times to verify the mass added before sealing the tubes. This was a disadvantage since the planned nominal mole fraction can differ based on the closeness of the pre-calculated mass required. Table 4-9 shows the weighing cycles of a cylinder when it is empty, after adding BTEX components to determine the amount of nitrogen used to flush the components into the cylinder, and finally, the weighing of the cylinder after nitrogen has been added.

Table 4-8: Weighing of capillary tubes to prepare 500 nmol/mol BTEX gas mixture

	Mass of empty capillary tube (mg)					
Capillary tube number	7	22	23	11	29	4
Component	Benzen e	Toluen e	Ethylbenzen e	o- xylen e	m- xylen e	p- xylen e
Number of weighing						
1	40.310	48.530	51.588	45.939	51.402	42.479
2	40.385	48.782	51.264	46.243	51.201	42.403
3	40.386	48.685	51.376	45.916	51.162	42.524
Average mass (mg)	40.360	48.666	51.409	46.033	51.255	42.469
Standard deviation (mg)	0.044	0.127	0.165	0.183	0.129	0.061
Relative Standard Deviation (%)	0.108	0.261	0.320	0.396	0.251	0.144
	Mass of capillary tube with component (mg)					
Capillary tube number	7	22	23	11	29	4
Component	Benzen e	Toluen e	Ethylbenzen e	o- xylen e	m- xylen e	p- xylen e
Number of weighing						
1	42.601	50.349	52.533	47.347	52.510	45.695
2	42.728	50.431	52.689	47.537	52.509	45.666
3	42.743	50.366	52.646	47.464	52.445	45.739
Average mass (mg)	42.691	50.382	52.622	47.449	52.488	45.700
Standard deviation (mg)	0.078	0.043	0.080	0.096	0.037	0.037
Relative Standard Deviation (%)	0.183	0.085	0.153	0.202	0.071	0.080
Mass of component added into a cylinder (mg)	2.330	1.716	1.213	1.417	1.233	3.232

Pre-calculated required mass of components (mg)	0.9742	1.1490	1.3240	1.3240	1.3240	1.3240
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Table 4-9: Cylinder weighing of 500 nmol/mol BTEX gas mixture

	Weighing cycle of cylinder FF9498		
	Mass empty cylinder (g)	Mass of cylinder with flushing nitrogen (g)	Mass of cylinder nitrogen balance (g)
1	7372.3981	7377.2097	7942.9484
2	7372.3993	7377.2095	7942.9464
3	7372.4002	7377.2129	7942.9459
4	7372.3968		7942.9468
5	7372.3965		7942.9465
6	7372.3994		7942.9466
7	7372.3992		7942.9485
8	7372.399		7942.9475
9	7372.3987		7942.9459
10	7372.3978		7942.9475
Average (g)	7372.399	7377.211	7942.947
Standard deviation (g)	0.001	0.002	0.001
Mass nitrogen added (g)		4.812	565.736
Total Mass nitrogen added (g)	570.548		

The mole fractions of the gas mixture in cylinder FF9498 are presented in Table 4-10. It can be seen from the results that the prepared mole fraction varied significantly from the planned 500 nmol/mol. This was due to the difficulty in the introduction of the required amount of each component into the capillary tube.

Table 4-10: Mole fraction of 500 nmol/mol BTEX (Cylinder FF9498)

Component	Cylinder Number	Gravimetric mole fraction (μmol/mol)	Gravimetric uncertainty (μmol/mol)
Benzene	FF9498	1469.06	112.71
Toluene		916.80	143.03
Ethyl benzene		562.10	169.29
m-xylene		571.39	124.04
p-xylene		1496.95	66.02
o-xylene		656.14	190.53

4.2.2 Gravimetric preparation results of 30 $\mu\text{mol/mol}$ BTX standard (NPL Method)

The loop weighing data of benzene into cylinders M517080, M518243, M395452, and M518191 is presented in Table 4-11. The loop weighing data of toluene and o-xylene into cylinders M517080, M518243, M395452, and M518191 is presented in Tables 4-12 and 4-13, respectively. The components were added to the cylinder individually. The mass of the component added to the cylinder was calculated by subtracting the average masses of the empty loop and the loop with a component. It should be noted that a loop of similar shape, material, and dimensions was used as a reference loop to monitor the balance's performance, check for balance drift, and to correct it if it occurred. The reference loop was only handled during the weighing process; therefore, it also served as an indication of the effect of sample loop handling during evacuation and filling at the gas manifold.

Table 4-11: Weighing of benzene in a loop (transfer vessel) for 30 $\mu\text{mol/mol}$ gas mixtures

	Benzene			
	Mass of loop with component (g)			
	Cylinder number			
	M518070	M518243	M395452	M518191
1	103.73712	103.68044	103.59214	106.13790
2	103.73712	103.68040	103.59216	106.13795
3	103.73724	103.68044	103.59221	106.13807
Average (g)	103.73716	103.68043	103.59217	106.13797
Standard deviation (g)	0.00007	0.00002	0.00004	0.00008
Relative Standard Deviation (%)	0.007%	0.002%	0.004%	0.008%
	Mass of loop after transfer of component (g)			
	Cylinder number			
	M518070	M518243	M395452	M518191
1	103.68580	103.62354	103.53799	106.08075
2	103.68591	103.62365	103.53816	106.08090
3	103.68596	103.62370	103.53807	106.08086
Average (g)	103.68589	103.62363	103.53807	106.08083
Standard deviation (g)	0.00008	0.00008	0.00009	0.00008
Relative Standard Deviation (%)	0.008%	0.008%	0.008%	0.007%
Mass of component added into a cylinder (g)	0.05127	0.05679	0.05410	0.05714

Table 4-12: Weighing of toluene in a loop (transfer vessel) for 30 $\mu\text{mol/mol}$ gas mixtures

	Toluene			
	Mass of loop with component (g)			
	Cylinder number			
	M518070	M395452	M518243	M518191
1	103.68560	103.60361	106.15221	106.35688
2	103.68570	103.60356	106.15226	106.35701
3	103.68564	103.60361	106.15232	106.35714
Average (g)	103.68565	103.60359	106.15226	106.35701
Standard deviation (g)	0.00005	0.00003	0.00006	0.00013
Relative Standard Deviation (%)	0.005%	0.003%	0.006%	0.013%
	Mass of loop after transfer of component (g)			
	Cylinder number			
	M518070	M395452	M518243	M518191
1	103.62228	103.53649	106.07971	106.29929
2	103.62231	103.53653	106.07972	106.29946
3	103.62227	103.53659	106.07980	106.29945
Average (g)	103.62229	103.53654	106.07974	106.29940
Standard deviation	0.00002	0.00005	0.00005	0.00009
Relative Standard (g) Deviation (%)	0.002%	0.005%	0.005%	0.009%
Mass of component added into a cylinder (g)	0.06336	0.06705	0.07252	0.05761

Table 4-13: Weighing of xylene in a loop (transfer vessel) for 30 $\mu\text{mol/mol}$ gas mixtures

	O-xylene			
	Mass of loop with component (g)			
	Cylinder number			
	M518191	M395452	M518243	M518070
1	103.70066	103.61921	106.15518	106.36657
2	103.70076	103.61927	106.15523	106.36667
3	103.70077	103.61922	106.15531	106.36672
Average (g)	103.70073	103.61923	106.15524	106.36665
Standard deviation (g)	0.00007	0.00003	0.00007	0.00007
Relative Standard Deviation (%)	0.006%	0.003%	0.006%	0.007%
	Mass of loop after transfer of component (g)			
	Cylinder number			
	M518191	M395452	M518243	M518070
1	103.62850	103.54992	106.08656	106.29902
2	103.62845	103.54990	106.08660	106.29901
3	103.62848	103.54983	106.08647	106.29898
Average (g)	103.62848	103.54988	106.08654	106.29900
Standard deviation (g)	0.00002	0.00005	0.00007	0.00002
Relative Standard Deviation (%)	0.002%	0.004%	0.006%	0.002%
Mass of component added into a cylinder (g)	0.07225	0.06935	0.06870	0.06765

The nitrogen component weighting data for cylinder M517080 is shown in Table 4-14, while those for cylinders M518191, M518243, and M395452 are shown in Tables 4-15, 4-16, and 4-17, respectively. As explained above, the mixture cylinder behaviour is monitored by weighing it against the reference cylinder (M395404), which is always held in the weighing room. The difference between the empty cylinder and the cylinder after adding nitrogen was used to calculate the mass of nitrogen added.

Table 4-14: Weighing of nitrogen cylinder M517080 for 30 µmol/mol BTX gas mixture

Weighing cylinder				
Date	2016 June 23			
Reference cylinder	M395404	Mixture cylinder	M518070	
EMPTY			NITROGEN	
Mass (g)			Mass (g)	
	M395404	M518070	M395404	M518070
1	7576.409	7592.114	7576.567	8203.268
2	7576.405	7592.115	7576.572	8203.273
3	7576.407	7592.115	7576.570	8203.273
4	7576.406	7592.115	7576.571	8203.277
Average	7576.407	7592.115	7576.570	8203.273
Standard Deviation	0.002	0.001	0.002	0.004
Relative Standard Deviation (%)	0.000023%	0.000007%	0.000029%	0.000045%
Nitrogen added				611.158

Table 4-15: Weighing nitrogen cylinder M518191 for 30 µmol/mol BTX gas mixture

Weighing cylinder				
Date	2016 June 23			
Reference cylinder	M395404	Mixture cylinder	M518191	
EMPTY			NITROGEN	
Mass (g)			Mass (g)	
	M395404	M518191	M395404	M518191
1	7576.406	7583.891	7576.561	8264.299
2	7576.408	7583.893	7576.563	8264.299
3	7576.408	7583.891	7576.567	8264.301
4	7576.409	7583.892	7576.567	8264.303
Average	7576.408	7583.892	7576.565	8264.301
Standard Deviation	0.001	0.001	0.003	0.002
Relative Standard Deviation (%)	0.000017	0.000013	0.000040	0.000023
Nitrogen added				680.409

Table 4-16: Weighing nitrogen cylinder M518243 for 30 $\mu\text{mol/mol}$ BTX gas mixture

Weighing cylinder				
Date	2016 June 23			
Reference cylinder	M395404	Mixture cylinder	M518243	
EMPTY			NITROGEN	
Mass (g)			Mass (g)	
	M395404	M518243	M395404	M518243
1	7576.583	7588.784	7576.529	8266.747
2	7576.578	7588.782	7576.528	8266.749
3	7576.582	7588.783	7576.532	8266.752
4	7576.581	7588.789	7576.534	8266.752
Average (g)	7576.581	7588.785	7576.531	8266.750
Standard Deviation (g)	0.002	0.003	0.003	0.002
Relative Standard Deviation (%)	0.000029	0.000041	0.000036	0.000030
Nitrogen added (g)				677.966

Table 4-17: Weighing nitrogen cylinder M395452 for 30 $\mu\text{mol/mol}$ BTX gas mixture

Weighing cylinder				
Date	2016 June 23			
Reference cylinder	M395404	Mixture cylinder	M395452	
EMPTY			NITROGEN	
Mass (g)			Mass (g)	
	M395404	M395452	M395404	M395452
1	7576.583	7588.784	7576.529	8266.747
2	7576.578	7588.782	7576.528	8266.749
3	7576.582	7588.783	7576.532	8266.752
4	7576.581	7588.789	7576.534	8266.752
Average (g)	7576.581	7588.785	7576.531	8266.750
Standard Deviation (g)	0.002	0.003	0.003	0.002
Relative Standard Deviation (%)	0.000029	0.000041	0.000036	0.000030
Nitrogen added (g)				677.966

The results of 30 $\mu\text{mol/mol}$ BTX gas standards of benzene, toluene and p-xylene are shown in Table 4-18. The loss of components, toluene in cylinder M518191 and p-xylene in cylinders M395452, M518191, and M518243, caused the variation of the planned mole fraction. The loss may have occurred due to the volatility of the components. The other factor that caused the loss was the incorrect use of the loop, which has a ball valve that

tends to hold residual liquid, resulting in inaccurate weighing. When the loop was weighed with that residual liquid mass, it was not transferred into the cylinder, causing a higher recorded mass than the actual mass transferred. This effect was minimised by turning the ball valve slightly to the opened position to allow the residual liquid to be removed, during the evacuation of the loop, before filling with liquid. This effect was also minimised by flushing the loop with nitrogen in a closed position.

Table 4-18: Gravimetric mole fraction results of 30 $\mu\text{mol/mol}$ BTX in nitrogen

Component	Cylinder Number	Gravimetric mole fraction ($\mu\text{mol/mol}$)	Gravimetric uncertainty ($\mu\text{mol/mol}$)
Benzene	M518070	30.08	0.12
	M395452	30.02	0.11
	M518191	30.12	0.11
	M518243	30.04	0.11
Toluene	M518070	31.52	0.10
	M395452	31.54	0.09
	M518191	25.74	0.09
	M518243	32.52	0.09
P-xylene	M518070	29.34	0.09
	M395452	28.15	0.08
	M518191	27.90	0.08
	M518243	26.84	0.08

4.2.3 Gravimetric preparation results of 10 $\mu\text{mol/mol}$ BTEX standard (NPL Method)

Gas mixtures containing BTEX at 10 $\mu\text{mol/mol}$ were prepared in September 2015. The procedure is detailed in section 3.3.2.2. For the gas mixtures under discussion, the NPL (loop) method was used to transfer the components into the cylinders. The results of four gas mixtures labelled M395461, M395412, M395469, and M395438 are presented in Tables 4-19 to 4-22, respectively. The components were added as follows, o-xylene, m-xylene, p-xylene, ethyl benzene, toluene and benzene, due to their vapour pressure, to minimise the loss of most volatile components. After the addition of each component, the vial was weighed three times. The drift of the balance was checked before and after each

weighing cycle by using 10 and 20 g mass pieces; no drift was observed during the vial weighing measurements. The mass difference between each component added to the vial was used to calculate the mass of that component. The total mass of the solution was the sum of all components added into the vial. This mass was essential to calculate the mass loss during the transfer of components into the cylinder.

Table 4-19: Addition of components into a single vial M395461 for 10 µmol/mol BTEX gas mixture

Cylinder number: M395461								
Preparation date	12092015							
Component addition sequence		1	2	3	4	5	6	
	Empty vial	o-xylene	m-xylene	p-xylene	Ethylbenzene	Toluene	Benzene	Total mass of solution
1	10.20110	10.22196	10.24870	10.27005	10.29465	10.31574	10.33356	
2	10.20106	10.22195	10.24568	10.27008	10.29463	10.31572	10.33357	
3	10.20104	10.22195	10.24566	10.27005	10.29465	10.31572	10.33354	
Average mass (g)	10.20110	10.22195	10.24668	10.27006	10.29464	10.31573	10.33356	
Mass of component (g)		0.02089	0.02473	0.02338	0.02458	0.02108	0.01783	0.13249
Standard Deviation	0.00003	0.00001	0.00175	0.00002	0.00001	0.00001	0.00002	
Relative Standard Deviation (%)	0.0003	0.0001	0.0171	0.0002	0.0001	0.0001	0.0001	

Table 4-20: Addition of components into a single vial M395412 for 10 µmol/mol BTEX gas mixture

Cylinder number: M395412								
Preparation date	12092015							
Component addition sequence		1	2	3	4	5	6	
	Empty vial	o-xylene	m-xylene	p-xylene	Ethylbenzene	Toluene	Benzene	Total mass of solution
1	10.20824	10.22941	10.25313	10.27723	10.30171	10.32273	10.34024	
2	10.20824	10.22939	10.25313	10.27720	10.30169	10.32274	10.34024	
3	10.20823	10.22937	10.25311	10.27720	10.30166	10.32272	10.34023	
Average mass (g)	10.20824	10.22939	10.25312	10.27721	10.30169	10.32273	10.34024	
Mass of component (g)		0.02115	0.02373	0.02409	0.02448	0.02104	0.01751	0.13200
Standard Deviation	0.00001	0.00002	0.00001	0.00002	0.00003	0.00001	0.00001	
Relative Standard Deviation (%)	0.00006	0.00020	0.00011	0.00017	0.00024	0.00010	0.00006	

Table 4-21: Addition of components into a single vial M395469 for 10 $\mu\text{mol/mol}$ BTEX gas mixture

Cylinder number: M395469								
Preparation date	12092015							
Component addition sequence		1	2	3	4	5	6	
	Empty vial	o-xylene	m-xylene	p-xylene	Ethylbenzene	Toluene	Benzene	Total mass of solution
1	10.15438	10.17534	10.19873	10.22319	10.24748	10.26845	10.28620	
2	10.15437	10.17536	10.19873	10.22320	10.24747	10.26844	10.28626	
3	10.15434	10.17533	10.19874	10.22320	10.24750	10.26843	10.28630	
Average mass (g)	10.15436	10.17534	10.19873	10.22320	10.24748	10.26844	10.28625	
Mass of component (g)		0.02098	0.02339	0.02446	0.02429	0.02096	0.01781	0.13189
Standard Deviation (g)	0.00002	0.00002	0.00001	0.00001	0.00002	0.00001	0.00005	
Relative Standard Deviation (%)	0.00021	0.00015	0.00006	0.00006	0.00015	0.00010	0.00049	

Table 4-22: Addition of components into a single vial M395438 for 10 µmol/mol BTEX gas mixture

Cylinder number: M395438								
Preparation Date	12092015							
Component addition sequence		1	2	3	4	5	6	
	MT vial	o-xylene	m-xylene	p-xylene	Ethylbenzene	Toluene	Benzene	Total mass of solution
1	10.21090	10.23215	10.25599	10.28061	10.30532	10.32633	10.34395	
2	10.21090	10.23213	10.25602	10.28061	10.30533	10.32633	10.34391	
3	10.21086	10.23217	10.25600	10.28060	10.30530	10.32631	10.34391	
Average mass (g)	10.21089	10.23215	10.25600	10.28061	10.30532	10.32632	10.34392	
Mass of component (g)		0.02126	0.02385	0.02460	0.02471	0.02101	0.01760	0.13304
Standard Deviation	0.00002	0.00002	0.00002	0.00001	0.00002	0.00001	0.00002	
Relative Standard Deviation (%)	0.00023	0.00020	0.00015	0.00006	0.00015	0.00011	0.00022	

The data for the mass of the components added into the cylinders is shown in Table 4-23. The weighing of the loop was repeated five times to ensure that repeatability was satisfactory (within the standard deviation of the balance) and that no mass loss due to evaporation occurred. The mass of solution added into the cylinder was the mass difference of the loop before transfer and the mass after transfer.

