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Mass Spectrometric Calibration for Real -Time Hydrocarbon Detection

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MASS SPECTROMETRIC CALIBRATION PROCEDURES FOR REAL-TIME HYDROCARBON DETECTION

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

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by
Makuachukwu Mbaegbu
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NOMENCLATURE

MS – Mass Spectrometer

GC – Gas Chromatography

FID – Flame Ionization Detector

APCI – Atmospheric Pressure Chemical Ionization

CVT – Consistent Volume Temperature

TOC – Total Organic Compound

LHC – Lighter Hydro-carbon

EI – Electron Impact

ESI – Electrospray Ionization

FAB – Fast Atom Bombardment

MALDI – Mass Assisted Laser Desorption Ionization

LC – Liquid Chromatography

QMS – Quadrupole Mass Spectrometer

FTMS – Fourier Transform Mass Spectrometer

VOCs – Volatile Organic Compound

AC- Alternate Current

DC – Direct Current

RF- Radio Frequency

H – Hydrogen

Ar – Argon

N – Nitrogen

CEC – Consolidated Engineering Corporation

ABSTRACT

Determining gas compositions from live well fluids on a drilling rig is critical for real time formation evaluation. However, development and utilization of a reliable mass spectrometric method to accurately characterize these live well fluids is always a challenging issue because of lack of a robust, quick and effectively selective instrument and method. The primary goal of this research is to understand reasons of such discrepancies in results between "good" spectra, and "poor" ones. The objectives are thus to identify the detection issues, calibrate and QA/QC the instruments, and analyze the results in lab settings. In this study, we used two mass spectrometers (loaned by Halliburton to LSU) to develop a more selective and precise method to quantitatively analyze low level lighter analytes like lighter hydrocarbon (C1- C6) with masses <75*m/z* at concentrations (10, 15, 100 & 500ppm). In addition, heavier hydrocarbons and non-hydrocarbons were also detected. The C1 to C10 compounds and other gases had *m/z* ranging from 2 to 200.

Our results suggest that using methane 15, ethane 26, propane 41, butane 43, pentane 73 and hexane 87 base masses can help detect these hydrocarbon components from gas streams in live well fluids. The mass spectrometers worked well and had good spectrometric resolutions and detection for some samples, however, the systems appeared to have issues with detection, spectra deconvolution, and quantification of analytes at lower concentrations (<20 ppm) for other samples, particularly for the lighter (<30 *m/z*) hydrocarbons. We were also able to successfully test the mass spectrometers for detection of complex hydrocarbons like butadiene, butene, benzene, heptane, toluene, octane, p-xylene, o-xylene and m-xylene, propylene, acetylene, pentene, ethylene, methyl-cyclohexene, and ethyl-benzene, as well as non-hydrocarbons like helium, carbon-dioxide, and oxygen.

CHAPTER 1. INTRODUCTION

Real-time analyses of hydrocarbon gases on-site at oil and gas rigs can allow for early detection of hydrocarbons, particularly the lighter species, as well as timely reservoir characterization based on fluid types. Wireline or logging-while-drilling (LWD) services can help obtain reservoir fluid information, but gas extraction from drilling fluid/mud and subsequent geochemical analyses can quantitatively determine reservoir fluid composition with higher accuracy during the drilling phase itself. Gas extraction equipment extracts gas from drilling fluid when the latter is circulated to the surface. After the extraction of gases, mass spectrometric analyses can help establish the composition. While gas chromatographic (GC) techniques can also analyze gas compositions, the ability to distinguish among wet gas, condensates, and oil can become very difficult, particularly at high rates of penetration when thin reservoir zones exist (Nair et al., 2009).Additionally GC techniques are not reliable for distinguishing free phase in pores versus those dissolved in pore fluids. GC also does not characterize a wide range of carbon species (Nair et al., 2009).Present-day surface and mud logging techniques thus employ mass spectrometric techniques for reservoir fluid characterization on-site with portable mass spectrometers (MS). The MS data when analyzed using statistical methods, ratios and cross plots can help characterize reservoirs and evaluate formations (Wicker, 2015). Compositional variations, reservoir compartmentalization, porosity trends are interpretable from MS data analyses.

Over the years, mass-spectrometers (MS) have been used to study the behavior of elements when bombarded with electrons at low voltage and then branched into its use in the petroleum industry to study hydrocarbons. The MS is capable of detecting minute changes in intermolecular arrangements, isotopes and ionization potential of pure gases (Hoover & Washburn 1941). These characteristics, when combined, lead to the multi-purposed tool that could be an asset in an oil field.

Mud gas analysis remains the first breath of a well, however, given the fact that processed data at the surface is often underutilized by formation fluid evaluation specialist. The limitations experienced from current technologies such as the gas trap method and post analysis of the gases in the mud logging cabin (Ferroni, 2016) can be offset by the use of the MS. The proposed methodology is real-time mass-spectrometric measurement- a more proficient and immediate way to analyze the well fluids (Rowe and Splapikas, 2017). Implementing such a method would lead to a better understanding of the reservoir, its characteristics and on-site safety.

The mass spectrometer used in this study belongs to the class of quadrupole mass spectrometer with a specific industrial name, jumping mass spectrometer (Rowe and Splapikas, 2017). It is called a jumping MS because of its ability to move from one mass peak to another during an analysis (Rowe and Splapikas, 2017). The brand name of the mass spectrometer used in this study is not stated due to proprietary reasons. The operational characteristics of this system include real-time measurement, low pressure, high voltage (70eV), and vacuum. In addition to these attributes, the tool is supposed to detect the presence of hydrocarbons with emphasis on the lighter ones in their lower concentrations (~10PPM – 15PPM). Unlike commonly used gas chromatography mass spectrometer (GC/MS), the MS used in this study does not have the extra dimension to separate masses based on their molecular weight/volatility, which has led to a deconvolution and mass interference problem. This problem needs to be resolved by the proper mass selection, calibration, and tuning, and improved resolution, position, and radiofrequency for the system.

The primary goal of this study is thus to test the quadrupole mass-spectrometers for calibration of the lower-molecular-weight hydrocarbons otherwise known as the lighter/volatile hydrocarbons. The second goal of this research is to determine the limit of detection for both MS, especially when analyzing lower concentration (~10 – 15PPM) of gases. The third goal is to test the mass spectrometers for their detection capabilities for more complex hydrocarbons like aromatics as well as non-hydrocarbons. The successful calibration of the tools and results generated thereof would help in the improved analysis of fluid components from a live well.

CHAPTER 2. LITERATURE REVIEW

During a drilling operation, the cuttings circulated through the annulus of the well emits signature gases (particular to the formation) at atmospheric pressure (Espitale et al, 1984). The gas extractor extracts the emitted gases, and techniques like gas chromatographic and/or mass spectrometric methods are then used to analyze the composition of these gases (Nair et al, 2009). Gases from drilling fluids are essential to gaining a more in-depth understanding of the subsurface, especially on the type of hydrocarbon contents. The information gathered from the gas analyses also provides insights into depositional environments for the formations, hydrocarbon types, and the estimated volume of hydrocarbons in the reservoir (Larter et al 1997).

2.1. Gas Extraction Process

Typically, the workflow follows the flow of fluids through the flow line, which contains drilling fluid and cuttings circulated bottoms up. From the flow line, differential pressure becomes higher and with the aid of gravity from the inclined connection of the bell nipple to the possum belly from which gases evolved flow into the gas trap (Figure 2-1). From the gas trap, it flows through the polyflowline in a vacuum, to the choice of surface logging tool, and then the display system.

2.2. Types of Gas Extractors

According to Rowe and Muirhead (2017), there are four common types of gas extractors - the legacy trap, the consistent volume extractor, the semipermeable membrane, and the consistent volume and temperature extractor. Although the various traps have a common goal of receiving gases through the flow line, the combination of more than one of these traps have not demonstrated an improvement in services (Rowe and Muirhead 2017).

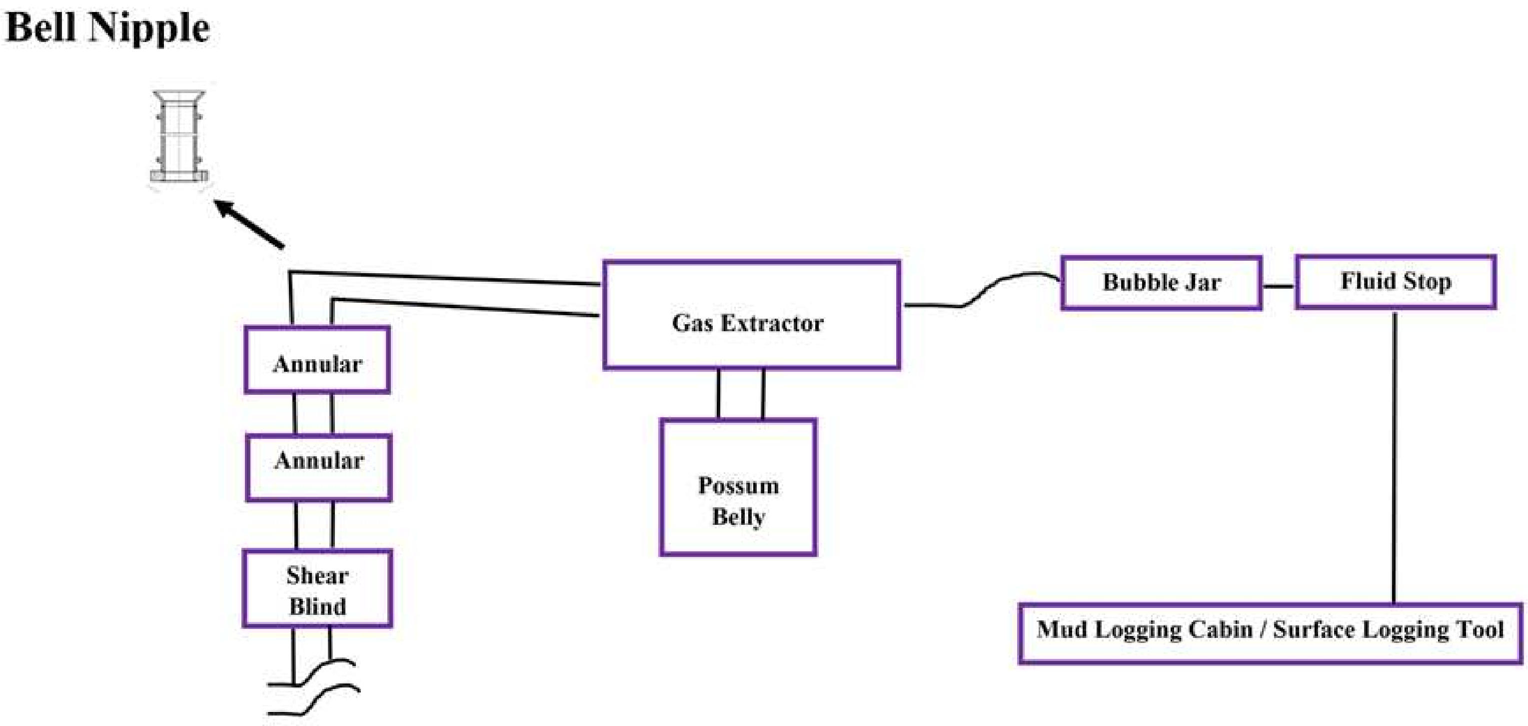


Figure 2.1. Current Practices on the Rig

2.2.1. Legacy Trap

The legacy trap was designed to meet standards of robustness, low cost, and ease of operation. As a result, it became and remained the standard gas extractor in the mud logging industry. The design of a legacy trap functions on spinning the impellers in a metal cylinder (Rowe and Muirhead 2017). The bottom of the legacy trap is exposed (Figure 2.2), allowing drilling fluid to enter the system. As the fluid is degassed, the leftover liquids exit the system through the spout on the upper part. In order to maximize the function of the legacy trap, it was recommended being placed in the header box or possum belly ensuring assess by drilling fluids. Due to the easy and uncontrolled access of fluids into the trap, degassed fluids become inconsistent. In addition to the unregulated volume, fluid temperature is inconsistent because of the exposure of fluids to environmental temperature.

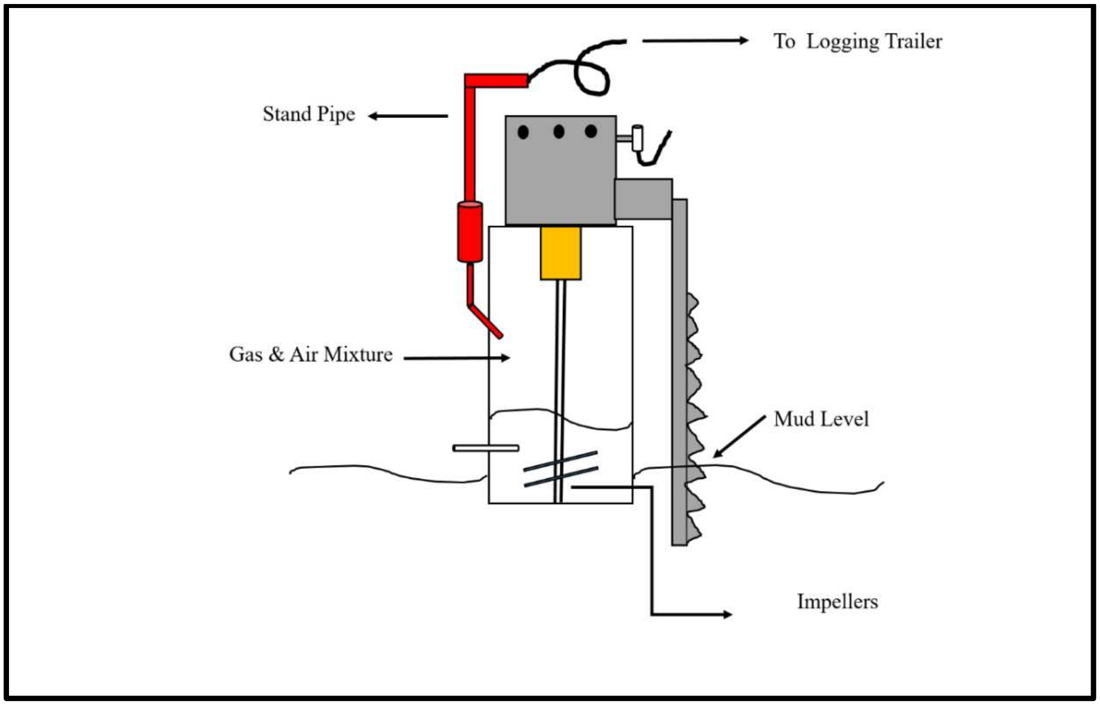


Figure 2. 2.LegacyTrap after Norbeck (2011)

2.2.2. Consistent Volume Extractor (CVE)

An extraction method created about 15 years ago with exposition to drilling fluids. Though called a consistent extractor, no published research justifies its ability to measure constant volumes (Rowe and Muirhead, 2017). CVE, as it is popularly known, collects drilling fluid samples through a pump, ensuring a certain amount is degassed each cycle. The pump solved the uncontrolled volume problem, which is the major contributor to issues related to false gas fluctuations (Rowe and Muirhead, 2017). Field implementation of the tool can however be expensive and is economics dependent.

2.2.3. Semipermeable Membrane

This design of the semipermeable membrane extractor worked to solve the issues of irregulated volume, temperature, and impeller issues (Norman 2006). Although it is an improvement to the problem from the CVE and legacy traps, the semipermeable membrane design had its challenges which included the mass flux with temperature (Forber et al. 2009). Due to the mass flux challenge, the semipermeable membrane turned out not very successful (Rowe and Muirhead, 2017).

2.2.4. Consistent Volume and Temperature (CVT)

The consistent volume and temperature extractor is the most commonly used gas extractor on the rigs but with an issue of fluid properties and volume changes at startup and shut down. The elevation of fluid temperature leads to the evolution of heavier hydrocarbons (NIST 2010). The CVT is a more technologically advanced and field adaptable tool because of the ability to regulate temperature and improved downhole fluid sampling. Due to CVT's functionality of downhole sampling, offshore operations adopt the tool (Rowe and Muirhead, 2017). As for maintaining a constant temperature, the fluids' temperature is raised higher than the fluid flow-out temperature.

Though there are different methods of heating, a common technique remains the heating of the vessel in which the fluid resides. CVT may solve temperature problems, but the implementation processes still have health and safety issues (Rowe and Muirhead, 2017).

Figure 2. 3. Semi-permeable Membrane 1(Brumboiu et al 2000)

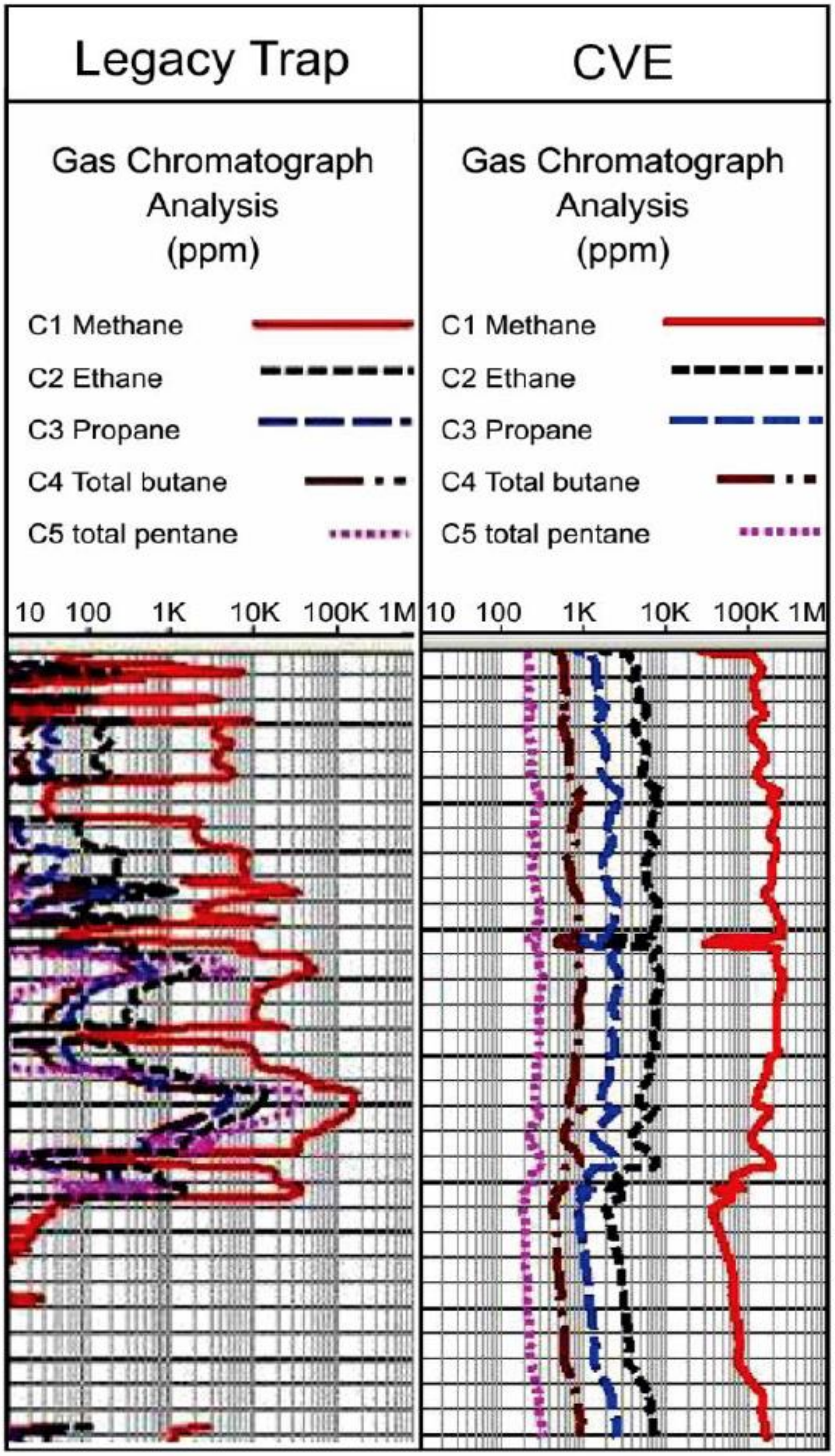


Figure 2. 4. Comparison of GC Analyses from Legacy Trap and CVE (Rowe and Muirhead,2017)

Limitation to the types of current gas extractors includes their inability to regulate fluid volume and temperature. The average kinetic energy of gas components is dependent on temperature, which is highly influenced by the temperature of the drilling fluids. Gases expelled, whether hydrocarbon or not, hamper the data acquisition processes and interpretation by professionals. Such constraints continue to be the basis for the opportunity for research and design growth of mudlogging tools used for mud gas analysis. Over the years, mud gas analysis has developed from observation of mud volumes to uses of tools like gas chromatogram-mass spectrometer (GC-MS), flame ionization detector (FID), and independent mass spectrometer (MS). Tools like GC-MS and FID requires two components: separation instrumentation and the detecting component. In the case of GC-MS, GC is the separation mechanism, and MS is for detection. However, the separation of instrumentation is dependent on the type of fluids analyzed. The more complex and bulkier the sample is, the more the need for the application of robust separation techniques (Niyonsaba et al. 2019).

2.2.5. Gas Detectors for Gas Analyses

Gas chromatography (GC) was invented in 1952 by Martin and James. It is one of the most widely used analytical tools in modern chemistry, especially for sample introduction to detecting tools like the mass spectrometer (MS). According to Keith and Myers, 2002, significant milestones have been attained over the past years. Such developments span improved column technology by infusing the columns with silica for better resolution, and the development of benchtop GC s. The gas chromatogram (GC) is a versatile instrument for separation of molecules and is compatible with mass spectrometers and other forms of detectors like the flame ionization detector (FID). flammable instrument, which influences and limits the placement options of the tool on the rig, an essential factor in the optimum use of rig tools used in the gas analysis (Mcglone et al. 2015).

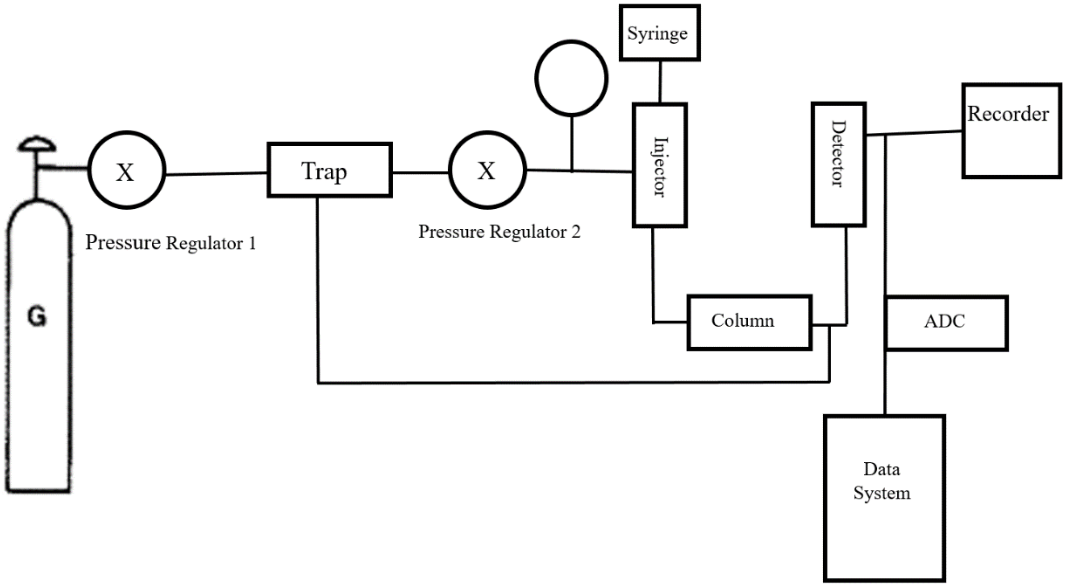


Figure 2. 5. Gas Chromatogram Adapted after Bartle et al. 2002

2.2.6. Flame Ionization Detector

Flame ionization detector operates as a qualitative instrument responsible for the detection of hydrocarbon. The instrument can only detect hydrocarbon and is designed to determine the global presence of hydrocarbon. Although the FID is a qualitative instrument, the detection range is broad and different (Chaulya et al., 2016). The FID tool does not read positive for moisture contents, hence preventing false readings. It is also capable of volatile organic compounds (VOCs) detections. Amongst all FID's positive uses, the tool has some limitations, such as its inability to identify VOC types and its non-functionality in high humidity regions. The FID is also a highly flammable instrument, which influences and limits the placement options of the tool on the rig, an essential factor in the optimum use of rig tools used in the gas analysis (Mcglone et al. 2015).

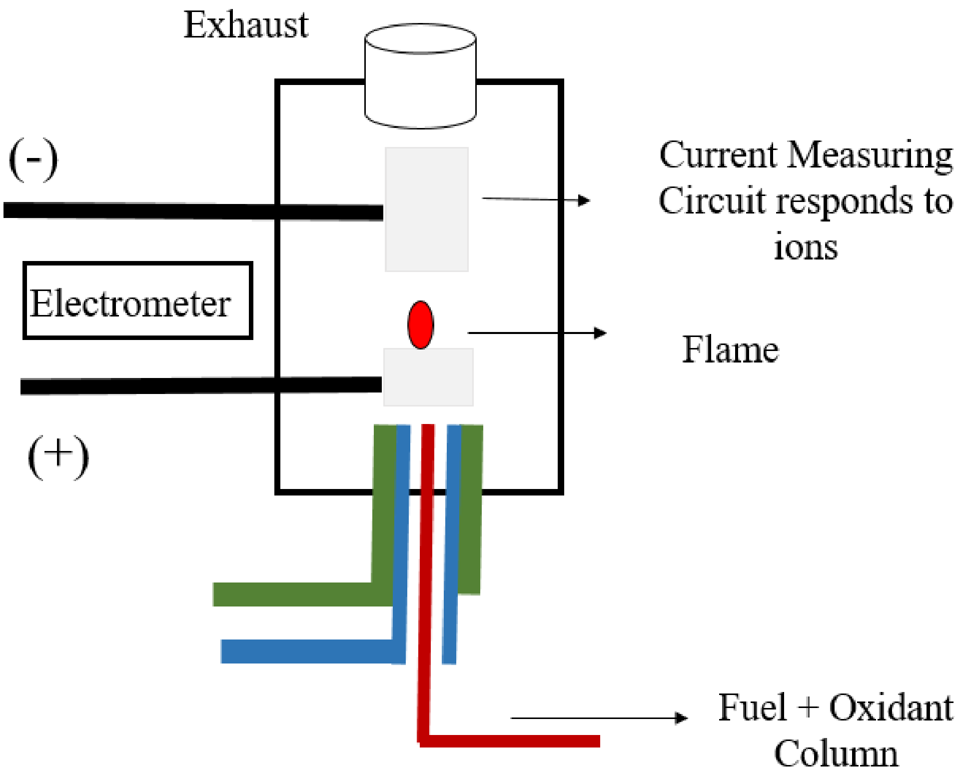


Figure 2. 6. Flame Ionization Detector (FID) Modified after Chaulya et al., 2016

2.3. Fundamentals of Mass Spectrometer

The mass spectrometer (MS) consists of three main components - an ion processing system, vacuum pumps, and control systems (Figure 2.7) (Clark, 2019). In order to ensure appropriately ionized and filtered ions, the ion processing system must consist of ionization, a mass analyzer, detection of ions, and signal processing (Clark, 2019). This component of the MS is responsible for the ionization process – bombarding of electrons with energy to produce ions, mass filtering – separation of ions based on the mass to charge ratio, detections and signal processing (Figure 2.7) – an amplifier amplifies the ions to detectable electrical signals. For the ions to travel faster in the MS system, there is a need for the vacuum system – creates an air-free environment. Finally, the control system (Figure 2.7) is in charge of ion detections and display. At this stage of analysis, components in the MS becomes individual components of the mixture.

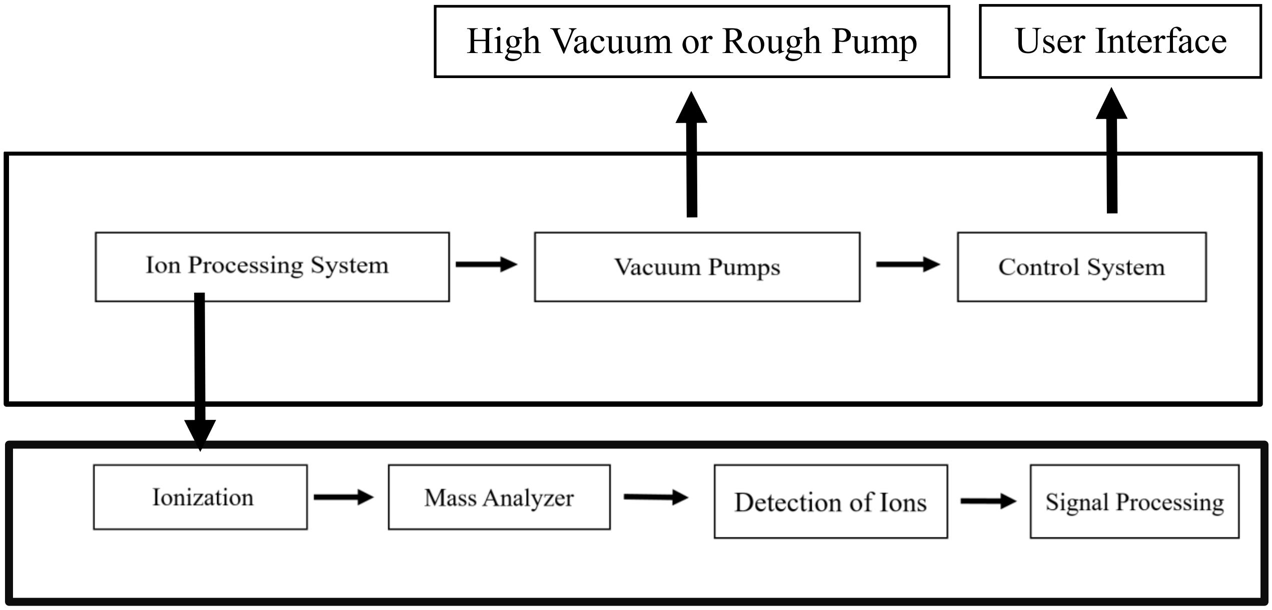


Figure 2. 7. Components of an MS

2.3.1. Mass Spectrometer

Mass spectrometer (MS) operates on the principle of bombarding the gaseous component with low voltage electrons, which a filament emits as temperature rises (Figure 2.8). The bombarded molecules ionize into positive ions and pass-through slit, which maintains a low negative potential. The electrons analyzed are displayed as peaks, also called fragments. These peaks become representative of unknown m/z ratios. In order to be optimal in the analysis of the unknown components, selection of the right peaks is essential considering that peaks could either be a parent or daughter (Figure 2.8). For the sake of this study, the peaks are fragments. Although the MS is a versatile tool, it is vital to know the goal for it during its design phase so that its uses are optimum.