Table 4-23: Mass of components added into cylinders (M395461, M395412, M395469, and M395438)

Number of weighing's (loop method)	Loop weighing before transfer	Empty loop weighing after transfer	Loop weighing before transfer	Empty loop weighing after transfer	Loop weighing before transfer	Empty loop weighing after transfer	Loop weighing before transfer	Empty loop weighing after transfer
	M395461		M395412		M395469		M395438	
1	100.19681	100.07581	100.21439	100.07828	106.41755	106.29304	100.20218	100.07565
2	100.19683	100.07587	100.21449	100.07834	106.41768	106.29303	100.20230	100.07563
3	100.19679	100.07593	100.21447	100.07827	106.41761	106.29301	100.20227	100.07565
4	100.19676	100.07592	100.21446	100.07830	106.41770	106.29306	100.20230	100.07573
5	100.19682	100.07597	100.21448	100.07836	106.41774	106.29309	100.20230	100.07576
Average mass (g)	100.19680	100.07590	100.21446	100.07831	106.41766	106.29305	100.20227	100.07568
Standard deviation (g)	0.00003	0.00006	0.00005	0.00004	0.00007	0.00002	0.00005	0.00001
Relative standard Deviation (%)	0.00003	0.00006	0.00005	0.00004	0.00006	0.00001	0.00005	0.00001
Mass of component added into cylinder(g)		0.12090		0.13615		0.12461		0.12659

The mass of each component added into a cylinder was calculated by multiplying the mass of the component transferred into the vial by the total mass, as shown in equation 4.9. The results of mass components added into the cylinder for all gas mixtures are presented in Table 4-24.

$$M_{ic} = \frac{M_{icv}}{M_{tsc}} \times M_{tsv} \quad 4.9$$

Where, M_{ic} is the mass of the component i added into the cylinder, M_{icv} is the mass of component i in the vial, M_{tsc} is the mass of the total solution added into the cylinder, M_{tsv} is the total mass of solution in the vial.

Table 4-24: Calculated mass of each component added into a cylinder

Calculated mass of component added into a cylinder (g)					
	Cylinder number	M395461	M395412	M395469	M395438
	Solution mass (g)	0.12090	0.13616	0.12461	0.12659
1	o-xylene	0.01906	0.02182	0.01982	0.02023
2	m-xylene	0.02256	0.02448	0.02210	0.02270
3	p-xylene	0.02134	0.02485	0.02311	0.02341
4	Ethylbenzene	0.02243	0.02525	0.02295	0.02351
5	Toluene	0.01924	0.02171	0.01980	0.01999
6	Benzene	0.01627	0.01806	0.01683	0.01675

The required mass of nitrogen was recalculated according to the mass of components added into the cylinder to ensure that the required mole fraction was achieved. The mass of nitrogen added was calculated by the mass difference of the empty cylinder and the mass of the cylinder with nitrogen. The results of nitrogen weighing are presented in Table 4-25.

Table 4-25: Weighing of cylinders for nitrogen addition for 30 mol/mol BTEX gas mixture

Mass of cylinder with BTEX components (g)	M395461	M395412	M395469	M395438
1	7576.149	7576.941	7576.891	7576.941
2	7576.144	7576.937	7576.893	7576.937
3	7576.150	7576.505	7576.892	7576.505
Average (g)	7576.148	7576.794	7576.892	7576.794
Standard deviation (g)	0.003	0.251	0.001	0.251
Relative Standard Deviation (%)	0.002	0.145	0.001	0.145
Mass of cylinder with nitrogen (g)	M395461	M395412	M395469	M395438
1	8124.582	8200.874	8134.523	8200.874
2	8124.579	8200.874	8134.523	8200.874
3	8124.580	8200.875	8134.523	8200.875
Average (g)	8124.580	8200.874	8134.523	8200.874
Standard deviation (g)	0.002	0.001	0.000	0.001
Relative Standard Deviation (%)	0.001	0.000	0.000	0.000
Mass of nitrogen added (g)	568.798	641.641	587.220	643.641

The final mole fraction and its corresponding measurement uncertainty of each gas mixture is calculated according to equation 4.8, the data is presented in Table 4-26. The mole fraction of m,p-xylene is presented by the sum of 2 individual mole fractions and the corresponding uncertainty is combined quadratically following GUM (JCGM 100, 2008). This was done to allow for comparison during analysis when using columns which elute m- and p-xylene as one peak.

Table 4-26: Gravimetric results of 10 µmol/mol gas mixtures of BTEX (M395461, M395412, M395469, M395438).

Component	Cylinder Numbers	M395461	M395412	M395469	M395438
Benzene	Gravimetric mole fraction (µmol/mol)	10.26	10.09	10.28	10.10
	Gravimetric uncertainty (µmol/mol)	0.06	0.06	0.06	0.06
Toluene	Gravimetric mole fraction (µmol/mol)	10.29	10.28	10.28	10.22
	Gravimetric uncertainty (µmol/mol)	0.05	0.05	0.06	0.05
Ethylbenzene	Gravimetric mole fraction (µmol/mol)	10.41	10.39	10.32	10.43
	Gravimetric uncertainty (µmol/mol)	0.05	0.04	0.04	0.04
o-xylene	Gravimetric mole fraction (µmol/mol)	8.82	8.95	8.89	8.84
	Gravimetric uncertainty (µmol/mol)	0.05	0.04	0.05	0.05
m,p-xylene	Gravimetric mole fraction (µmol/mol)	20.38	20.30	20.33	20.47
	Gravimetric uncertainty (µmol/mol)	0.07	0.06	0.07	0.06

4.2.4 Gravimetric preparation results of 10 $\mu\text{mol/mol}$ BTEX standard (KRISS Method)

Another set of eight gas mixtures of mole fraction 10 $\mu\text{mol/mol}$ of BTEX was prepared in February 2017. The procedure for the preparation of the batch is detailed in Section 3.3.2.3. The set consisted of 2 batches of four gas mixtures, where a batch of four gas mixtures was each prepared from one mixture solution. Batch 1 gas mixtures were PRGM50005393, NMISA30005428, PRGM20005422, PRGM30005374, and batch 2 gas mixtures were PRGM40005417, PRGM2005462, PRGM20005415, and PRGM70005690. The weighing results of component addition into the vial for gas mixtures PRGM50005393, NMISA30005428, PRGM20005422, and PRGM30005374 are shown in Table 4-27 and those of gas mixtures PRGM40005417, PRGM2005462, PRGM20005415, and PRGM70005690 are presented in Table 4-28. The weighing of each component after addition into the vial was repeated three times to ensure that there was no loss of components due to the volatility of components. The main difference in this method was that one solution was used to prepare four gas mixtures, whereas each gas mixture was prepared independently with the NPL method.

Table 4-27: Vial weighing data for 10 µmol/mol BTEX gas mixtures prepared following KRISS method (PRGM50005393, NMISA30005428, PRGM20005422, and PRGM30005374).

Gas mixture certificates: PRGM50005393, NMISA30005428, PRGM2005422, PRGM30005374								
Preparation date:	12022017							
Component addition sequence		1	2	3	4	5	6	
	Empty vial (g)	o-xylene	m-xylene	p-xylene	Ethylbenzene	Toluene	Benzene	Total mass of solution
1	14.01362	14.55032	15.08631	15.62236	16.15938	16.62265	17.01415	
2	14.01360	14.55026	15.08616	15.62220	16.15926	16.62254	17.01403	
3	14.01344	14.55021	15.08618	15.62221	16.15919	16.62245	17.01409	
Average mass (g)	14.01355	14.55026	15.08622	15.62226	16.15928	16.62255	17.01409	
Filled mass (g)		0.53671	0.53595	0.53604	0.53702	0.46327	0.39154	3.00054
Standard deviation (g)	0.00010	0.00006	0.00008	0.00009	0.00010	0.00010	0.00006	
Relative Standard Deviation (%)	0.00070	0.00038	0.00054	0.00057	0.00059	0.00060	0.00035	

Table 4-28: Vial weighing data for 10 $\mu\text{mol/mol}$ BTEX gas mixtures prepared following KRISS method (PRGM40005417, PRGM2005462, PRGM20005415, and PRGM70005690).

Cylinder numbers PRGM40005417, PRGM2005462, PRGM20005415, and PRGM70005690								
Preparation date	12022017							
Component addition sequence		1	2	3	4	5	6	
	Empty vial (g)	o-xylene	m-xylene	p-xylene	Ethylbenzene	Toluene	Benzene	Total mass of solution
1	14.01391	14.55032	15.08631	15.62236	16.15938	16.62265	17.01415	
2	14.01379	14.55026	15.08616	15.62220	16.15926	16.62254	17.01403	
3	14.01362	14.55021	15.08618	15.62221	16.15919	16.62245	17.01409	
Average mass (g)	14.01377	14.55026	15.08622	15.62226	16.15928	16.62255	17.01409	
Filled mass (g)		0.53649	0.53595	0.53604	0.53702	0.46327	0.39154	3.00032
Standard deviation (g)	0.00015	0.00006	0.00008	0.00009	0.00010	0.00010	0.00006	
Relative Standard Deviation (%)	0.00104	0.00038	0.00054	0.00057	0.00059	0.00060	0.00035	

The weighing data for adding components into the cylinders is shown in Table 4-29 for batch 1 and Table 4-30 for batch 2. The syringe weighing measurements were repeated three times before and after transfer to ensure that there is no loss of component due to the volatility.

Table 4-29: Mass of solution transferred into the cylinder for BTEX gas mixtures (PRGM50005393, NMISA30005428, PRGM20005422, and PRGM30005374).

Syringe weighing with solution before transfer of BTEX into the cylinder				
Certificate number	PRGM50005393	NMISA30005428	PRGM2005422	PRGM30005374
1	19.91739	20.94702	20.95289	20.95179
2	19.91743	20.94703	20.95275	20.95159
3	19.91747	20.94699	20.95278	20.95151
Average mass (g)	19.91743	20.94701	20.95281	20.95163
Standard Deviation (g)	0.00004	0.00002	0.00007	0.00014
Relative Standard Deviation (%)	0.00020	0.00010	0.00035	0.00069
Syringe weighing after transfer of BTEX into the cylinder				
Certificate number	PRGM50005393	NMISA30005428	PRGM2005422	PRGM30005374
1	19.78808	20.82265	20.82660	20.82598
2	19.78821	20.82271	20.82646	20.82593
3	19.78806	20.82270	20.82657	20.82599
Average mass (g)	19.78812	20.82269	20.82654	20.82597
Standard Deviation (g)	0.00008	0.00003	0.00007	0.00003
Relative Standard Deviation (%)	0.00041	0.00015	0.00035	0.00015
Solution mass into cylinder (g)	0.12931	0.12433	0.12626	0.12566

Table 4-30: Mass of solution transferred into the cylinder for BTEX gas mixtures (PRGM40005417, PRGM2005462, PRGM20005415, and PRGM70005690).

Syringe weighing with solution before transfer of BTEX into the cylinder				
Certificate number	PRGM40005417	PRGM20005462	PRGM20005415	PRGM70005690
1	20.94986	20.94638	20.94954	20.94973
2	20.94983	20.94640	20.94959	20.94978
3	20.94987	20.94646	20.94960	20.94974
Average mass (g)	20.94985	20.94641	20.94958	20.94975
Standard Deviation (g)	0.00002	0.00004	0.00003	0.00003
Relative Standard Deviation (%)	0.00010	0.00020	0.00015	0.00013
Syringe weighing after transfer of BTEX into the cylinder				
Certificate number	PRGM40005417	PRGM20005462	PRGM20005415	PRGM70005690
1	20.82571	20.82304	20.82610	20.82620
2	20.82575	20.82311	20.82608	20.82616
3	20.82568	20.82317	20.82602	20.82614
Average mass (g)	20.82571	20.82311	20.82607	20.82617
Standard Deviation (g)	0.00004	0.00007	0.00004	0.00003
Relative Standard Deviation (%)	0.00017	0.00031	0.00020	0.00015
Solution mass into cylinder (g)	0.12414	0.12331	0.12351	0.12358

The results of cylinder weighing of gas mixtures PRGM50005393, NMISA30005428, PRGM20005422, and PRGM30005374 are shown in Table 4-31, and those of PRGM40005417, PRGM20005462, PRGM20005415 and PRGM70005690 are shown in Table 4-32. It is important to mention that after the solution was injected into the heated syringe injector, it was flushed into the cylinder with approximately 200 kPa of nitrogen.

Table 4-31: Weighing cycles of cylinders 10 $\mu\text{mol/mol}$ of BTEX gas mixtures (empty and after all components added, PRGM50005393, NMISA30005428, PRGM20005422, and PRGM30005374).

Mass empty cylinders				
Certificate number	PRGM50005393	NMISA30005428	PRGM2005422	PRGM30005374
1	7553.228	7561.315	7549.211	7552.624
2	7553.228	7561.314	7549.211	7552.627
3	7553.226	7561.317	7549.21	7552.622
4	7553.227	7561.315	7549.21	7552.62
Average mass (g)	7553.227	7561.315	7549.210	7552.623
Standard deviation (g)	0.00096	0.00126	0.00058	0.00299
Relative Standard Deviation (%)	0.00001	0.00002	0.00001	0.00004
Mass of cylinder after flushing BTEX with nitrogen				
1	7582.931	7595.852	7578.414	7580.292
2	7582.932	7595.851	7578.415	7580.295
3	7582.930	7595.851	7578.414	7580.292
4	7582.931	7595.851	7578.415	7580.294
Average mass (g)	7582.931	7595.851	7578.414	7580.293
Standard deviation (g)	0.00082	0.00050	0.00058	0.00150
Relative Standard Deviation (%)	0.00001	0.00001	0.00001	0.00002
Mass N ₂ flushing components (g)	29.704	34.536	29.204	27.670
Mass of cylinder after addition of nitrogen balance				
1	8159.605	8154.031	8174.336	8174.336
2	8159.605	8154.03	8174.333	8144.475
3	8159.603	8154.03	8174.333	8144.473
4	8159.602	8154.03	8174.332	8144.473
Average mass (g)	8159.603	8154.030	8174.3335	8144.474
Standard deviation (g)	0.00150	0.00050	0.00173	8144.473
Relative Standard Deviation (%)	0.00002	0.00001	0.00002	0.00096
Nitrogen Added (g)	576.672	558.179	595.919	564.180
Total mass N ₂ added (g)	606.3765	592.715	625.123	591.850

Table 4-32: Weighing cycles of cylinders 10 $\mu\text{mol/mol}$ of BTEX gas mixtures (empty and after all components added, PRGM40005417, PRGM20005462, PRGM20005415 and PRGM70005690).

Mass empty cylinders				
Cylinder number	PRGM40005417	PRGM20005462	PRGM20005415	PRGM70005690
1	7557.498	7566.703	7560.653	7523.408
2	7557.504	7566.610	7560.650	7523.407
3	7557.503	7566.611	7560.649	7523.408
4	7557.501	7566.700	7560.649	7523.406
Average mass (g)	7557.501	7566.656	7560.650	7523.407
Standard deviation (g)	0.00265	0.05255	0.002	0.00096
Relative Standard Deviation (%)	0.00004	0.00069	0.00003	0.00001
Mass of cylinder after flushing BTEX with nitrogen				
1	7584.859	7596.672	7590.732	7553.896
2	7584.858	7596.672	7590.735	7553.892
3	7584.862	7596.677	7590.733	7553.890
4	7584.861	7596.675	7590.730	7553.889
Average mass (g)	7584.860	7596.674	7590.733	7553.892
Standard deviation (g)	0.00183	0.00245	0.00208	0.00310
Relative Standard Deviation (%)	0.00002	0.00003	0.00003	0.00004
Mass N ₂ flushing components (g)	27.3585	30.018	30.082	30.484
Mass of cylinder after addition of nitrogen balance				
1	8131.786	8146.516	8137.825	8108.258
2	8131.786	8146.518	8137.832	8108.253
3	8131.787	8146.514	8137.831	8108.250
4	8131.787	8146.516	8137.832	8108.256
Average mass (g)	8131.787	8146.516	8137.830	8108.254
Standard deviation (g)	0.00058	0.00163	0.00337	0.00350
Relative Standard Deviation (%)	0.00001	0.00002	0.00004	0.00004
Nitrogen Added (g)	546.926	549.842	547.097	554.362
Total mass N ₂ added (g)	574.285	579.860	577.180	584.847

4.3 Verification of gas mixtures

After completing the gravimetric preparation of reference gas mixtures, their gravimetric composition was validated. Since the preparation was completed following robust preparation methods, the guidelines for validation or verification of prepared gas mixtures were done according to ISO 6143- Gas analysis - Comparison methods for determining and checking the composition of calibration gas mixtures (ISO 6143, 2001). Validation was confirmed using equation 4.10:

$$|x_g - x_a| \leq 2\sqrt{u(x_g)^2 + u(x_a)^2} \quad 4.10$$

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

The approach used for verifying reference gas mixtures of similar mole fractions was one-point calibration, by choosing one mixture as a reference at random and the rest as unknowns (samples). The mole fraction of reference gas mixtures chosen to be unknowns was calculated using equation 4.11:

$$C_{sample} = \frac{A_{sample}}{A_{reference}} \times C_{reference} \quad 4.11$$

Where C_{sample} is the mole fraction of the sample, A_{sample} is the peak area of the sample, $A_{reference}$ is the peak area of the reference and $C_{reference}$ is the mole fraction of the reference.

One of the methods used to verify the gas mixture components at a similar mole fraction is the measure of internal consistency. The ratio of detector response to the gravimetric value of the components in the gas mixture calculated the internal consistency. The sensitivity ratio factors were used to evaluate the internal consistency of prepared gas mixtures with similar mole fractions shown in equations 4.12 and 4.13.

$$Sensitivity_{reference} = \frac{Area_{Ref}}{C_{Ref}} \quad 4.12$$

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

$$Sensitivity_{sample} = \frac{Area_{Sample}}{C_{Sample}} \quad 4.13$$

where $Sensitivity_{sample}$ is the sensitivity of the sample, $Area_{sample}$ and C_{sample} represents the average peak area from the instrument response and the mole fraction of the sample cylinder. The sensitivity ratio of the sample and the reference is given by equation 4.14, with the value close to unity (1) representing a good comparison.

$$Sensitivity_{ratio} = \frac{Sensitivity_{Sample}}{Sensitivity_{Reference}} \quad 4.14$$

where $Sensitivity_{ratio}$ is the ratio of the sensitivity calculated for the sample and the reference, $Sensitivity_{Sample}$ is the sensitivity of the sample and $Sensitivity_{Reference}$ is the sensitivity of the reference. The calculation formulae of the average, the standard deviation, and relative standard deviation are not included since they are well known.

4.3.1 Verification of 500 nmol/mol BTEX gas mixture

The verification results of FF9498 are shown in Table 4-32. The components were separated using a AT-WAX HELIFLEX (60 m x 0,32 mm id x 0,2 µm df) column. The gas mixture was verified against the BTEX primary reference gas mixtures CAL-11248 and CAL-11250. The verification was performed on the 16th and 19th October 2015. Both CAL11248 and CAL-11250 contained five components except ethylbenzene, at a nominal mole fraction of 500 nmol/mol. The mole fraction of FF9498 varied between 1496 to 571 nmol/mol due to the varying masses of each component added into the cylinder. The verification results of FF9498 against CAL11248 show a difference of -2,57 % for benzene, -5,36 % for toluene, 9,17 % for m-xylene, -48,09 % for p-xylene and -6,96 % for o-xylene. The results against CAL11250 show a difference of -10,15 % for

benzene, 3,74 % for toluene, 16,99 % for m-xylene, -41,41 % for p-xylene and 6,70 % for o-xylene.

The results are also presented in Figures 4-11 and 4-12. In both figures, the zero line represents the gravimetric values. The circles are differences between the gravimetric and the verification (predicted) values, each component with its colour as shown on the x-axis. The error bars are combined relative expanded uncertainty values, with the largest contribution from gravimetric preparation due to uncertainty components of weighing the capillary tubes. P-xylene showed the largest deviation compared to other components. This could be attributed to the loss of this component during transfer into the cylinder, where the component might not have swept completely into the cylinder during flushing with nitrogen. The capillary method is the most challenging compared to the other two (NPL and KRISS), however it does carry one advantage that lower mole fraction gas mixtures could be prepared directly without dilution. Efforts were made to repeat the method in South Africa, however time did not allow. The capillary method carries many risks of component loss due to volatility. Preference is rather to use NPL or KRISS, preparing a higher mole fraction and diluting down to atmospheric levels, even though the uncertainty will be higher compared to the capillary method. Serial dilution increases the uncertainty due to law of propagation of uncertainty.. Balances were well maintained, calibrated and checked before and after use.

Table 4-33: Verification results of 500 nmol/mol BTEX gas mixture FF9498

Component	Cylinder Number	Gravimetric mole fraction (μmol/mol)	Gravimetric uncertainty (μmol/mol)	Verification mole fraction (μmol/mol)	Verification uncertainty (μmol/mol)	% Difference	Combined Expanded uncertainty (U) (k=2)	% Relative expanded uncertainty (%REU)
Benzene	CAL11250	425.10	1.00					
	FF9498	1469.06	112.71	1320.01	18.30	-10.15	228.37	15.55%
	CAL-11248	508.50	1.00					
	FF9498	1469.06	112.71	1431.33	40.38	-2.57	239.45	16.30%
Toluene	CAL11250	485.90	1.00					
	FF9498	916.80	143.03	951.11	10.10	3.74	286.76	31.28%
	CAL-11248	506.40	1.00					
	FF9498	916.80	143.03	867.70	11.77	-5.36	287.02	31.31%
Ethylbenzene	CAL11250							
	FF9498	562.10	169.29					
	CAL-11248							
	FF9498	562.10	169.29					
M-xylene	CAL11250	448.80	1.00					
	FF9498	571.39	124.04	668.44	5.81	16.99	248.35	43.46%
	CAL-11248	517.10	1.00					
	FF9498	571.39	124.04	623.80	9.17	9.17	248.76	43.54%
P-xylene	CAL11250	450.90	1.00					
	FF9498	1496.95	66.02	877.01	7.63	-41.41	132.92	8.88%
	CAL-11248	505.80	1.00					
	FF9498	1496.95	66.02	777.09	14.46	-48.09	135.17	9.03%
O-xylene	CAL11250	438.10	1.00					
	FF9498	656.14	190.53	663.68	6.38	6.00	381.27	58.11%
	CAL-11248	508.80	1.00					
	FF9498	656.14	190.53	612.23	8.51	-6.96	381.43	58.13%

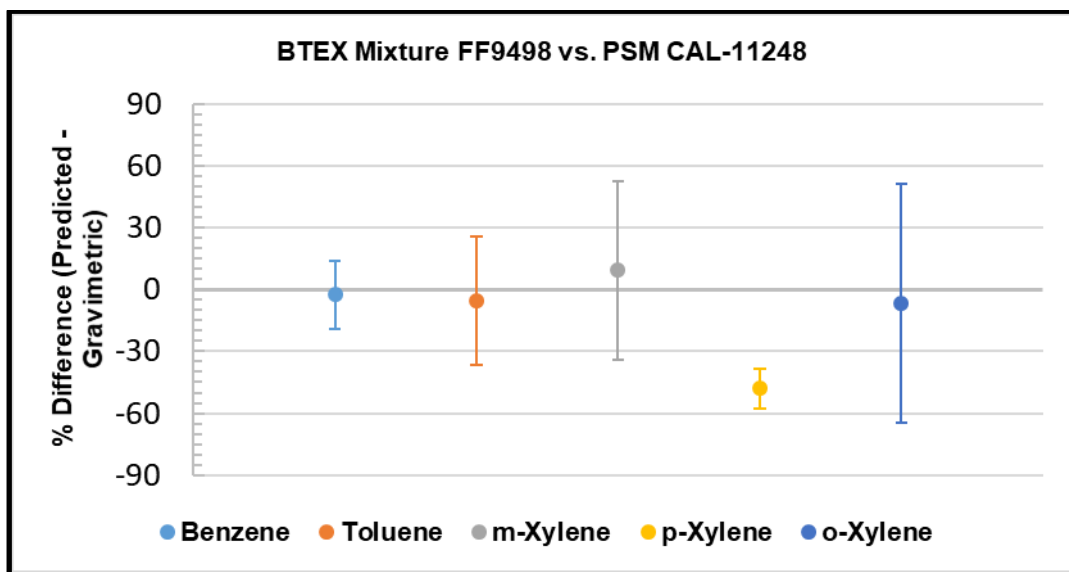


Figure 4-11: Verification results of FF9498 against CAL11248

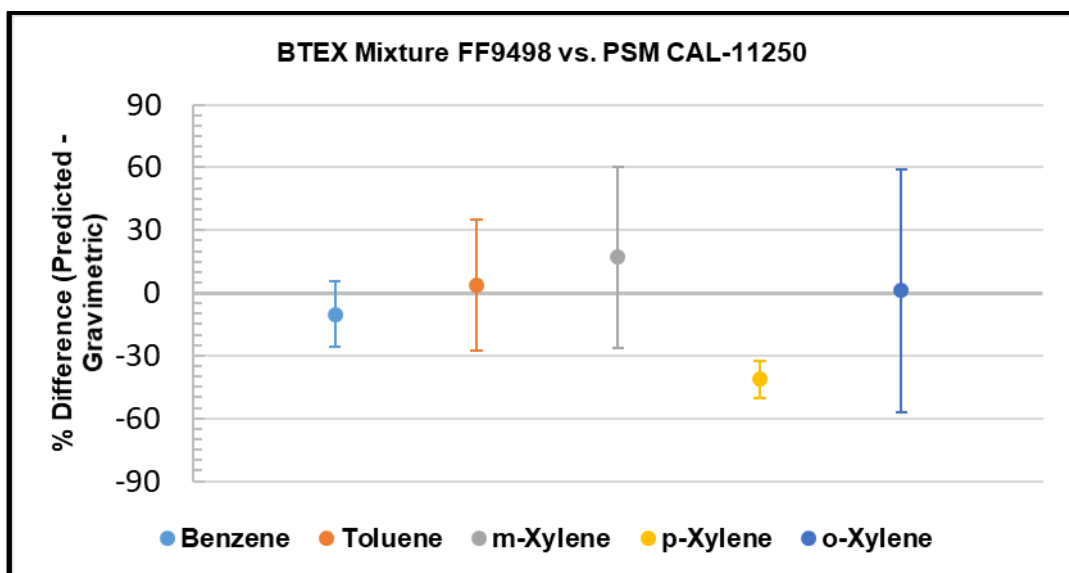


Figure 4-12: Verification results of FF9498 against CAL11250

4.3.2 Verification of 30 $\mu\text{mol/mol}$ BTX gas mixtures

Gas mixtures containing three components of benzene, toluene, and p-xylene (BTX) at a nominal mole fraction of 30 $\mu\text{mol/mol}$ were prepared and analysed by gas chromatography with flame ionisation detection. The separation was achieved by using a Restek Rxi624SilMS (60 m x 0,32 mm id x 1,8 μm df) column. The gas mixtures at this nominal mole fraction were prepared due to customer demand in South Africa for the calibration of equipment for ambient pollution monitoring. Four gas mixtures were analysed, and the superimposed chromatogram of all gas mixtures is shown in Figure 4-

13. The chromatogram shows the separation of benzene, toluene and p-xylene in that elution order. The marks on the chromatogram are set integration parameters applied in the method to achieve consistent baseline allocation.

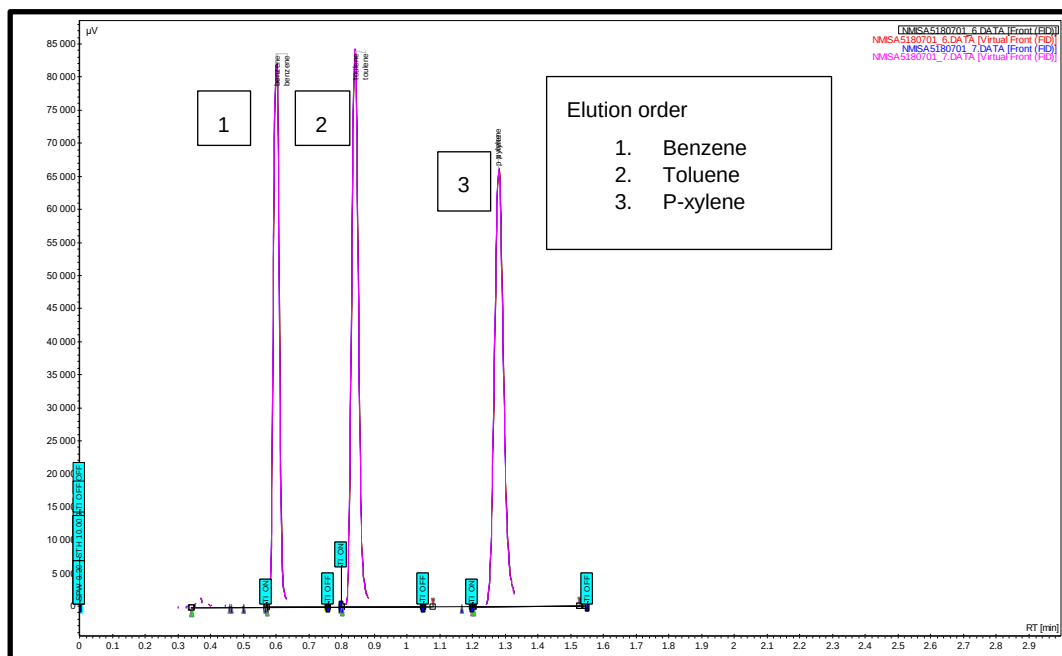


Figure 4-13: Superimposed chromatogram of four gas mixtures (M518070, M395452, M518191, M518243)

The gas mixtures were prepared using the NPL loop method, with components added to the gas cylinder using the cylinder vacuum and were added individually. The verification results are presented in Table 4-33, with cylinder number D517080 chosen randomly as a reference to analyse the other three cylinders. For benzene, the verification between the gravimetric and the verification values were all within 1%. The difference was 0,81% for M395452, 0,04 % for M518191, and 0,62 % for M518243, respectively, indicating good agreement between the gravimetric and the verification values. The verification results of toluene also showed an agreement of within 1% between the gravimetric and the verification values for M395452 and M518191; however, for M518243, the difference was 1,03%. The verification results of p-xylene showed a large difference of -4,30 % for M395452 and -19,83 % for M518243. The significant differences could be attributed to the loss of components during the transfer from the loop into the cylinder. The causes of mass loss were explained in Section 4.2.2.

Table 4-34: Verification results of gas mixtures containing 30 µmol/mol of BTX

Component	Cylinder Number	Gravimetric mole fraction (µmol/mol)	Gravimetric uncertainty (µmol/mol)	Verification mole fraction (µmol/mol)	Verification uncertainty (µmol/mol)	% Difference	Combined Expanded uncertainty (U) (k=2)	% Relative expanded uncertainty (%REU)
Benzene	M518070	30.08	0.12					
	M395452	30.02	0.11	30.27	0.13	0.81	0.34	1.15%
	M518191	30.12	0.11	30.13	0.13	0.04	0.33	1.10%
	M518243	30.04	0.11	30.23	0.13	0.62	0.34	1.13%
Toluene	M518070	31.52	0.10					
	M395452	31.54	0.09	31.53	0.11	-0.06	0.29	0.92%
	M518191	25.74	0.09	25.85	0.09	0.41	0.26	1.01%
	M518243	32.52	0.09	32.19	0.11	-1.03	0.29	0.88%
P-xylene	M518070	29.34	0.09					
	M395452	28.15	0.08	26.94	0.08	-4.30	0.24	0.83%
	M518191	27.90	0.08	27.89	0.09	-0.06	0.24	0.86%
	M518243	26.84	0.08	21.52	0.07	-19.81	0.21	0.80%

The results of the internal consistency tests are presented in Table 4-34 and graphically in Figure 4-14, with M518070 as a reference. The internal consistency was within 1%, consistent with data presented in Table 4-33. Data presented in Tables 4-32, 4-33, 4-34, 4-35, and 4-36 were obtained from the GC peak area data.

Table 4-35: Internal consistency of benzene in mixtures (M518070, M395452, M518191, M518243).

Benzene					
Cylinder number	Sensitivity Ratio	Standard uncertainty of sensitivity ratio (%)	Expanded Uncertainty of sensitivity ratio (%)	Expanded Uncertainty of sensitivity ratio	Difference
M518070	1.0000	0.2696	0.5391	0.0054	
M395452	1.0081	0.2696	0.5391	0.0054	-0.8134
M518191	1.0006	0.1773	0.3547	0.0035	-0.0613
M518243	1.0062	0.2250	0.4500	0.0045	-0.6210

The calculated expanded uncertainty of the internal consistency shown by the error bars in Figure 4-14, confirmed consistency with the gravimetric values.

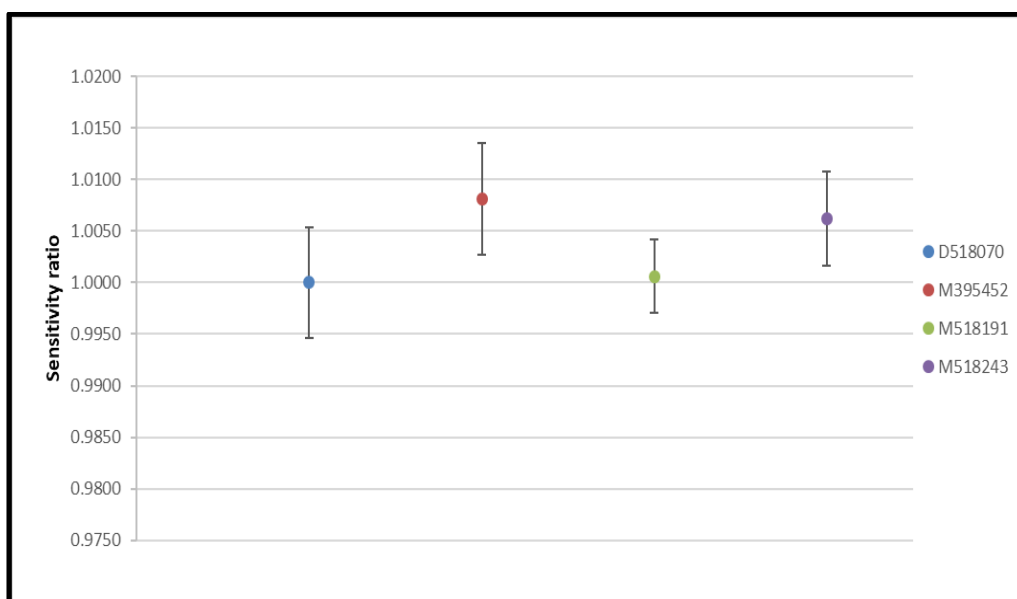


Figure 4-14: Sensitivity ratio graph of benzene as a measure of internal consistency

The internal consistency results of toluene are shown in Table 4-35 and Figure 4-15. The results showed that M518070, M395452 and M518191 were consistent with each other except M518243, with more than 1%, although it is within the uncertainty of M518070 and M395452, it is not acceptable.

Table 4-36: Internal consistency of toluene in mixtures M518070, M395452, M518191, M518243.

Toluene					
Cylinder number	Sensitivity Ratio	Standard uncertainty of sensitivity ratio (%)	Expanded Uncertainty of sensitivity ratio (%)	Expanded Uncertainty of sensitivity ratio	Difference
M518070	1.0000	0.3603	0.721	0.0072	
M395452	0.9994	0.3434	0.687	0.0069	0.0587
M518191	1.0046	0.3049	0.610	0.0061	-0.4629
M518243	0.9884	0.3805	0.761	0.0075	1.1571

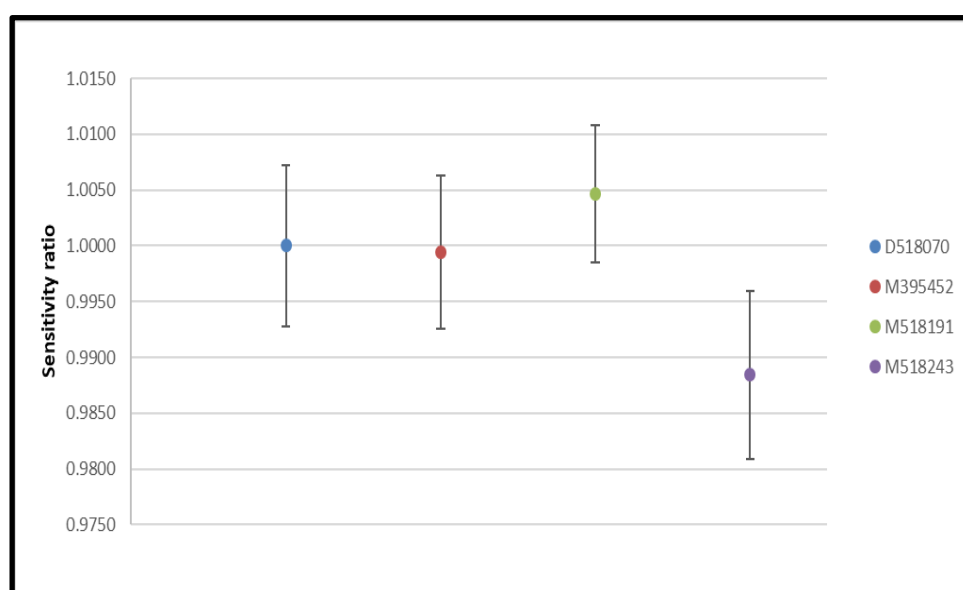


Figure 4-15: Sensitivity ratio graph of toluene as a measure of internal consistency

The internal consistency results of p-xylene are presented in Table 4-36 and Figure 4-16. Similar to the discussion of benzene and toluene, the internal consistency of p-xylene showed a deviation of 20% for M518243 and 4% for M395452. The two mixtures did not pass the verification criteria and were thus rejected.