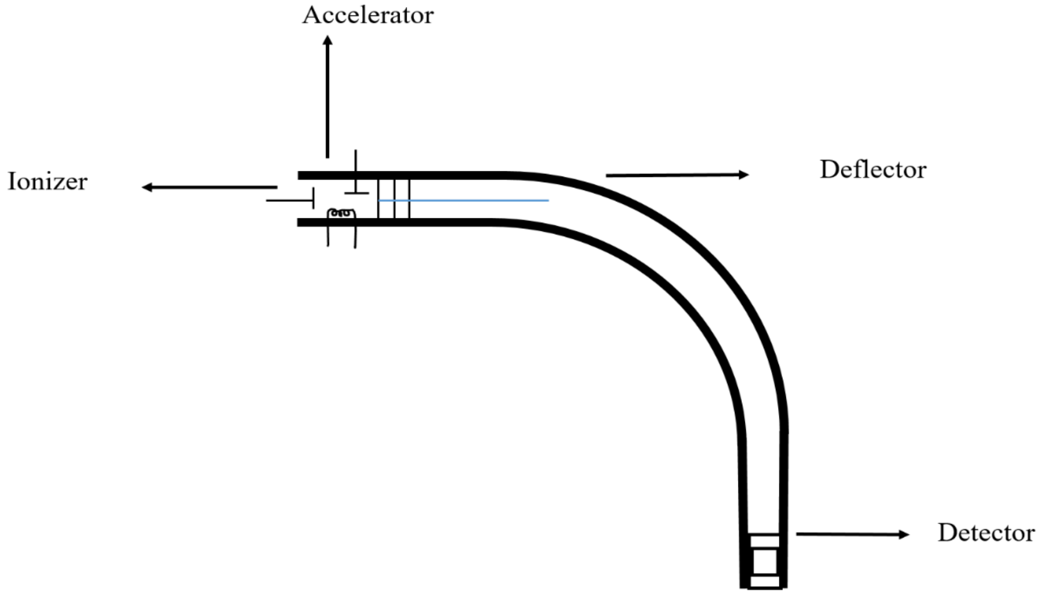
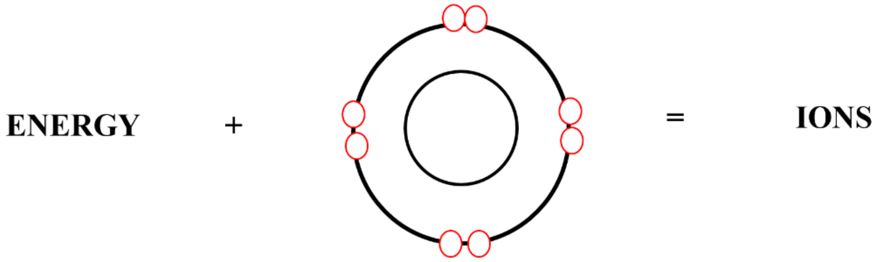


Figure 2. 8. Schematic of an MS after Clark 2000

2.4. Ionization Processes

Ionization is the process of creating ions either by the gain or loss of electrons from the molecule or atom. The gain of an electron creates a negatively charged ions, whereas the loss of electron is the positively charged ions. For the case of the mass spectrometer, positive ions are a result of the samples introduced to the system (Clark, 2000). In Figure 2.9 below, the vaporized sample – gaseous sample is heated to excite the electrons in the outer most electron shell (Figure 2.9) – ionization energy. The emitted electrons are trapped and stored in the electron trap so the ions can travel through the accelerator (Figure 2.9) – part of the ionizer responsible for maintaining the kinetic energy of the ions (Clark, 2000). There are different types of ionization processes for mass spectrometry. They include electron impact (EI), electrospray ionization (ESI), fast atom bombardment (FAB), atmospheric pressure chemical ionization (APCI), and mass assisted laser desorption ionization (MALDI). In addition to the types of ionization techniques, ionization processes could be hard or soft.



$$M + e^{-} \longrightarrow M^{\cdot +} + 2e^{-}$$

Figure 2. 9. Molecular level of Ionization

2.4.1. Electron Impact (EI)

Electron impact ionization is one of the more commonly used ionization processes — the EI functions in the presence of a vacuum system responsible for volatilizing the samples. The typical voltage at the filament is 70 volts. The EI is the highest fragment ion-producing technique and more compatible with volatile compounds (Down, 2016).

2.4.2. Fast Atom Bombardment (FAB)

Fast atom bombardment ionization, was an early form of ionization. This method of ionization required the use of a matrix. Like the electron impact ionization, there is also a need for voltage supply. However, in this method, ionization is achieved by bombarding the molecules or atoms with inert gases like argon charged to kilovolts. This method of ionization functions better with non-volatile components and secondary ion mass spectrometry (SIMS) (Down, 2016).

2.4.3. Electrospray Ionization (ESI)

This form of ionization works by combining high voltage and flow of liquid at atmospheric pressure (Down, 2016). As a result of the combination, spray ionization becomes possible. The high voltage liquid is desolvated, resulting in the ejection of ions from the droplets of the spray. The ejected ions accelerate through the accelerator thereby being detected. This form of ionization also ionizes molecules at low flow where a low voltage liquid can be used. This technique is more compatible with the separation process - liquid chromatography (LC), large molecules, and nonvolatile substances (Down, 2016). The technique's sensitivity is also highly dependent on the concentration of the samples. Sensitivity is low because of the limited mass to charge ration ranges.

2.4.4. Atmospheric Pressure Chemical Ionization (APCI)

This method of ionization is similar to the ESI with a difference of voltage applied to the needle, unlike ESI with the liquid. The needle used in APCI is called a corona needle that operates at atmospheric pressure by discharging ions (Down, 2016). Typically, the ions produced by the corona needle are protonated H3O+. The technique also has a variety of atmospheric pressure photoionization (APPI). Also, one of APCI's advantage over traditional methods like EI lies in the ease of use and less carryover of samples.

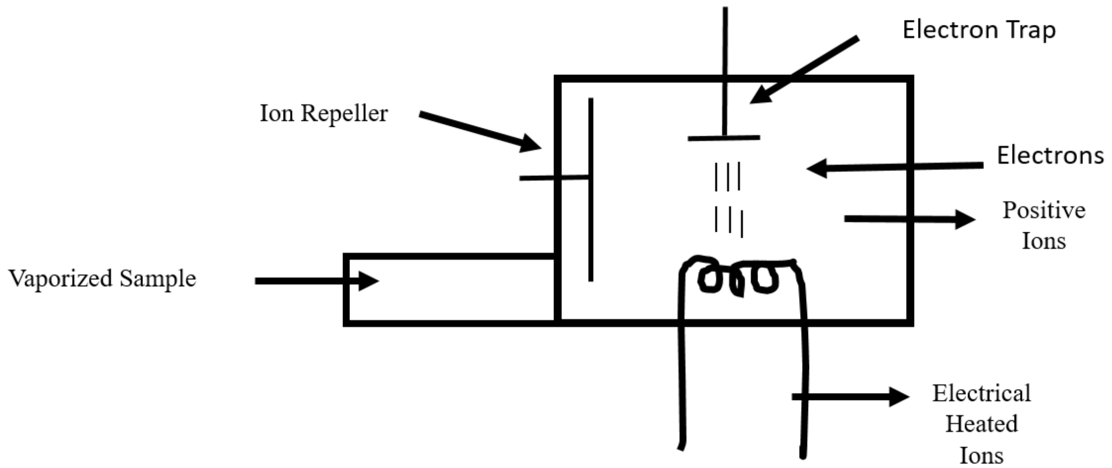


Figure 2. 10. Ionizer Adapted from Clark 2000

2.5. Accelerator

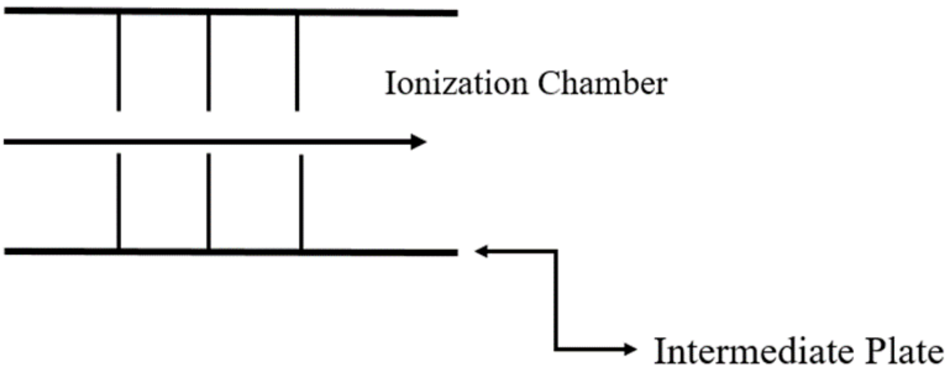


Figure 2. 11. Accelerator Modified after Clark 2000.

This component of the MS maintains the kinetic energy of the ions.

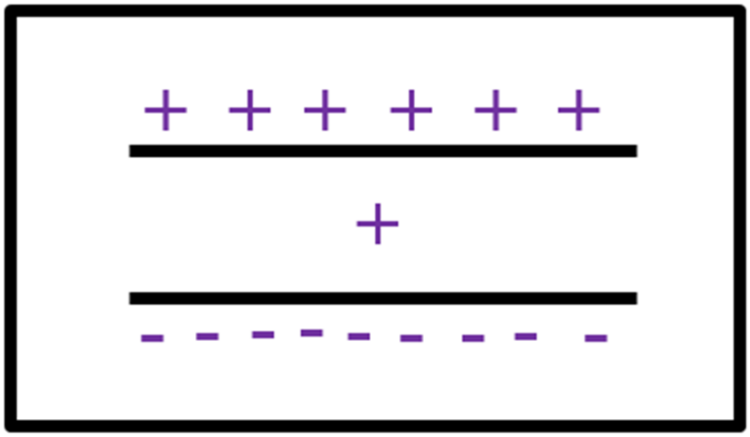


Figure 2. 12. Accelerator Molecular level

2.6. Types of Mass Analyzers

The mass analyzers are also known as deflectors or mass filters. The component of the MS that filters the ions according to their mass to charge ratios (m/z) (Cooks, 1393). Mass analyzers are crucial to the successful operation of an MS because it ensures that ions are available for detection (Clark, 2019). The mass analyzer also ensures that noise in the spectra results is minimal. Most mass analyzers consist of a magnetic and electric field. In addition, a combination of more than one mass analyzer supports the phenomenon of tandem mass spectrometry – a combination of more than one form of mass filtering. There are four common types of mass analyzers: magnetic sector instruments, quadrupole mass spectrometers (QMS), ion trap mass spectrometer, Time of flight mass spectrometer, Fourier transform mass spectrometry (FTMS), and, Orbitrap.

2.6.1. Magnetic sector instrument

The sector type of instrument is a pioneering analyzer (Gross, 2013). In the sector, there is the presence of a magnetic and electric field in the curved section. The curvature of the sector, in combination with the fields, acts as a guide for the ions to the detector. Due to the curvature of the analyzer, space between the ions exists as a result decreases the sensitivity of the tool. Although there are sensitivity issues, the analyzer remains useful in the analysis of dioxins. The analyzer is capable of high-resolution analysis after ions are selected.

2.6.2. Quadrupole Mass Spectrometers

The most common ionizer because of simplicity, sensitivity, and fast scanning. All of these characteristics laid the foundation for use with GC-MS and LC-MS. The QMS consists of 4 rods connected by the radio frequency and direct current voltage. Most times, the voltage of the ion is adjustable through a computer – user interface. Due to the structural design of QMS (Figure 4.3), a mass analyzer could be a tandem MS – mass spectrometer capable of multi-stage analysis, improving resolutions. The mass analyzer is also an ideal method for quantifying ions; hence, it is the focus of their research.

2.7. Other Types of Mass Spectrometers

2.7.1. Ion Trap Mass Spectrometer

Ion trap mass spectrometers are similar to the QMS, except it is a 3D instrument. It stores and manipulates ions. Hence the reason for its high sensitivity compared to other analyzers. Though sensitive in its analysis, the instruments lack the ability of extensive fragmentation, especially at the front end of the tool. It is also expensive to maintain a 3D tandem MS.

2.7.2. Time of Flight Mass Spectrometer (TOF)

This form of analyzer measures the ion travel time. The larger mass to charge ratios is theoretically slower. Due to slow TOF of a larger m/z ratio, sensitivity becomes relatively slower in its response, which indirectly affects the sensitivity.

2.7.3. Fourier Transform Mass Spectrometer (FTMS)

Although other analyzers have used the Fourier transform in analyzing their output data, the instrument functions by measuring the cyclotron motion of ions caused by the magnetic field. Typically the lighter the ion, the more vibrational motion (higher frequency) hence, more m/z ratio to measure. Due to the fundamental operation of the FTMS through the cyclotron measurement, the instrument is high resolution and efficient at scanning ions.

2.7.4. Orbitraps

Orbitrap is a newer and youngest generation mass analyzer responsible for the measurement of ionization energy during the ionization process. Similar in its function with the FTMS, the orbitrap functions without the magnetic field. The instrument measures the frequency of ions in an electrostatic trap. The movement of ions in the trap is harmonic, hence there is no noise in the output.

2.8. Detection of ions

At this point, ionization and mass filtering - the significant components of the mass spectrometer are complete. As a result, the ions deposited on a metal plate are now connected to wires of the amplifier (Figure 2.13). As evidenced (Figure 2.13) in the detector system, valence electrons become a conductive path between the collecting plate and the amplifying wire.

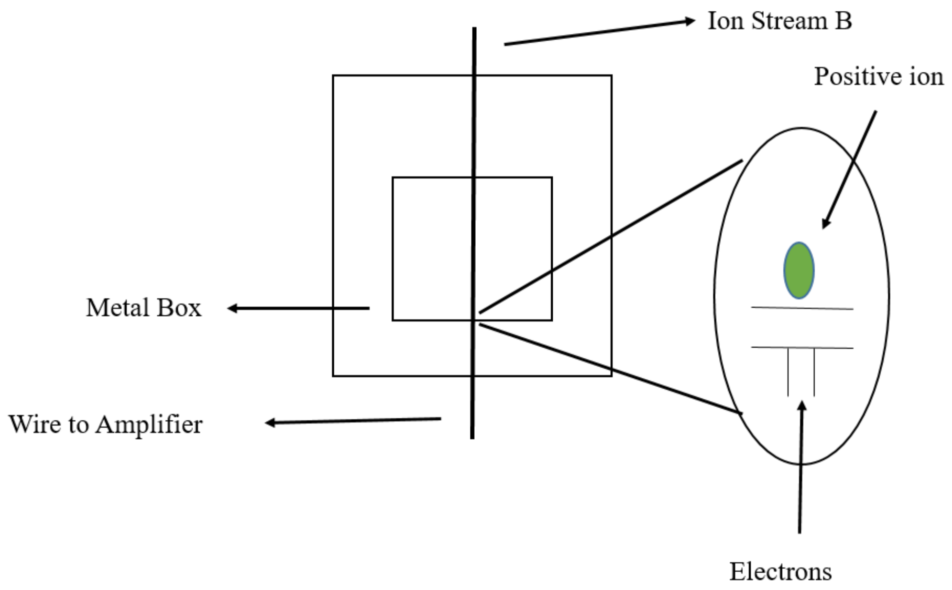


Figure 2. 13. Detector Modified after Clark 2000

2.9. Signal Processing and Control Systems

Atoms are the building blocks of matter. The combination of more than one atom forms molecules. Ions lose or gain electrons. As a result, the molecules are either positively or negatively charged (equation1-1). In the case of mass spectrometry, it usually is a loss of an electron, so the ions are positively charged. The size of ions depends on the chemical reaction that occurs. In order words, positive ions are lighter because of the loss of an electron. Sizes of atoms increase top to bottom of the periodic table. The trend – like the behavior of atoms, provides a relative representation for ions. Ions of bigger atoms are relatively bigger in comparison to smaller atoms. All these factors act on the strength of the signal delivered on a detector in an MS. For this reason, signal processing of ions mostly include an amplifying wire - double insulated wires made of fiber optics material, so the ions processed are accurate and of high resolution. The control system is the last stage in ion processing. It is the component of the MS that are based on the choices of computer systems. It is responsible for displaying the output results making the analyses of ions possible.

2.10. Geochemistry and Oil Finger Printing

Geochemical analysis and fingerprinting are the standard methods used in the petrochemical analytical method, focused on the compositional makeup of a sample. The method also provides information on fragmentation patterns of the compounds. These patterns improve the knowledge of the elemental composition of the hydrocarbon compound. The oil fingerprinting is unable to provide wholesome information on analytes. As a result, the need for in-depth knowledge of the molecular rearrangement of ions – as known as Mclafferty rearrangement is imperative. Understanding the expected rearrangement of the molecules during the ionization process improves the interpretation of data detected by the instrument ((Niyonsaba et al. 2019).

2.11. Mud Gas Analysis

Mud gas analysis is the first breath of a well and a form of monitoring reservoir fluids in drilling fluids. However, processed data at the surface during circulation remains underutilized by formation fluid evaluation specialist. The reason for the existence of the shortcomings are results of current technology (Ferroni, 2016). Mud gas analysis is also a method that has existed for about 80 years (Baroid 1961). In the past, gas monitoring was by observing mud volume and bubble in returned drilling fluids (Baroid 1961). However, as times progressed, rig operations became more complex; hence; its need to be equipped with the right tools. As a result tool like gas chromatogram – mass spectrometer, Flame ionization detectors, and mass spectrometers are norms. Amongst the classes of tools, data underutilization remains a problem.

Lighter hydrocarbons are volatile and would readily escape to the atmosphere unlike heavier hydrocarbon compounds. Due to the lightness of some of the hydrocarbons, quantitative analysis of the gases remains a challenge. Thus, this research focuses on the LHCs' and the quantitative analysis using MS.

LHCs typically evolve from the drilling fluids at lower concentrations example (< 30PPM). Current challenges are quantitative analyses of LHCs. Due to the characteristics such as high volatility and low boiling point, volatile organic compounds (VOCs) prefer to exist in a gaseous state. For this reason, the post-analysis of fluids at the mudlogging cabin is an unfavorable method for VOC characterization. The new technology of measuring gas composition real-time using the calibrated and optimized mass spectrometer solves the problem because it captures VOCs at concentrations as low as <30ppm. Historically, the MS has shown its capability to identify isotopes and ionization potentials of pure gases (Faber,1983). Also, it proved its sensitivity to low concentration likes <30ppm (Haworth et al, 1984). Thus, the mass spectrometer is versatile and reliable. (Hoover 1940) in regards to the problem at hand.

On drilling sites, gases are measured and examined using (daughter peak) fragment-peaks method. An advantage of the fragment peak style is the opportunity to cross-compare and correlate the information with other formation evaluation methods. There are two significant challenges to the choice of peak analysis: the deconvolution matrix of the binary gas standard and the quantitative validation of the gases to gas standards. The corroboration of the LHC s against gas standards would solidify the knowledge of the MS response to the gases at varying concentrations. Considering the operating characteristics of the MS, it is a necessary tool for fieldwork in the oil and gas industry (Hoover & Washburn 1941). Possessing the added capabilities to serve multiple purposes and still provide reliable results concerned with detection and sensitivity (Hoover & Washburn 1941) makes the tool and its operational use invincible.

The real-time MS detection method allows gaining a more in-depth understanding of characteristics like reservoir compartmentalization. Real-time formation evaluation provides countless privileges for faster, easier, accurate decision-making while on a job. However, there are challenges in detecting and quantifying lower concentrations (<30ppm). Such concerns are one of the main reason for which the MS on the rig site contains an ISO file, which helps generate the calibration and tune file.

2.12. History of Mass Spectrometers

Until the 1940s, physicists had significant control of the MS and used it in to study the nature of atoms. Separation of elemental isotopes became essential to the Alfred Nier debuted an MS that combined the electrostatic and magnetic analyzers Manhattan Project and World War II before the 1940's (Meyerson 1986). As a result, the use of MS became more popular. Concurrently, (Meyerson 1986). One of his early achievements from publicizing was within the biologist group by providing a method to measure carbon 13 (13C). Shortly after, the geochemists dated the age of the earth by quantifying the lead (^{207}Pb / ^{206}Pb) present using the MS. Nier was also able to attract the community of nuclear scientists, who separated the uranium (^{235}U) using the MS during WWII, hence, the birth of nuclear energy.

Biemann discovered the mass spectrometer's ability to determine the structures of complex molecules and was also the first to test unknown compounds using the MS (Griffith, 2008). Through Biemann's work Djerassi, another natural products scientist developed an interest in mass spectrometry and its uses in protein sequencing (Griffth, 2008). The scientists, Mclafferty, Djerassi, and Biemann, are recognized as the fathers of MS methods because of their pioneering works (Meyerson 1986). By 1980, the MS proved useful in the study of smaller organic molecules, though the bigger molecules remained a challenge. Around the same time, the electrospray ionization (ESI) and mass assisted laser desorption ionization (MALDI) became a classified ionization technique.

2.13. Petroleum Industry and Mass Spectrometers

The advances of mass spectrometers encouraged, the petroleum industry to increase its application in the oil field. In the year 1945, Consolidate Engineering Corporation (CEC) learned of an abortive project from the California Institute of Technology (CALTECH) that focused on the use of mass spectrometer to analyze refinery streams (Meyerson 1986). Due to CEC's business focus on oil prospecting, they embarked on the journey of the same project from CALTECH. As an active step, the company hired the student and the tool used in the CALTECH lab. CEC proceeded to test the tool and its ability to analyze gases from the soil. The soil- gas analysis faded, but the use of the MS in the refinery stream was a success. This success led to the rise in competition amongst MS manufacturers. However, none was able to perfect the technology as the CEC. As a result, CEC proceeded to launch its first model (CEC Model No. 21- 101). The company also installed its first mass spectrometer successful in Atlantic refining company during the same year. This act led to the acknowledged market presence of MS amongst others in petroleum industry.

Although, the early suppliers of the MS were primarily CEC. Other companies like the Westing House and Wiley ventured in the business of MS systems; however, the tools proved to be lacking in vital functions (Meyerson 1986). For example, the first model of the MS from Westing House was at the Standard Oil of Louisiana. The installed MS had some significant challenges – one of them being the faulty inlet. The inlet failed that rebuilding the tool onsite was the only alternative at the time (Meyerson 1986). The set back on the path of the Westing House kept CEC as the dominant provider of MS services to the oil and gas industry.

The MS is known as an analytical tool from 1935, the year exploration of MS uses in Petroleum began. However, the extent of its uses was unknown and has improved over the years. From its initial uses for soil gas analysis to the use in refinery streams. In addition to the mass spectrometer's uses in the oil and gas industry, other industries such as the food industry proved its use in measuring components of fruits, especially during their oxidation process. This success reinforces the use of MS in the petroleum industry.

2.14. Improvements in MS in Petroleum Industry

As the years went by, the demands of mass spectrometers in the market evolved. As a result, the tools were designed to fit customers' needs. Some of the improvements were the sensitivity of the tool. The tool had a problem with continuous gas sensitivity — the inefficiency of the tool to detect gases leading to reduced detection of compositional and structures of gases (Meyerson 1986). With multiple lab experiments, Sharkey, Friedel, and Robinson from the Bureau of Mines and CEC respectively eventually related the MS sensitivities to purity levels of gases emitted from the tungsten filament (Meyerson 1986). They also observed that the tungsten detected gases in the presence of impurities like carbides, oxides, and carbon deposits without affecting detection of gases that matter. Altering the composition of the tungsten filament resulted in significant improvements to the sensitivity of the MS (Meyerson 1986).

Following the improvement in gas sensitivity, accurate mass and elemental composition were proved to be a function of the mass spectrometer by John Beynon in 1954 (Gross 2013). As a result, oil companies invested in at least one MS (Meyerson 1986). Atlantic refining company being the first to install a machine on the refinery site in Pennsylvania (Meyerson 1986). Their reported success with the tool encouraged other companies like Shell to invest. As the industrial needs for the MS increased, other manufacturers like General Electric became suppliers. About five years later, the number of MS uses in the petroleum industry led as number one amongst all other industries with 35 installed mass spectrometers. Shell Oil also reported satisfaction with the MS on heavy oil identification (O' Neal 1955) though the first generation of mass spectrometers was built to analyze low boiling point liquids and gases. These breakthroughs in the use of MS to analyze heavier oil encouraged the growth in resolution, amplification, and stability in research. In addition to the operational improvements, quantitative analysis of the gases and liquid became feasible (Meyerson 1986).

2.15. Miniature MS Development

The miniaturization of the mass spectrometer began in the year 2000. As the exploration of possible miniaturization of the tool began, the attention on small-sized mass spectrometers improved, which eventually led to more appreciation of the complex challenges related to producing small devices. The debut of the small devices led to the production of more devices for on-site applications. However, with the increase of use of a miniature mass spectrometer, other challenges presented itself, namely, methods of ionization so the ambient ions are available to the mass analyzers. From the year 2000 till 2009, miniaturized mass analyzers produced with an estimated m/z ratio exceeding 60,000 (Cook et al. 2009).

2.16. Optimization of MS Data Acquisition

Optimization of data acquired through the MS is challenging but continues to prove useful. With the data acquisition, reliability, and validation of the tool becomes a significant concern. Also, proof of concept is imperative for the standardization of gas data acquisition processes across the industry. However, the opportunity to achieve such levels requires the consolidation of multiple data collection methods across the industry. As a result of the challenges in sharing the data with competitors, exploration of mass spectrometers, and its use in the evaluation of the formation remains minimized.

2.17. Jumping MS and Real-Time Measurements

The jumping MS debuted in 2017 with goals of comparing the results to the other mud gas analyses methods. The testing focused on validating the use of mass spectrometer in measuring gases (Rowe 2017). According to the experimental study, a mass spectrometer (MS), Common quadrupole (CQ) and Gas Chromatogram (GC) were compared. Comparatively the efficiency of the tools was analyzed based on methane and pentane gases - methane being representative of the lighter hydrocarbon and pentane the heavier gas. The test proved that the mass spectrometer detected the gas components at different concentrations.

With the introduction of the mass spectrometer for gas composition measurements, the problem of fragment deconvolution arose. The deconvolution problem is the situation where the fragments of the gases analyzed overlaps. As a result, the peak selections become challenging at the rig site. Also, the longer the hydrocarbon chain, the more the deconvolution problem. For these reasons, this study uses the QMS to develop a calibration methodology validated in the laboratory, ensuring the peaks corresponds to the correct masses. This calibration methodology when used on the on the rig will give higher confidence in the resolution of the deconvolution problem, and can be successfully used in the field.

CHAPTER 3. STUDY GOALS

The primary goal of this study is to test the quadrupole mass-spectrometers (QMS) for calibration of the lower-molecular-weight hydrocarbons otherwise known as the lighter/volatile hydrocarbons. Mud gas samples are complex mixtures of “overlapping hydrocarbon species” (Turner et al., 2004). While QMS are employed for detection of analytes down to levels of parts per billion (PPB), the accuracy of these measurements depend primarily on the robustness of the calibration method, and whether cross-sensitivity of analytes have been studied, and accounted for. Cross sensitivity occurs when a previously exposed gas changes the response and accuracy of the instrument to the next gas or gases. Thus, the primary goal of this study is to generate and test a robust calibration method for hydrocarbon gases, particularly the low molecular weight species.

The second goal is to test the calibration method to the detection of the lighter hydrocarbons particularly at lower concentrations (~10 – 15PPM) of gases. The gas used for calibration will have different concentrations levels (10, 15, 100, and 500ppm) with different constituents in different balances. These gases will generate peaks at specific m/z ratios. These resulting fragment peaks will be compared to preselected base peaks from the fragmentation pattern process. As long as there is minimal interference and peaks match the selected peak, the m/z ratio will be considered appropriate for the hydrocarbon compound. The most suitable peak will be queried statistically by calculating the %Relative Standard Deviation (%RSD). The peaks of choice, the sensitivity of the tool, and repeatability of the experiment will constitute the QA/ QC process, improving the reliability of the tool as well as its operations. Ultimately, the successful calibration of the MS would lead to identifying the m/z ratios and the base mass peaks for C1 to C6 components which can then be directly used and applied in the field for an improved analysis of fluid components from a live well.

In pursuing the two main goals of this study, an understanding into the performance of the MS is gained, particularly when lighter gases are passed through the system. Thus the fragmentation patterns of select elements and compounds are studied, primarily focusing on hydrocarbons (C1-C6), on each instrument by using binary standards that contain lighter hydrocarbons balanced in either nitrogen or argon. This step will then be followed by calibration of the instruments using mixed gas standards, to estimate sensitivity of the MS in terms of percentage relative standard deviation (%RSD) for the selected base peaks/masses for each hydrocarbon compound present in the mixture.

A third and final goal of this study is to extend the calibration method to detecting heavier hydrocarbons and non-hydrocarbons using the same MS to test the extent of their detection capabilities of components encountered in well fluids. This is accomplished to directly using gas mixtures, and not binary standards as in C1-C6 analyses.

CHAPTER 4. ESTABLISHMENT OF METHODOLOGY

There is minimal room for error in the oil industry because of the cost- efficiency-driven incentives. For this reason, the mass spectrometer helps reduce rig time while still providing reliable information. Another added advantage of using mass spectrometers (MS) is the reduction of offsite time spent conducting experimental procedures on well fluids. The use of the improved and streamline workflow (ref. fig 1.17) is expected to cut the overall cost of operations and rig time, which are typically a primary concern for the operators; owners of the wells (Ferroni, 2016). Safety is also another motivation because of the opportunity to prevent blow out situations. Additionally, the use of real-time mass spectrometers improves knowledge on productive formations using lighter hydrocarbons as indicators.

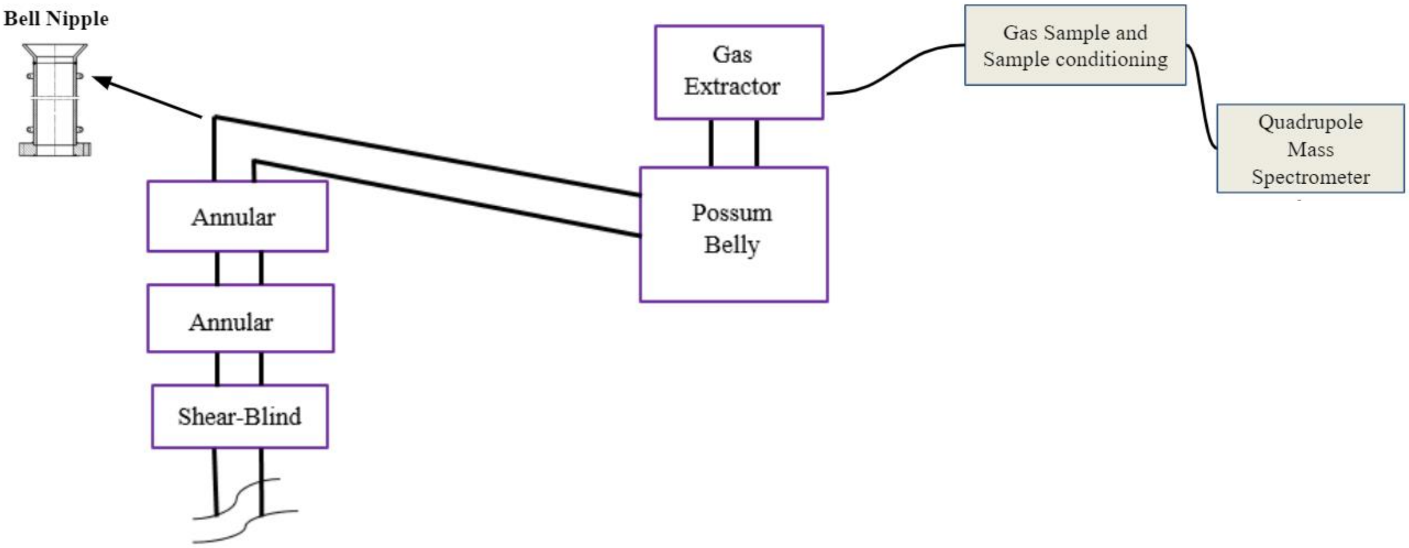


Figure 4. 1. Proposed Methodology

In the early days of mud gas analysis, methane was an indicator gas, but due to increased use of crude oil in drilling fluids, identification of other hydrocarbons became useful (Baroid 1961). Instrumentation of the MS has existed for more than 70 years, but the limit of detection is ~ 50PPM. In this chapter, we discuss the quadrupole mass spectrometer (QMS), and establish the methodology used in this study for calibration, setting detection limits, and analyses of data.

4.1. Design of Quadrupole Mass Spectrometer

Due to proprietary information, the internal design of the mass spectrometer used in this study is confidential but it is known to be a quadrupole mass spectrometer (QMS). Wolfgang Paul developed the QMS in the nineties. The motivation of his invention stemmed from the challenge of magnetic field destroying tools that worked in conjunction with the MS. In response to the problem, Paul developed a method of passing electricity using quadrupoles - hence the name Quadrupole Mass Spectrometer (QMS). The QMS consists of an ionizer, an ion accelerator, and a mass filter. The ionizer is the component of QMS responsible for bombarding molecules with electrons from hot filament producing ionized gas. The gases are accelerated through the ion accelerator and filtered by the four parallel poles with alternating electricity in the forms of alternating current (AC) and direct current (DC) (March, 1997).