Table 4-37: Internal consistency of p-xylene in mixtures M518070, M395452, M518191, M518243.

P-xylene					
Cylinder number	Sensitivity Ratio	Standard uncertainty of sensitivity ratio (%)	Expanded Uncertainty of sensitivity ratio (%)	Expanded Uncertainty of sensitivity ratio	Difference
M518070	1.0000	0.2818	0.5635	0.00564	
M395452	0.9553	0.3896	0.7791	0.00744	4.469
M518191	1.0001	0.3897	0.7795	0.00780	-0.011
M518243	0.8010	0.1508	0.3016	0.00242	19.901

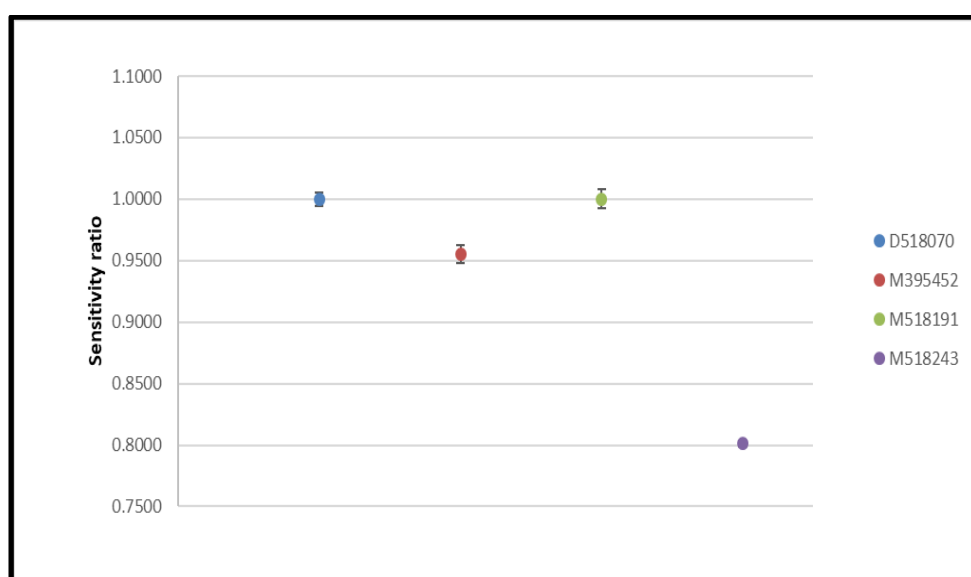


Figure 4-16: Sensitivity ratio graph of p-xylene as a measure of internal consistency

4.3.3 Verification of 10 $\mu\text{mol/mol}$ BTEX mixture (prepared by NPL method)

Four gas mixtures containing six components of benzene, toluene, ethylbenzene, m-xylene, p-xylene, and o-xylene (BTEX) at a nominal mole fraction of 10 $\mu\text{mol/mol}$ were prepared and analysed by gas chromatography with a flame ionisation detector. The separation was accomplished by using a Restek Rxi624SilMS (60m x 0,32mm ID x 1.8 μm) column, where m,p-xylene eluted as one peak. The analysis was done in March 2016, six months after preparation. The verification results for benzene, toluene, and ethylbenzene are presented in Table 4-37 and in Table 4-38 for m,p-xylene, and o-xylene. Cylinder number M395461 was chosen randomly as a reference against cylinders M395412, M395469, and M395438. The analysis sequence followed was

reference 1>sample 1>reference 1>sample 2>reference 1, etc., to ensure that the detector response was constantly monitored during the analysis. The detector drift is measured by the difference of peak area of a component of a reference at the beginning of analysis to a peak area of the same reference after each sample analysis. The detector drift is calculated according to Equation 4-15.

$$Drift_{\%} = \frac{Peak\ area_{Ref\ (B)} - Peak\ area_{Ref\ (A)}}{Peak\ area_{Ref\ (A)}} \times 100 \quad 4.15$$

Where *Drift*; is the measure of the changes in detector response to the same analyte during analysis, *Peak area_{Ref (B)}* is the peak area of the reference mixture analysed after the sample mixture and *Peak area_{Ref (A)}* is the peak area of the reference mixture analysed before the sample mixture. A difference of less than 1% showed that the detector drift was within the accepted limit for long analysis methods such as those of BTEX.

For benzene (Table 4-37), the verification between the gravimetric and the verification values were -2,69%, for M395412, -0,06% for M395469 -2,26% for M395438. For toluene, the verification between the gravimetric and the verification values were -0,57%, for M395412, -0,55% for M395469 -1,20% for M395438. For ethylbenzene, the verification between the gravimetric and the verification values were -0,15%, for M395412, -1,32% for M395469 -0,16% for M395438. For m,p-xylene (Table 4-38), the verification between the gravimetric and the verification values were -0,10%, for M395412, -0,48% for M395469 -0,00% for M395438. For o-xylene, the verification between the gravimetric and the verification values were 2,02%, for M395412, 0,62% for M395469 1,26% for M395438.

Table 4-38: Verification results of 10 µmol/mol BTEX (M395461, M395412, M395469 and M395438, for benzene, toluene and ethyl benzene)

Component	Cylinder Number	Gravimetric mole fraction (µmol/mol)	Gravimetric uncertainty (µmol/mol)	Verification mole fraction (µmol/mol)	Verification uncertainty (µmol/mol)	% Difference	Combined Expanded uncertainty (U) (k=2)	% Relative expanded uncertainty (%REU)
Benzene	M395461	10.26	0.06					
	M395412	10.09	0.06	10.36	0.07	-2.69	0.17	1.70%
	M395469	10.28	0.06	10.29	0.07	-0.06	0.18	1.74%
	M395438	10.10	0.06	10.32	0.07	-2.26	0.18	1.76%
Toluene	M395461	10.29	0.05					
	M395412	10.28	0.05	10.34	0.06	-0.57	0.15	1.46%
	M395469	10.28	0.06	10.34	0.06	-0.55	0.17	1.66%
	M395438	10.22	0.05	10.34	0.06	-1.20	0.16	1.53%
Ethylbenzene	M395461	10.41	0.05					
	M395412	10.39	0.04	10.40	0.07	-0.15	0.15	1.49%
	M395469	10.32	0.04	10.45	0.07	-1.32	0.16	1.58%
	M395438	10.43	0.04	10.45	0.06	-0.16	0.15	1.43%

Table 4-39: Verification results of 10 µmol/mol BTEX (M395461, M395412, M395469 and M395438, for m,p-xylene and o-xylene)

Component	Cylinder Number	Gravimetric mole fraction (µmol/mol)	Gravimetric uncertainty (µmol/mol)	Verification mole fraction (µmol/mol)	Verification uncertainty (µmol/mol)	% Difference	Combined Expanded uncertainty (U) (k=2)	% Relative expanded uncertainty (%REU)
m,p-xylene	M395461	20.38	0.07					
	M395412	20.30	0.06	20.32	0.09	-0.10	0.22	1.09%
	M395469	20.33	0.07	20.43	0.11	-0.48	0.25	1.22%
	M395438	20.47	0.06	20.47	0.10	0.00	0.24	1.17%
o-xylene	M395461	8.82	0.05					
	M395412	8.95	0.04	8.77	0.05	2.02	0.14	1.54%
	M395469	8.89	0.05	8.83	0.06	0.62	0.15	1.73%
	M395438	8.95	0.05	8.84	0.05	1.26	0.14	1.58%

The graphical representation of the verification data is shown in Figures 4-17 to 4-21. The figures are a plot of the sensitivity ratio calculated by equation 4.14, with the error bars representing the estimated expanded uncertainty of the sensitivity ratio.

It was observed that the largest deviation was for benzene, followed by o-xylene and toluene. The internal consistency of ethylbenzene and m,p xylene were acceptable, to within 1.5% as the largest deviation. A factor could be that benzene is the most volatile component, while for o-xylene, it could have been the errors arising from weighing, which were not noticed.

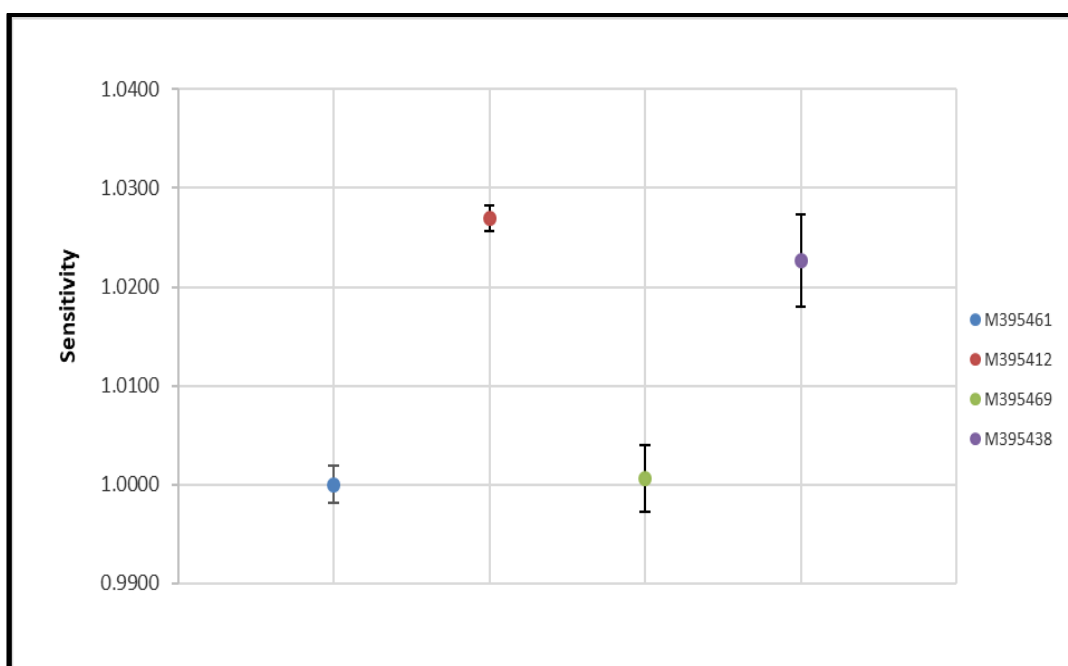


Figure 4-17: Sensitivity ratio graph of benzene as a measure of internal consistency

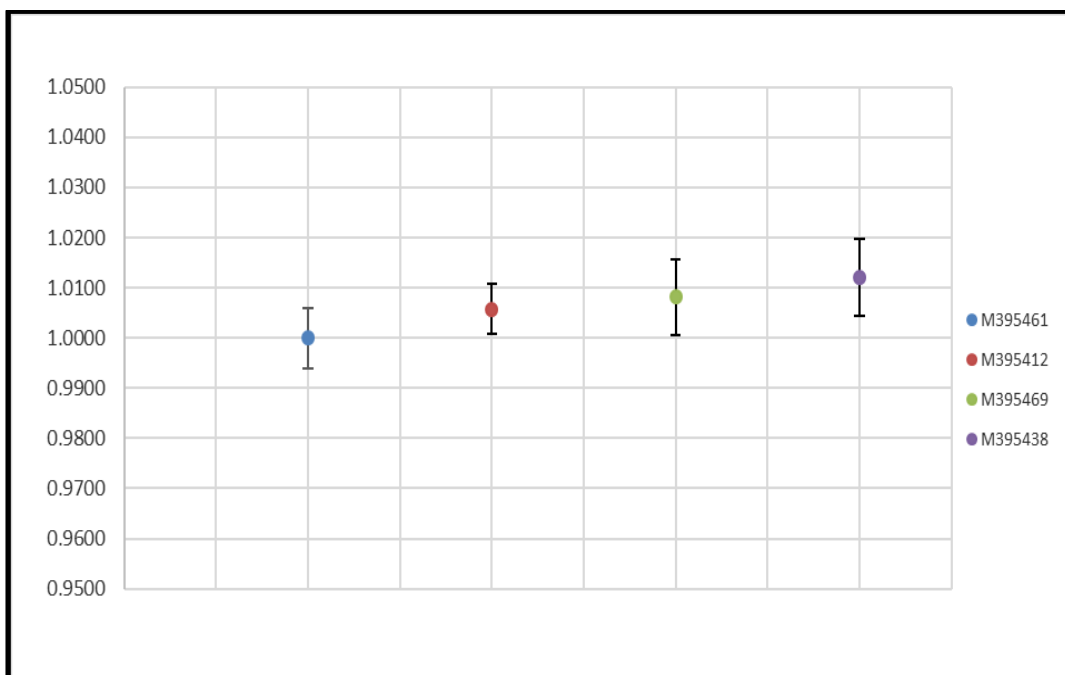


Figure 4-18: Sensitivity ratio graph of toluene as a measure of internal consistency

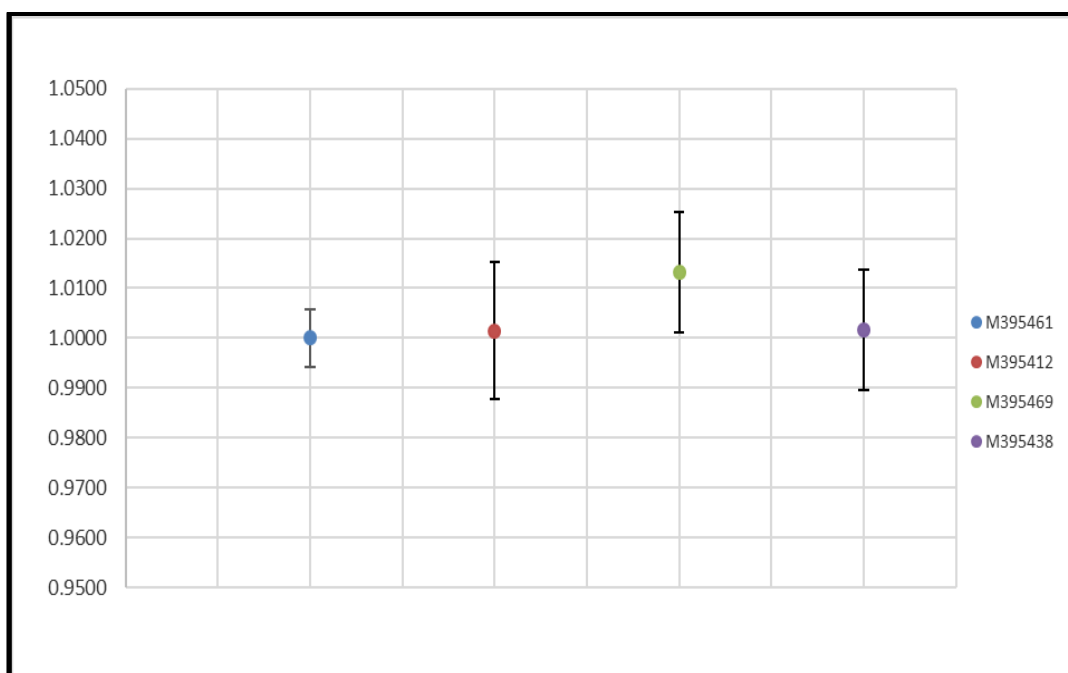


Figure 4-19: Sensitivity ratio graph of ethylbenzene as a measure of internal consistency

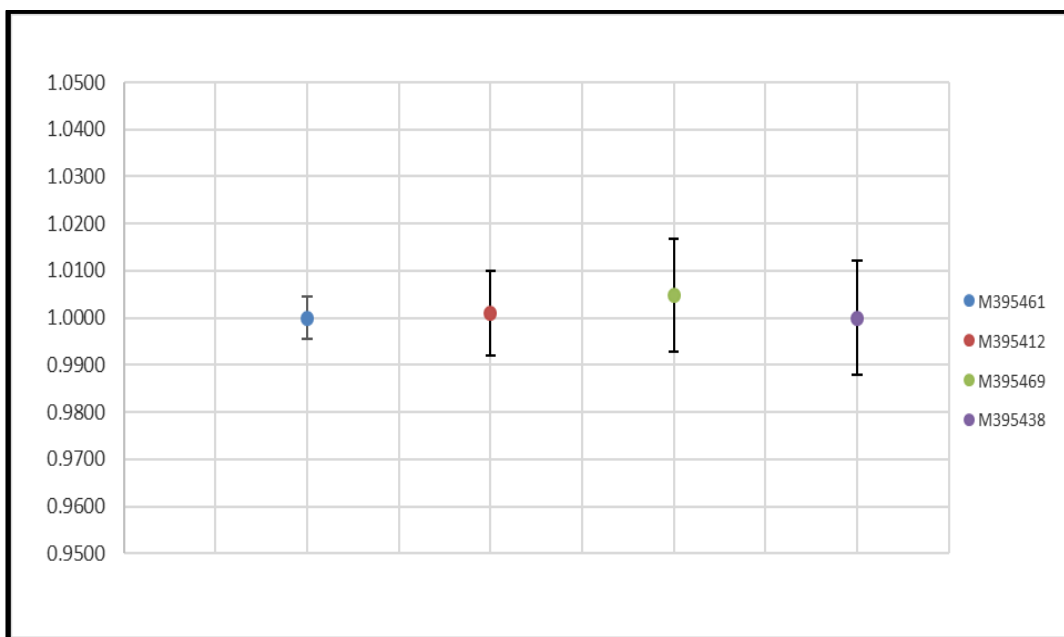


Figure 4-20: Sensitivity ratio graph of m,p-xylene as a measure of internal consistency

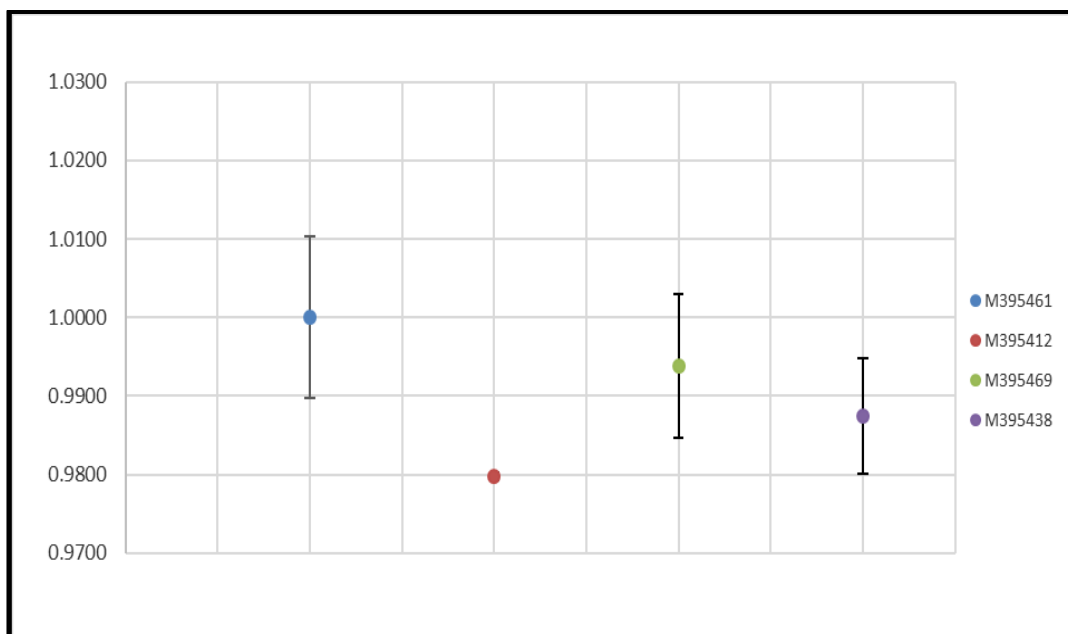


Figure 4-21: Sensitivity ratio graph of o-xylene as a measure of internal consistency

4.3.4 Verification of 10 $\mu\text{mol/mol}$ BTEX mixture (prepared by KRISS method)

Eight gas mixtures were prepared in February 2017 using the KRISS method and verified from February until March 2017. The four gas mixtures were analysed by gas chromatography with a flame ionisation detector. The separation was achieved by using

Agilent DB-624 (60m x 0,32mm id 1.8 μ m df) column. The chromatogram of the gas mixture used as a reference cylinder is shown in Figure 4-16, including the elution order of components with their respective retention times. M,p-xylene elute together as one component, their individual mole fractions were summed, and their corresponding measurement uncertainties were combined quadratic following the GUM guidelines (JCGM 100, 2008). The verification results are presented in Table 4-40; PRGM20005415 was chosen randomly as a reference to analyse the other three cylinders. The analysis was performed over five consecutive days. The data presented in Table 4-40 was the analysis of three other cylinders chosen randomly from two batches.

The results of all BTEX components in all cylinders showed satisfactory consistency. The difference between the gravimetric and the verification values were less than 0,5%, with the highest difference being 0,29% for benzene on mixture PRGM50005422. The internal consistency results of benzene are shown in Table 4-41 and graphically in Figure 4-23. The error bars represent the expanded uncertainty of the internal consistency.

The results suggest that the KRISS method displays better accuracy than the NPL method, probably due to the simple operation of filling the components into the cylinder by syringe followed by flushing with 200 kPa of nitrogen. The NPL method achieved the transfer by drawing the components in the loop by cylinder vacuum. The method has critical steps that require care to ensure that the loss of components is minimal and accurately accounted for. In the KRISS method, the solution mixed with components in the vial was used to prepare four cylinders, while with the NPL method, each cylinder is prepared independently.

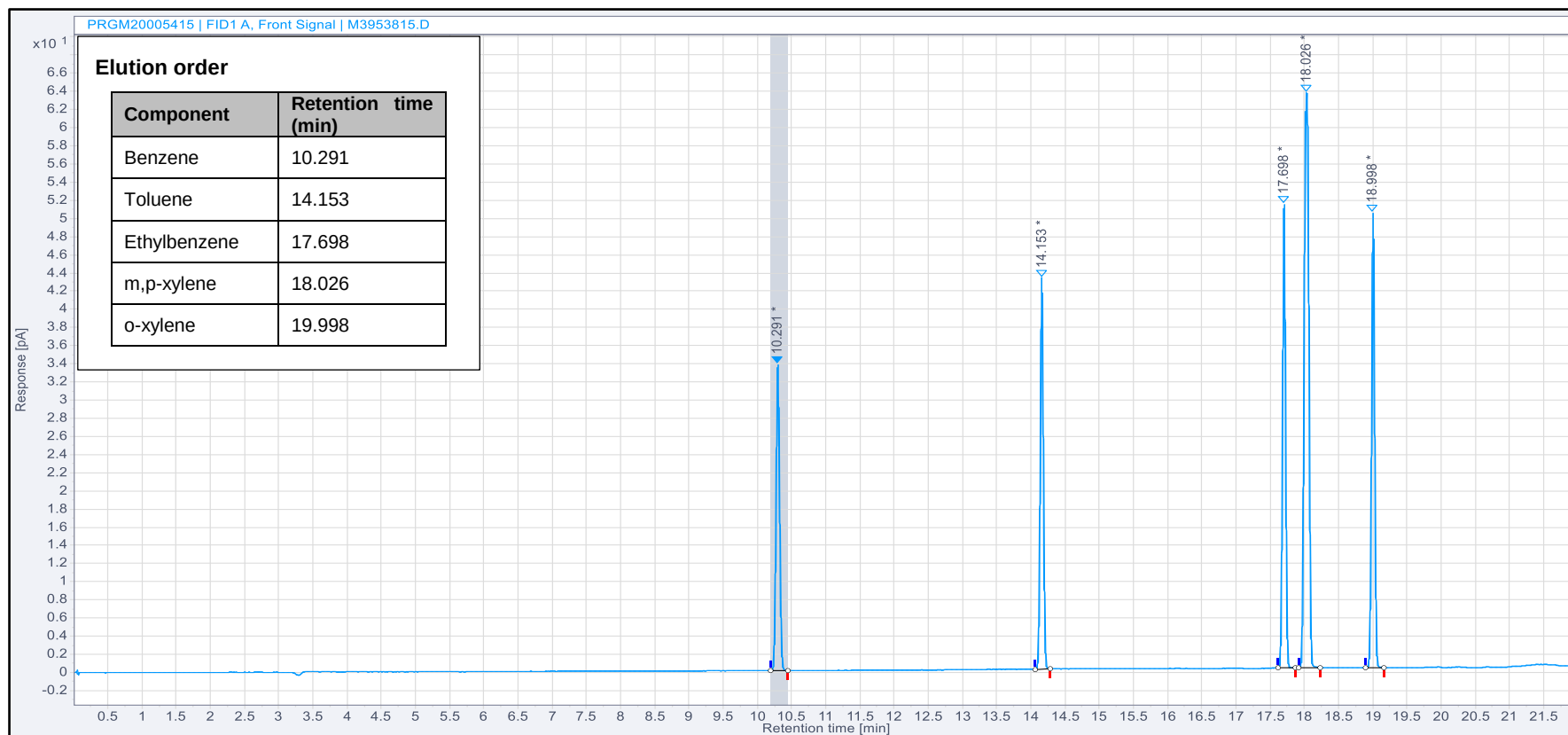


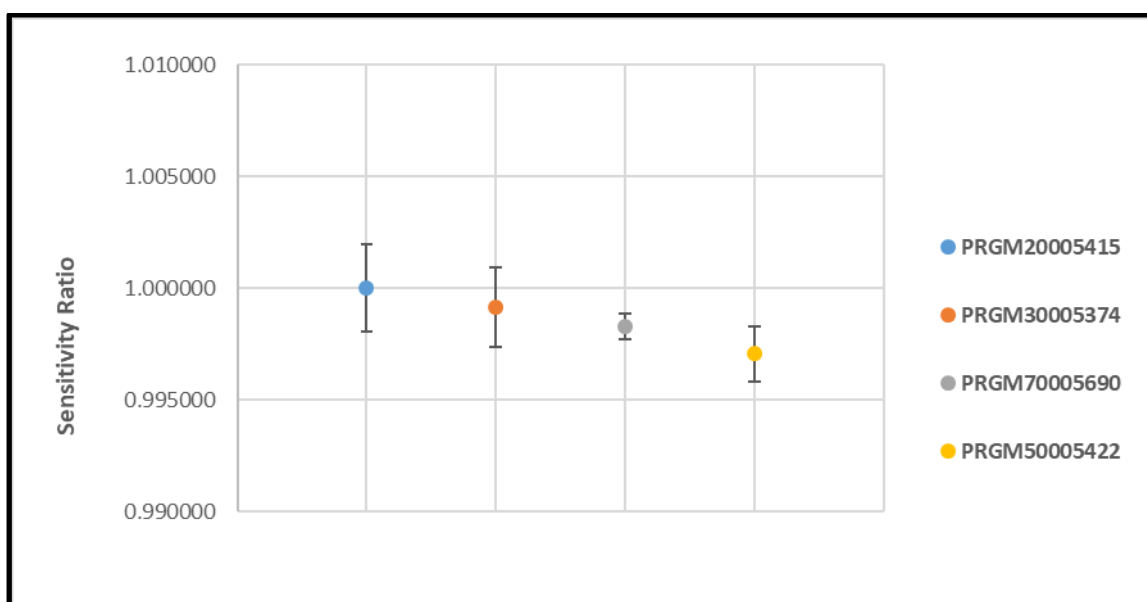
Figure 4-22: Chromatogram of BTEX verification in March 2017 (cylinder # PRGM20005415)

Table 4-40: Verification results of 10 µmol/mol BTEX (PRG20005415, PRGM30005374, PRGM70005690 and PRGM50005422)

Component	Cylinder Number	Gravimetric mole fraction (µmol/mol)	Gravimetric uncertainty (µmol/mol)	Verification mole fraction (µmol/mol)	Verification uncertainty (µmol/mol)	% Difference	Combined Expanded uncertainty (U) (k=2)	% Relative expanded uncertainty (%REU)
Benzene	PRGM20005415	10.02	0.12					
	PRGM30005374	9.94	0.12	9.93	0.12	0.08	0.35	3.48%
	PRGM70005690	9.89	0.12	9.87	0.12	0.17	0.35	3.51%
	PRGM50005422	9.45	0.11	9.43	0.12	0.29	0.33	3.47%
Toluene	PRGM20005415	10.05	0.11					
	PRGM30005374	9.97	0.10	9.98	0.11	-0.15	0.29	2.95%
	PRGM70005690	9.92	0.10	9.90	0.10	0.17	0.29	2.97%
	PRGM50005422	9.48	0.10	9.47	0.10	0.10	0.28	2.93%
Ethylbenzene	PRGM20005415	10.11	0.09					
	PRGM30005374	10.03	0.09	10.03	0.09	-0.02	0.25	2.54%
	PRGM70005690	9.98	0.09	9.98	0.09	0.07	0.26	2.56%
	PRGM50005422	9.54	0.08	9.56	0.09	-0.14	0.24	2.54%
m,p-xylene	PRGM20005415	20.19	0.13					
	PRGM30005374	20.04	0.13	20.07	0.13	-0.18	0.37	1.83%
	PRGM70005690	19.94	0.13	19.98	0.13	-0.18	0.37	1.84%
	PRGM50005422	19.06	0.12	19.05	0.12	0.02	0.35	1.81%
o-xylene	PRGM20005415	10.07	0.09					
	PRGM30005374	10.00	0.09	9.98	0.09	0.22	0.26	2.61%
	PRGM70005690	9.95	0.09	9.92	0.09	0.26	0.26	2.62%
	PRGM50005422	9.51	0.09	9.53	0.09	-0.20	0.25	2.60%

Table 4-41: Internal consistency of 10 µmol/mol benzene

Benzene					
Certificate number	Sensitivity Ratio	Standard Uncertainty (%)	Expanded Uncertainty (%)	Expanded Uncertainty of sensitivity ratio	Difference (%)
PRGM20005415	1.000000	0.098013	0.196026	0.001960	
PRGM30005374	0.999162	0.090251	0.180501	0.001803	0.08
PRGM70005690	0.998303	0.028556	0.057113	0.000570	0.17
PRGM50005422	0.997060	0.062676	0.125352	0.001250	0.29

**Figure 4-23:** Graphical internal consistency of 10 µmol/mol benzene

The internal consistency results of toluene are shown in Table 4-42 and graphically in Figure 4-24. The verification results were consistent with the gravimetric values to within 0,17 %.

Table 4-42: Internal consistency of 10 µmol/mol toluene

Toluene					
Certificate number	Sensitivity Ratio	Standard Uncertainty (%)	Expanded Uncertainty (%)	Expanded Uncertainty of sensitivity ratio	Difference (%)
PRGM20005415	1.000000	0.157852	0.315704	0.003157	
PRGM30005374	1.001472	0.087131	0.174261	0.001745	-0.15
PRGM70005690	0.998312	0.097518	0.195037	0.001947	0.17
PRGM50005422	0.999024	0.074691	0.149382	0.001492	0.10

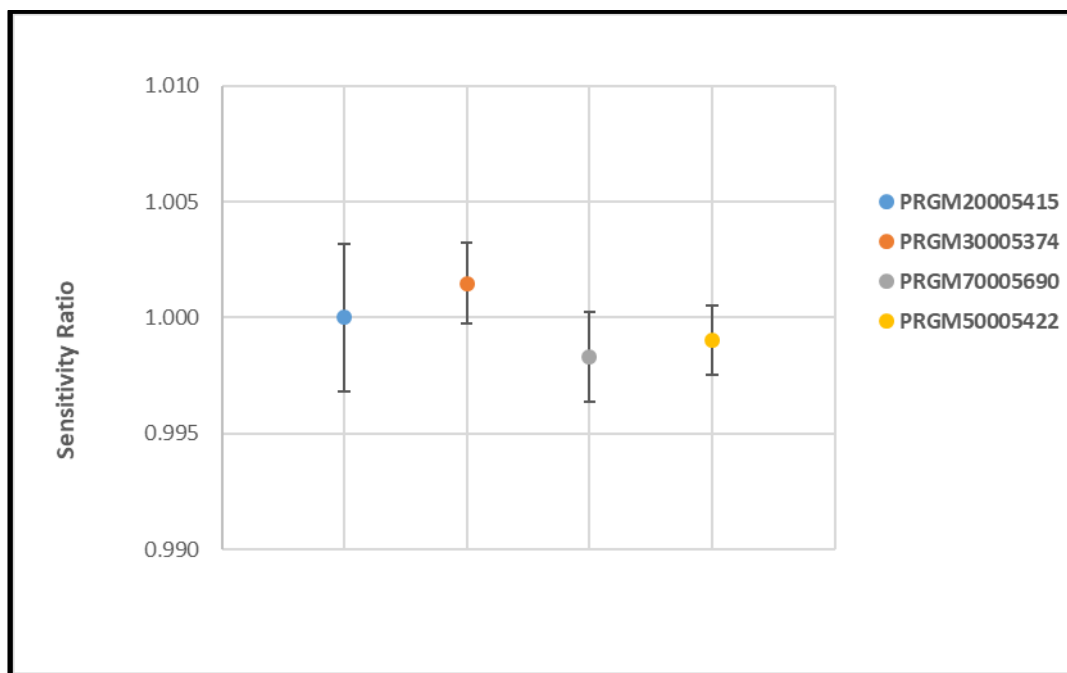


Figure 4-24: Graphical internal consistency of 10 µmol/mol toluene

The internal consistency results of ethylbenzene are shown in Table 4-43 and graphically in Figure 4-25. The verification results were consistent with the gravimetric values to within 0,14 %. The larger sensitivity ratio uncertainty contributed to the verification of the repeatability of the peak area.

Table 4-43: Internal consistency of 10 µmol/mol ethylbenzene

Ethylbenzene					
Certificate number	Sensitivity Ratio	Standard Uncertainty (%)	Expanded Uncertainty (%)	Expanded Uncertainty of sensitivity ratio	Difference (%)
PRGM20005415	1.000000	0.212328	0.424655	0.004247	
PRGM30005374	1.000193	0.057932	0.115864	0.001159	-0.02
PRGM70005690	0.999313	0.044619	0.089238	0.000892	0.07
PRGM50005422	1.001409	0.065684	0.131368	0.001316	-0.14

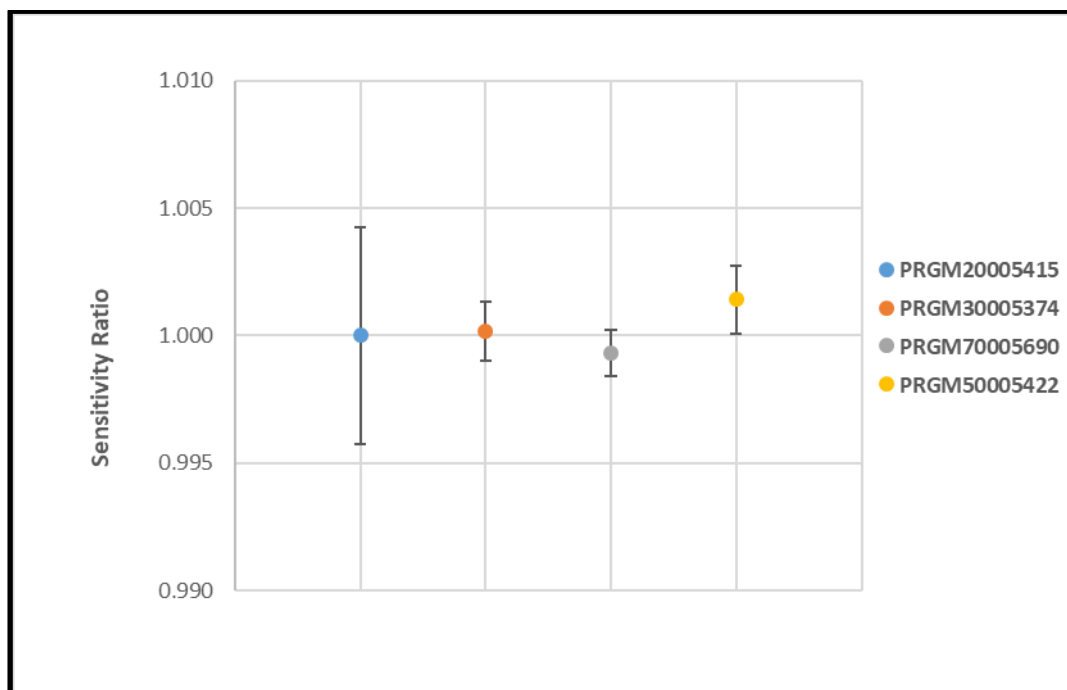


Figure 4-25: Graphical internal consistency of 10 µmol/mol ethylbenzene

The internal consistency of m,p-xylene is shown in Table 4-44 and graphically in Figure 4-26. The verification results were consistent with the gravimetric values to within 0,20 %.