The poles act as mass filters after applying opposing potentials on the opposite ends of the rods. A potential of $U+V\cos(\omega t)$ is applied to two rods, and $-(U+V\cos(\omega t))$ to the other two rods. Here U is the DC voltage and $V\cos(\omega t))$ is the AC voltage, and ω the angular frequency. The trajectories of the ions are affected by voltage, especially while the ion travels through its flight path. QMS provides the opportunity to adjust the current to improve the detection of ions based on mass to charge ratios. For a range of DC and AC voltages, only ions belonging to a particular mass-to-charge ratio pass through the filter whereas the others are deflected from their original paths. By varying ω and keeping U and V constant, or by varying U and V with (U/V) fixed for a constant angular frequency, ω, the ions passing through the filter are monitored which in turn generate the mass spectrum (March, 1997).

Newton's equation of motion is the governing equation, which states that the force is equivalent to the ion charge and the electric field. The angular frequency is implemented through the Mathieu's equation which relates the magnitude of the electron (e), distances between the electrodes (r02), mass (m), and charge (q).

$$\frac{d2x}{dt2} = -\frac{e}{m}[U + Vcos(\omega t)] * \frac{X}{r02}$$

$$\frac{d2y}{dt2} = \frac{e}{m}[U + Vcos(\omega t)] * \frac{y}{r02}$$

Equation 4-1 Mathieu's Governing

The QMS operates in two directions; X and Y (Equation 4-1). Stability of the ion trajectories is affected by the weight of the ions, likewise the flight path. Heavy ions follow the high pass mass filter and lighter ions the low pass mass filter. High pass mass filter ions oscillate increasingly in the X direction without striking X electrodes-electrodes in the x-direction. Unlike the latter, low-pass mass filter caters to ions of lighter mass without striking the electrodes in the Y direction. The ion's path is highly determined by its mass after the supply of a radiofrequency – direct current (RF-DC) leads to ions that are capable of operating in both the X and Y path. The RF-DC character of the QMS is the primary contributor to the tuning abilities of the tool (March, 1997). Although the QMS is tunable, ions are expected to be within a theoretically stable envelope to be detected (Figure 4-2).

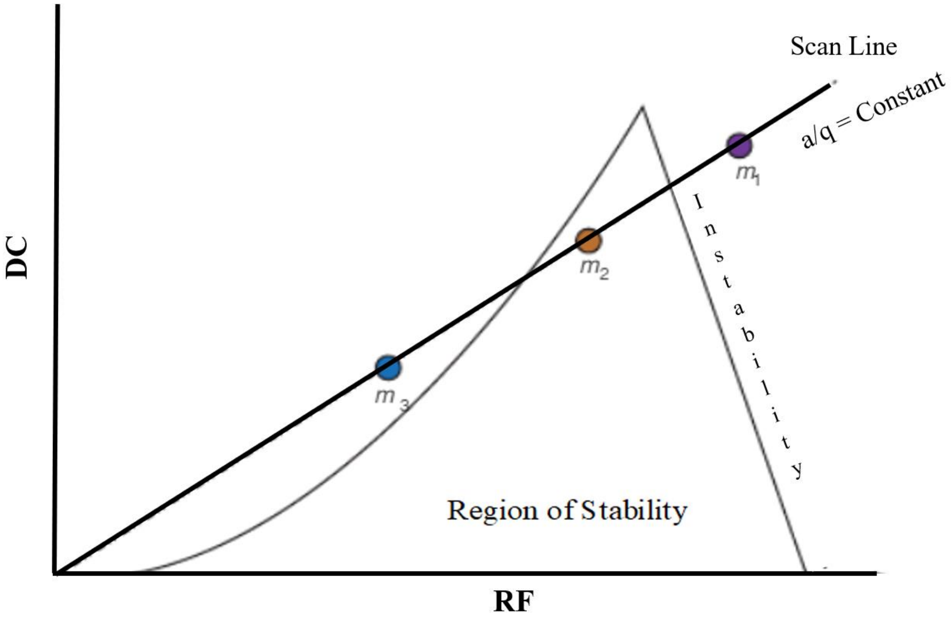


Figure 4. 2. Possible Trajectories for Ions after Ceballos et al 2017

Although the gasses detected are selected based on their mass to charge, m/z ratio, known amount of electric current and radiofrequency voltage (RF) passes through the rod with a DC offset that acts as a filter for masses detected or otherwise. It is essential to understand that the MS detects ions, not the atomic masses of the gases. The rods are significant in the design of the quadrupole MS because of the opportunity to adjust the designs based on the manufacturer's needs and justifications of physics, another characteristic in the quadrupole MS to fine-tune or tune the tool accordingly.

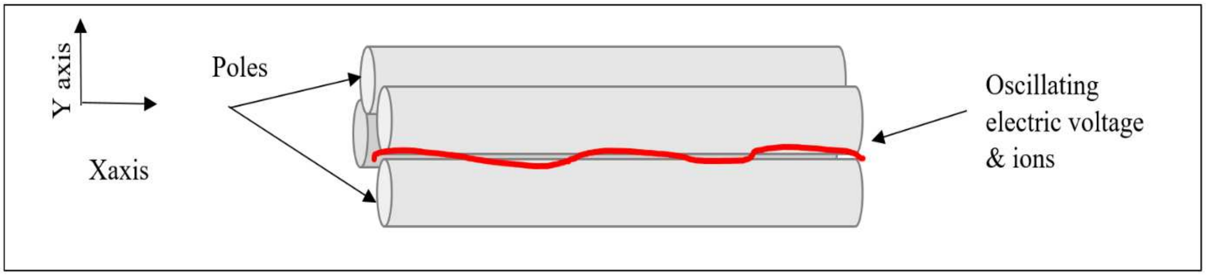


Figure 4. 3. Schmatic Picture of a Quadrupole Mass Analyzer

4.2. Binary and Mixed Standards

There are two types of standards used for this study; mixed and binary standards balanced in either Hydrogen (H), Nitrogen (N), Helium (He) or Argon (Ar). Mixed standards (table1) is the compressed mixture of more than one gas balanced at varied concentrations. It is also known as "blend." Binary standards contain the compressed gas of interest and its balance. The balance is necessary because it maintains equilibrium in the cylinder. Gases used as balance gases are typically inert and abundant in nature, ensuring the safety of compressed gases.

In this study, we used Airgas supplier of gases and a third party company guaranteeing purity measured at 99.99%. There are three gas standards used in this experiment; standard 1 (ST1), standard 2 (ST2), standard 3 (ST3). ST1 (Table1) consisted of lighter and heavier hydrocarbons balanced in Helium, ST2, and ST3 (Table 1) consisted of heavy and lighter hydrocarbon as well as non-hydrocarbons. Due to the inability of the supplier to produce $C_7 - C_{10}$, these gases are not tested. For this reason, the study tests only $C_1 - C_6$.

Table 1. List of Blends Used in this Study at Various Concentrations

Standard 1		**Standard 2**			**Standard 3**			
Component	**Concentration**	**Component**	**Concentration**		**Component**	**Concentration**		
1 Butene	10PPM	Benzene	50PPM	50.90PPM	Methyl Cyclohexane	199	2%	200PPM
1 Pentene	10PPM	ethylene	50PPM	49.10PPM	Benzene	505	2%	500PPM
1,3,Butadiene	10PPM	Helium			Ethylene	507	2%	500PPM
Acetylene	10PPM	Methylene	50PPM	49.60PPM	Helium	503	2%	500PPM
Benzene	10PPM	propylene	50PPM	50.70PPM	N- Octane	498	2%	500PPM
Ethane	10PPM	toluene	50PPM	49.70PPM	Propylene	503	2%	500PPM
Ethylbenzene	10PPM	Argon	100PPM	50.80PPM	Toluene	508	2%	500PPM
Ethylene	10PPM	ethane	100PPM	99.20PPM	Hexane	993	2%	1000PPM
Hexane	10PPM	Hexane	100PPM	100.90ppm	N- Heptane	997	2%	1000PPM
Isobutene	10PPM	N- Butane	100PPM	100.20PPM	Carbon Dioxide	3027	2%	3000PPM
Isoprene	10PPM	N Heptane	100PPM	107.2PPM	Argon	4964	2%	5000PPM
M Xylene	10PPM	N Octane	100PPM	101.2PPM	Ethane	4961	2%	5000PPM
Methane	10PPM	N Pentane	100PPM	100.4PPM	N- Butane	4969	2%	5000PPM
Methyl acetylene	10PPM	Propane	100PPM	99.90PPM	N- Pentane	501	2%	5000PPM
N-Butane	10PPM	Carbon Di Oxide	300PPM		Propane	4987	2%	5000PPM
N-Pentane	10PPM	Methane	0.10%		Methane	1.01%	2%	1%
O-Xylene	10PPM	Oxygen	1%		Oxygen	5.01%	2%	5.00%
P- Xylene	10PPM	Nitrogen	98.76%	Balance	Nitrogen	90.67%	2%	90.68%
Propane	10PPM							
Propylene	10PPM							
Toluene	10PPM							
Helium	Balance							

4.3. Flowline

The material for the connecting wire from the gas cylinders to the mass spectrometer is silicon, which is about half an inch in diameter. The choice of material and size of the connecting wires ensures fast and sufficient delivery of gases to the inlet valve of the MS. One other major equipment in this experimental study is the regulators for pressure maintenance. Two regulators are connected to the cylinder; as shown in figure 4.4 below. One of the regulators provides information on the amount of pressurized gas remaining, and the other regulator maintains the fluid pressure of gases at the inlet of the MS system.

Figure 4. 4. Mixed Standard Cylinder used in Experiment

4.4. Operational Conditions of Mass Spectrometer

Like most tools, the MS has its operating conditions. They include a fixed amount of voltage of about 70eV in the filament and average surface temperature at 80 degrees Fahrenheit. It also comes with a gas column with an operating pressure of 15 – 20 psia for gas analyses purposes. The MS also has a software characteristic providing the instrument an opportunity to be tuned. Tuning of the MS includes peak adjustment and positioning, which improves the resolution of results diminishing levels of uncertainties. This also offers the opportunity to adjust the dwell time and mass to charge ratio.

Figure 4. 5. Pressure Regulators used in the Study

4.5. Gas Standards and Fragmentation Pattern

The behavior of binary gases is understood through the MS fragmentation pattern. Information gathered on the style of fragmentation improves the interpretation of lighter hydrocarbon constituents. In order to ensure that resulting fragmentation pattern contains minimal discrepancies. Afterward, the study of the gas mixed standards at various concentration (10, 15,100, and 500) ppm are passed through the MS system as well. Another reason to understand the behavior of the lighter hydrocarbons at varied concentrations is to observe the detection limits of the MS. The use of mixed gas standards works to simulate the evolution of lighter hydrocarbons from the drilling mud, especially in the presence of other gases. All preparation of the gases studied were at purity levels of 99.9%, limiting any concerns of impurities existence in the gases.

The fragmentation of hydrocarbon studied was C1 through C6 and Propylene. In order to understand in detail, the fragmentation style, the first step is to know the preferred theoretical peaks for the studied hydrocarbons. Furthermore, the supposed peak (theoretical peak) is cross-checked with results from the MS, in order to determine any potential relationships between the expected and experimental mass to charge ratio peak. Afterward, the selected peaks amongst the tested and analyzed hydrocarbons are QA/QC ed to ensure that there is minimal interference within the group of lighter hydrocarbons.

Some of the precautions include ensuring that the gas allowed flows at 15-20 psi; otherwise, the filament may be damaged. There are many methods to ensure that the pressure never exceeds the required pressure. In the case of these experiment, the addition of an extra valve served the purpose (see Figure 4.6 for valves). The fact that we chose silica as a connecting line is also important. The choice of wire type connection for flow of gas is vital when using the tool because PVC pipes are known to absorb particular types of hydrocarbons unlike the Teflon/silicon membrane that remains inert to lighter (very volatile) hydrocarbon improving detection possibilities (Ferroni 2016). For this reason, gases detected will present lower statistical uncertainties.

4.6. QA/QC of Fragmentation Pattern

The fragmentation pattern is representative of the structures of the compounds analyzed. Typically, the signals are in millivolts. Signals are amplified and displayed as the spectra or fragment patterns. In order for the fragment pattern to be displayed, fragment ions must be present. The fragmentation ions are secondary ions of the parent – molecule ion. To achieve fragmentation of ions, we bombarded the molecules at about 50eV – 70eV, in which the upper bound of 70eV is the operational frequency for both the QMS tested in this research. There are different types of ions produced after the ionization process. Example of the ions are the parent ion, molecule ion, fragment ion, metastable ions, rearrangement ion, multiply charged ions, and negative ions (Down, 2006). The parent ion is the loss or removal of a single electron from the molecule. An example reaction that forms the parent ion is equation 2-1. The parent ions are the first group of ions in a system as well as the ions that depleted in the presence of fragmentation. Some chemical species do not produce parent ions; as a result, could lead to some false result in the mass of the molecule. The molecule ion is created as a result of losing two-electrons from the outer shell. Molecule ions could be rearrangement ions, fragment ion, or parent ions. As a result, there is no particular classification of ions formed by electron removal. The rearrangement ions are a subsect of molecule ions. These types of ions weigh less than the parent molecules. Also, this form of ionization occurs in the presence of a hydrogen atom in the saturated form or unsaturated. For this reason, rearrangement ion is typical when electrons impact hydrocarbons. This form of ionization is responsible for the base peak – peaks with the most and intense ion in a spectrum. Amongst all the forms of the fragmentation process the rearrangement ionization process uses the most energy.

4.7. Base Peak Selection

Base peak is ions with higher intensity on the spectra or result. The base peaks are made up of metastable ions or fragment ions. However, the intensity of the ions determines the percentage of the spectra occupied by the ions. For example, base peaks made of metastable ions make up of (0.1 – 1) % of the base peak (Kiser, 1932). In the case of the fragment ions, the base peak intensity is more with a relative intensity of 100. These base peaks serve as the guide in determining the precise mass to charge ratio of ions in a fragmentation process. The base peak technique also improves the qualitative preselection of ions before statistically analyzing the data for errors of uncertainty. This method of peak selection used in this study is as a result of the fragmentation overlap exhibited by the gaseous compounds. During the base peak selection, it is important to select peaks with minimal interference (from other ions) because of possibilities of more than one peak existing at the base mass. For the study, one of the main ways of enforcing minimal interference amongst base peak selection is quantification of percent mass of the gases at the initially selected peaks for the binary gas standards. Afterwards, the base mass peak is checked for %RSD associated with it at that mass before it is used in the gas mixed standards.

4.8. Verification of Peaks against Standards

Due to the fragmentation overlap, verification of gas standards against laboratory methods is crucial. The calibration method developed helps in the verification of mass peaks. Another reason for the base peak and verification processes is to create a precise spectrum of mass to charge ratio that corresponds to the compounds of interest thus improving real-time identification of lighter hydrocarbons on rig sites.

4.9. Limit of Detection

The calibration gas tested has concentration levels at (10, 15, 100, and 500ppm) with different constituents in different balances. These gases generate peaks at specific *m/z* ratios. The resulting fragment peaks are compared to preselected base peaks from the fragmentation pattern process. As long as there is minimal interference and peaks match the selected peak, the *m/z* ratio becomes appropriate for the hydrocarbon compound. Additionally, the most suitable peak is queried statistically by calculating the %Relative Standard Deviation (%RSD). The peaks of choice, the sensitivity of the tool, and repeatability of the experiment are QA/ QC steps that improve the reliability of the tool as well as its operations. All these steps are adopted in this study for the calibration of the QMS – thus establishing a robust methodology that operators and service personnel can use onsite.

4.10. Statistical Analyses of Data

The testing of the mass spectrometer resulted in the creation of datasets (Results and Discussion) with a statistical spread. As the QMS records and displays the detected signals in millivolts ranging from 10^{-9} – 10^{-13} filtering the data is essential for the statistical processing. In order to optimize the information from the gas measurement, simple statistical analyses including the sum of averages, variance, standard deviation, and the relative standard deviation (%RSD) are performed on data generated. In this study %RSD is set to be 10%.

4.11. Procedural Steps

The steps below outline how the calibration process was achieved for the QMS under study.

4.11.1. Set Instrument up and Tune the Instrument

The instrument is first set-up following the directions of the manufacturer. Multiple iterations of QA/QC are required to ensure successful set-up and follow up operation. The tuning of the instrument is possible through the software component of the MS, a part of the control system. Tuning is vital for the peak positioning, resolution, and detection period. Tuning of MS generates a file, which becomes useful on multiple devices over time.

4.11.2. Create a Folder for the Day on the Computer

The creation of a folder that provides the opportunity to store every information from each gas run through the mass spectrometer.

4.11.3. Run the Blank (air) through the Instrument

In order to run the blank through the instrument, both inlet and outlet valves are mechanically opened as well as from the computer. The primary purpose of blank running is to flush the system of any leftover gases which may be contaminating samples. Although blank running is useful in its ability to cleanse the system of contaminating gases, it is optional to record the blank.

4.11.4. Connect the Gas Balance

Gas balances serve as a method of communication in the MS, so gases are differentiable during analysis in the mass spectrometer. Besides serving as a form of calibration on type of gases, the balances help to maintain the analyte's integrity, especially under the compressed conditions. The system of choice for a gas introduction to the system was a silicon membrane flowline. The reason for the silicon membrane is because of its inability to absorb gases like PVC, ensuring that the gases are delivered to the inlet (Feronni et al. 2016).

4.11.5. Connect Gas Standard to the MS (Mixture or Binary)

The gas standards are the main contributors to the calibration of the mass spectrometer. The standards either mixed or binary, are passed through the MS after the balance. The membrane of choice remains the silicon flowline, so no gases are absorbed, ensuring 100% introduction of gases and its components to the mass spectrometer.

4.11.6. Run Gas at Pressure of 15 – 20 PSI through the System

There are two interchangeable steps to follow in order to ensure that gases passed through the MS are maintained at 15- 20 PSI. They include flushing the system with the gas balance of choice by uncapping the exhaust of the tool for about 5 – 8 minutes, or capping the exhaust of the instrument to save gas or connect a tube from the exhaust to the fume hood. Also, the use of two gas valves (Figure 4.6) ensures that analyte gases are at 15-20 PSI so that the instrument is not damaged.

4.11.7. Scan and Record Data

Records all the mass to charge ratios scanned by the quadrupole mass analyzer are saved on the computer. The scanning and recording of the data can last as long as is needed; however, a recommended time of ~ 5 – 8 minutes ensures the efficiency in detection of the ions by the MS. In order to stop recording, uncap the exhaust if it was capped then connect the tube to the exhaust and the fume hood. Lastly, turn off the gas cylinder and wait until the gauge reads 0 PSI to disconnect, so no gas leaks occur. Repeat the procedure for all gas standards (mixed and binary) to ensure valid calibration of the tool before field use.

CHAPTER 5. RESULTS AND DISCUSSION I LIGHTER HYDROCARBONS

All gas standards, both binary and mixed standards are analyzed for best peak, average standard error, percent relative standard deviation and calibrated masses of the gases. The fact that we were able to minimize the relative standard errors to acceptable values (< 10%) imply that these instruments and the calibration procedures developed will be able to detect the lighter hydrocarbons at fairly low concentrations – a challenge that the oil and gas currently faces. In this chapter we present the results from the calibration procedure developed in Chapter 4 for the lighter hydrocarbons. Chapter 6 presents the results from the heavier hydrocarbons and non-hydrocarbons,

5.1. Methane

Methane is the shortest alkane group with a molecular mass of 16g/mol. It is also a volatile organic compound- it evaporates at atmospheric pressure. Methane is also a good indicator for wetter gas reservoirs. It is one of the simplest hydrocarbons compounds with four hydrogen atoms to one carbon atom. Besides being a hydrocarbon, methane is a greenhouse gas that makes up about 1.8% of the atmospheric gas because of the lower density being less than air. Due to the lightness of the gas, it burns once in contact with oxygen and slightly dissolves in water. It is also a very flammable gas, because the longer the gas is in contact with air or a form of heat the more likely it is to ignite into flames or burst like a rocket if in a compressed state. These characteristics of methane are some of the significant reasons for monitoring methane real-time on rig sites.

The quadrupole mass spectrometer fragments the compound as soon as the gas arrives at the mass analyzer. In the test leading to the spectra of methane, the gas balance used was argon (inert) so that methane properties were maintained. Figure 5.1 shows that the methane compound fragments into molecular masses 14, 15, 16, 17, and 18. However, the theoretical molecular mass of methane is16.04 g/mol. Figure 5.1, reinforces that the fragmentation of compounds is non-conformal to the known molecular masses which is another reason for developing a robust calibration method as well as validating the use of gas standards. In this case, methane is at mass 15 which is the appropriate peak candidate for the study. Another point to consider is that the selected peak must have minimal interference with other hydrocarbons during fragmentation. Methane 15 demonstrates a minimal interference and is the peak of choice.

A major guiding factor for the peak selection was the compatibility of the gases passed through the mass spectrometers tested. Both mass spectrometers were expected to detect the presence of the gases for the peak candidate to be 15. According to Figure 5.1, mass 16, 17, and 18 were detected by mass spectrometer 2 only, which automatically discredits the peak at 16, 17, or 18, deductively guiding the fact that mass 15 due is a good peak choice due to its relative abundance mass and response factors for both mass spectrometers 1 & 2.

According to Figure 5.1, methane balanced in argon has two central base peak potentials at 14 and 15. However, based on the % mass recorded by both mass spectrometers, the decision to use methane at 15 is reliable. In addition to the satisfying MS responses, the difference in the detected % mass for methane at 15 between both mass spectrometers is ~ 4%, indicative of the similarity of MS 1 & MS 2. This also establishes % mass difference as of the analytical methods to justify similarity between the mass spectrometers.

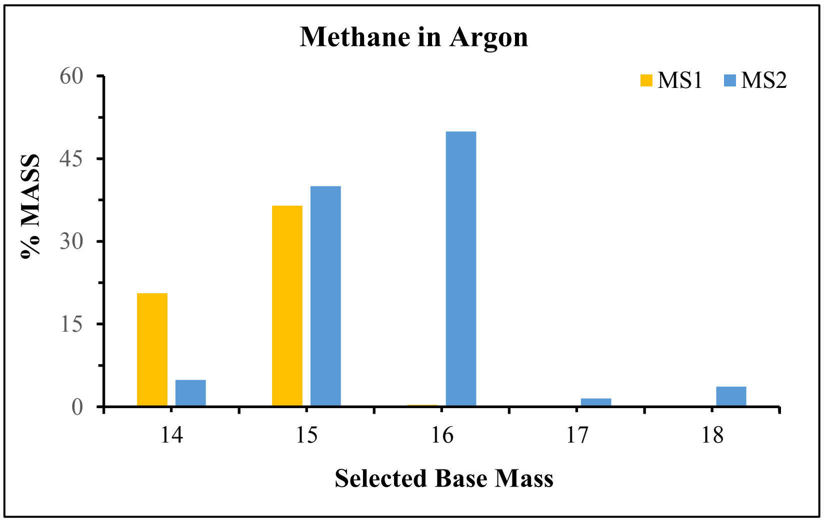


Figure 5. 1. Spectra of Methane in Argon

5.2. Ethane

Ethane is the second member of the alkane group with a molecular formulation of C_2H_6 and molecular mass of 30.070 g/mol. It is also the second shortest hydrocarbon chain of the alkane group. The molecule ethane is a volatile organic compound with boiling and melting point at –127.3°F and -297°F respectively. Based on these properties, ethane can act as refrigerant and plant metabolite. It is also colorless and odorless gas with the characteristic to easily ignite. Also, ethane acts an asphyxiator because of its denser characteristics in comparison to air. One primary reason for the monitoring of the gas at the wellsite is also vital to ensuring a safe work environment for the personnel on sites. In the petroleum industry, ethane is a significant indicator of wetter gas reservoirs. With the shale oil boom in the continental United States, there has been significant growth in ethane production. Besides the significance of ethane in the petroleum industry, the chemical industry fracs the natural gas liquid to make plastic.

In this experimental study, ethane balanced in nitrogen and argon is the candidate for base peak selection. Like methane at 15, ethane fragments, however, it fragments much more than methane making the peak selection process tedious. Based on our results (Figures 5.2 & 5.3), ethane is detectable from masses 25, 26, 27, 29, and 30. However, it also fragments into the mass 15 indicative of the presence of methane. The mass spectrometers' responses (Figures 5.2 & 5.3) show the relative abundance of ethane at different molecular masses making the selection of the most suitable peak for ethane a far more challenging problem. Based on the result displayed in the observed spectra, the ethane sample in both balances are fragmented, however, the relative abundances are varied. Ethane fragment is detected in abundance when balanced in argon. Like methane, there are multiple candidates for base peak selection. The selected mass for ethane 26 is favorable to both mass spectrometers as well as the components of the gases detected. The masses 27, 29, and 30 could potentially be a selected peak for the masses; however, nitrogen was observed to fragment at 29. For this reason, a peak preceding the masses 29 & 30 were favorable to avoid interference from nitrogen should it be present in the gas stream. A similar principle based on avoiding interference from similarly weighted ions is used for the remainder of the study in choosing base mass peaks – the base masses should be detectable by both MS, they should have minimal interference, and they should have masses less than the interfering or theoretical masses of the gases that are being detected and quantified.

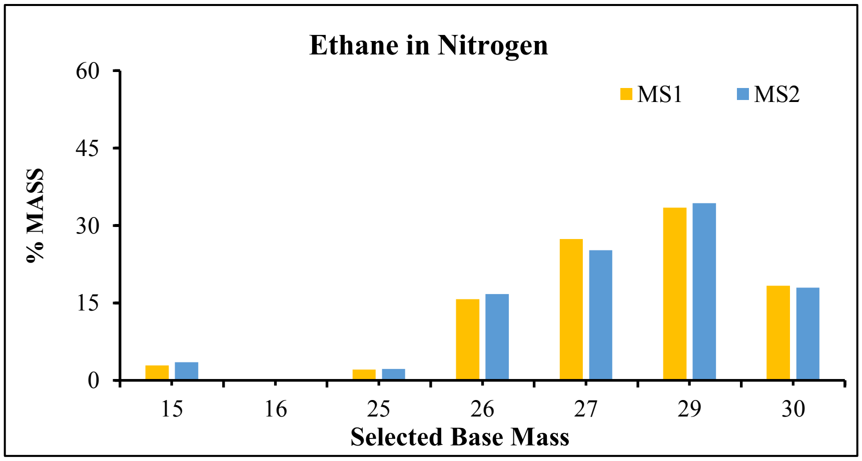


Figure 5. 2. Spectrum of Ethane balanced in Nitrogen

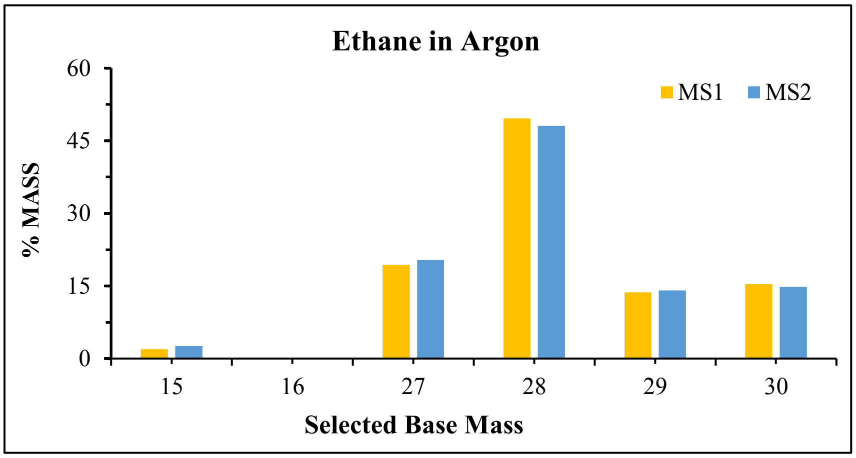


Figure 5. 3. Spectrum of Ethane balanced in Argon

5.3. Propane

Propane is a three-carbon alkane. It comprises of three carbon atoms and eight hydrogens. It has a molecular mass of 44.09 g/mol with a melting point at – 187.7^{o}F and boiling point at -42.25^{o}F. It is typically a compressed gas used for cooking but is also a by-product of refinery streams. Due to propane's ability to be liquefied, propane gas exists dissolved in crude oil. As a result, it provides the opportunity to be evolved from the drilling fluid at the surface of the wellbore allowing for the potential to analyze the gas using the Mass Spectrometer. Based on results shown in Figures 5.4 & 5.5 below, it is challenging to decipher the compound and its corresponding molecular mass – in this case, propane.

Propane fragments into 15, 16, 25, 26, 27, 30, 39, 40, 41, 42, 43 and 44. Overall both mass spectrometers responded to the propane gas present in the MS, which helped lead to the decision to select mass 41 for propane. In other words, the presence of 41 means that there are traces of propane. In addition to the contributing factor of the molecular mass present, longer chains such as propane act to evolve gases at the earlier stages, just like in figures 5.4 & 5.5 like ethane, the balance for propane does not affect the behavior of the gas of interest, which in this case is propane.

The base peak for propane is 41, according to figures 5.4 – 5.5, which contains mass spectrometric responses from the components of gases detected by MS1 & MS2. In the case of propane, the peaks are less visible compared to the other compounds analyzed, with masses at 40, 41, 42, 43 & 44 — the masses are potential representatives for propane in the mass spectrometer. Due to the importance of using peaks with minimal interference from other components capable of fragmentation at the masses 42, 43 and 44, propane 41 is the best peak. Also, the validation of the instruments similarity in designs becomes relatively quantifiable based on the detection of gases.