Table 4-44: Internal consistency of 10 µmol/mol m,p-xylene

m,p-xylene					
Certificate number	Sensitivity Ratio	Standard Uncertainty (%)	Expanded Uncertainty (%)	Expanded Uncertainty of sensitivity ratio	Difference (%)
PRGM20005415	1.000000	0.178282	0.356565	0.003566	
PRGM30005374	1.001791	0.139343	0.278685	0.002792	-0.18
PRGM70005690	1.001815	0.116474	0.232949	0.002334	-0.18
PRGM50005422	0.999779	0.046489	0.092977	0.000930	0.02

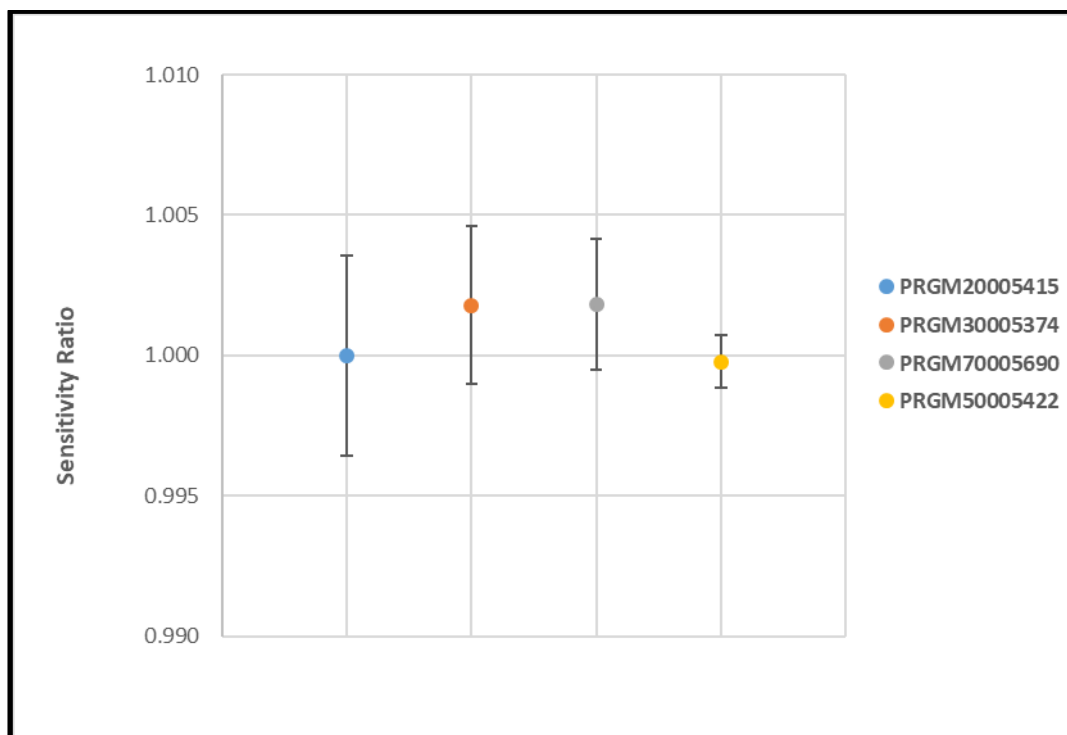


Figure 4-26: Graphical internal consistency of 10 µmol/mol m,p-xylene

The internal consistency of o-xylene is shown in Table 4-45 and graphically in Figure 4-27. The verification results were consistent with the gravimetric values to within 0,26 %.

Table 4-45: Internal consistency of 10 µmol/mol o-xylene

o-xylene					
Certificate number	Sensitivity Ratio	Standard Uncertainty (%)	Expanded Uncertainty (%)	Expanded Uncertainty of sensitivity ratio	Difference (%)
PRGM20005415	1.000000	0.232810	0.465619	0.004656	
PRGM30005374	0.997761	0.231882	0.463765	0.004627	0.22
PRGM70005690	0.997437	0.162546	0.325092	0.003243	0.26
PRGM50005422	1.001975	0.228751	0.457502	0.004584	-0.20

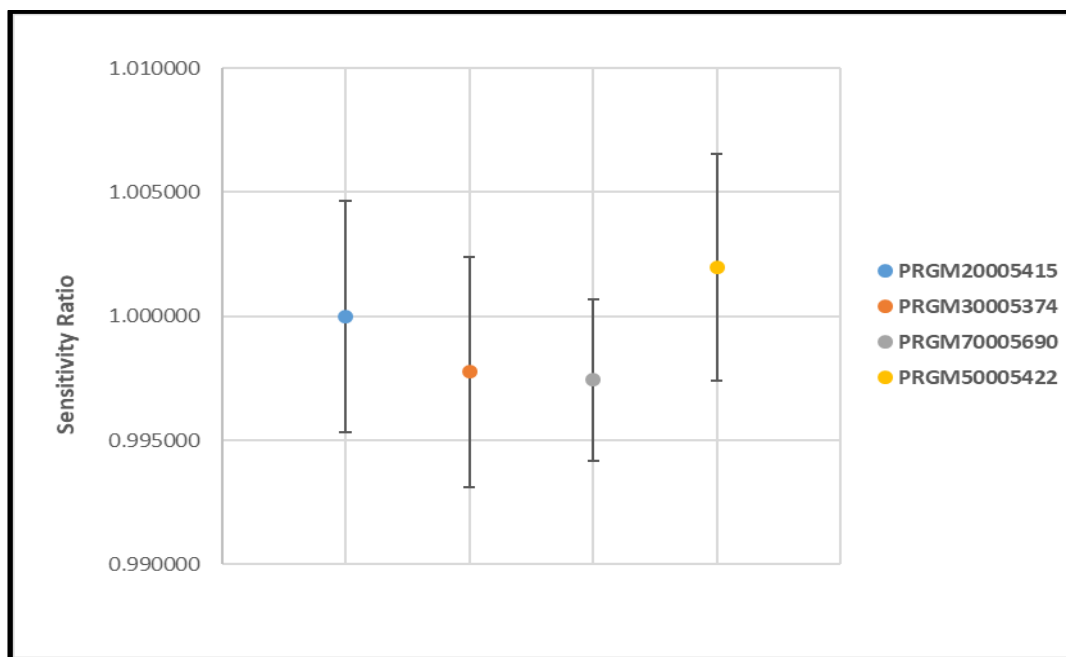


Figure 4-27: Graphical internal consistency of 10 µmol/mol o-xylene

4.4 Establishment of measurement equivalence

After the preparation and verification (analysis) of primary reference gas mixtures, the analysis method can further be validated by analysing reference gas mixtures using different techniques and personnel. This exercise was done to estimate the variation of the method when it is performed using similar parameters and different personnel within the same laboratory. A method validation principle based on the European Association of National Metrology (EURACHEM) document recommends parameters to be investigated to achieve results that are fit for purpose (Sengoku et al., 1999). In the case of reference standards preparation, the matrix of the material is well characterised based on purity analysis performed before preparation. For metrology institutes, this is particularly important to establish measurement capability for a defined parameter, in this case, it is the preparation and analysis of BTEX reference standards. The exercise is common and performed under the Mutual Recognition Agreement (MRA) as explained in Chapter 2. There were three international comparisons in which NMISA participated to establish the measurement capability for BTEX gas mixtures in nitrogen and the hazardous air pollutants gas mixtures. The names of the comparison were the following:

- The Air Pacific Metrology Programme (APMP.QM-S12) comparison of BTEX at nominal mole fraction of 100 nmol/mol (benzene, toluene, ethylbenzene, m-xylene and o-xylene)
- The Air Pacific Metrology Programme (APMP.QM-S14) comparison of HAPs at nominal mole fraction of 100 nmol/mol (benzene, toluene, ethylbenzene, o-xylene, m-xylene, styrene, 1,3-butadiene, tetrachloroethylene, trichloroethylene, methylchloroform, 1,1-dichloroethane, carbon tetrachloride, chloroform, dichloromethane)
- The Consultative Committee for Amount of Substance (CCQM-K10) comparison of BTEX at nominal mole fraction of 100 nmol/mol (benzene, toluene, ethylbenzene, m-xylene, p-xylene and o-xylene).

The results obtained from the international comparison studies are discussed in Sections 4.4.2 and 4.4.2.

4.4.1 Measurement equivalence of BTEX at 100 nmol/mol

4.4.1.1 The APMP.QM-12 (BTEX in nitrogen at 100 nmol/mol)

The components of interest were benzene, toluene, ethylbenzene, m-, o-xylene, and styrene. Although styrene was not included in the NMISA studies of BTEX, it was included in the Asian BTEX programme as an indoor air pollutant. The GC chromatogram of the reference cylinder (D155858) is shown in Figure 4-28, and that of a sample cylinder (APEX 121845) is in Figure 4-29. The separation was achieved using Agilent HP INNOWAX (60 m x 0,32 mm id x 0,5 µm df) column to separate the m- and p-xylenes. In Figures 4-28 and 4-29, the elution order of components with their respective retention times was included. The main difference between the two chromatograms is the size of p-xylene in cylinder APEX 121845, which is smaller than in cylinder D155858. The reason was that p-xylene was not included in the comparison protocol; it was observed in the chromatogram of APEX 121845 instead as an impurity of m-xylene and o-xylene.

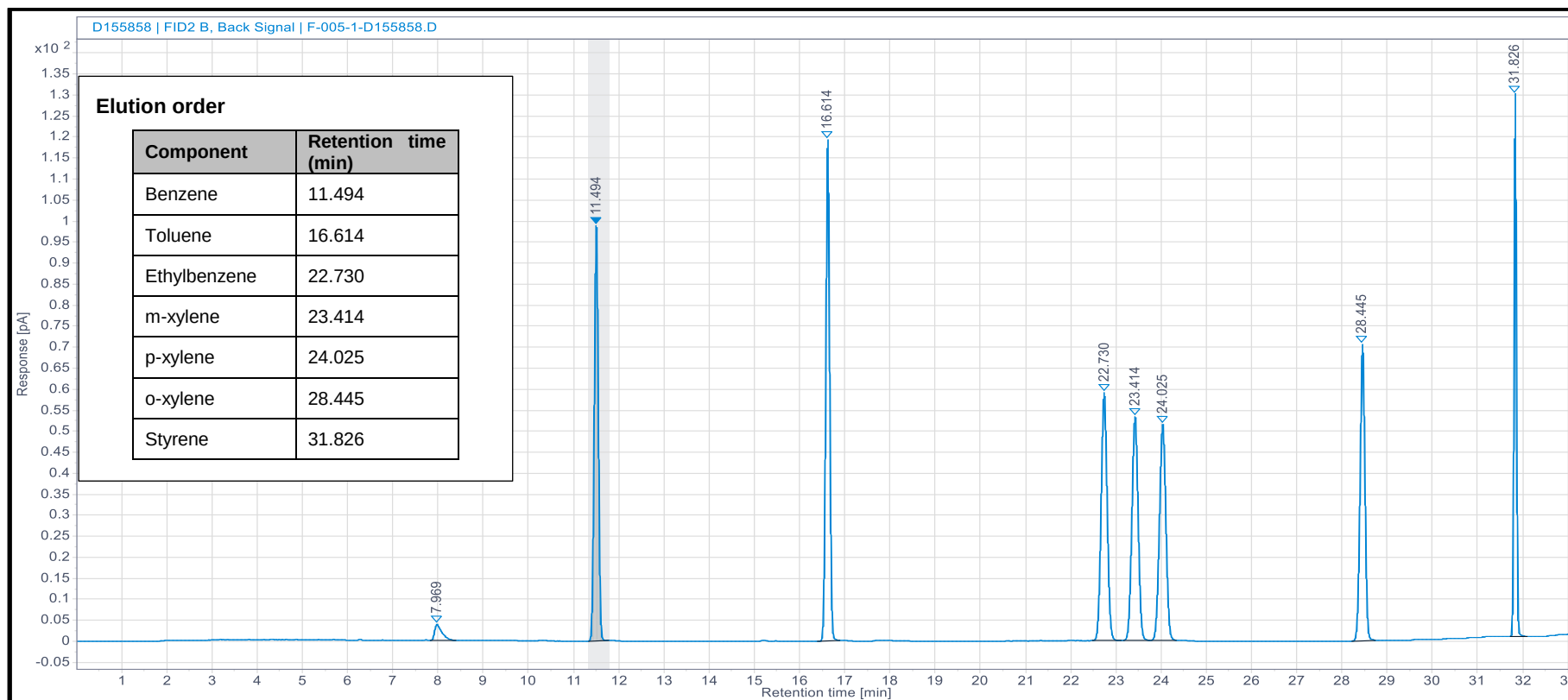


Figure 4-28: Chromatogram of reference cylinder D155858 at 100 nmol/mol BTEX for APMP comparison

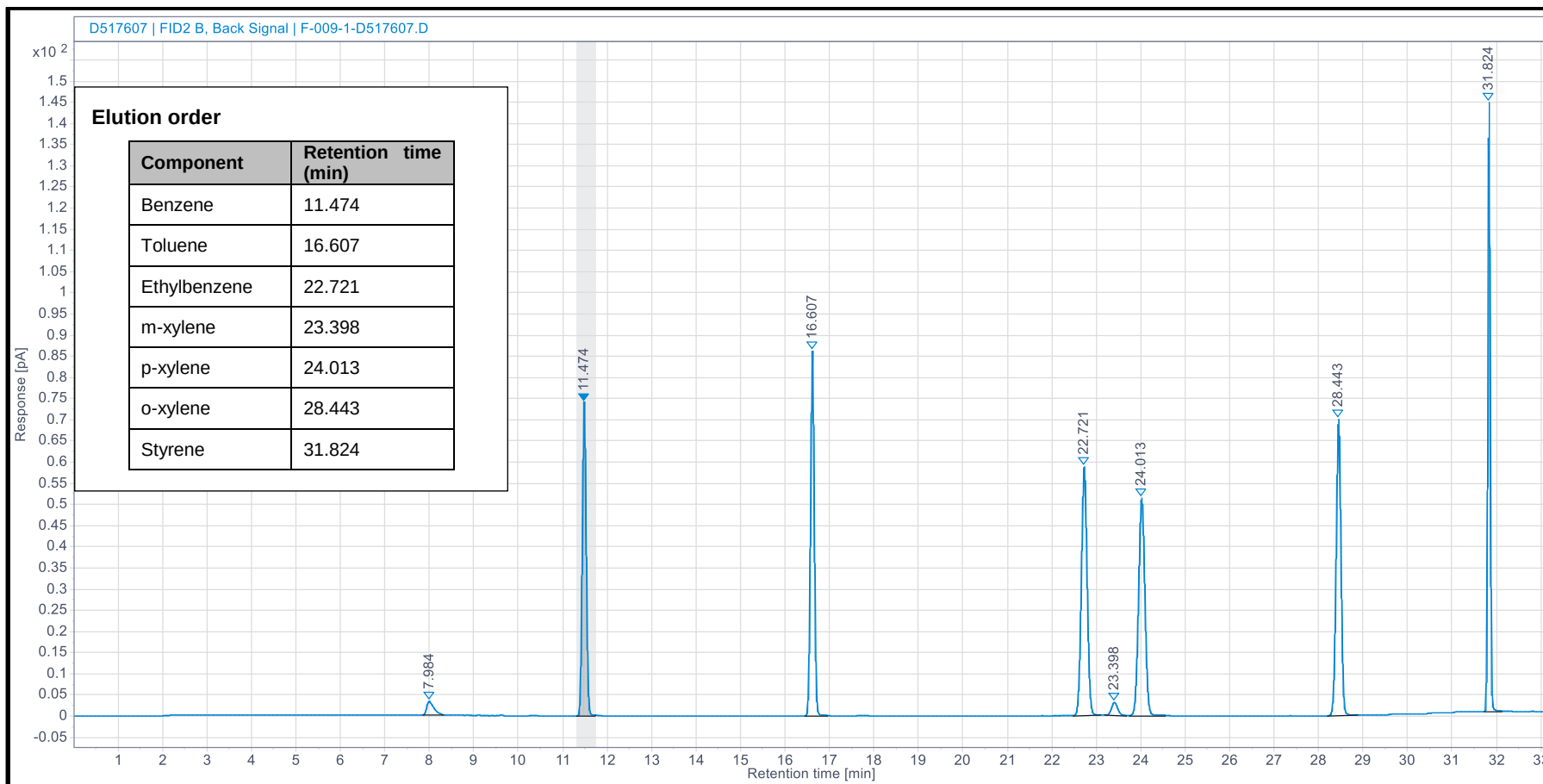


Figure 4-29: Chromatogram of sample cylinder APEX 121845 at 100 nmol/mol BTEX for APMP comparison

The gas chromatography analysis peak area results of D155858 are shown in Tables 4-44, 4-46 and 4-48 and those of APEX 121845 are shown in Tables 4-45 and 4-47 respectively. The results are average peak areas of three repeated injections obtained under repeatability conditions. Cylinder D155858 was used as the standard reference to analyse APMP cylinder APEX 121845. In addition, cylinder D155858 was one of the two reference standards procured from KRIS to validate the method of BTEX analysis. During the APMP comparison, NMISA had not reached the preparation of 100 nmol/mol.

The calibration approach used was a one-point calibration method using a similar mole fraction of 100 nmol/mol. The analysis sequence was reference (D155858a)- sample (APEX 121845a)- reference (D155858b)- sample (APEX 121845b)- reference (D155858c). The mole fraction of the APMP cylinder was calculated using equation 4.11. The average sensitivity and peak area in Tables 4-45 and 4-47 were calculated by combining the values of D155858 in Tables 4-44, 4-46, and 4-48. This method is used mostly when nominal mole fractions are similar, and the drift is calculated to measure the change in response of the flame ionisation to the same sample after some time. The highest drift obtained was 6% in the analysis of styrene due to the inconsistent peak area in Table 4-44. Typically the drift of 1% or less is achievable during a short analysis time. The analysis of BTEX at nano-mol was long due to the pre-concentration step with a duration of 18 to 25 minutes followed by column separation of between 25 to 35 minutes.