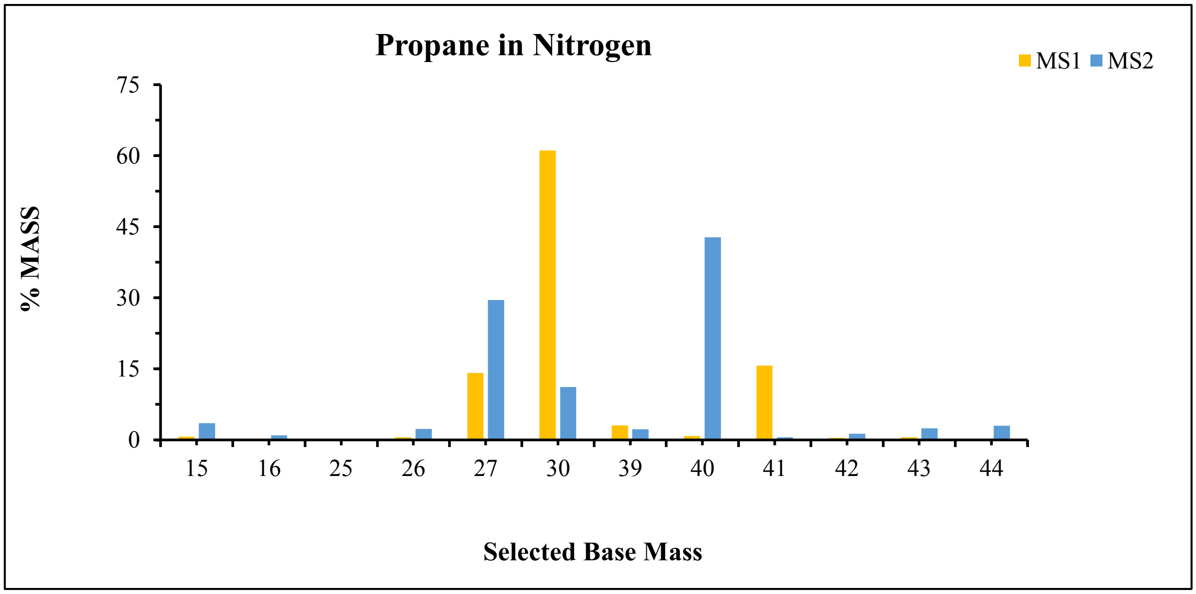


Figure 5. 4. Spectra of Propane in Nitrogen

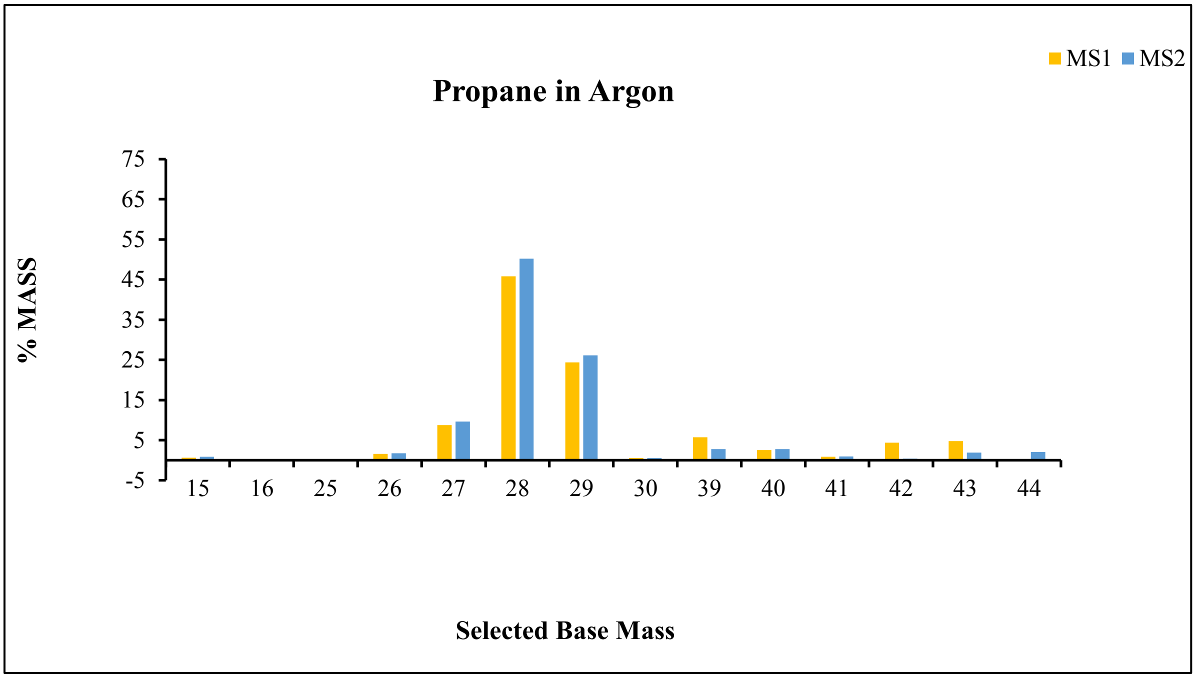


Figure 5.5. Spectra of Propane in Argon

5.4. Butane

Butane is a four-carbon compound alkane (C_4H_{10}) with the boiling and melting points at 30.2°F and 216.4°F respectively. It also serves as a blend with propane and is known as the liquefied petroleum gas (LPG). Again, Butane can exist in the liquid and gaseous state – as a result, is dissolved in the drilling fluids at a higher pressure and evolved at lower pressure and temperature. Based on the characteristics of butane as an alkane, it is also possible to capture it on rig sites and analyze through a mass spectrometer. Also, butane serves as a form of energy for campsites, lighter fluids, and cooking. Unlike methane through propane, butane has a smell similar to gases.

Butane follows the trend of the other alkanes by fragmenting from methane 15 through 59 but selected mass 43 as the N- butane peak. However, the peaks at methane are smaller compared to those analyzed against ethane and propane. This characteristic serves as an indicator that longer hydrocarbon chains fragment slower, ensuring a more accurate output of data. Butane's peak is at 43, for mass spectrometers 1 & 2 with a difference in % mass between the mass spectrometers averaging about 11%. Although the % mass difference is high, it is not a positive reflection on the sensitivity of the tool. Instead it reflects the ability of the tool to detect butane in particular, especially at lower concentrations. The significant disparity between the % mass detected by the MS 1 and MS 2 is independent of the tool's functions in gas detection.

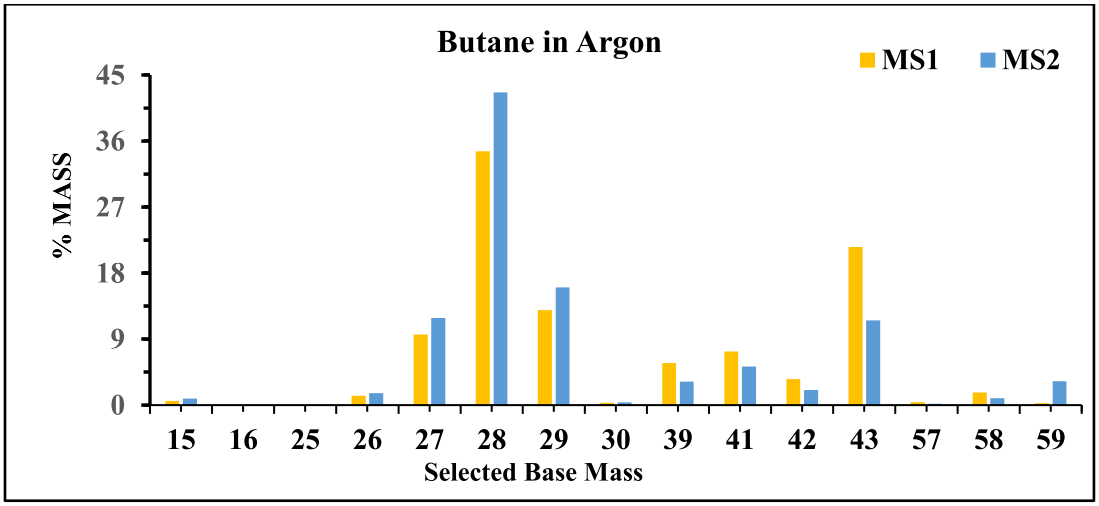


Figure 5.6. Spectra of Butane in Argon

5.5. Pentane

Pentane is a five alkane; C_5H_{12} hydrocarbon with boiling and melting point at 96.98°F and -201.6°F respectively. Pentane is the second-longest chain studied in this experiment with a molar mass of 72.15 g/ mol. Although the theoretical mass of pentane exists at 72.15, the experimental deduction for this study uses 73g/mol for identification of pentane. In Figure 6.8 below, at 72, pentane is not detected by MS2, but at 73 both MS 1 & 2 could detect the five-chain hydrocarbon. Thus, 73 is chosen as the base mass of pentane. The selection of pentane is guided and reinforced by the detections of the gas by both MS1 & MS 2 - a significant indicator for higher confidence on the chosen base peak. As observed in the results of the previous tests and results, the balance is inert. In the case of pentane's peak selection, the mass is at 73 for both tools; however, there were no multiple candidates to beat, resulting in a faster and decisive peak selection process for the five-carbon alkane.

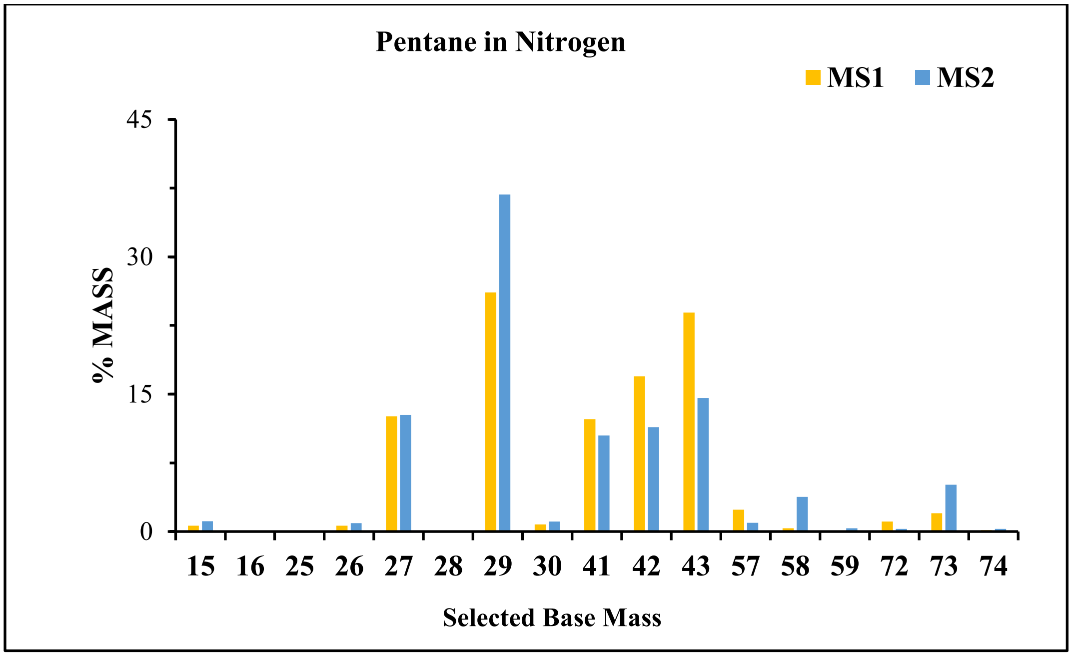


Figure 5. 7. Spectra of Pentane in Nitrogen

5.6. Hexane

The longest and last hydrocarbon; C_6H_{14} alkane with a molecular mass of 86.18 g/mol is also tested in this study. Besides being a longer chain, hexane is also a neurotoxin and nonpolar carbon chain. It has the highest boiling point recorded at 154.4^0F and no melting point. The absence of a melting point indicates that the substance does not change state. According to the spectra of hexane, it is evident that the inability for the chain in the alkane group to fragment represents the preferred state of the compound as a liquid. In the spectra (Figure 5.9 below), there are no fragments at methane 15 and 16, as well as ethane but begins to present of ions in abundance at 39 – a fingerprint for argon, the inert balance. Although there are spectra at 41, 42, 43, 57 and 58, the mass peak selection has a minimal interference at 87. The peak selection for hexane was one of the easier ones because of the lack of other masses with fragments.

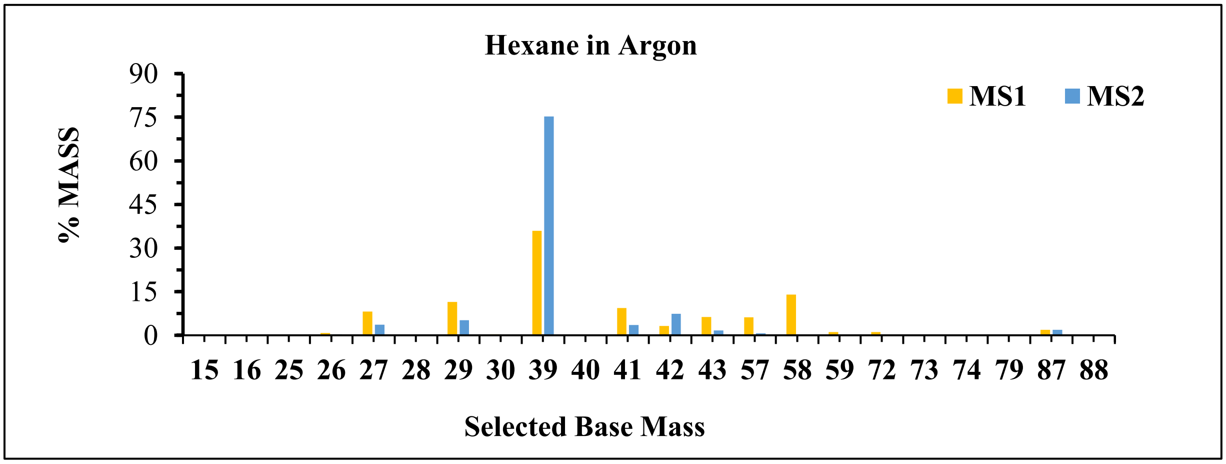


Figure 5. 8. Spectra of Hexane in Argon

Fragmentation of binary standards is an essential step in creating a calibration system for the MS. Understanding fragmentation patterns guides decisions in selecting the initial base peaks of the hydrocarbons studied. The use of binary standards to the hydrocarbon served as a pre-screening sensitivity scan. The fragmentation process revealed that each MS behaved differently but was consistent within itself. The two MS however behaved similarly within % mass difference error for the six hydrocarbons discussed in this chapter.

One of the major challenges faced in MS analyses of live fluids is that of deconvolution. Deconvolution occurs when base masses overlap due to fragmentation of components. In gas mixtures this generates a problem, viz. which base mass repesents what component, and how much of that component? For example, if propane fragments into methane, ethane and propane masses, then should we conclude that the gas is only propane, or should we conclude that the gas is a mixture of methane, ethane and propane? Because the fragmentation occurs due to ionization of the gas in the MS – are the methane, ethane and propane components registered because of the ionization process or because they were originally present in the gas stream from the well. The calibration method developed in this study addresses and resolves this problem by identifying the base mass peaks that need to be used to detect C1-C6 components irrespective of deconvolution. Our results suggest that using methane 15, ethane 26, propane 41, butane 43, pentane 73 and hexane 87 base masses can help detect true hydrocarbon components from gas streams in live well fluids. While we solved the deconvolution problem by plotting the % masses, the %RSD provides the opportunity to quantify the response of the tools to the binary gas standards, which serve as a foundation for the mixed gas standard calibration process.

Besides the deconvolution problem, the limit of detection of the gases was a challenge as well. It is a critical contributor to development of the calibration process of the mass spectrometer because of the trace quantities of gases measured on the field. In order to account for the variability, all gas mixed standards containing the tested binary compounds focused on upper bounds of concentration values. The concentrations were 10, 15, 100, and 500 PPM. According to the figures, 5.8 – 5.13, the % relative standard deviation (%RSD) versus the concentrations were determined. In the analyses below, the observed pattern is that lower concentration gases (~10 – 15 PPM) have higher %RSD values. The values were an average of ~2% greater than RSD values of higher concentrations (100 – 500) PPM because, at a higher concentration, the mass spectrometric analyses of gases becomes easier. At higher concentrations, the mass spectrometer becomes populated with gas that quickly fragments to produce abundant ions, which as a result decreases the variations in numbers and errors or RSD values. Estimating the %RSD values for different ranges of gas concentration helps determine a metric for uncertainty, given that lower concentrations of lighter hydrocarbons can have higher uncertainty in measurements.

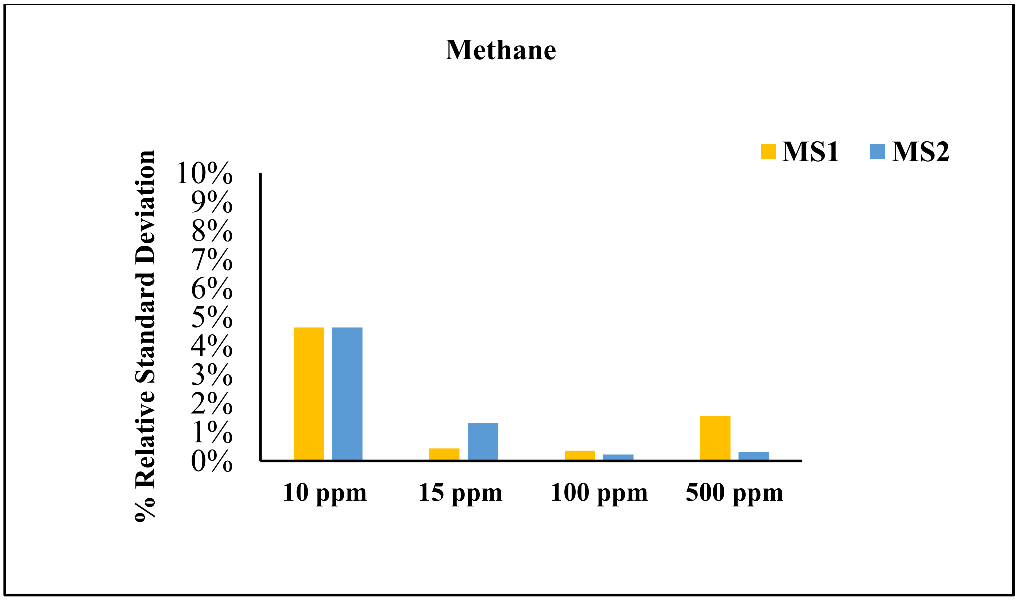


Figure 5. 9. Precent Relative Standard Deviation versus Concentration of Methane

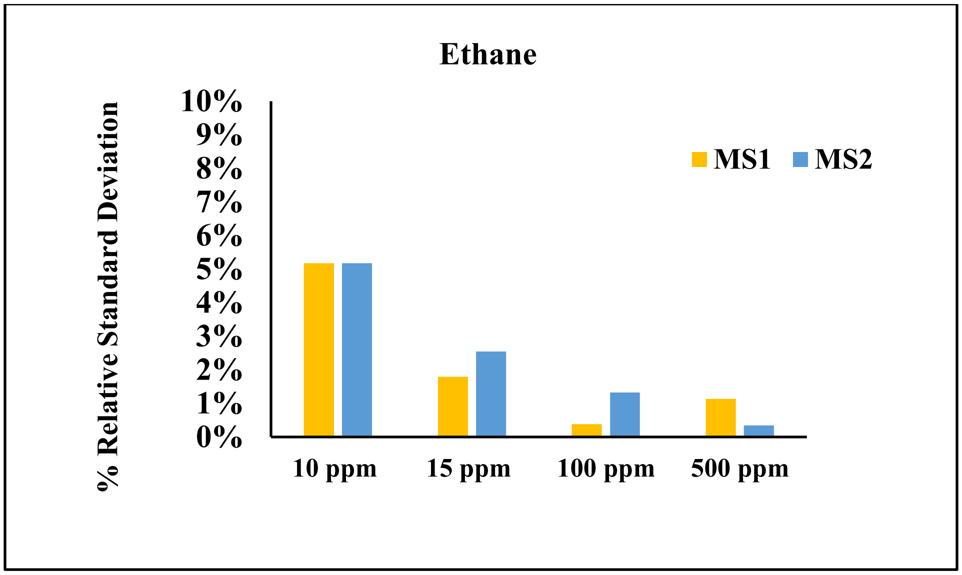


Figure 5. 10. Precent Relative Standard Deviation versus Concentration of Ethane

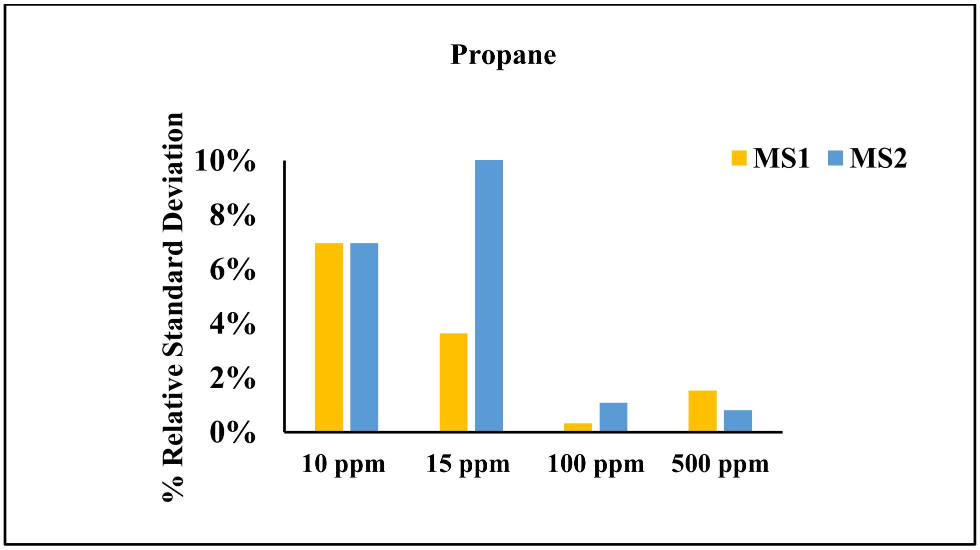


Figure 5. 11. Precent Relative Standard Deviation versus Concentration of Propane

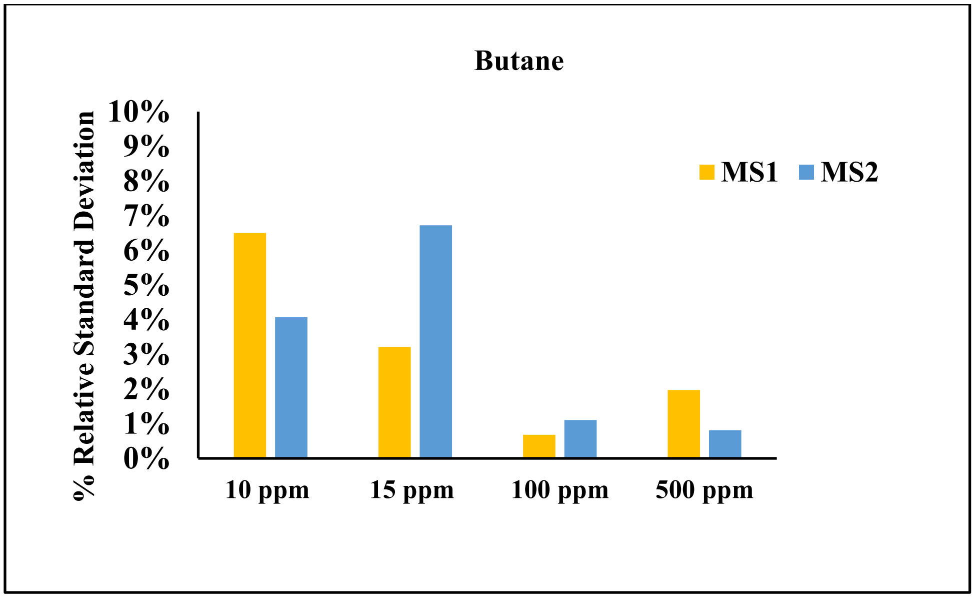


Figure 5. 12. Precent Relative Standard Deviation versus Concentration of Butane

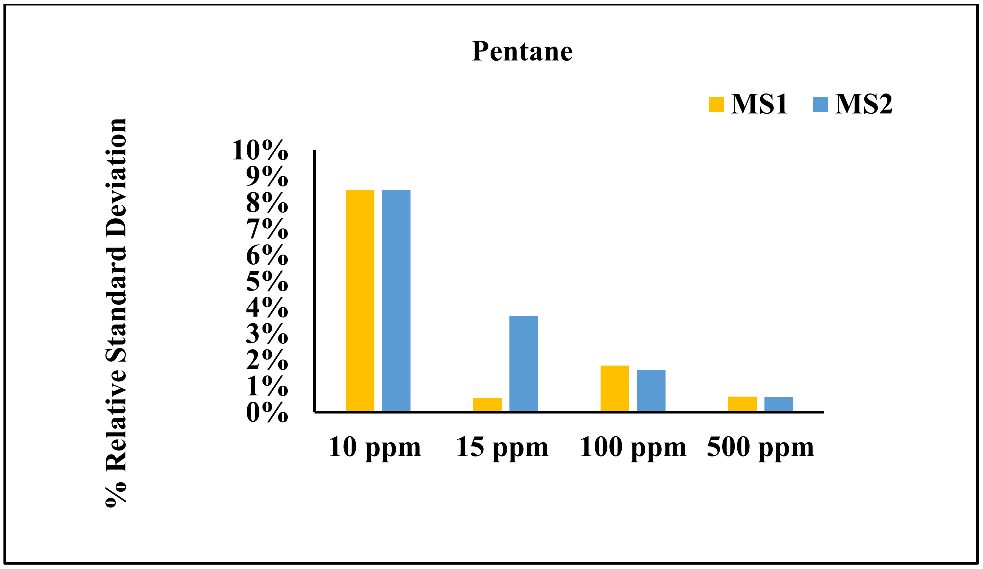


Figure 5. 13. Precent Relative Standard Deviation versus Concentration of Pentane

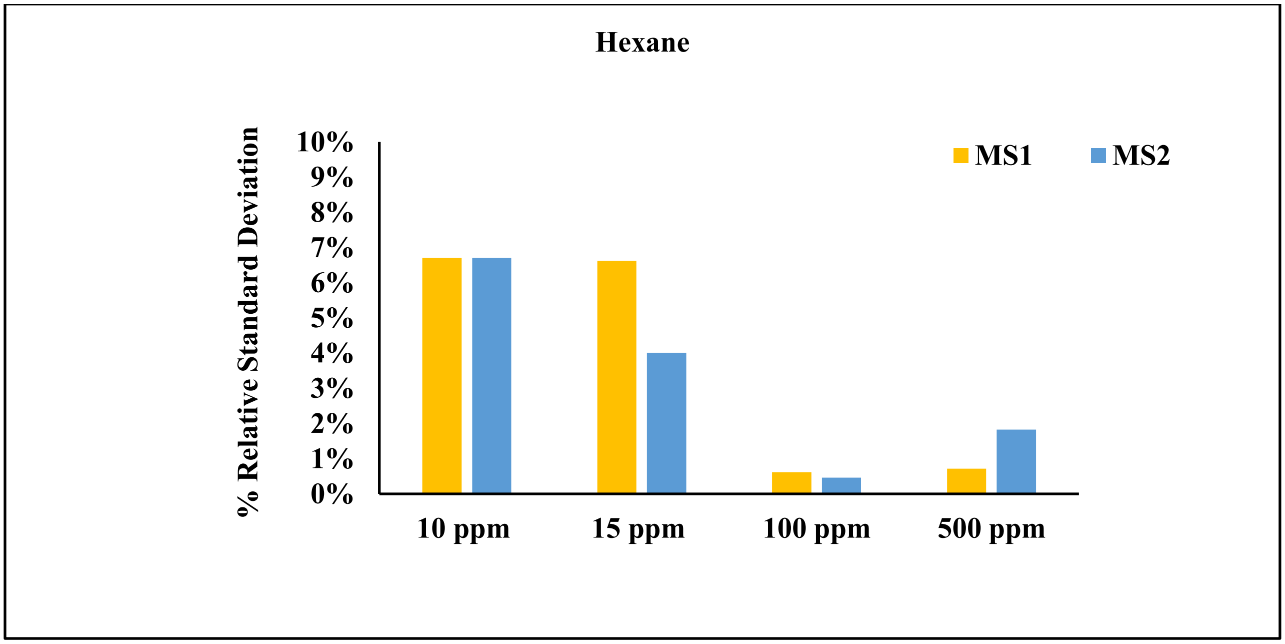


Figure 5. 14. Precent Relative Standard Deviation versus Concentration of Hexane

5.6.1. Average Mass Spectrometer Binary Gas Standards Response for MS1 and MS 2

In this study, each gas standard was run for 3 trials. The responses were averaged for each of the trials, and then averaged for each of the gas standard tests for both the MS. This final average is called the average mass spectrometric response for the two instruments tested. In order to validate the calibration process, address and reduce uncertainty and ensure repeatability, the average mass spectrometric responses were determined. Sensitivity must be measurable and reproducible; otherwise, the improvement of the tool's design becomes essential. All gases used in the study were the same for both the instruments. As a more natural method of testing sensitivity before statistical analysis, binary gas standards used in the mass spectrometer were tested and results observed for consistency of gas detection from methane through hexane. Results were found to be consistent for both the MS.

In addition to the interpretation of the data received as output from the gas detection in the mass spectrometer, statistical methods like average, standard deviation, and relative standard deviation were used to analyze the data. Based on past exploratory use of the mass spectrometers, 10% and 5% are boundaries conditions set for the % relative standard deviation. The limits 10% and 5 % serve as a guide for higher and lower concentrations. Lower concentration gases were difficult to detect and thus a higher error margin is used. Lighter hydrocarbons at rig sites would occur in trace elements, which typically is ~ (10 – 15) PPM. At such concentrations, detection of gases becomes a challenge; for this reason, the sensitivity of the MS is prioritized and validated through the % RSD method.