Table 4-46: Results of D155858a reference cylinder

	Benzene	Toluene	Ethyl-benzene	p-xylene	m-xylene	o-xylene	Styrene
Injection number	Peak areas						
1	654.4	713.2	602.1	567.9	559	512.9	389
2	653.4	714.5	598.7	571.5	568.9	518.6	496.2
3	635.3	711	588.5	559.6	557	567.1	487.4
Average	647.70	712.90	596.43	566.33	561.63	532.87	457.53
Standard deviation	10.75	1.77	7.08	6.10	6.37	29.78	59.51
%RSD	1.66	0.25	1.19	1.08	1.13	5.59	13.01
ESDM	6.21	1.02	4.09	3.52	3.68	17.20	34.36
Sensitivity	6.46	6.95	5.95	5.60	5.62	5.18	4.61
CRM Conc. (nmol/mol)	100.20	102.60	100.20	101.10	100.00	102.90	99.33
CRM std. uncertainty (nmol/mol)	2.51	2.57	2.51	2.53	2.50	2.57	2.48

Table 4-47: Results of APEX 121845a comparison cylinder

	Benzene	Toluene	Ethyl-benzene	p-xylene	m-xylene	o-xylene	Styrene
Injection number	Peak areas						
1	467	520	545.6	31.7	530.2	544.8	515.8
2	466.7	517.3	544.5	27	529.6	544.1	517.6
3	461.3	509	537.9	23.2	524.1	537.4	514.7
Average	465.00	515.43	542.67	27.30	527.97	542.10	516.03
Standard deviation	3.21	5.73	4.16	4.26	3.36	4.09	1.46
%RSD	0.69	1.11	0.77	15.60	0.64	0.75	0.28
ESDM	1.85	3.31	2.40	2.46	1.94	2.36	0.85
Sensitivity							
Average sensitivity	6.425	6.929	5.691	5.515	5.563	5.299	4.752
Average area	643.8	711.0	590.8	557.6	556.3	545.3	472.0
Conc. Calculated (nmol/mol)	72.38	74.38	95.36	4.95	94.91	102.30	108.59
Calculated std. uncertainty (nmol/mol)	3.87	4.49	4.57	0.68	4.89	4.51	5.28

Table 4-48: Results of D155858b reference cylinder

	Benzene	Toluene	Ethyl-benzene	p-xylene	m-xylene	o-xylene	Styrene
Injection number	Peak areas						
1	642.8	711.3	583.6	544.1	548.7	554.8	482.3
2	639.3	706	586.1	550.5	552	558.3	488.2
3	637.4	709.7	585.9	552.1	552	560	489
Average	639.83	709.00	585.20	548.90	550.90	557.70	486.50
Standard deviation	2.74	2.72	1.39	4.23	1.91	2.65	3.66
%RSD	0.43	0.38	0.24	0.77	0.35	0.48	0.75
ESDM	1.58	1.57	0.80	2.44	1.10	1.53	2.11
Sensitivity	6.39	6.91	5.84	5.43	5.51	5.42	4.90
CRM Conc.(nmol/mol)	100.20	102.60	100.20	101.10	100.00	102.90	99.33
CRM std. uncertainty (nmol/mol)	2.51	2.57	2.51	2.53	2.50	2.57	2.48
Drift	-1.21	-0.55	-1.88	-3.08	-1.91	4.66	6.33

Table 4-49: Results of APEX 121845b comparison cylinder

	Benzene	Toluene	Ethyl-benzene	p-xylene	m-xylene	o-xylene	Styrene
Injection number	Peak areas						
1	465.5	521.6	553.4	30.9	539.1	554.9	532.6
2	467.3	520.6	553.7	26.7	539.2	555	533.8
3	463.8	512	548.2	22	533.2	549.8	531.7
Average	465.53	518.07	551.77	26.53	537.17	553.23	532.70
Standard deviation	1.75	5.28	3.09	4.45	3.44	2.97	1.05
%RSD	0.38	1.02	0.56	16.78	0.64	0.54	0.20
ESDM	1.01	3.05	1.79	2.57	1.98	1.72	0.61
Sensitivity							
Average sensitivity	6.365	6.917	5.702	5.541	5.581	5.581	5.238
Average area	637.7	709.7	590.8	555.7	558.1	565.9	492.8
Conc. Calculated (nmol/mol)	73.14	74.90	96.77	4.79	96.26	99.14	101.69
Calculated std. uncertainty (nmol/mol)	3.92	3.98	4.37	0.69	4.61	5.59	4.38
Drift	0.11	0.51	1.68	-2.81	1.74	2.05	3.23

Table 4-50: Results of D155858c reference cylinder

	Benzene	Toluene	Ethyl-benzene	p-xylene	m-xylene	o-xylene	Styrene
Injection number	Peak areas						
1	636.1	707.7	589.5	551.7	556.7	563.6	493.9
2	634.1	709.1	598.1	565.9	569	576.9	495.2
3	636.7	714.2	601.6	569.7	569.9	581.7	508.4
Average	635.63	710.33	596.40	562.43	565.20	574.07	499.17
Standard deviation	1.36	3.42	6.23	9.49	7.37	9.38	8.02
%RSD	0.21	0.48	1.04	1.69	1.30	1.63	1.61
ESDM	0.79	1.98	3.59	5.48	4.26	5.41	4.63
Sensitivity	6.34	6.92	5.95	5.56	5.65	5.58	5.03
CRM concentration (nmol/mol)	100.20	102.60	100.20	101.10	100.00	102.90	99.33
CRM std. uncertainty (nmol/mol)	2.51	2.57	2.51	2.53	2.50	2.57	2.48
Drift	-0.66	0.19	1.91	2.47	2.60	2.93	2.60

The comparison results are shown in Table 4-49, in which column three is reported results from Tables 4-45 and 4-47, with their associated measurement uncertainties in column four. The reference values were analysed by the coordinating laboratory (KRISS) in column five and the associated uncertainty in column 6. The degree of equivalence is shown in column seven, which is the difference between the reported value by the participating laboratory and the value of the coordinating laboratory. According to the results, it was observed that the largest deviation was obtained for benzene (-35%) and toluene (-32%), followed by ethylbenzene and o-xylene at 12% each. M-xylene and styrene were consistent with the comparison reference value; the reported values were within the uncertainty of the reference value. The investigation into the deviating results was attributed to the poor recovery of the pre-concentrator system. A large variation of FID response to cylinder D155858 used when analysed on different days. There could have been a leak in the system (flow line of cylinder APEX 121845) before the sample entering the preconcentration unit, where the more volatile components would be lost more significantly compared to the less volatile components. This effect was seen only in that comparison gas mixture but not for other gas mixtures. This could have been the case since the largest deviation was seen on benzene, followed by toluene.

Table 4-51: APMP.QM-S12 comparison results

Cylinder Number	Component	Reported value (nmol/mol)	Reported uncertainty (nmol/mol)	APMP reference value (nmol/mol)	APMP uncertainty (nmol/mol)	Degree of equivalence (nmol/mol)	Degree of equivalence uncertainty (k=1)
APEX 121845	Benzene	72.48	4.33	106.88	2.39	-34.40	9.89
	Toluene	74.48	4.86	106.14	2.47	-31.66	10.91
	Ethyl benzene	94.43	4.91	105.59	2.28	-11.16	10.83
	m-xylene	102.03	5.15	104.21	2.79	-2.18	11.73
	o-xylene	95.05	4.92	107.07	2.76	-12.02	11.30
	Styrene	107.43	5.74	106.39	2.39	1.04	12.44

4.4.1.2 The APMP.QM-14 (HAPs in nitrogen at 100 nmol/mol)

NMISA also participated in the APMP.QM-S14 for analysing hazardous air pollutants (HAPs) gas mixture containing benzene, toluene, ethylbenzene, m-xylene, styrene, o-xylene, chloroform, 1,1,2-trichloroethane, trichloroethylene, tetrachloroethylene, 1,1-dichloroethane, carbon tetrachloride, 1,3-butadiene and dichloromethane in nitrogen at a nominal mole fraction of 100 nmol/mol. The components of interest were benzene, toluene, ethylbenzene, m-xylene and o-xylene, which are discussed, the other components were not included in the discussion.

The results of the comparison are shown in Table 4-50 in which column three contains the reported results, with their associated measurement uncertainties presented in column four. The reference values were analysed by the coordinating laboratory (KRISS) in column five and the associated uncertainty in column 6. The degree of equivalence is shown in column seven, which is the difference between the reported value by the participating laboratory and the value of the coordinating laboratory. According to the result, it was observed that the largest deviation was obtained for benzene (13%) and m-xylene (12%), followed by o-xylene (-11%), ethylbenzene (7%) and toluene (2%). Toluene was the only component that was consistent with the comparison reference value. The results showed improvement from the previous results of APMP.QM-S12 for the components mentioned above. The gas mixture used as a reference standard was prepared by NMISA, diluting BTEX and HAPs gas mixtures to 100 nmol/mol. The improvement can be attributed to the improved preparation procedure of the components using a syringe method, where the losses of components during weighing and transferring into the cylinder could be accounted for. The analysis was also performed using the NUTECH 8900 pre-concentrator with better recoveries than the ENTECH 7200 model. The rest of the data for the other components is included in the APMP.QM-S14 report (Lee et al., 2021). The comparison involved three participating laboratories, including the coordinating laboratory that prepared, analysed, and distributed the comparison cylinders.

Table 4-52: APMP.QM-S14 HAPs in nitrogen comparison results at 100 nmol/mol

Cylinder Number	Component	Reported value (nmol/mol)	Reported uncertainty (nmol/mol)	APMP.QM-S14 reference value (nmol/mol)	APMP.QM-S14 uncertainty (nmol/mol)	Degree of equivalence (nmol/mol)	Degree of equivalence uncertainty (k=2)
APMP 1218321	Benzene	118.6	3.50	105.42	0.44	13.18	7.00
	Toluene	108.3	3.40	105.96	0.44	2.34	6.90
	Ethyl benzene	112.6	3.00	105.16	0.47	7.44	6.00
	m-xylene	116.4	2.80	104.31	0.47	12.09	5.60
	o-xylene	93.8	2.50	104.81	0.19	-11.01	5.10

4.4.2 Measurement equivalence of BTEX at 5 nmol/mol

NMISA participated in the CCQM-K10 (2018) preparative BTEX comparison at 5 nmol/mol mole fraction. The aim was to compare the gas mixtures prepared by the gravimetric method at different NMI's and compare them by the analysis against calibration standards at NIST. This comparison was thus aimed at establishing the preparation comparability of NMI's for gas components containing BTEX in nitrogen to support the WMO-GAW project. The components of BTEX are part of the selected VOCs being monitored by the WMO-GAW program, as mentioned in Chapter 1. The comparison was a repeat of CCQM-K10 conducted from 2001 to 2002. It is worth mentioning that in the preparative comparison, the gas mixtures are prepared and analysed similarly with the analysis comparison; however, the values reported are gravimetric. The results of the comparison (Final report) (Cecelski et al., 2022) are presented in Table 4-51 and graphically in Figure 4-30. NMISA-reported values are shown in column three, with their respective uncertainty in column four. Comparison values were obtained using NIST gas standards according to their ratio method. The calculated ratios of control gas mixture and the participant gas mixture were used to predict the participant values using the gravimetric values of the control gas mixtures.

The results presented in Table 4-51 showed a negative deviation of 0.297 nmol/mol from the preparation value for benzene. The other components showed a positive deviation of 0,302 nmol/mol for toluene, 0,362 nmol/mol for ethylbenzene, 0,952 nmol/mol for m-xylene, 0,584 nmol/mol for p-xylene and 0,690 nmol/mol for o-xylene. The blue error bars in Figure 4-30 represent the expanded uncertainty of the degree of equivalence, showing that NMISA values are inconsistent with the reported values. The green line represents the Key Comparison Reference Value (KCRV), based on the decision to use the ratio prediction approach. The deviation is consistent with the effect of vaporisation explained previously, where the loss of benzene is prevalent due to its high volatility compared to the other components. The results also indicate that there has been an improvement in the preparation of BTEX gas mixtures based on the comparison data of APMP.QM-S12, APMP.QM-S14 and CCQM-K10. The deviations of CCQM-K10 were considerably smaller than the two APMP comparisons.

Table 4-53: Results of CCQM-K10 in the final report

Cylinder Number	Component	Reported value (nmol/mol)	Reported uncertainty (nmol/mol)	CCQM-K10 reference value (nmol/mol)	CCQM-K10 uncertainty (nmol/mol)	Degree of equivalence (nmol/mol)	Degree of equivalence uncertainty (k=2)
D62 6613	Benzene	5.017	0.23	4.720	0.06	-0.297	0.233
	Toluene	5.019	0.22	5.321	0.06	0.302	0.224
	Ethyl benzene	5.021	0.21	5.383	0.05	0.362	0.206
	m-xylene	5.033	0.25	5.985	0.05	0.952	0.222
	p-xylene	5.021	0.31	5.605	0.06	0.584	0.219
	o-xylene	5.023	0.23	5.713	0.05	0.690	0.217

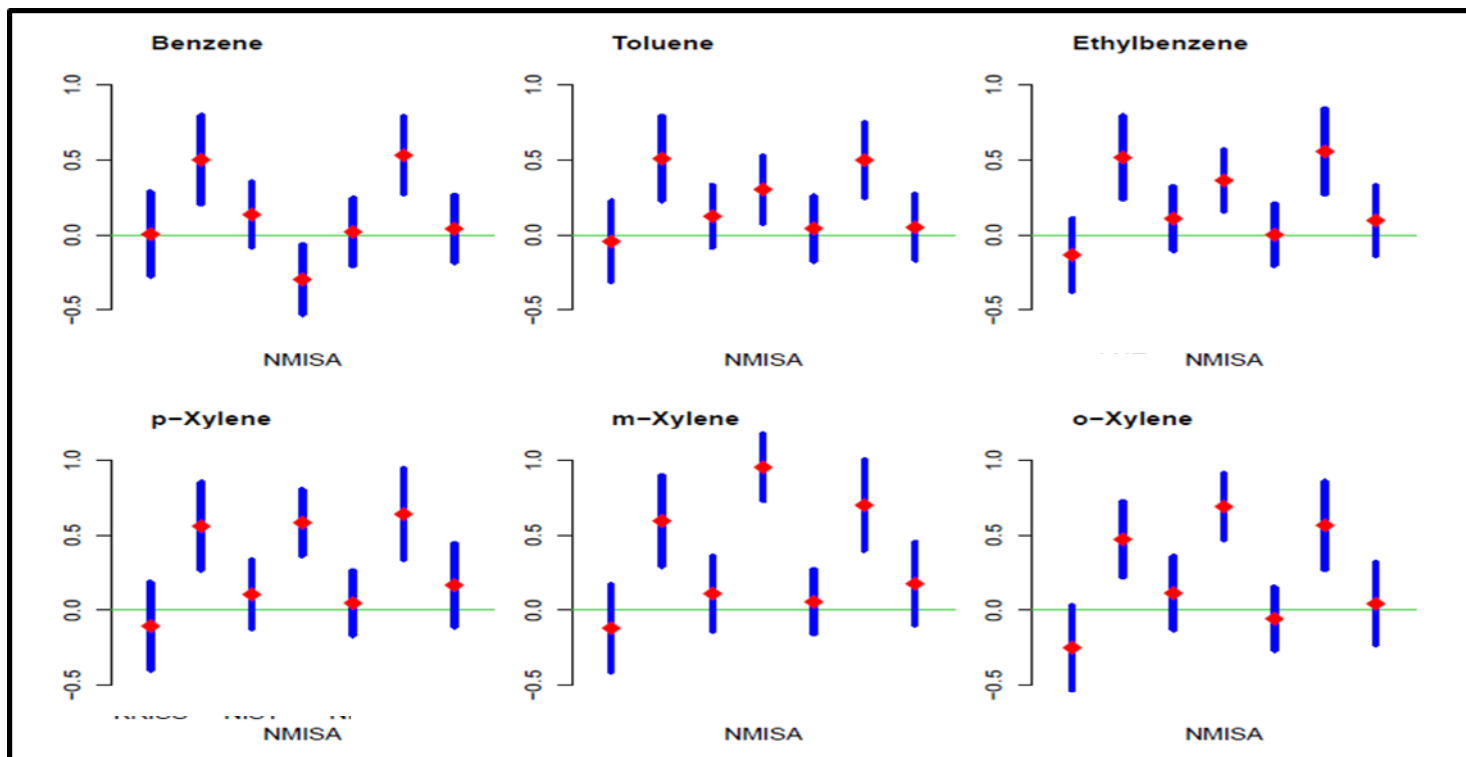


Figure 4-30: Graphical representation of BTEX results (Copied from official final report CCQM-K10)

4.4.3 Stability results

The stability of a gas mixture is the measurement of the drift rate from the date of preparation until it is used up, measured at set time intervals. The stability depends on the behaviour of the gas components due to the following factors:

- The reaction of components with the internal walls of the cylinder (adsorption)
- The possible reaction of components with each other.

The stability is assessed by analysing the gas mixture against a newly prepared mixture containing the same components at similar nominal mole fractions. The preparation of new gas mixtures can be done by following a similar preparation method, followed by verification immediately after the preparation (typically within 2 days). The newly prepared gas mixture is then used to determine the stability of the gas mixture with the stated shelf life.

The BTEX mixtures' stability was assessed using a 30 µmol/mol cylinder (PRGM1000395452) against a newly prepared cylinder (PRGM50005468). The method used to prepare PRGM50005468 was similar to that of PRGM1000395452, prepared in 2016. The cylinder under investigation was prepared on 23 June 2016 followed by analysis on 8 July 2016, the results were discussed in the in Section 4.3.2. The stability results are presented in Table 4-52 and graphically in Figure 4-31. The stability results showed a loss of -0,130 µmol/mol for benzene and -0,151 µmol/mol for toluene over 24 months. The outlier in the stability of p-xylene since the initial verification showed a -4 % difference from the gravimetric value, with the subsequent value 24 months later being close to the gravimetric value. The lower value obtained for the initial verification could have been due to the loss of p-xylene due to adsorption on the regulator or transfer line connecting the gas mixture to the sampler valve. However, this effect was not thoroughly investigated. No other data was obtained to explain the deviation for results of p-xylene.