5.6.2. Average Mass Spectrometer Mixed Gas Standards Response for MS1 and MS 2

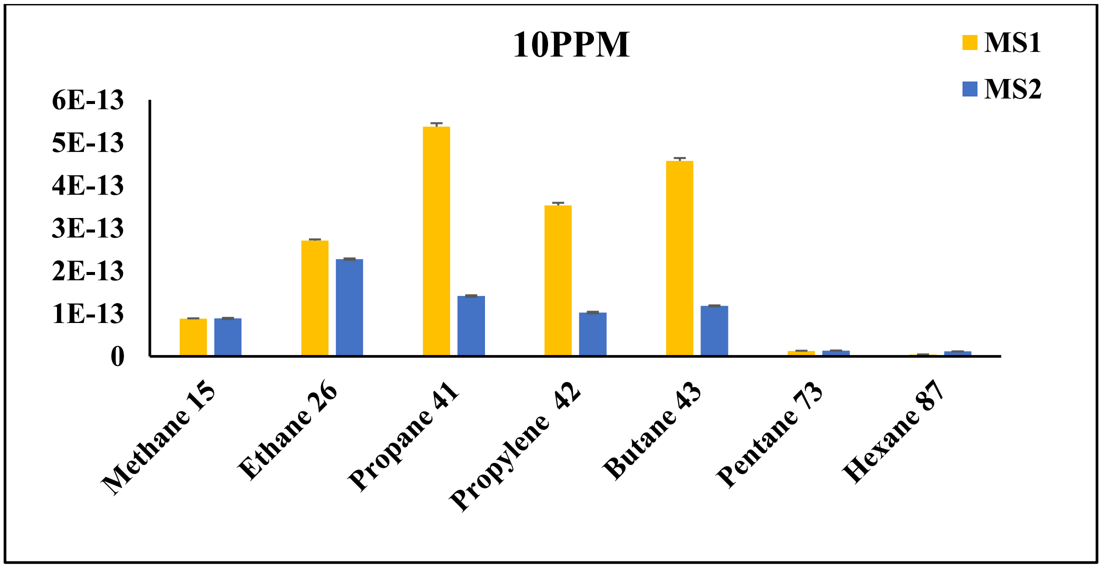


Figure 5. 15. Average MS response for 10ppm mixed standard in MS1 & MS2

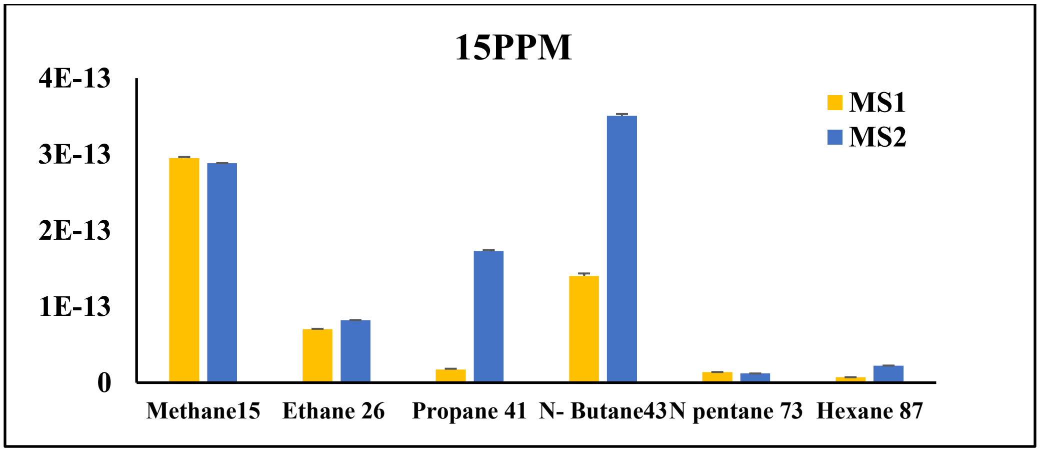


Figure 5. 16. Average MS response for15ppm mixed standard in MS1 & MS2

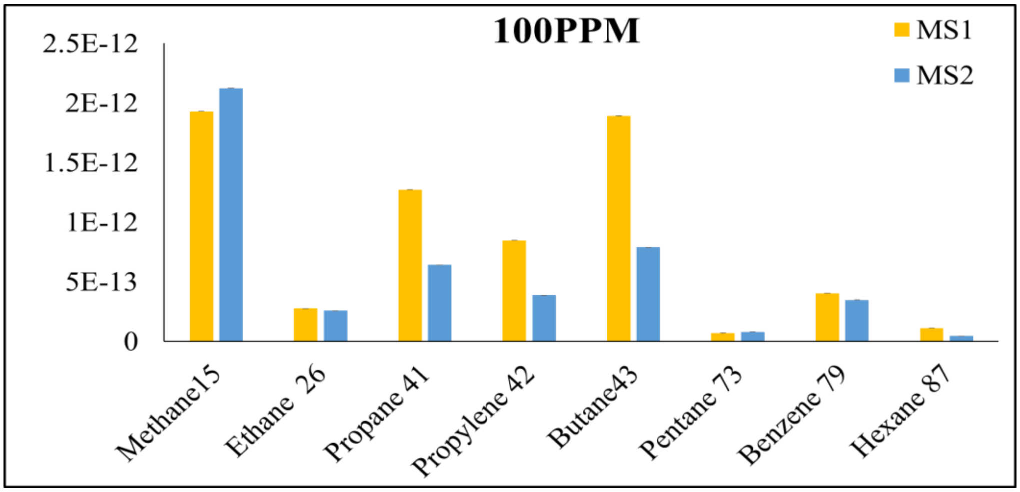


Figure 5.17. Average MS response for 100ppm mixed standard in MS1 & MS2

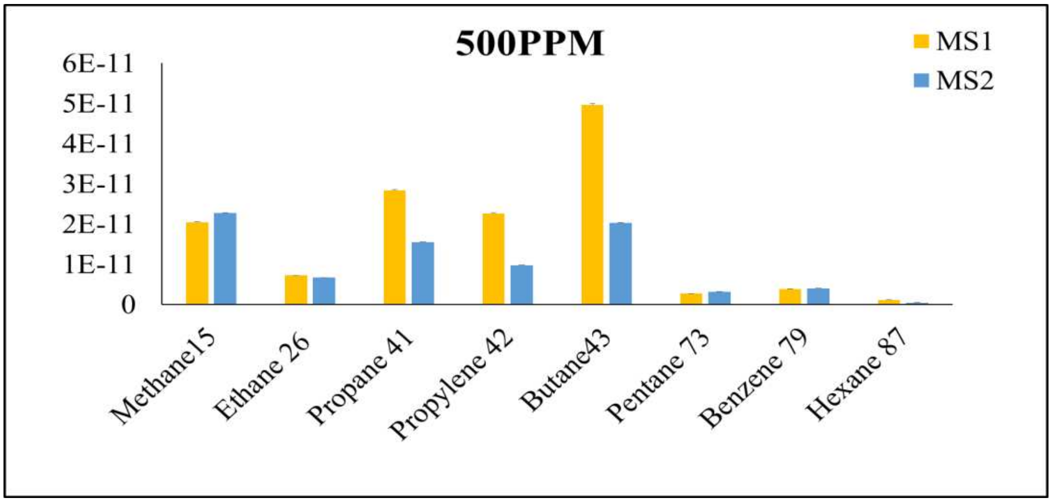


Figure 5. 18. Average MS response for 500ppm mixed standard in MS1 & MS2

Another conclusion of this testing and calibration process is that the base mass peak selections from the binary standards facilitated the analyzes from the mixed standards. The combination of knowledge from binary fragmentation and base peak selections improved confidence in the representative masses selected for calibration. The average of gas mixed standards, followed by standard deviation and the %RSD calculation for each selected base peak adds to the reliability of the detection capability of the mass spectrometers. During the process of calculating %RSD, the error limit of five to ten percent RSD served as a decision guide for testing sensitivity, and whether the best peak is indeed the best. As shown in the figure (5.14 – 5.17), the deviation from the average is minimal in each case, which in turn validates the reliability of the peaks selected for each MS and the mixed standards. The figures (5.14 – 5.17) also demonstrate that the MS instruments are highly responsive and sensitive irrespective of the concentrations of the blend.

5.7. Relative Standard Deviation versus Concentration

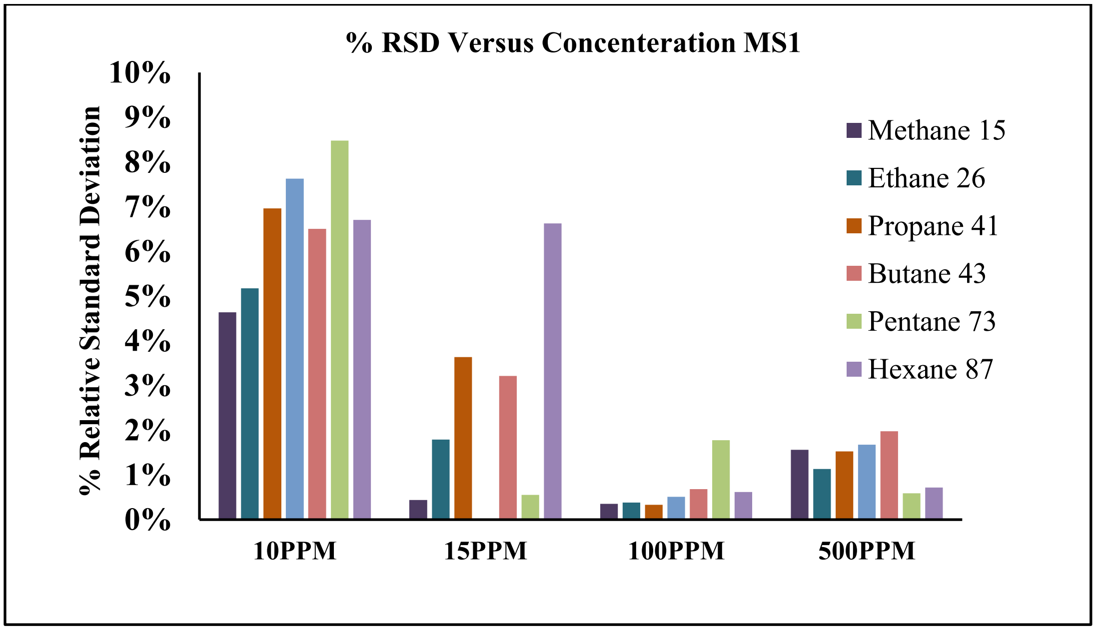


Figure 5. 19. Precent RSD versus Concentration for Gas Mixed Standard MS1

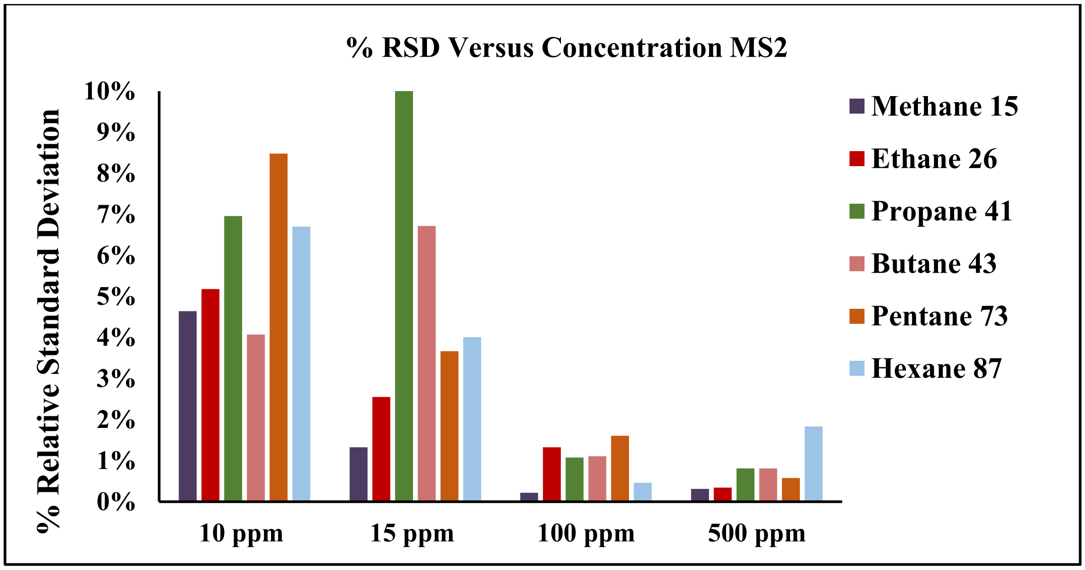


Figure 5. 20. Precent RSD versus Concentration for Gas Mixed Standard MS2

Figures 5.19 – 5.20 represents the cumulative responses of the mass spectrometers individually analyzed as MS 1 and MS 2. The results in figures 5.19 – 5.20 support the results of RSD values versus concentrations above. The plots (RSD versus Concentration) showed that higher concentrations had lower variation from the average MS response, which the cumulative plots above reinforce. The fitting of a curve on the cumulative responses of each class of concentration 10, 15, 100, and 500 PPM is normal in distribution reflecting natural composition/population of data. However, fitting of one curve over the entire plots (5.19 – 5.20) projects the data as slight skewed to the right, indicating that gas component detection is greatly affected by concentration.

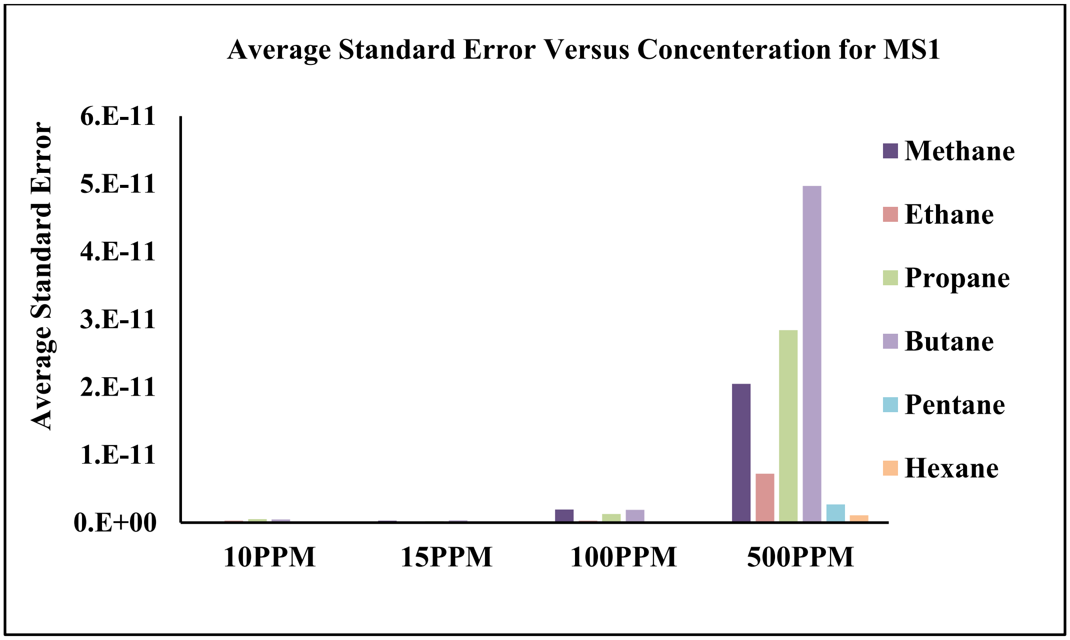


Figure 5. 21. Average Standard Error versus Concentration for Gas Mixed Standard MS1

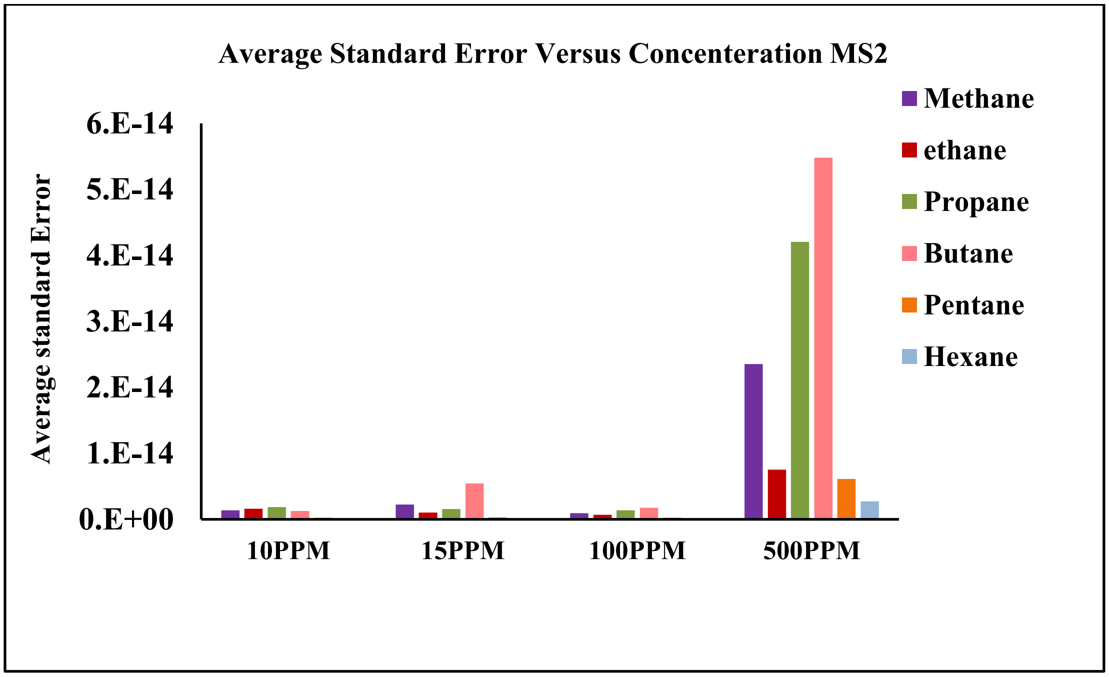


Figure 5. 22. Average Standard Error versus Concentration for Gas Mixed Standard MS2

Figures 5.21 - 5.22 above show the cumulative responses of the gas behavior in both the mass spectrometers 1 and 2. According to the cumulative graphical representation of percent relative standard deviation versus concentration at 10, 15, 100, and 500 PPM, the higher the concentration, the lower the % relative standard deviation. It also implies the reliability and accuracy of the tool increases by the percent standard deviation for the specific gas at either 10, 15, 100, or 500 PPM.

5.8. Standard Error Plots of Lighter Hydrocarbons Gases in the Mixed Standards

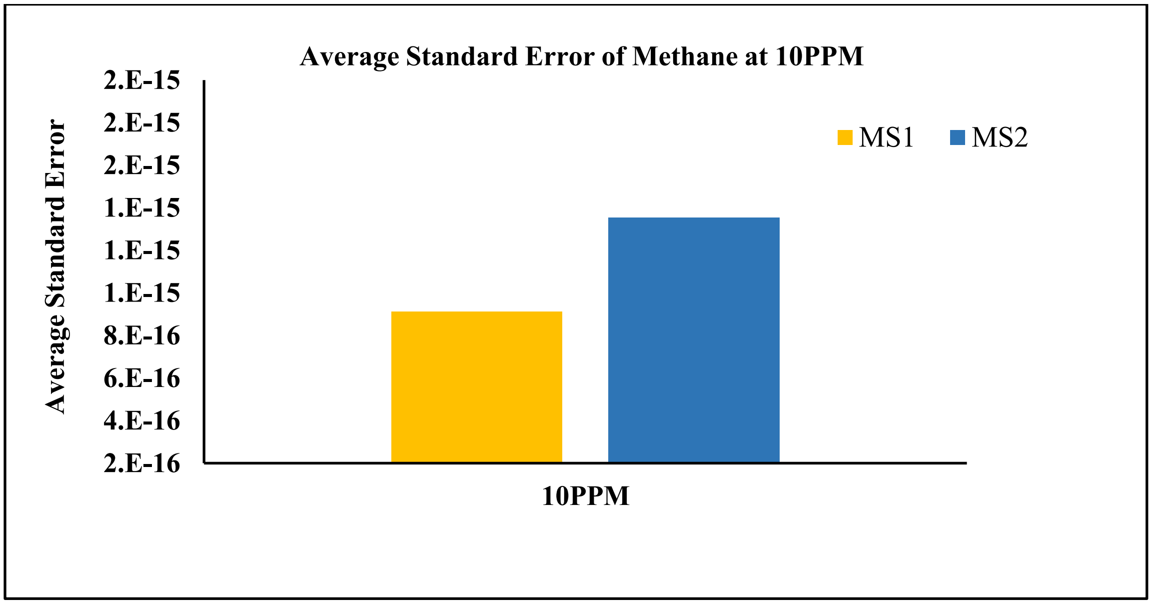


Figure 5. 23. Average Standard Error Methane in MS1 and MS 2

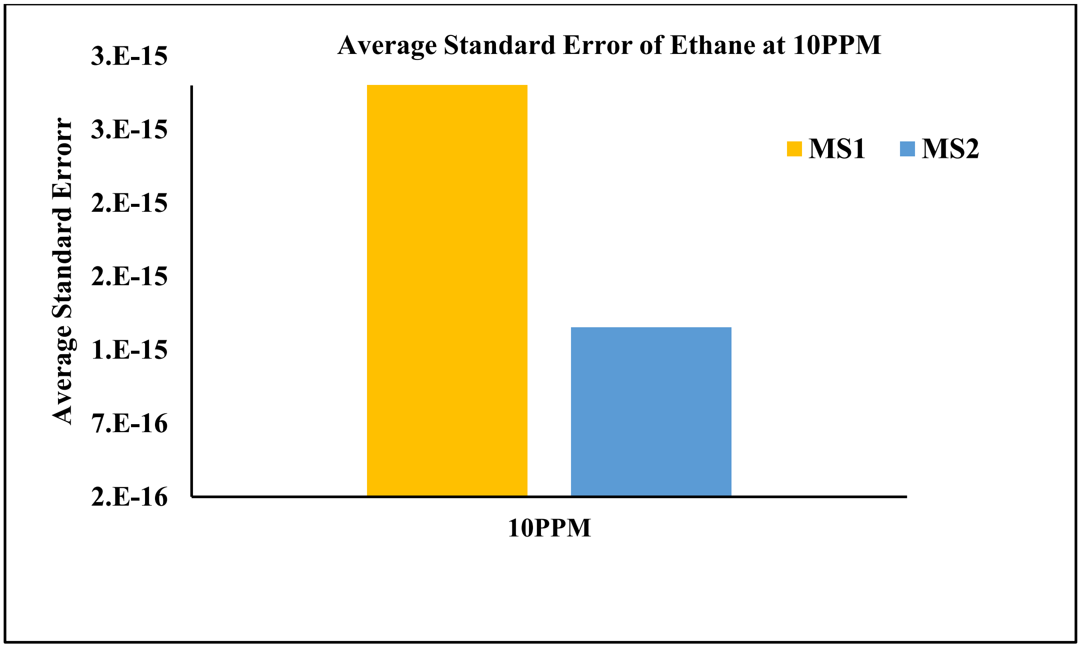


Figure 5. 24. Average Standard Error Ethane in MS1 and MS 2

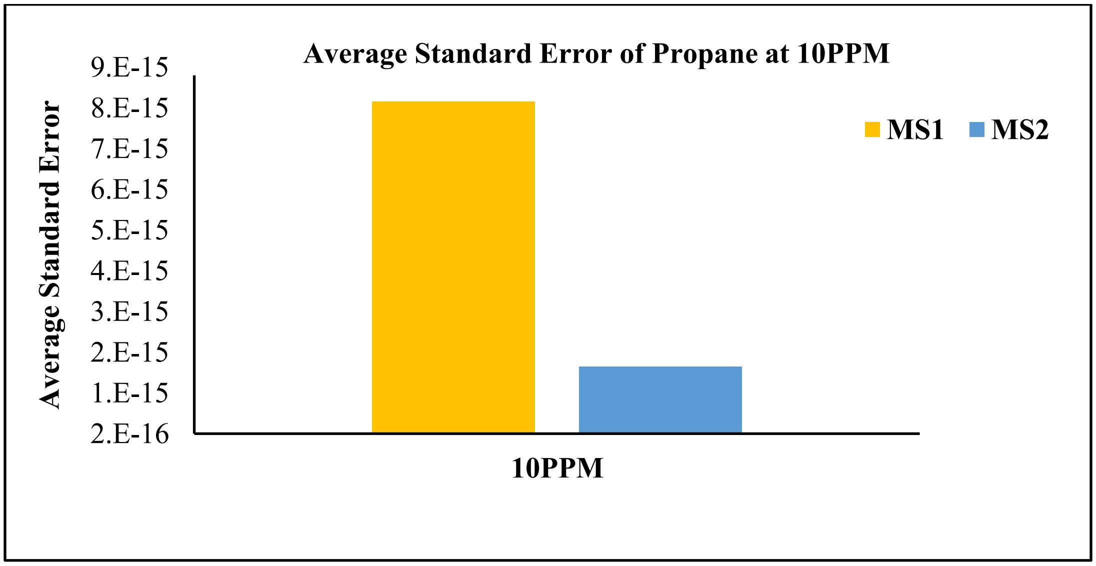


Figure 5. 25. Average Standard Error Propane in MS1 and MS 2

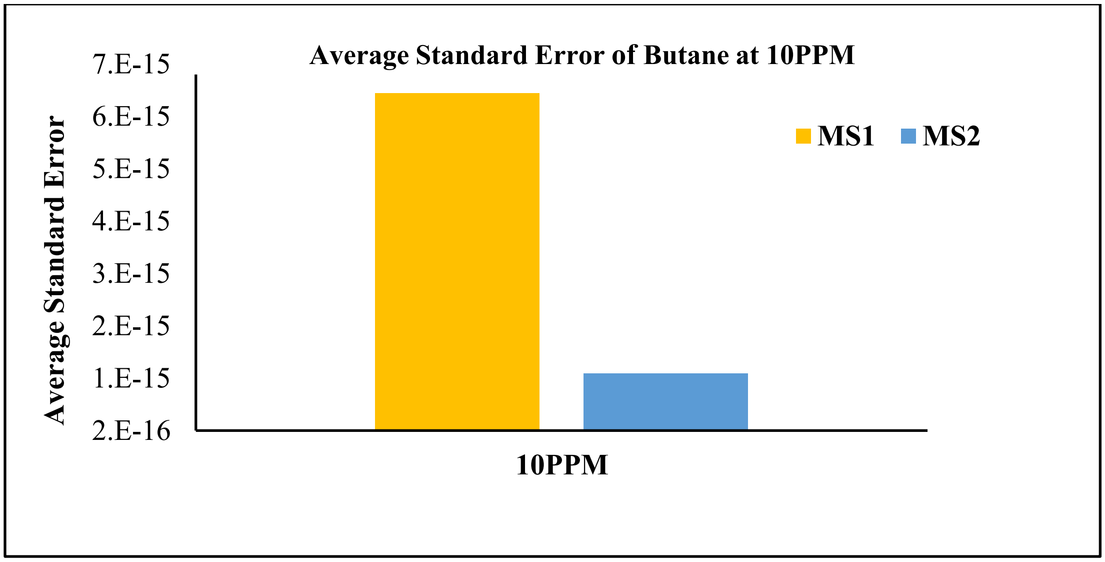


Figure 5. 26. Average Standard Error Butane in MS1 and MS 2

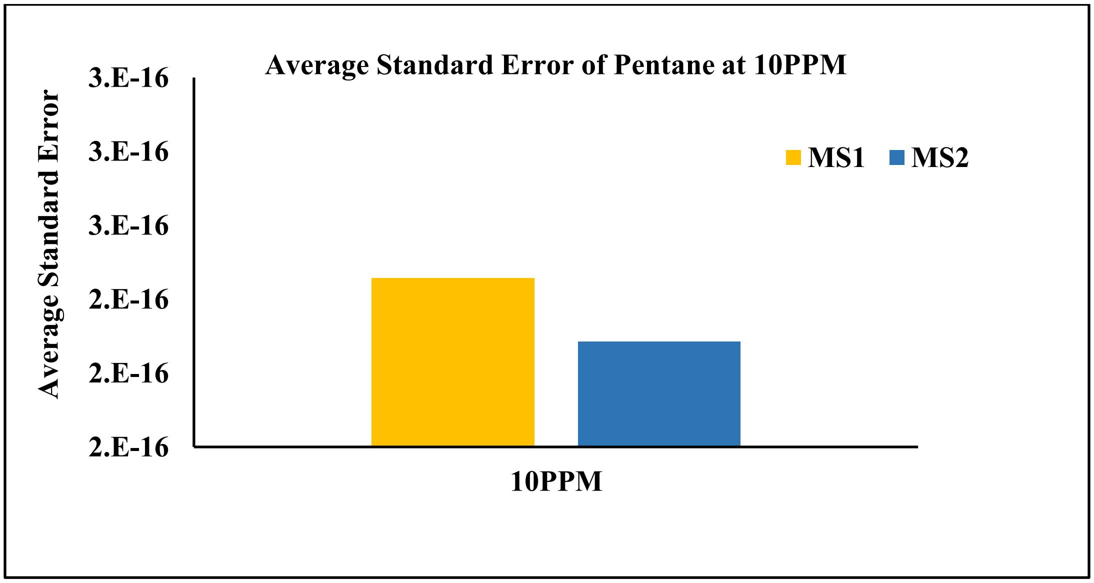


Figure 5. 27. Average Standard Error Pentane in MS1 and MS 2

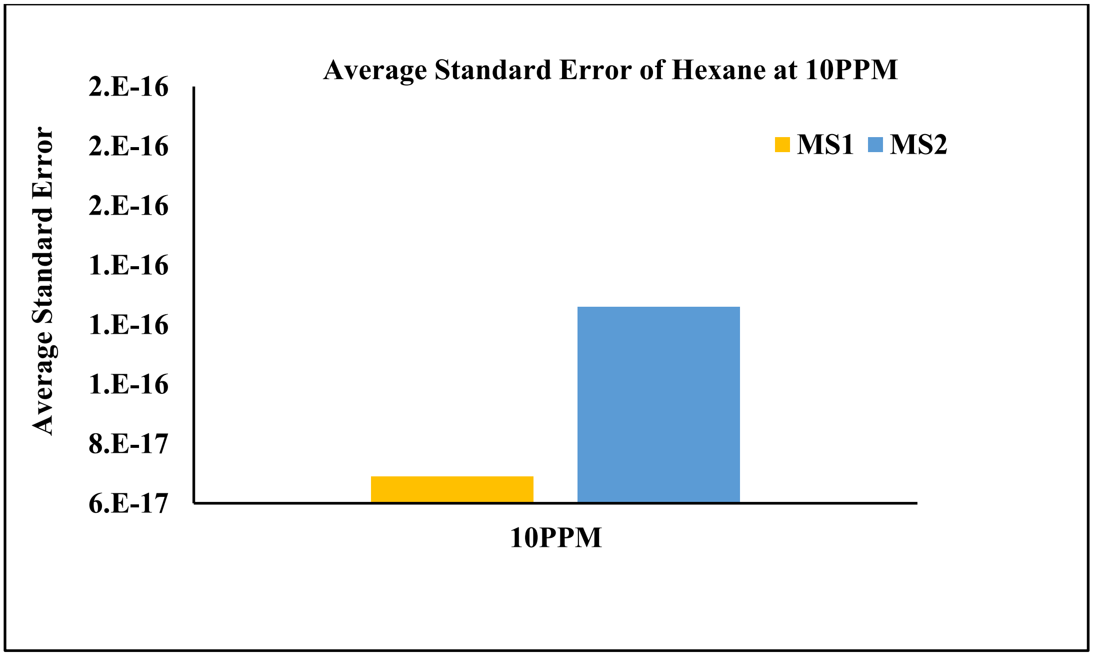


Figure 5. 28. Average Standard Error Hexane in MS1 and MS 2

Figures 5.23 – 5.28 shows the average standard error of methane through hexane. As is known, percentages give a sense of false representation. As a result for every percent value analyzed, the raw standard must be plotted and compared to %RSD to ensure consistency. In the case of 10 PPM, it is safe to estimate the accuracy of about ~ 0.99 or 99%. The value of accuracy indicates that the tools ability in detecting gases methane through hexane at 10PPM from a mixed gas in the laboratory is reliable.

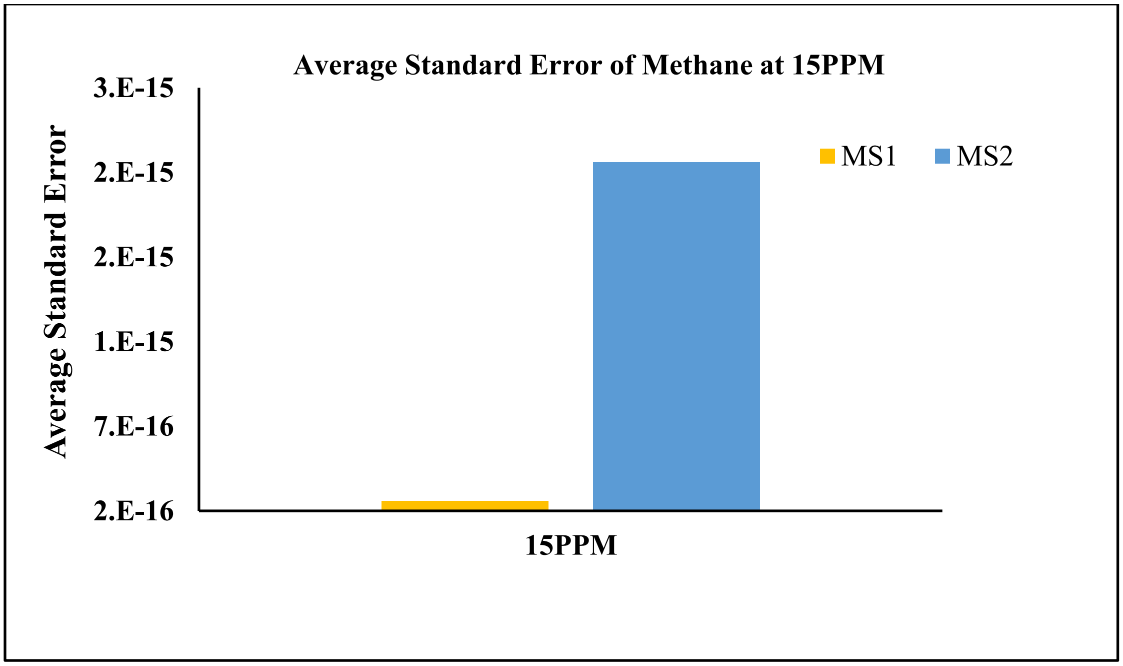


Figure 5. 29. Average Standard Error Methane in MS1 and MS 2

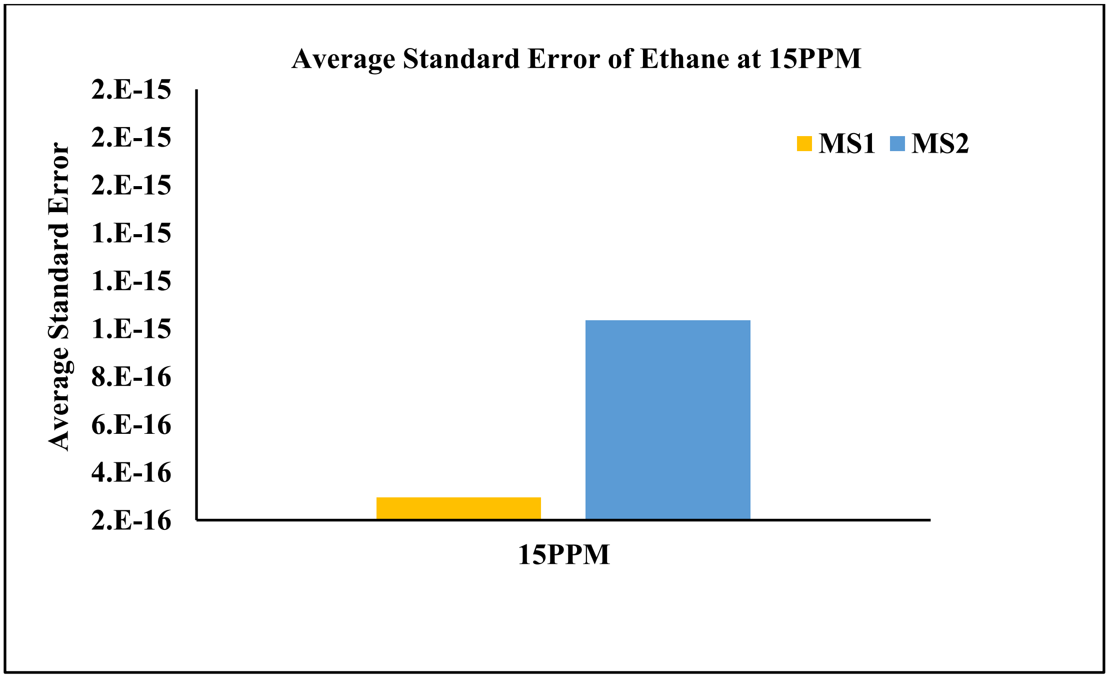


Figure 5. 30. Average Standard Error Ethane in MS1 and MS 2

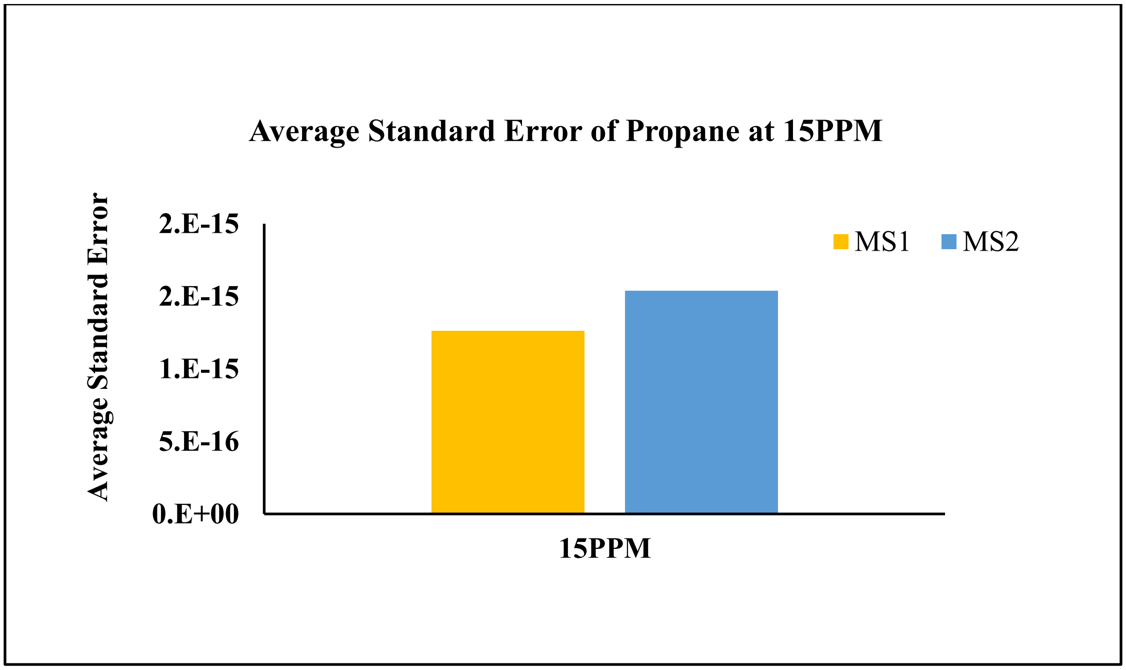


Figure 5. 31. Average Standard Error Propane in MS1 and MS 2

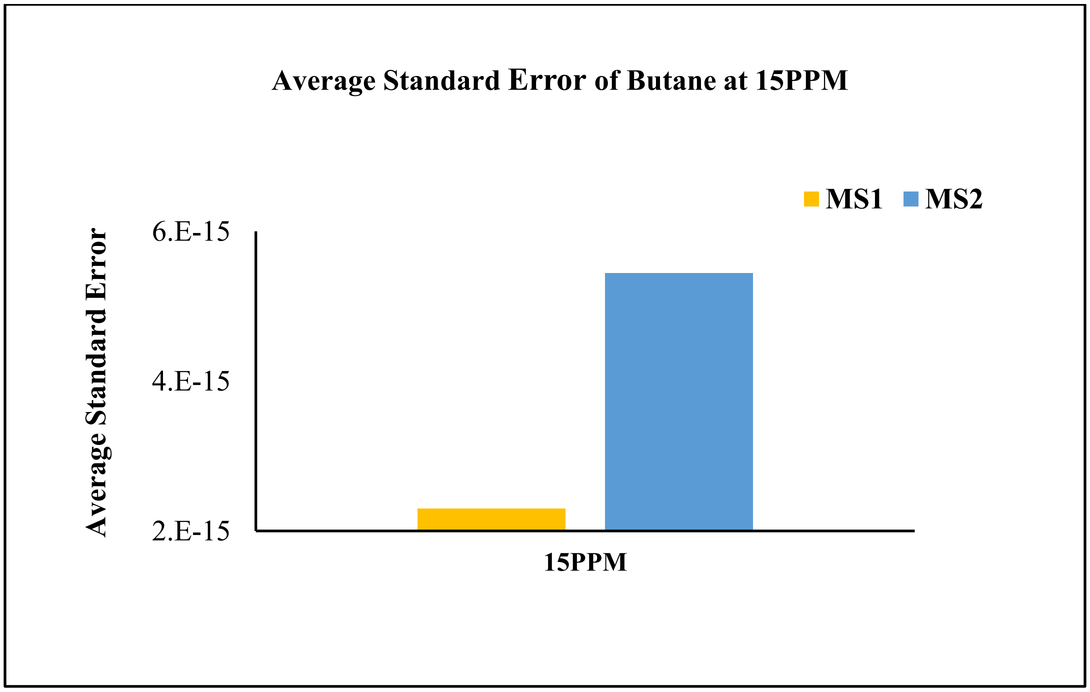


Figure 5. 32. Average Standard Error Butane in MS1 and MS 2

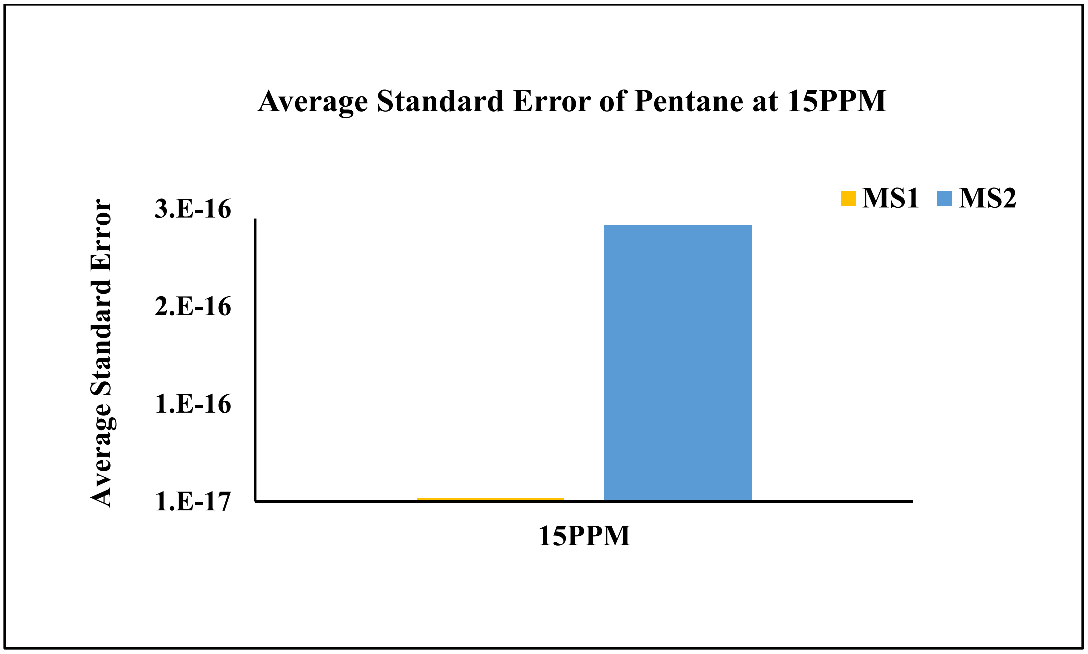


Figure 5.33. Average Standard Error Pentane in MS1 and MS 2

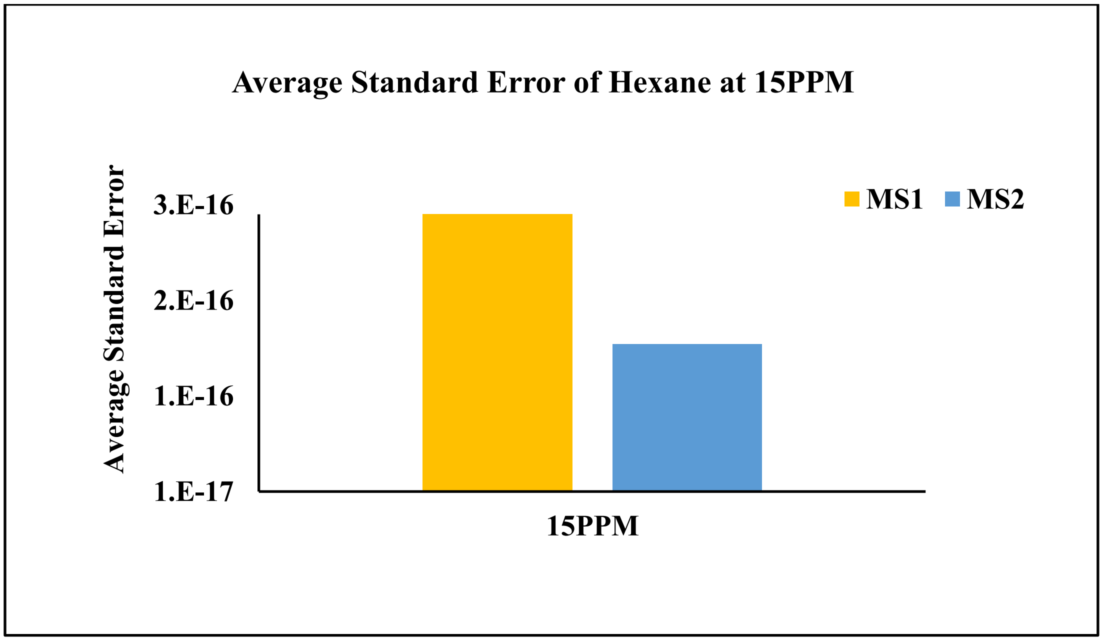


Figure 5. 34. Average Standard Error Hexane in MS1 and MS 2

Figures 5.29 – 5.34 shows the average standard error of methane through hexane at 15PPM. The order remains constant at 10^{-15} for shorter carbon chains (C1 through C3) but gains more variability from butane through hexane (C4 – C6). The trend in the order of average standard error (ASE), proves the tools detection ability for shorter carbon chains. Compared to the concentrations 10PPM, there is an improvement in average standard error, confirming the initial hypothesis of higher concentration better detection.