Table 4-54: Twenty-four-month stability results for 30 µmol/mol of BTX

Cylinder number	Component	Mole Fraction (µmol/mol)	Verification analytical value (µmol/mol) 8 July 2016	Stability analytical value (µmol/mol) 19 July 2018	% RSD	Difference (µmol/mol)	Preparation date	Combined Expanded uncertainty (U) (k=2)
PRGM1000395452	Benzene	30.021	30.265	30.135	0.92%	-0.130	23/06/2016	0.34
	Toluene	31.545	31.526	31.375	0.87%	-0.151	23/06/2016	0.28
	p-xylene	28.265	26.944	28.158	0.72%	1.214	23/06/2016	0.23

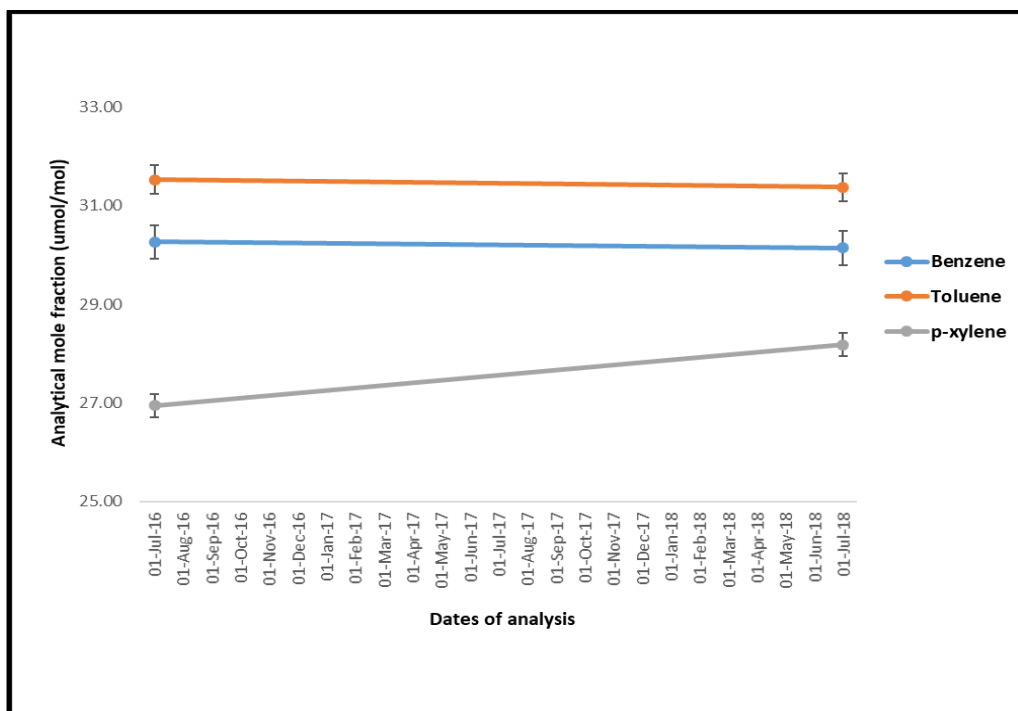


Figure 4-31: Stability results (over 24 months) of 30 $\mu\text{mol/mol}$ of BTX

5. Conclusion and recommendations

Three methods of gravimetric preparation of BTEX reference gas mixtures were compared. NIST uses the micro-gravimetric method for the preparation of BTEX gas standards from low $\mu\text{mol/mol}$ to nmol/mol levels (Rhoderick et al., 2010). The method used glass capillary tubes of different sizes to add required aliquots of BTEX components into the pre-evacuated cylinder in sequence via vacuum followed by a small flush of nitrogen gas. The method is challenging to repeat, and the attainment of components at similar nominal mole fractions in the mixture is difficult because of the fact that the capillary tubes do not have markings to measure the volume of components added. The preparation on other mole fractions, for example $10 \mu\text{mol/mol}$, was not done because there was no availability of reference standards to verify concentrations at NIST. There was another challenge of preparing the BTEX standards using the micro-gravimetric method at NMISA, in that the gas laboratory did not allow the installation of a burner due to safety concerns regarding the storage of flammable gases. The main advantage of the method is that a gas mixture at 250 nmol/mol can be prepared without dilution; however, the process is long and requires extreme care in the various stages of the preparation. In the experiment performed at NIST in 2015, the verification in some components showed the largest deviation.

The second method used stainless steel loops (transfer vessels). The method was patented at NPL in 2010 based on the technique's advantage in reducing the dead volume between the cylinder valve and the loops (Grenfell et al., 2010). This method can prepare mole fractions of $500 \mu\text{mol/mol}$ down to $1 \mu\text{mol/mol}$. This was demonstrated by the preparation of $10 \mu\text{mol/mol}$ in 2015 and $30 \mu\text{mol/mol}$ in 2016 and 2018, respectively. The method is simple to use; however, care should be taken regarding the operation of the valves to avoid loss of components to the atmosphere or vacuum. The other challenge is working with mixed liquid components with similar vapour pressure to avoid unaccounted losses during the preparation. This method can be used for the addition of single components or a mix of components.

The KRISS method employs the addition of liquid components into the cylinder using a syringe connected to a special connector with a heated line to vaporise heavier components and is followed by the flushing of components into a cylinder by a small

amount of nitrogen gas. This method was demonstrated by preparing 10 $\mu\text{mol/mol}$ gas mixtures. Components may also be added as a mix or as a single component. The analysis data obtained demonstrated that the most highly volatile component (namely benzene) showed larger variation compared to other components.

The capability demonstrated in this study was the analysis of the prepared components at similar mole fractions following a one-point calibration using a sequence of reference>sample>reference to account for detector drift caused by changing environmental conditions. Often the changes are due to room pressure, where the number of gas molecules in a specified volume changes, leading to poor repeatability. The effect is minimised by the employment of mass flow controllers upstream before the sampling loop in the injection valve of the gas chromatograph. The analysis of the components was achieved using the separation by gas chromatography, and it was found that a wax column is best used to separate the meta and para xylene isomers which co-elute when using other columns such as DB1 and DB 624.

To achieve the measurement equivalence, NMISA participated in international key comparisons, namely APMP.QM-S12 and APMP.QM-S14, at 100 nmol/mol nominal mole fraction. In the APMP.QM-S12 comparison, the analysis was conducted using a BTEX reference gas mixture from KRISS, however, there was a large deviation of NMISA results from the reference value. This was attributed to poor recovery of the ENTECH 7200 pre-concentrator and larger deviation was observed for benzene and toluene. On the other hand, there was an improvement during the participation of APMP.QM-S14 was attributed to the use of reference standards prepared by NMISA. NMISA also participated in the CCQM-K10 comparison at 5 nmol/mol in which the participating laboratories prepared the gas mixtures and sent them to NIST for analysis. NMISA obtained much improved values considering the comparison was below 10 nmol/mol. In the CCQM-K10 comparison, NMISA prepared a combination of 10 and 2 $\mu\text{mol/mol}$ BTEX gas standards and verified these concentrations using GC-FID. After the analysis and comparisons, the cylinders for which good data was obtained were selected to prepare 5 nmol/mol BTEX reference gas standards in a series of two dilutions (100 and 200 nmol/mol) as intermediate mole fractions.

NMISA has successfully developed the traceable primary reference gas material containing BTEX in nitrogen. The capability was demonstrated by comparing the gravimetrically prepared BTEX gas mixture to those around the world through participation in international comparison. The availability of these BTEX reference gas mixtures allows for their use in the calibration of equipment to support air pollution monitoring activities in South Africa.

5.1 Recommendations and future work

The preparation of BTEX gas mixtures showed a typical negative deviation for benzene from the calculated gravimetric value, evident from some 10 nmol/mol gas mixtures and in the CCQM-K10 comparison. This effect should be investigated to account for the significant losses of benzene due to its volatility compared to the other components, even though it is added last in the preparation steps. It is recommended that a study be conducted with benzene prepared as a single component using any of the methods tested in this study, followed by verification. The benzene standard should be diluted to lower mole fraction from a binary gas mixture.

The analysis of BTEX gas mixtures at 100 nmol/mol using the ENTECH 7200 pre-concentrator showed large variations in trapping efficiency. Therefore, parameters should be investigated to obtain reproducible results with satisfactory accuracy. Although the stability results indicated little degradation of BTEX, the adsorption studies immediately after the preparation should be investigated to account for losses of material due to weighing errors or physical adsorption into cylinder walls of valves.

The stability monitoring could be done at shorter intervals to demonstrate the period of significant losses (if any). The specific challenge in the stability analysis was that there were many projects which required cylinder sharing, therefore, unfortunately, some of the old gas mixtures were blown off.

6. References

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Appendices

A.1 Certificate of analysis of BTEX

SIGMA-ALDRICH®

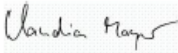
Riedstrasse 2, D-89555 Steinheim/Germany
Tel: +49 73 2997 2550 Fax: +49 73 2997 2557

Certificate of Analysis

Product Name: BENZENE
Product Number: 270709
Product Brand: Sigma-Aldrich
Molecular Formula: C₆H₆
Molecular Mass: 78.11
CAS Number: 71-43-2

TEST	SPECIFICATION	LOT STBB0083 RESULTS
APPEARANCE (COLOR)	COLORLESS	COLORLESS
APPEARANCE (FORM)	LIQUID	LIQUID
COLOR (IN APHA)	≤ 20 APHA	5 APHA
PURITY (GC AREA %)	≥ 99.90 %	99.95 %
WATER (COULOMETR.)	≤ 0.020 %	0.020 %
RESIDUE (EVAPORATION)	≤ 0.0005 %	< 0.0005 %
INFRARED SPECTRUM	CONFORMS TO STRUCTURE	CONFORMS
UV-ABSORBANCE	400 NM ≤ 0.01	0.001
UV-ABSORBANCE	350 NM ≤ 0.01	0.002
UV-ABSORBANCE	330 NM ≤ 0.02	0.019
UV-ABSORBANCE	300 NM ≤ 0.06	0.027
UV-ABSORBANCE	290 NM ≤ 0.15	0.071
UV-ABSORBANCE	280 NM ≤ 1.0	0.363

QC RELEASE DATE 22/SEP/09



Claudia Mayer, Manager
Quality Control
Steinheim, Germany

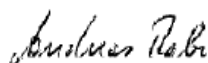
Sigma-Aldrich warrants, that its products conform to the information contained in this and other Sigma-Aldrich publications. Purchaser must determine the suitability of the product for its particular use. See reverse side of invoice for additional terms and conditions of sale. The values given on the 'Certificate of Analysis' are the results determined at the time of analysis.

Figure 0-1: Benzene certificate of analysis (Sigma Aldrich)

Certificate of Analysis

SIGMA-ALDRICH

Product Name	Toluene, CHROMASOLV [®] , for HPLC, 99.9%
Product Number	34888
Product Brand	SIAL
CAS Number	108-88-3
Molecular Formula	C ₆ H ₅ CH ₃
Molecular Weight	92.14
TEST	
assay (GC)	99.9 %
non-volatile matter	< 0.0005 %
water (Karl Fischer)	0.003 %
free acid (as HCl)	< 0.001 %
thiophene	< 0.0005 %
transmittance at 290 nm	> 50 %
transmittance at 310 nm	> 90 %
transmittance from 350 nm	> 99 %
	product replaces Fluka 89683 and Aldrich 270377
Production Date	04.Apr.10
Expiry Date	09.Mar.15



Dr. Andreas Rabe
Quality Management
Seelze / Germany

Figure 0-2: Toluene certificate of analysis (Sigma Aldrich)

Certificate of Analysis

SIGMA-ALDRICH

Product Name Ethylbenzene,
anhydrous, 99.8%
Product Number 298848
Product Brand SIAL
CAS Number 100-41-4
Molecular Formula C_8H_{10}
Molecular Weight 106.17

TEST

Appearance (Form)
Infrared spectrum
Purity (GC)
Water (by Karl Fischer)
Residue on Evaporation
Specification Date:
Date of QC Release:
Print Date:

SPECIFICATION

Liquid
Conforms to Structure
 $\geq 99.75\%$
 $\leq 0.002\%$
 $\leq 0.0005\%$

LOT 00496PK RESULTS

Liquid
Conforms
 99.90%
 $< 0.001\%$
 0.0002%
JUN 2010
NOV 2009
JUN 10 2010



Jeff Becker, Senior Chemist
Quality Control
Sheboygan Falls, Wisconsin, USA

Figure 0-3: Ethylbenzene certificate of analysis (Sigma Aldrich)

Certificate of Analysis

Product Name: O-XYLENE
puriss. p.a.
Product Number: 95662
Product Brand: Sigma-Aldrich
Molecular Formula: C_8H_{10}
Molecular Mass: 106.17
CAS Number: 95-47-6

TEST	SPECIFICATION	LOT 1421425 RESULTS
APPEARANCE (COLOR)	COLORLESS	COLORLESS
APPEARANCE (FORM)	CLEAR LIQUID	CLEAR LIQUID
PURITY (GC AREA %)	≥ 99.0 %	99.1 %
REMARKS ON GC	TOLUENE ≤ 0.4 %, M- AND P-XYLENE ≤ 0.6 %	0.813 % P-XYLENE, 0.012 % M-XYLENE, 0.005 % ETHYLBENZENE, NO TOLUENE DETECTED
REFRACTIVE INDEX N20/D	1.504 - 1.508	1.508
RESIDUE (EVAPORATION)	≤ 0.002 %	< 0.0001%
INFRARED SPECTRUM	CONFORMS TO STRUCTURE	CONFORMS
METAL TRACE ANALYSIS (ICP)	CORRESPONDS TO REQUIREMENTS	PASSED
ALUMINIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
BARIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
BISMUTH (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
CALCIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
CADMIUM (ICP)	≤ 0.05 MG/KG	< 0.05 MG/KG
COBALT (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
CHROMIUM (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
COPPER (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
IRON (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
POTASSIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
LITHIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
MAGNESIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
MANGANESE (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
MOLYBDENUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
SODIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG

Figure 0-4: O-xylene certificate of analysis (Sigma Aldrich)

Certificate of Analysis

Product Name: *M*-XYLENE
 puriss. p.a., ≥ 99.0 % (GC)
 Product Number: 95672
 Product Brand: Sigma-Aldrich
 Molecular Formula: C₈H₁₀
 Molecular Mass: 106.17
 CAS Number: 108-38-3

TEST	SPECIFICATION	LOT BCBC1553 RESULTS
APPEARANCE (COLOR)	COLORLESS	COLORLESS
APPEARANCE (FORM)	CLEAR LIQUID	CLEAR LIQUID
PURITY (GC AREA %)	≥ 99.0 %	99.7 %
REMARKS ON GC	O- AND P-XYLENE ≤ 0.5 %, TOLUENE ≤ 0.5 %	0.123 % O-XYLENE, 0.118 % P-XYLENE
REFRACTIVE INDEX N _{20/D}	1.496 - 1.498	1.497
RESIDUE (EVAPORATION)	≤ 0.002 %	< 0.0001 %
INFRARED SPECTRUM	CONFORMS TO STRUCTURE	CONFORMS
METAL TRACE ANALYSIS (ICP)	CORRESPONDS TO REQUIREMENTS	PASSED
ALUMINIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
BARIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
BISMUTH (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
CALCIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
CADMIUM (ICP)	≤ 0.05 MG/KG	< 0.05 MG/KG
COBALT (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
CHROMIUM (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
COPPER (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
IRON (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
POTASSIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
LITHIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
MAGNESIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
MANGANESE (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
MOLYBDENUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
SODIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
NICKEL (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG

Figure 0-5: M-xylene certificate of analysis (Sigma Aldrich)

Certificate of Analysis

Product Name: *P*-XYLENE
 puriss. p.a.
 Product Number: 95682
 Product Brand: Sigma-Aldrich
 Molecular Formula: C₈H₁₀
 Molecular Mass: 106.17
 CAS Number: 106-42-3

TEST	SPECIFICATION	LOT 1432941 RESULTS
APPEARANCE (COLOR)	COLORLESS	COLORLESS
APPEARANCE (FORM)	CLEAR LIQUID	CLEAR LIQUID
PURITY (GC AREA %)	≥ 99.0 %	99.7 %
REMARKS ON GC	O- AND M-XYLENE ≤ 0.5 %, TOLUENE ≤ 0.5 %	0.041% O-XYLENE, 0.132% M-XYLENE, 0.007% TOLUENE, 0.072% ETHYLBENZENE
REFRACTIVE INDEX N _{20/D}	1.494 - 1.496	1.496
RESIDUE (EVAPORATION)	≤ 0.002 %	0.0019 %
INFRARED SPECTRUM	CONFORMS TO STRUCTURE	CONFORMS
METAL TRACE ANALYSIS (ICP)	CORRESPONDS TO REQUIREMENTS	PASSED
ALUMINIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
BARIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
BISMUTH (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
CALCIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
CADMIUM (ICP)	≤ 0.05 MG/KG	< 0.05 MG/KG
COBALT (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
CHROMIUM (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
COPPER (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
IRON (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
POTASSIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG
LITHIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
MAGNESIUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
MANGANESE (ICP)	≤ 0.02 MG/KG	< 0.02 MG/KG
MOLYBDENUM (ICP)	≤ 0.1 MG/KG	< 0.1 MG/KG
SODIUM (ICP)	≤ 0.5 MG/KG	< 0.5 MG/KG

Figure 0-6: P-xylene certificate of analysis (Sigma Aldrich)

A.2 Certificate of 100 nmol/mol of BTEX used in APMP.QM-S12

Certificate No.: 1307-00919-002

Page 1 of 2 Pages

CERTIFICATE OF REFERENCE MATERIAL

Indoor air pollutants in N₂, 10 L, 9.5 MPa

Reference Material Code: 110-06-002

Serial No.: D15 5858

Description of Certification

- Intended Use: Calibration
- Instructions and Notices: Not Applicable
- Information for Hazardous Situation: Please check related MSDS prior to its use as the CRM is a highly compressed gas.
- Homogeneity: The CRM is mixed homogeneously.
- Methods of Certification: The CRM was prepared and certified according to "Preparation and Certification Procedure of Primary Reference Gas Mixtures by Gravimetric Method.(R-112-001-2012)
- Certified Values and Uncertainty : Please refer to the next page for certified values uncertainty in CRM
- Traceability: Gravimetry
- Uncertified Values and Further Information: Not Applicable

Manufacturer: KRISS, 267 Gajeong-no, Yuseong-gu, Daejeon 305-340 Republic of Korea

(Applicant): Gas Metrology Laboratory, National Metrology Institute of South Africa (NMISA)

Date of Certification: 28 February, 2014

Valid until: 27 February, 2015

We certify that the above CRM is traceable to the national measurement standards of the KRISS in accordance with the provision of Article 13 of the Framework Act on the National Standards.

This certificate is consistent with the calibration and measurement capabilities (CMCs) that are included in Appendix C of the Mutual Recognition Arrangement (MRA) drawn up by the International Committee for Weights and Measures (CIPM). Under the MRA, all participating institutes recognize the validity of each other's calibration and measurement certificates for the quantities, ranges and measurement uncertainties specified in Appendix C ([for details see http://www.bipm.org](http://www.bipm.org)).

Date of issue: 28 February, 2014

For the President of KRISS

Certified by :

Byungmoon Kim

+82-42-868-5359

bmkim@kriss.re.kr

Approved by :

Oh, Sang-Hyub

+82-42-868-5341

shoh@kriss.re.kr

Certificate No.: 1307-00919-002

Page 2 of 2 Pages

Certification Results

• Certified Values and Uncertainty :

Benzene	100.2 nmol/mol
Toluene	102.6 nmol/mol
Ethylbenzene	100.2 nmol/mol
<i>m</i> -xylene	100.0 nmol/mol
<i>p</i> -xylene	101.0 nmol/mol
Styrene	99.33 nmol/mol
<i>o</i> -xylene	102.9 nmol/mol
Nitrogen	Balance

Relative Expanded Uncertainty: 5 % (level of confidence: about 95 %, $k = 2$)

End of Certificate.