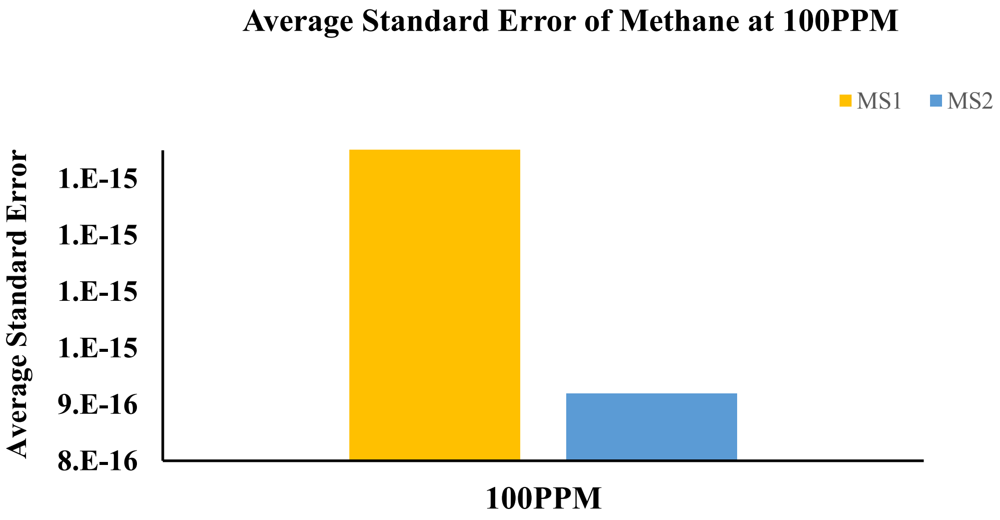


Figure 5. 35. Average Standard Error Methane in MS1 and MS 2

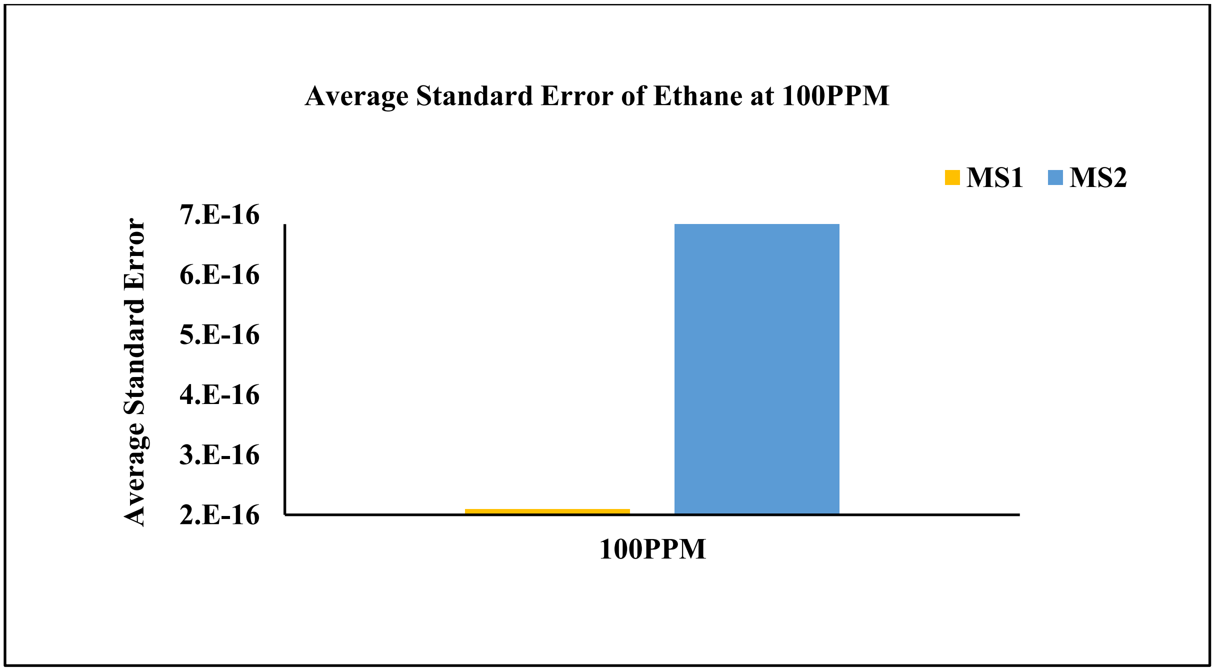


Figure 5. 36. Average Standard Error Ethane in MS1 and MS 2

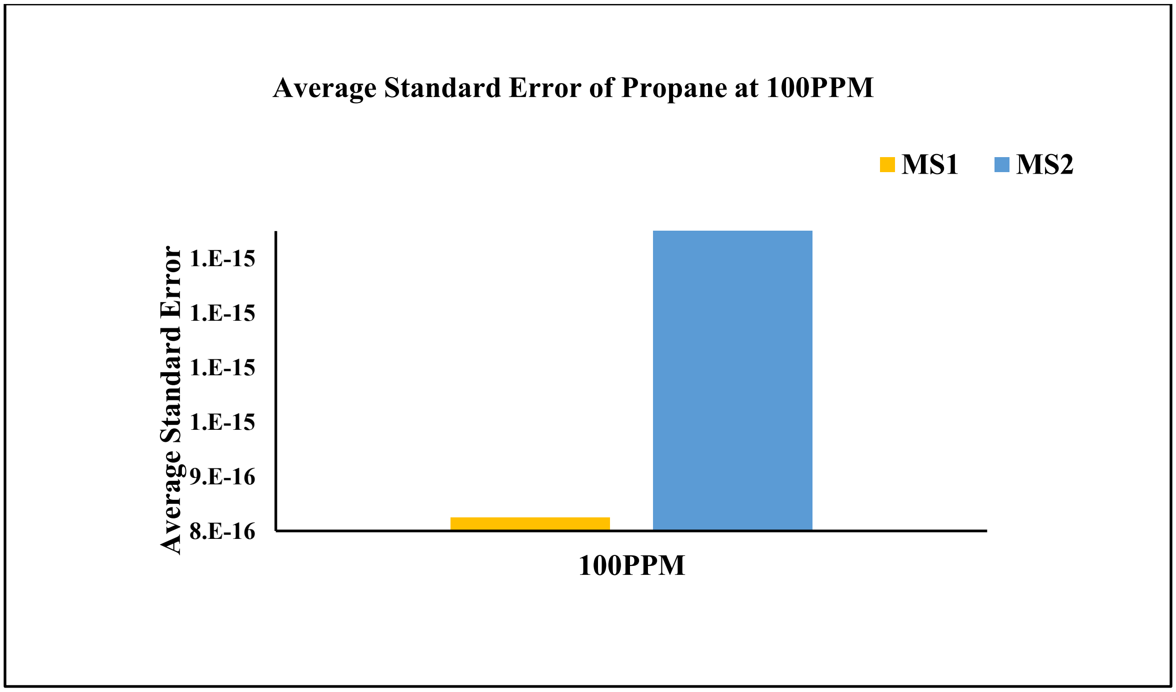


Figure 5.37. Average Standard Error Propane in MS1 and MS 2

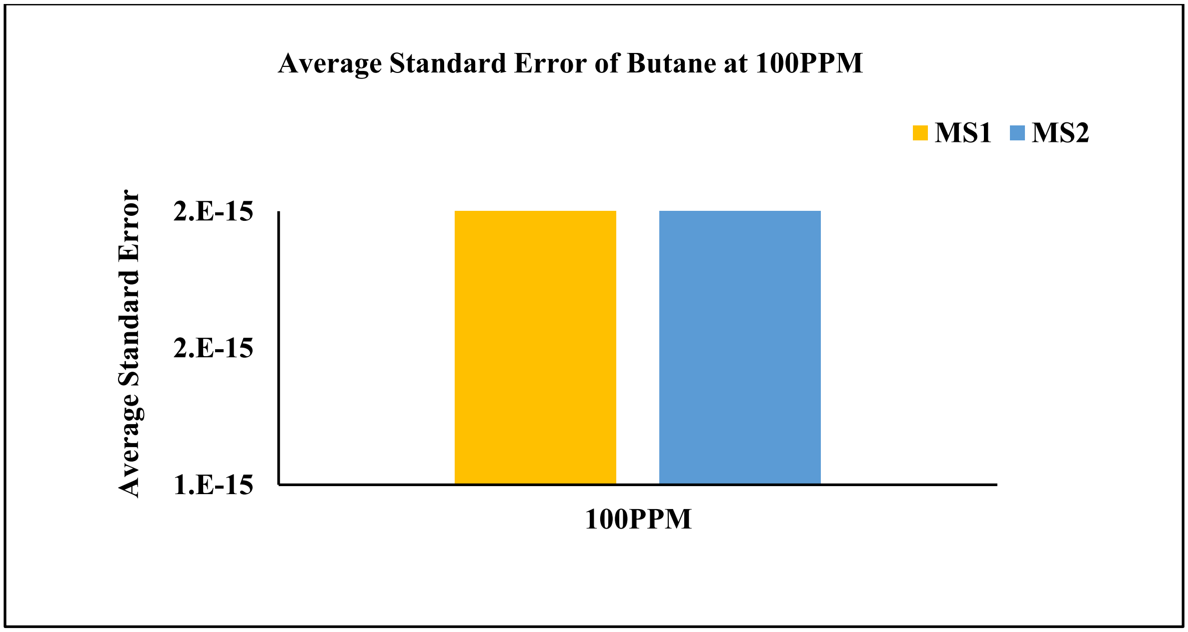


Figure 5. 38. Average Standard Error Butane in MS1 and MS 2

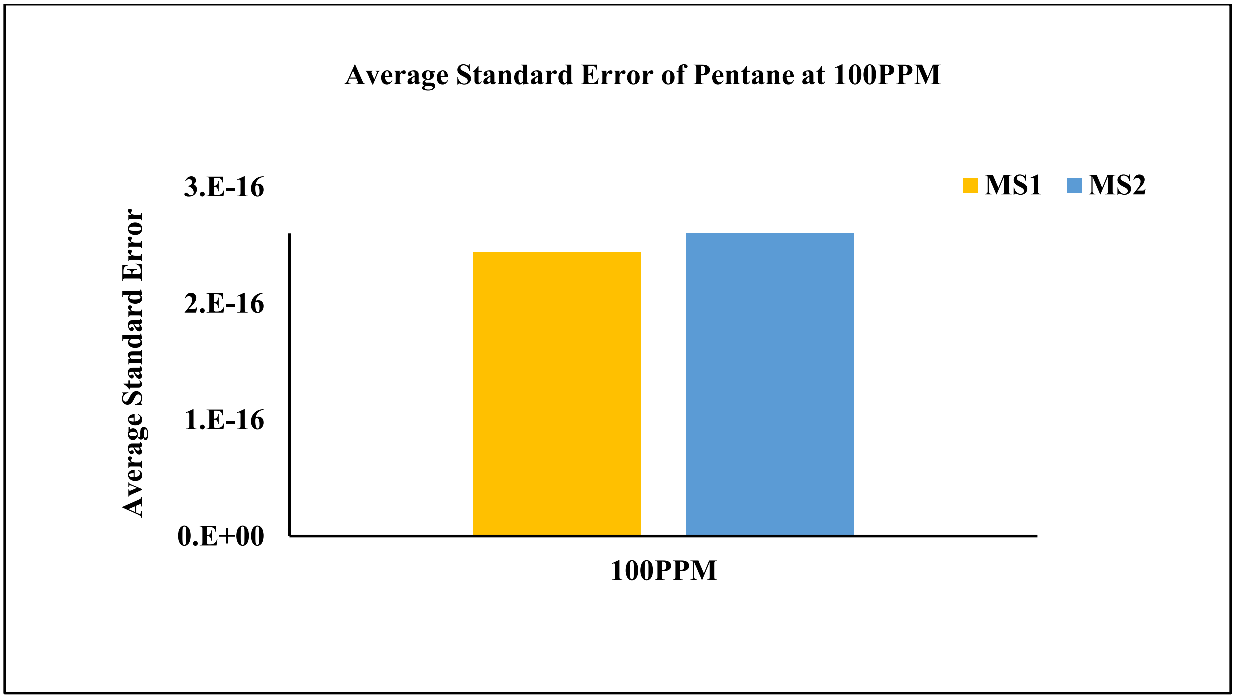


Figure 5. 39. Average Standard Error Pentane in MS1 and MS 2

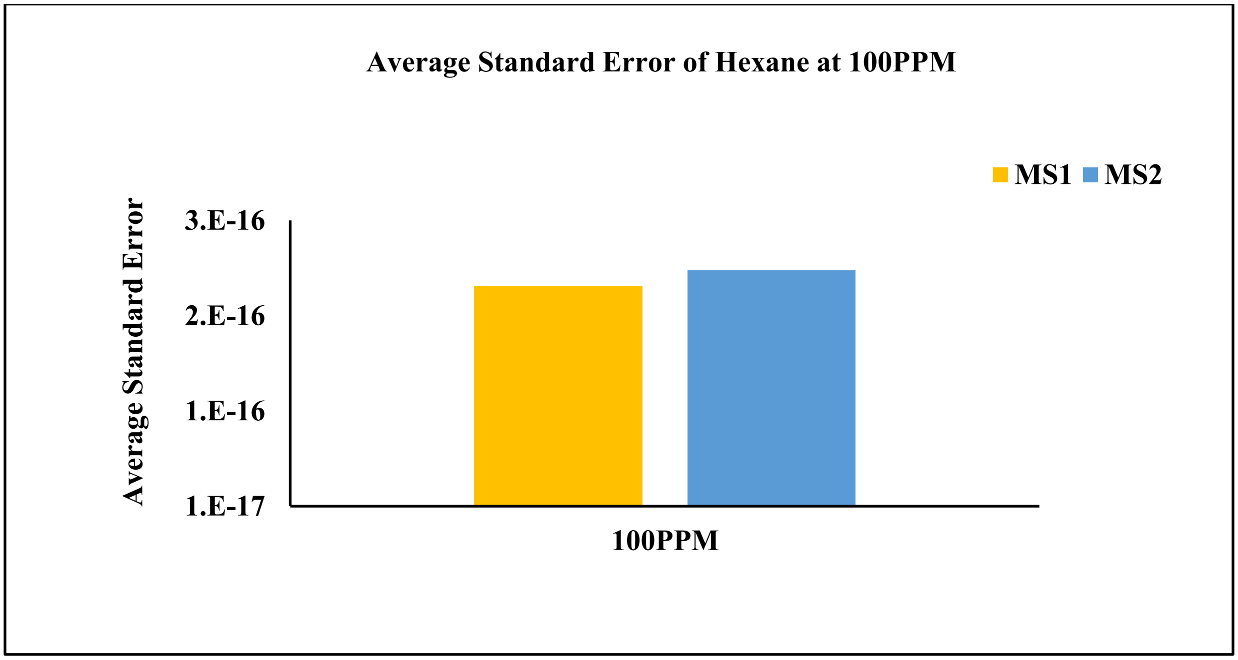


Figure 5. 40. Average Standard Error Hexane in MS1 and MS 2

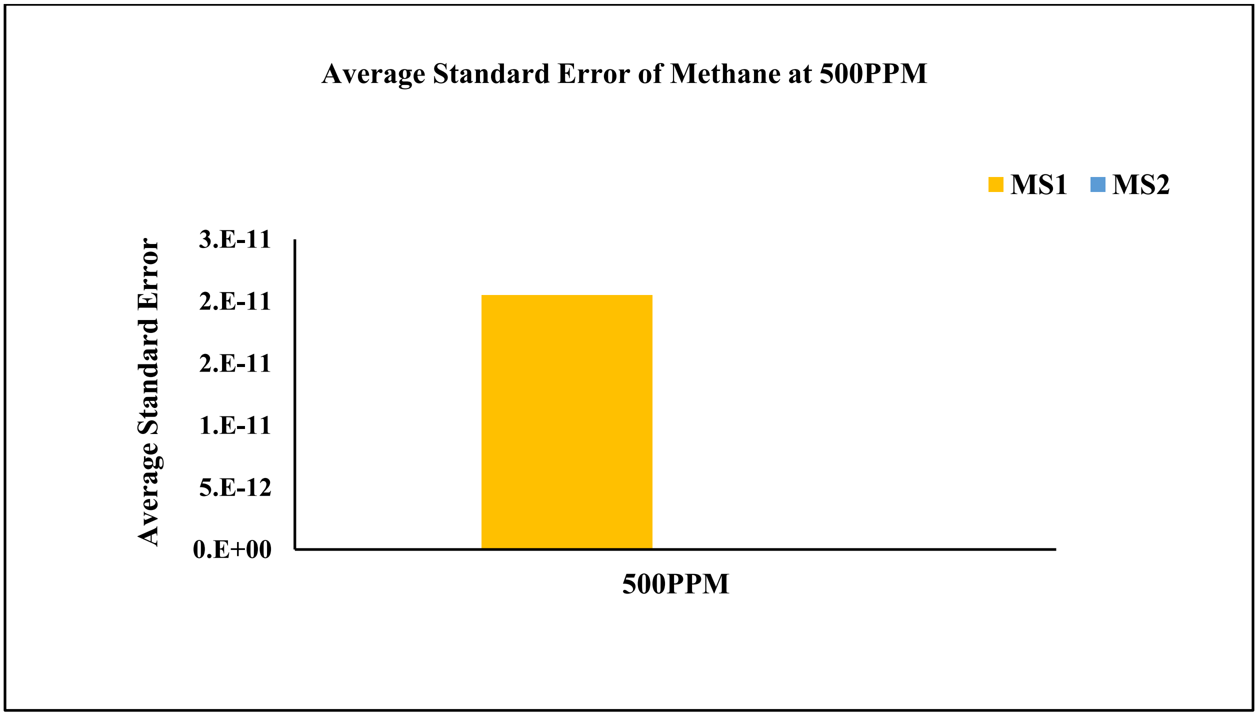


Figure 5. 41. Average Standard Error Methane in MS1 and MS 2

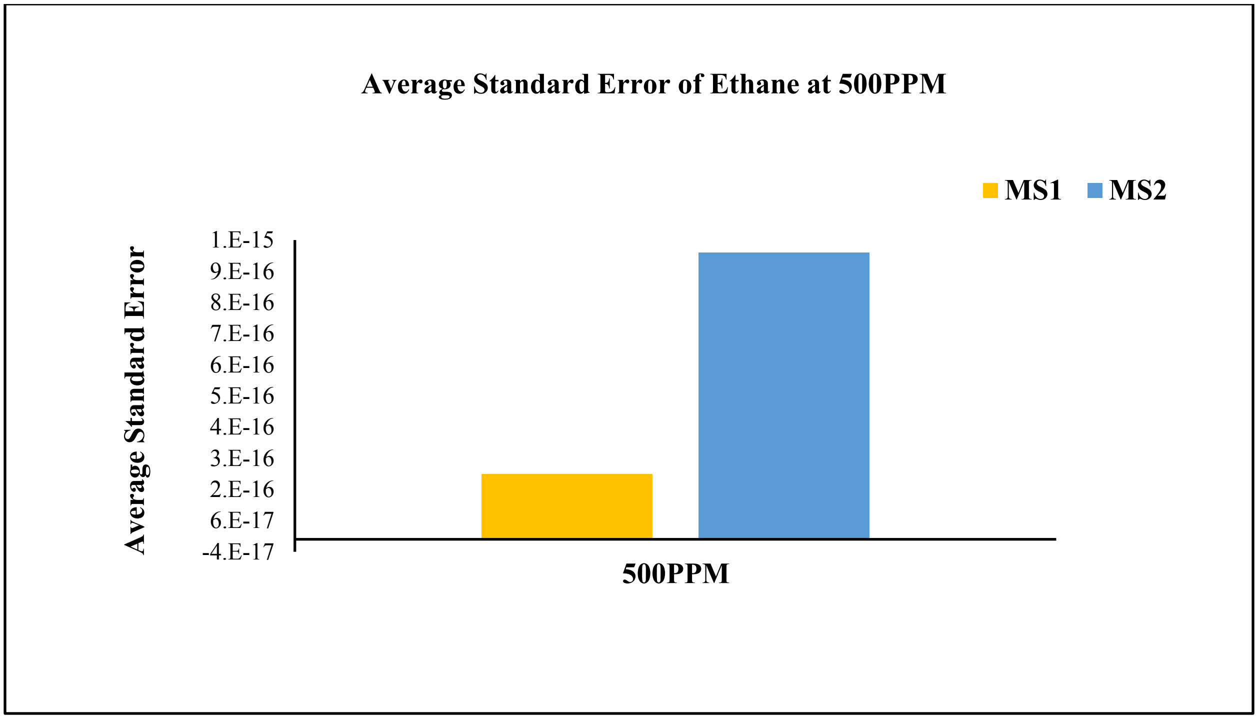


Figure 5. 42. Average Standard Error Ethane in MS1 and MS 2

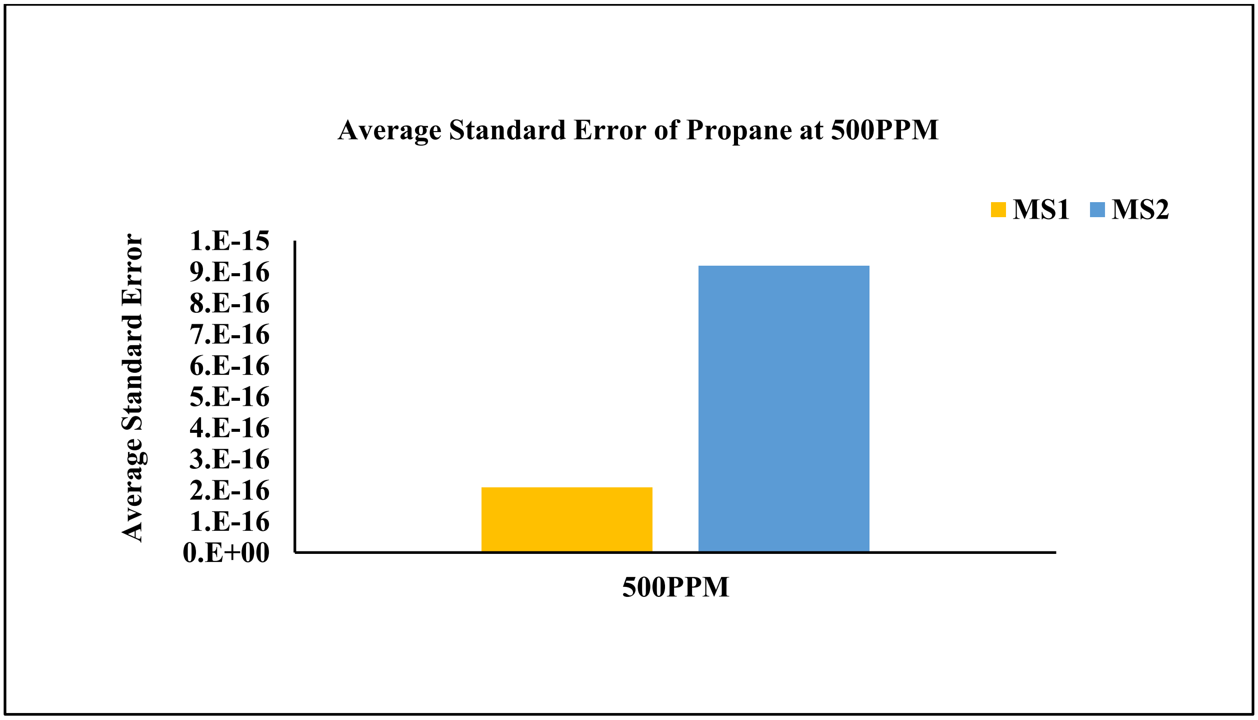


Figure 5. 43. Average Standard Error Propane in MS1 and MS 2

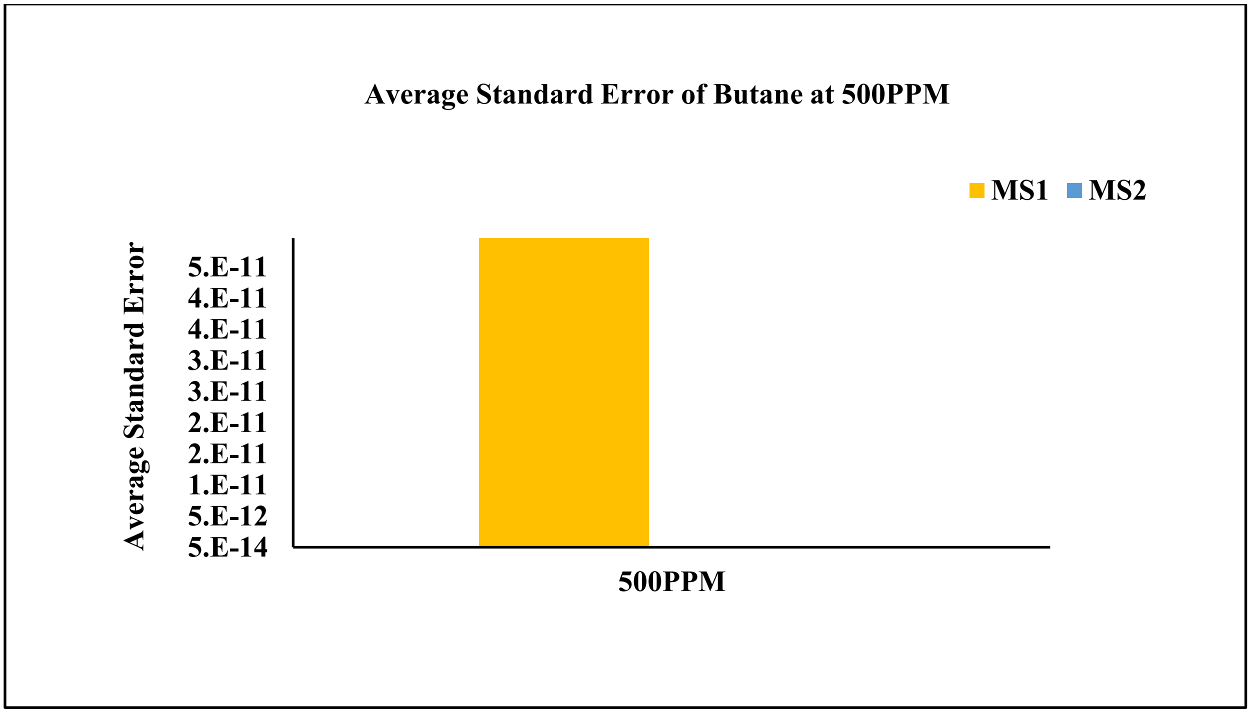


Figure 5. 44. Average Standard Error Butane in MS1 and MS 2

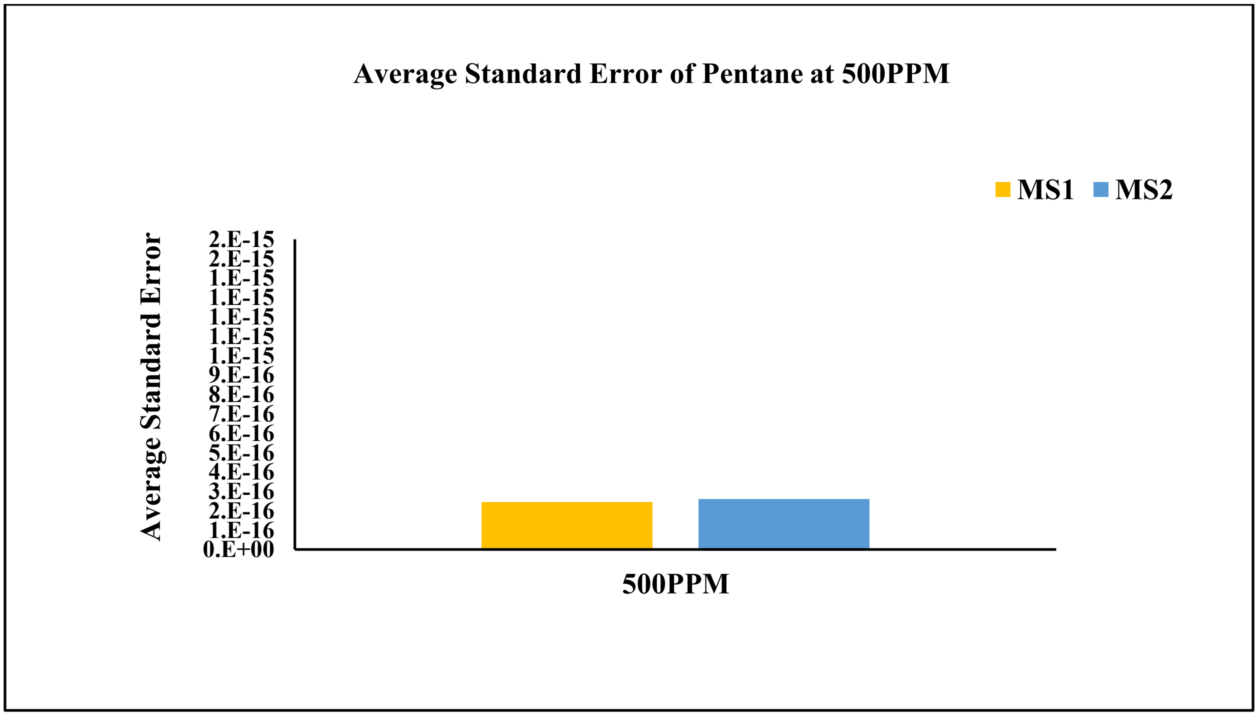


Figure 5. 45. Average Standard Error Pentane in MS1 and MS 2

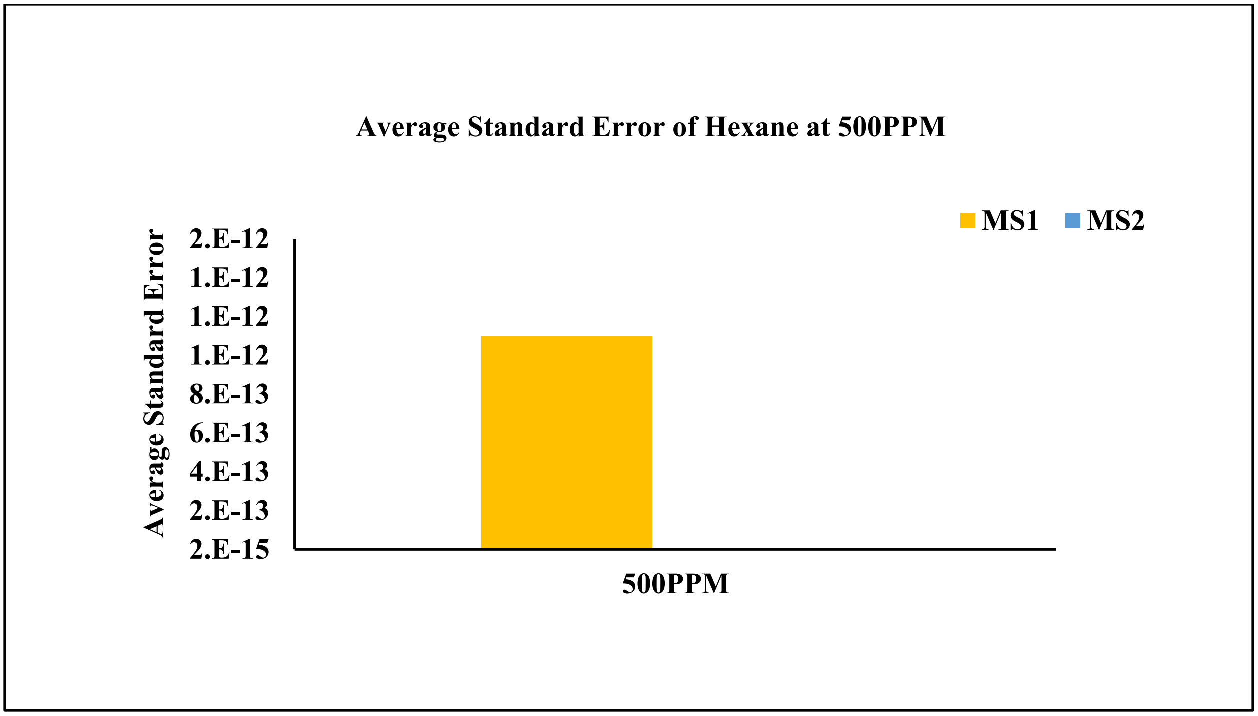


Figure 5.46. Average Standard Error Hexane in MS1 and MS 2

Figures 5.35 - 5.46 show the average standard error against the concentrations, 100PPM, and 500PPM. The order of magnitude ranges from 10^{-15} – 10^{-17}, which is minimal to insignificant considering the concentration of gases passed through the mass spectrometer — another indicator of the reliability of both mass spectrometers one and two. In addition to the minimal errors, there is a relationship between the standard error and the concentration. As the gas concentration increased, the standard error becomes minimal and approximately insignificant to the operational use of the mass spectrometers. Although the mass spectrometers are accurate in their measurements, each of the tools exhibits its own of accuracy – for example, for hexane at 500PPM, the mass spectrometer one and two used to deliver different types of average standard error values. In the case of hexane at 500PPM, MS 2 is more accurate in its measurement. However, the differences observed from the tool 1 to 2 do not distort the results at lower and higher concentrations.

5.9. Statistical Values for MS1

Table 2. Percent Relative Standard Deviation of Mass Spectrometer 1

MASS SPECTROMETER 1																	
Components	Mass Number	10 PPM				15 PPM				100 PPM				500 PPM			
		Average	Stdev.p	Variance	%RSD	Average	Stdev.p	Variance	%RSD	Average	Stdev.p	Variance	%RSD	Average	Stdev.p	Variance	%RSD
Methane	15	8.81E-14	4.08E-15	1.67E-29	4.64%	2.88E-13	3.91E-15	1.53E-29	0.44%	1.93E-12	6.84E-15	7.02E-29	0.35%	2.05E-11	3.20E-13	1.53E-25	1.56%
Ethane	29	4.03E-13	1.40E-14	1.96E-28	0.69%	2.00E-11	1.79E-15	3.21E-30	1.22%	1.79E-11	1.06E-15	1.68E-30	0.62%	5.84E-11	8.18E-14	1.00E-26	1.32%
Propane	41	5.37E-13	3.74E-14	1.40E-27	6.96%	1.71E-13	2.66E-15	7.08E-30	3.64%	1.27E-12	4.18E-15	2.62E-29	0.33%	2.84E-11	4.34E-13	2.82E-25	1.53%
N-Butane	43	4.57E-13	2.97E-14	8.83E-28	6.50%	3.52E-13	9.43E-15	8.89E-29	3.21%	1.89E-12	1.29E-14	2.48E-28	0.68%	4.97E-11	9.81E-13	1.44E-24	1.97%
N pentane	73	1.30E-14	1.10E-15	1.21E-30	8.48%	1.22E-14	5.07E-16	2.57E-31	0.55%	6.94E-14	1.23E-15	2.29E-30	1.78%	2.68E-12	1.58E-14	3.75E-28	0.59%
Hexane	87	4.60E-15	3.08E-16	9.50E-32	6.70%	2.27E-14	2.84E-16	8.09E-32	6.62%	1.11E-13	6.87E-16	7.07E-31	0.62%	1.10E-12	7.86E-15	9.27E-29	0.72%

5.10. Statistical Values for MS2

Table 3. Percent Relative Standard Deviation of Mass Spectrometer 2

MASS SPECTROMETER 2																	
		10 ppm				**15 ppm**				**100 ppm**				**500 ppm**			
Components	**Mass number**	**Average**	**Stdev.p**	**Variance**	**%RSD**	**Average**	**Stdev.p**	**Variance**	**%RSD**	**Average**	**Stdev.p**	**Variance**	**%RSD**	**Average**	**Stdev.p**	**Variance**	**%RSD**
Methane	15	1.30E-10	4.08E-15	1.67E-29	4.64%	2.90E-13	1.26E-15	1.59E-30	1.33%	2.10E-12	4.60E-15	3.17E-29	0.22%	2.20E-11	7.06E-14	7.48E-27	0.31%
Ethane	26	4.20E-14	1.40E-14	1.96E-28	5.18%	7.00E-14	1.45E-15	2.10E-30	2.55%	2.50E-13	3.42E-15	1.76E-29	1.33%	6.70E-12	2.26E-14	7.63E-28	0.34%
Propane	41	1.30E-13	3.74E-14	1.40E-27	6.96%	1.70E-14	6.21E-15	3.86E-29	35.68%	6.40E-13	6.92E-15	7.18E-29	1.08%	1.50E-11	1.26E-13	2.39E-26	0.81%
N-Butane	43	NA	2.97211E-14	8.83345E-28	NA	1.40E-13	1.13E-14	1.28E-28	6.72%	7.80E-13	8.80E-15	1.16E-28	1.11%	2.00E-11	1.64E-13	4.06E-26	0.81%
N pentane	73	4.30E-15	1.10E-15	1.21E-30	8.48%	1.30E-14	6.70E-17	4.49E-33	3.67%	8.00E-14	1.30E-15	2.54E-30	1.61%	3.10E-12	1.84E-14	5.07E-28	0.58%
Hexane	87	3.20E-13	3.08E-16	9.50E-32	6.70%	7.00E-15	1.51E-15	2.27E-30	4.01%	4.40E-14	2.08E-16	6.47E-32	0.46%	4.40E-13	8.13E-15	9.91E-29	1.83%

5.11. Comparison, Validation, and Reliability of MS 1 and MS2

Based on the binary and mixed gas standard information above, both tools are similar to each other with minimal differences. Both tools also exhibit and fulfill two significant objectives of the research – to check the sensitivity and reliability of the tool. All of these are achieved and justified based on the results from the testing of the calibration process described in the sections earlier.

5.12. Applications of Mass Spectrometry on the Field

The use of mass spectrometers on the field has been around for a while. However, the placement of calibrated mass spectrometer on the same floor as the possum is new. So far, the use of Gas Chromatogram Mass Spectrometers (GC-MS) on the field remains in the mud logging cabin because of the tool's incapability to handle the external and rig conditions. Typically, on a rig site, the mud logger or well site geologist is responsible for operating tools like the GC-MS.

During drilling operations, especially offshore, kick detections remain rudimentary because of lacking innovations to improve kick indication (Johnson et al. 2014). Kick indicator and reactions are unstandardized across the industry. The response plans remain more reactive than proactive, which is not ideal in operations costing millions of dollars. Innovation typically improves as the need arises. After the Macondo indent in 2010, the regulatory boards have worked and keep working to standardize worst-case discharge calculations as well as response plans. However, the efforts are applauded and taken seriously. The response plans and standardized calculations remain a post solution with the hopes on contingency plans. As a result, methods to monitor the process of drilling would raise levels of safety on rig sites by offering the opportunity to monitor lighter hydrocarbon components. These components also serve as fingerprint information on the reservoir and the overburden of the reservoir, which improves the field development plan, typically made before drilling begins. As is known, the subsurface is one of the least studied places on earth; hence, the need for technological advancements like the calibrated mass spectrometer and the developed methodology.

CHAPTER 6. RESULTS AND DISCUSSION II – HEAVIER HYDROCARBONS AND NON-HYDROCARBONS

In this chapter, we discuss results for detecting more complex hydrocarbons (butadiene, butene, benzene, heptane, toluene, octane, p-xylene, o-xylene and m-xylene, propylene, acetylene, pentene, ethylene, methyl-cyclohexene, and ethyl-benzene) as well as the non-hydrocarbons (helium, carbon-dioxide, and oxygen). The testing for the heavier hydrocarbons and non-hydrocarbons were conducted directly using gas mixtures (as opposed to using binary standards), and thus is purely a detection method. Similar statistical parameters (% RSD, average mass spectrometer responses, and average standard errors) are also used here for the detection of these components and their statistical analyses.

According Figures 6.1 – 6.10, the base masses of the heavier hydrocarbons and nonhydrocarbons are detected. However, the concentration remains a direct proportion of ion abundance (representative of the population of gases passed through the quadrupole mass analyzer), indirectly affecting the signals measured in electro-volts. The detected samples are analyzed, and the percent relative standard deviation calculated and plotted – Figures 6.1 – 6.10. In the cases where no responses are plotted, the gas component is not present in the gas mixed standards. For example, 1, 3 butadiene at 15PPM has no response plotted because of its absence in the gas tanks. Other gas samples with no response in some of the tanks include; Octane at 15PPM, Butene at 15PPM, Oxygen at 10PPM, Acetylene at 15PPM, and Carbon di Oxide at 10PPM. Although the samples are absent at the concentration, its sister samples at different concentrations contribute to the analyses of gases.

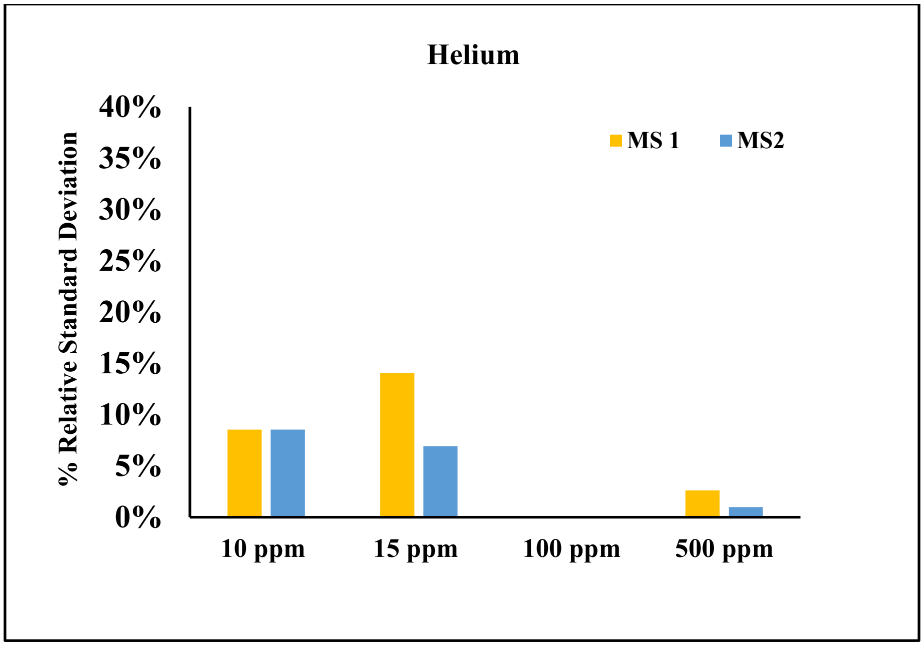


Figure 6. 1. Precent Relative Standard Deviation versus Concentration of Helium

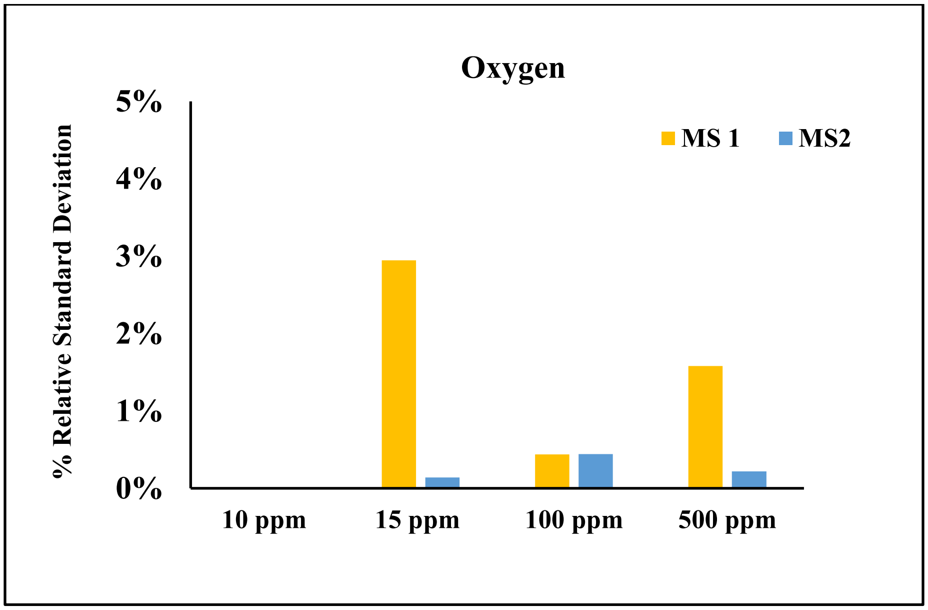


Figure 6. 2. Precent Relative Standard Deviation versus Concentration of Oxygen

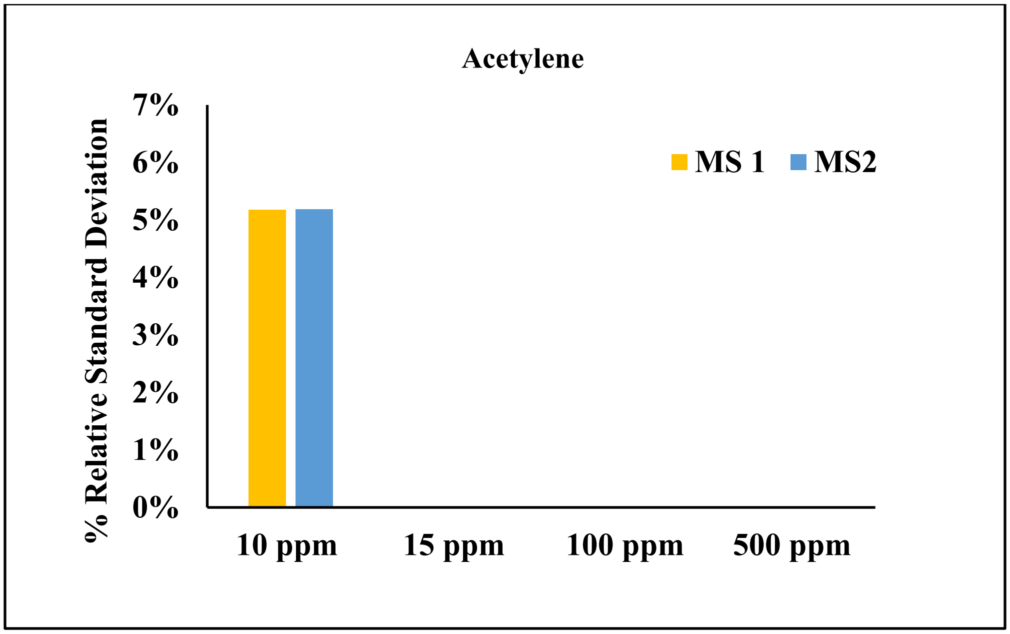


Figure 6. 3. Precent Relative Standard Deviation versus Concentration of Acetylene

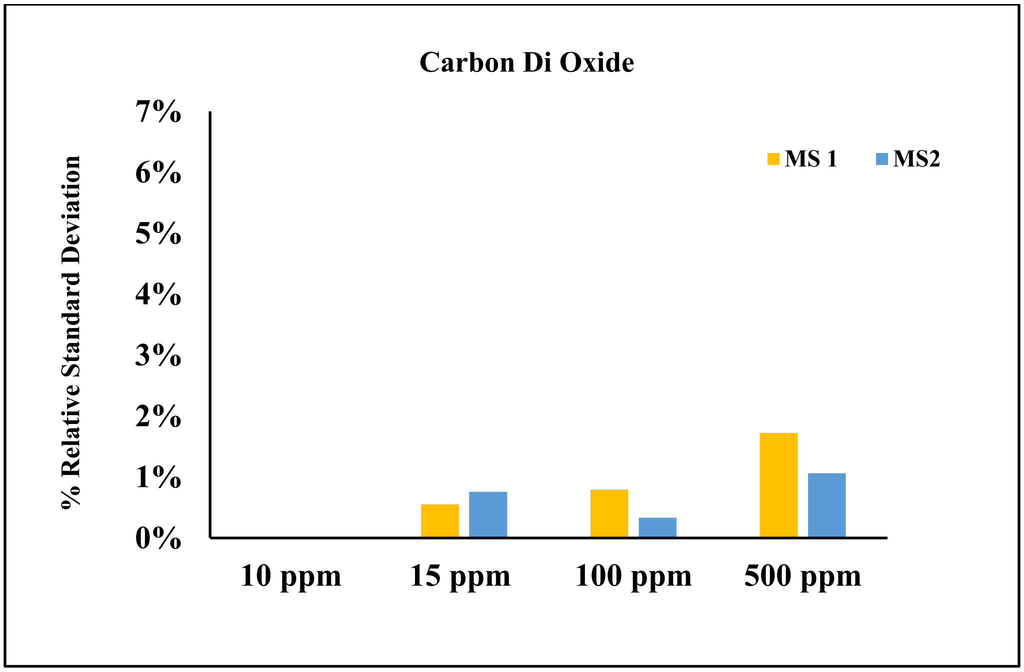


Figure 6. 4. Precent Relative Standard Deviation versus Concentration of Carbon Di Oxide

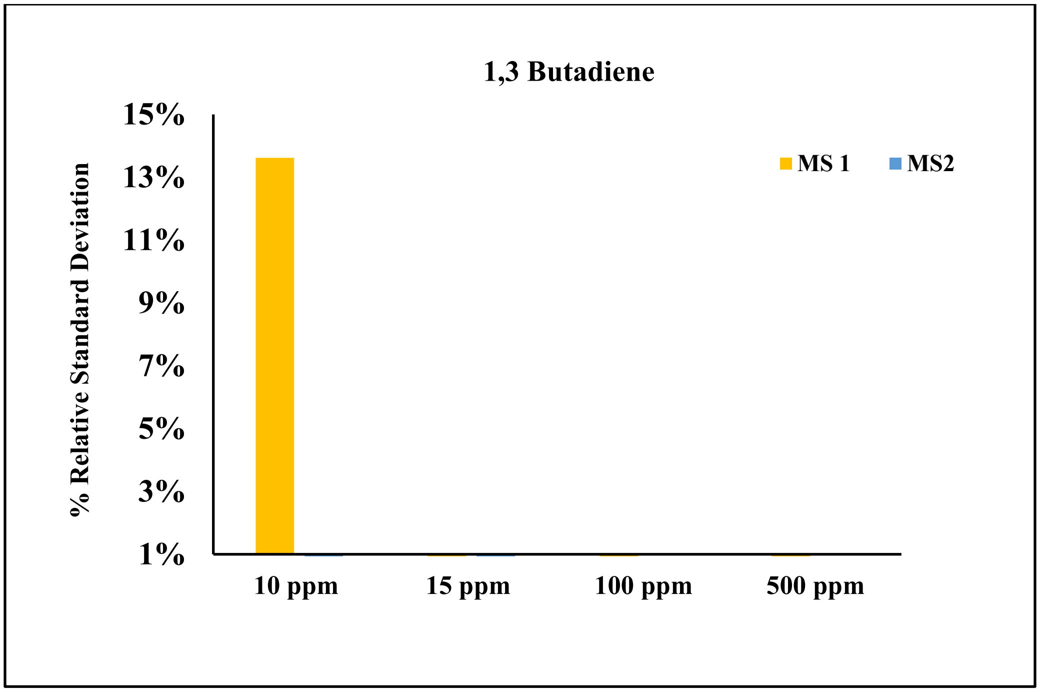


Figure 6. 5. Precent Relative Standard Deviation versus Concentration of 1,3 Butadiene

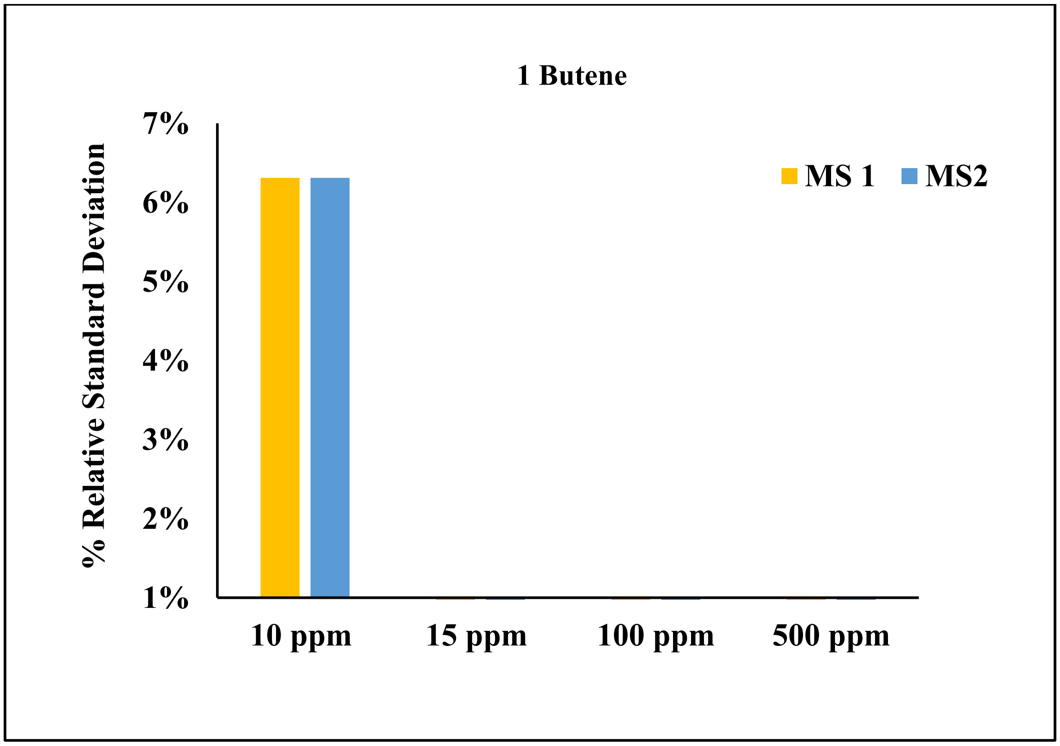


Figure 6. 6. Precent Relative Standard Deviation versus Concentration of   1 Butene

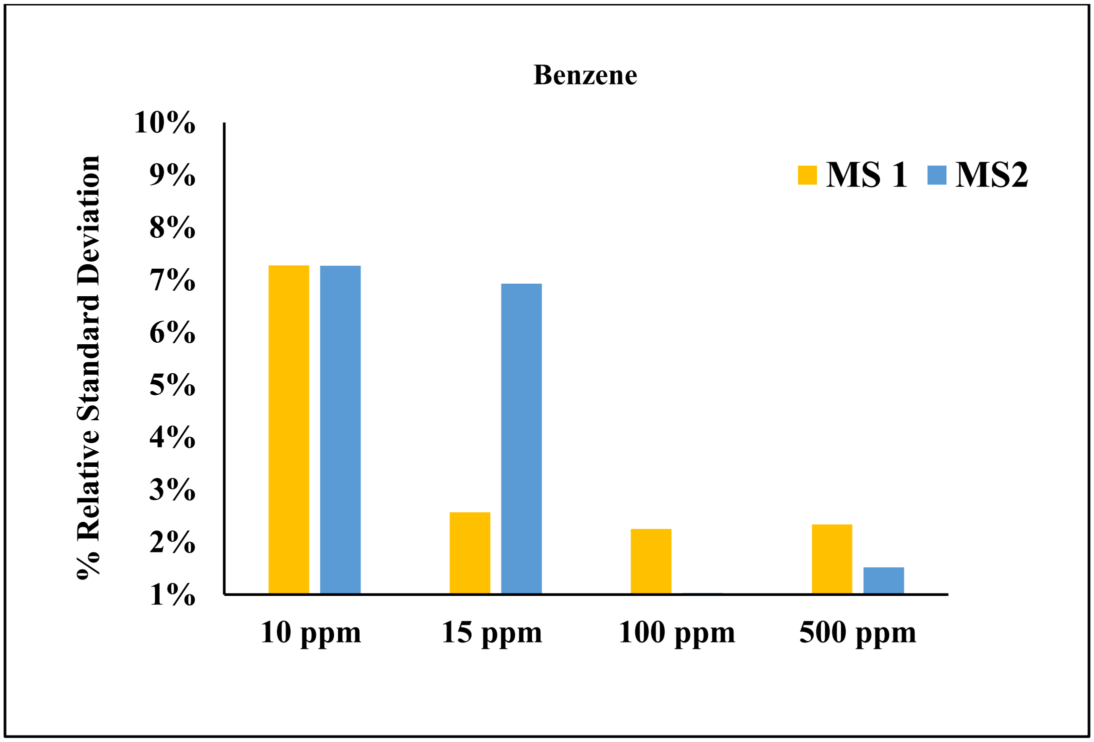


Figure 6. 7. Precent Relative Standard Deviation versus Concentration of Benzene

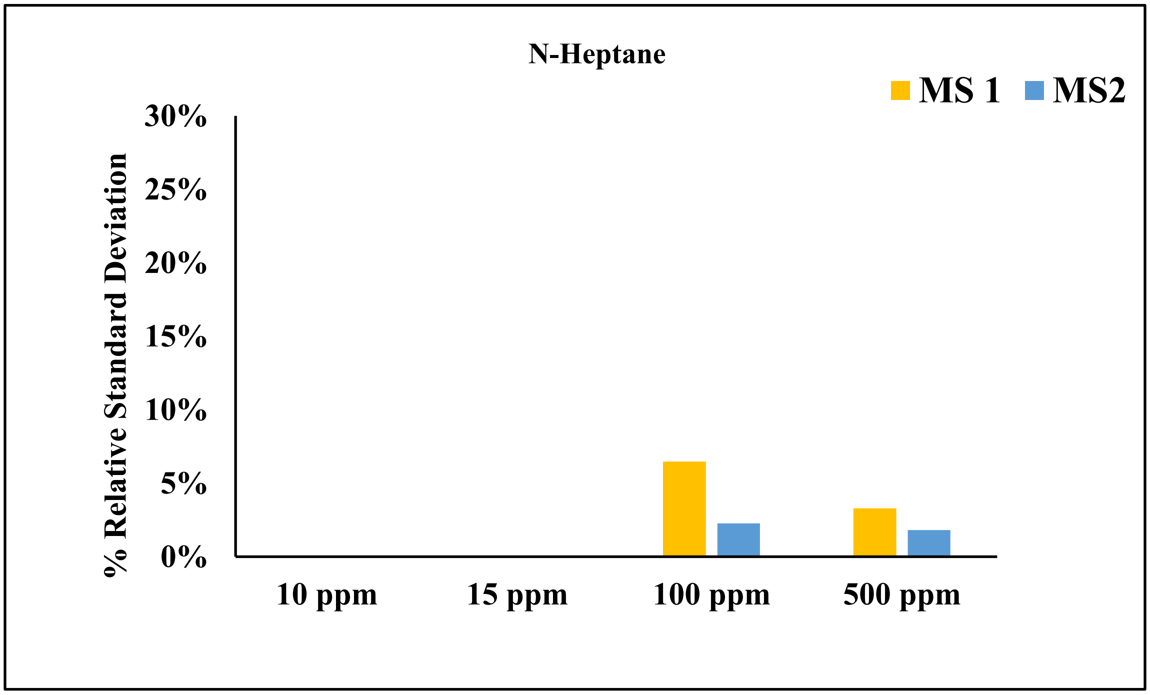


Figure 6. 8. Precent Relative Standard Deviation versus Concentration of N-Heptane

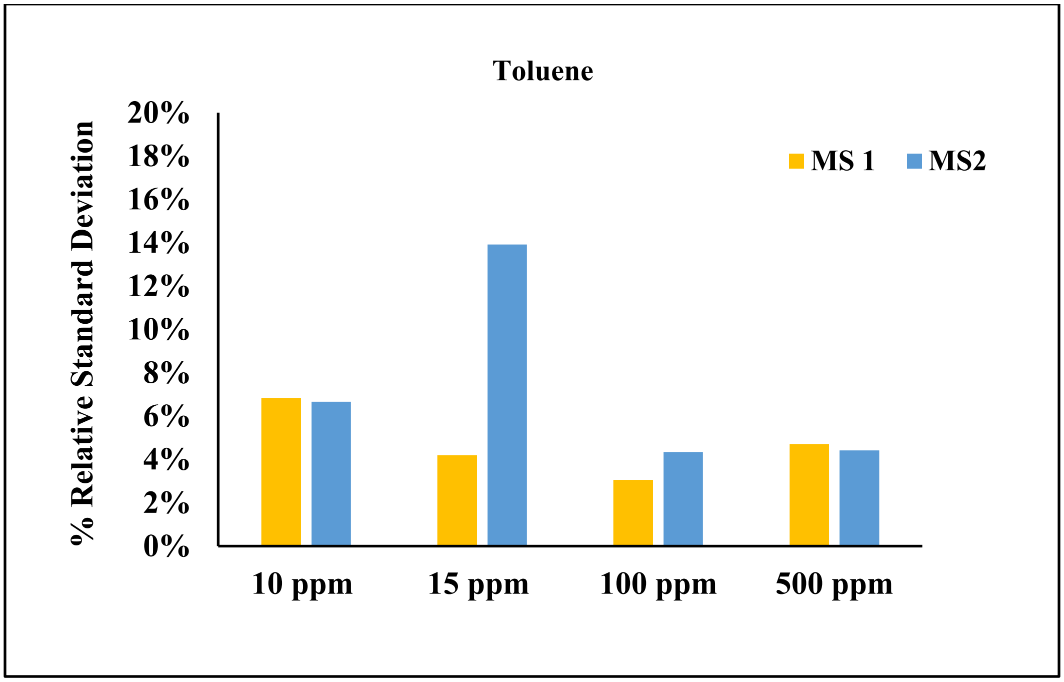


Figure 6. 9. Percent Relative Standard Deviation versus Concentration of Toluene

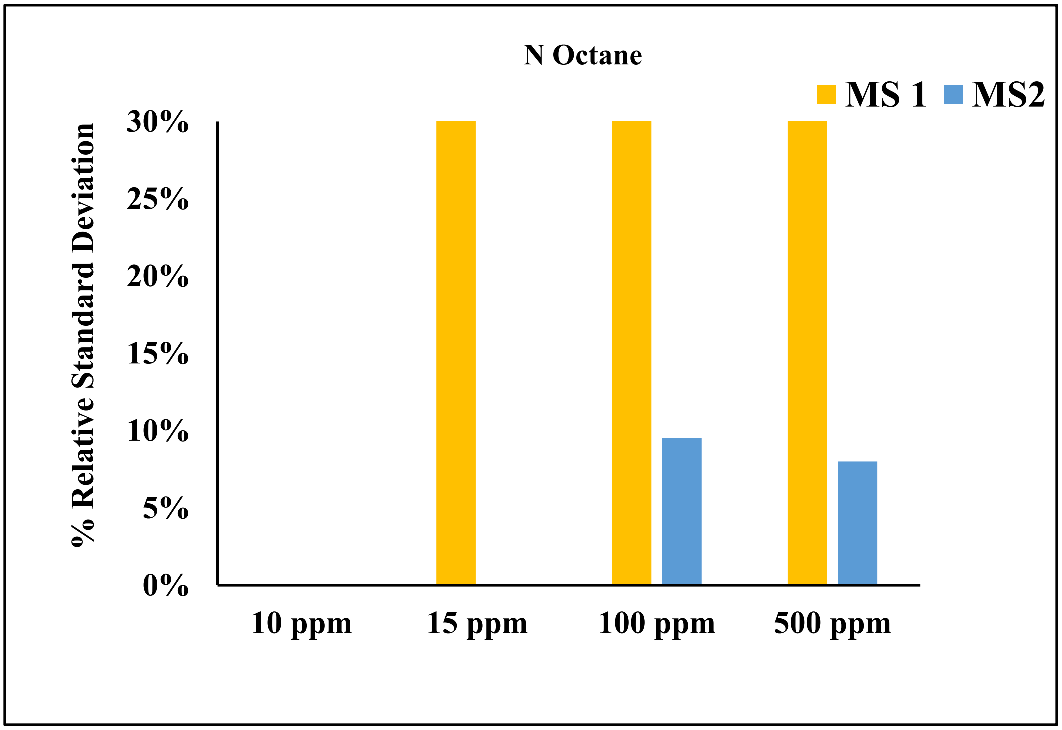


Figure 6. 10. Percent Relative Standard Deviation versus Concentration of N-Octane

In the case of the gas response factors above in figure 6.1 – 6.10, the gases did not have binary standards associated with the base peak selections. As a result, some gas samples in its response, for example N-Octane, figure 6.10, shows a percent RSD as high as ~30% for mass spectrometer 1 and ~10% for mass spectrometer 2. In addition to the potential overestimation, figure 6.10 is an example that highlights the sensitivity variability of the mass spectrometers. The mass spectrometers however proved their capability to detect the BTEX- Benzene, Toluene, Ethylene, and Xylene (the aromatic compounds). These aromatics are known for the complexness of the rings, and their resistance to breaking the double bond. The ability for the mass spectrometer to fragment BTEX demonstrates that voltage supplied by the mass spectrometer is sufficient to fragment aromatics.

Figures 6.1 – 6.10 also show that the cumulative average % relative standard deviation for heavier hydrocarbons is ~ 10%. The nonhydrocarbons – helium, oxygen and carbon dioxide contained in the mixed standards at the different concentration show a percent relative standard ~ 3% which is more accurate than the lighter hydrocarbons.

The figures 6.11 and 6.12 show the relationship between the % relative standard deviation and concentration. As seen in the figure in the figures 6.11 and 6.12, the curve skewed positively is indicative of the mean concentrated to the right, which contains the higher concentrations (~100 – 500)PPM, which is the same as results obtained from the lighter hydrocarbons. Higher concentrations lead to lower percent relative standard deviations because of the complete saturation of the mass analyzer by the gas analyte.

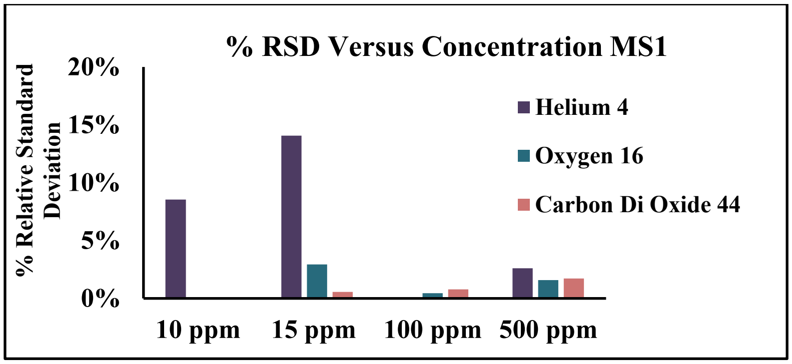


Figure 6. 11. Cumulative Percent RSD Versus Concentration MS1 for Non-Hydrocarbons

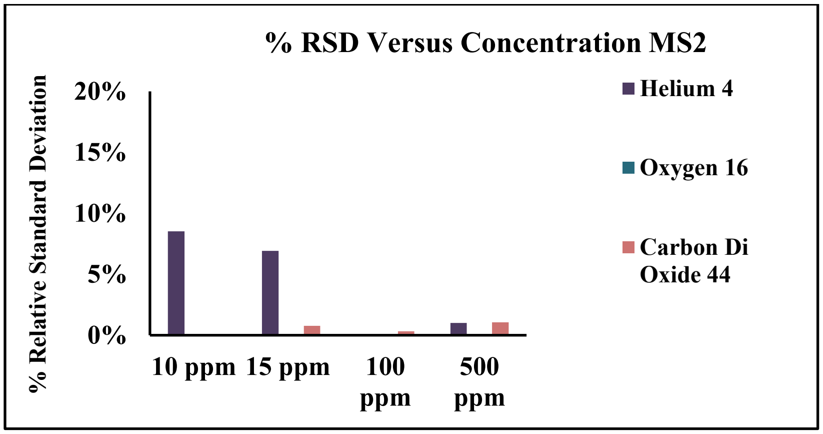


Figure 6. 12. Cumulative Percent RSD versus Concentration MS2 for Non-Hydrocarbons

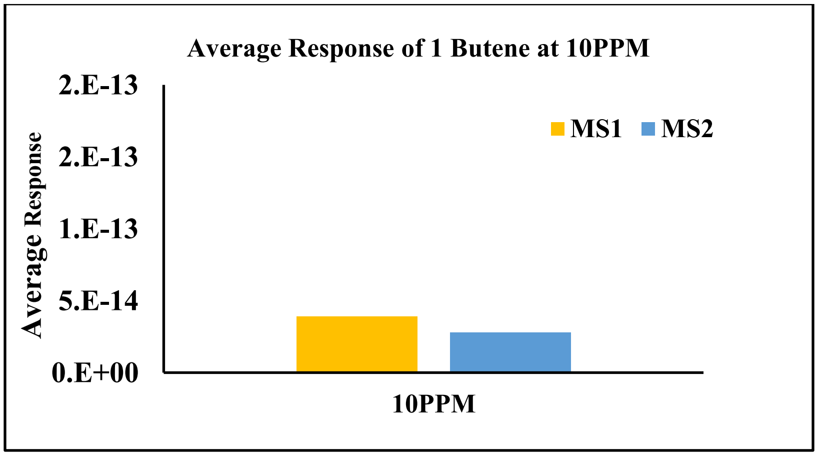


Figure 6. 13. Average Mass Spectrometer Response to 1, Butene

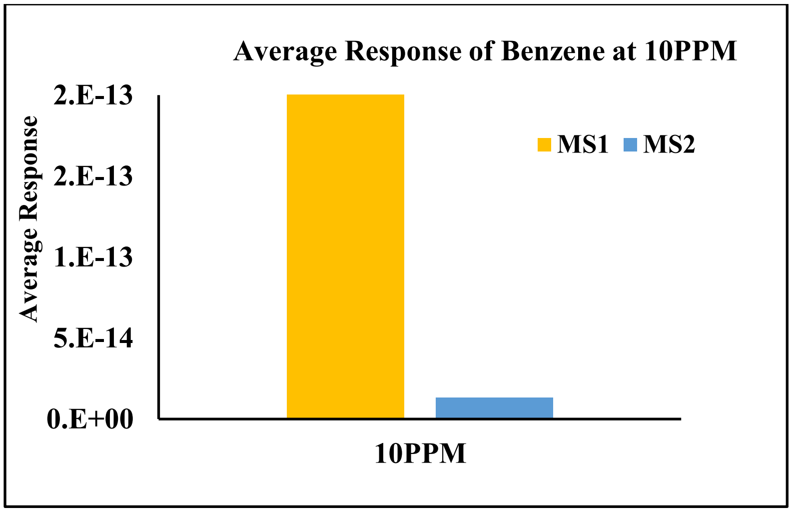


Figure 6. 14. Average Mass Spectrometer Response to Benzene

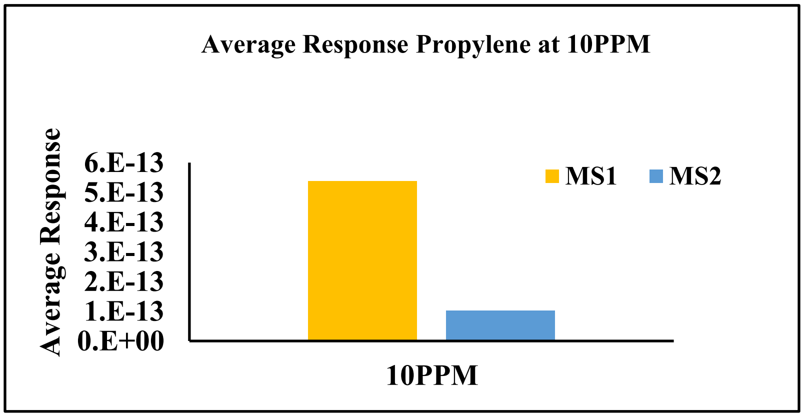


Figure 6. 15. Average Mass Spectrometer Response to Propylene

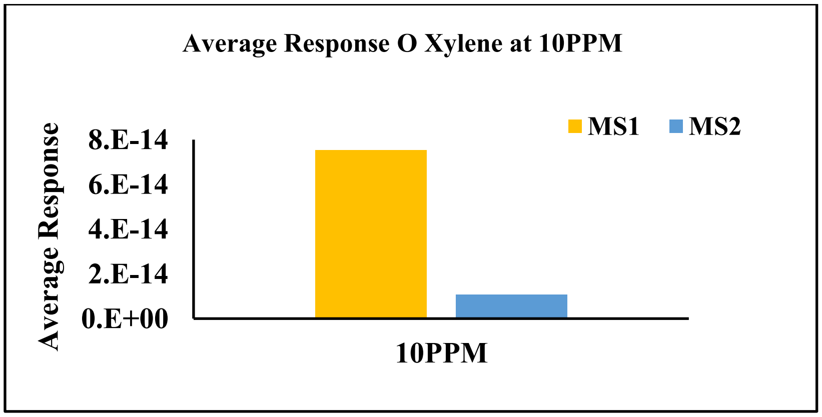


Figure 6. 16. Average Mass Spectrometer Response to O Xylene

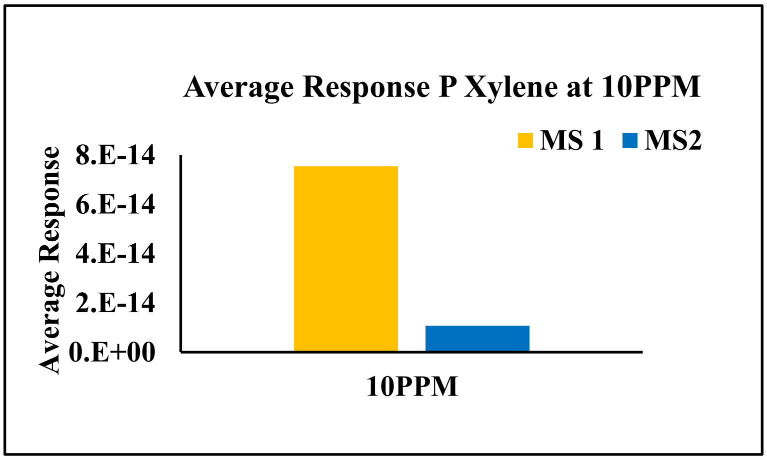


Figure 6. 17. Average Mass Spectrometer Response to P Xylene

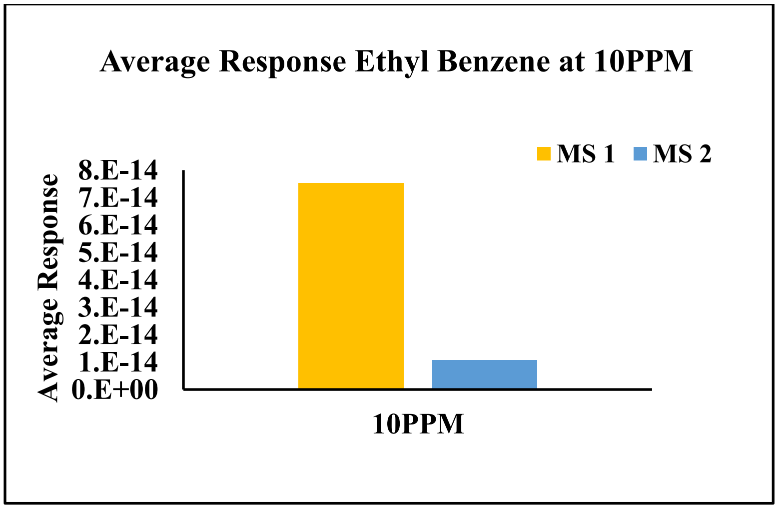


Figure 6. 18. Average Mass Spectrometer Response to Ethyl- Benzene

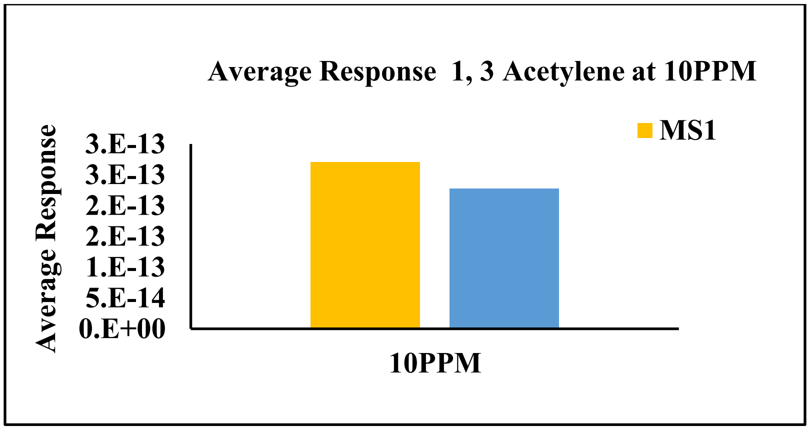


Figure 6. 19. Average Mass Spectrometer Response to 1, 3 Acetylene

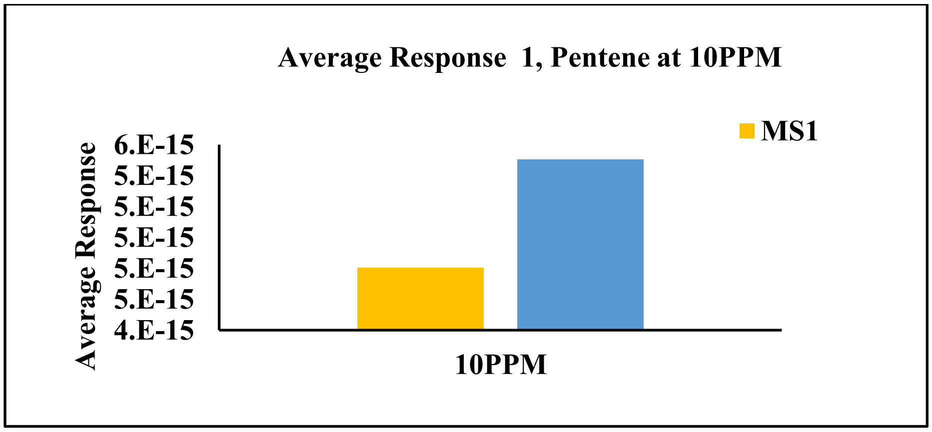


Figure 6. 20. Average Mass Spectrometer Response to 1, Pentene

Based on figure 6.13 – 6.20, the average mass spectrometer response for 1 and 2 ranges from 10^{-14} – 10^{-15}, with helium being the most abundant in the mixed standard one because it is the balance of the gas mixed standard. The MS response of the gases in the order 10^{-14} – 10^{-15}, is indicative of the inverse relationship between the order of magnitude of the detection and concentration of gas analytes. P-Xylene and O-Xylene are isomers which are also detected by both the instruments (Figures 6.18 & 6.19) although no established trend could be identified.

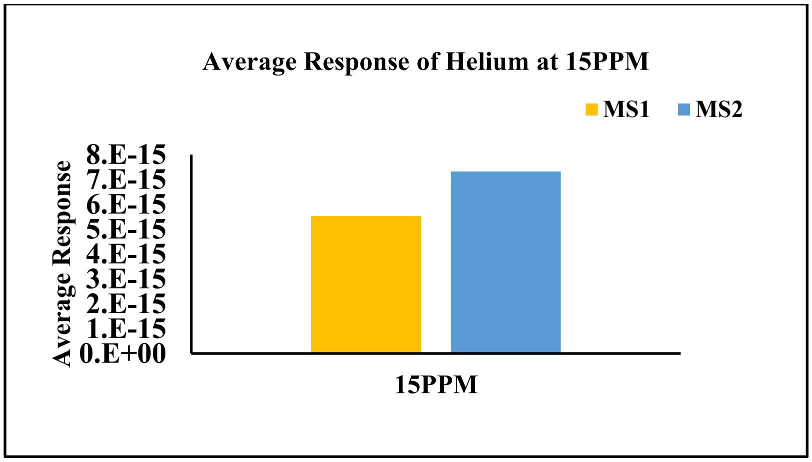


Figure 6. 21. Average Mass Spectrometer Response to Helium

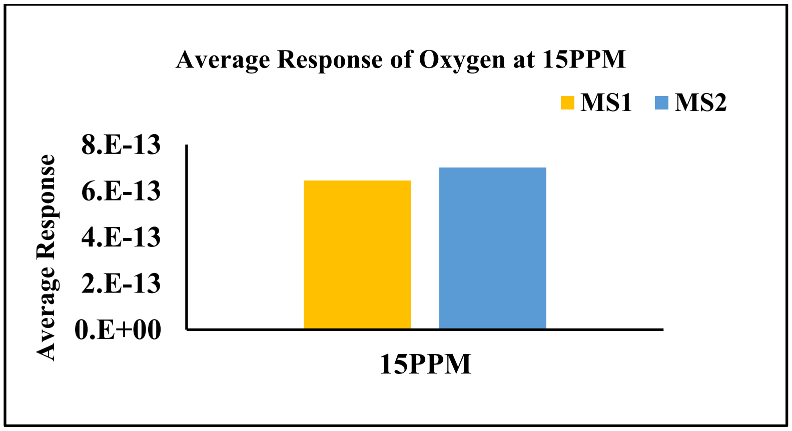


Figure 6. 22. Average Mass Spectrometer Response to Oxygen

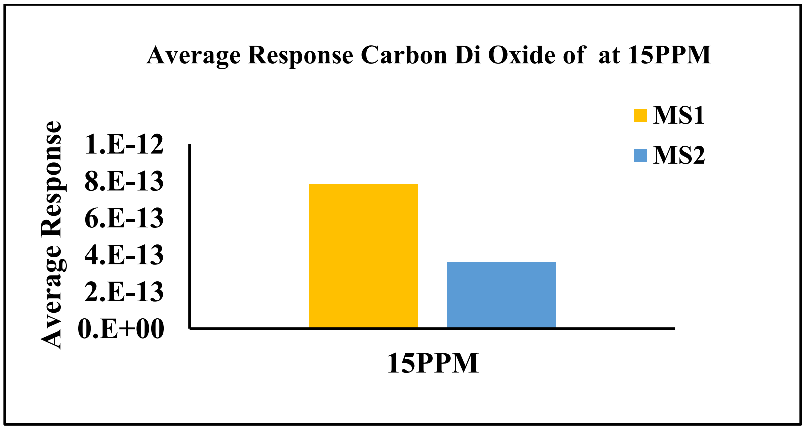


Figure 6. 23. Average Mass Spectrometer Response to Carbon Di Oxide

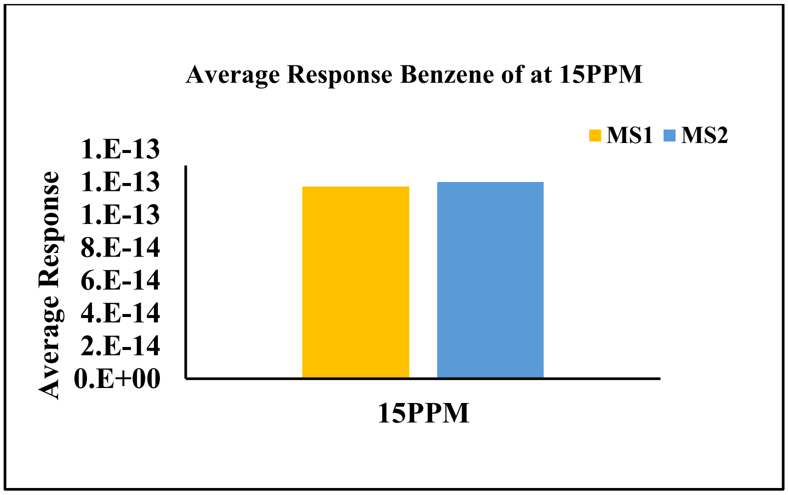


Figure 6. 24. Average Mass Spectrometer Response to Benzene

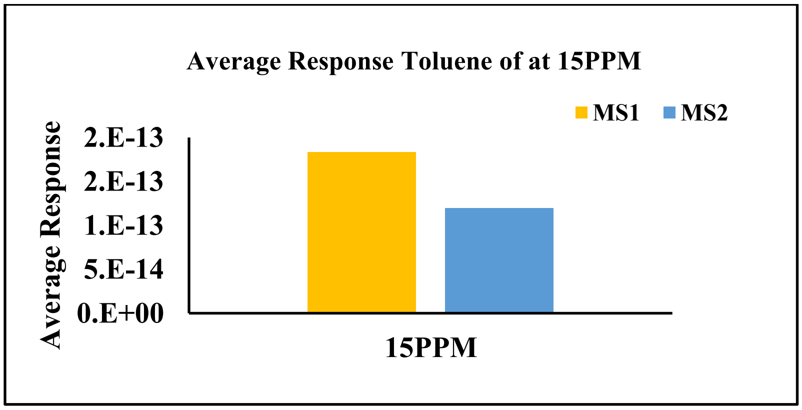


Figure 6. 25. Average Mass Spectrometer Response to Toluene

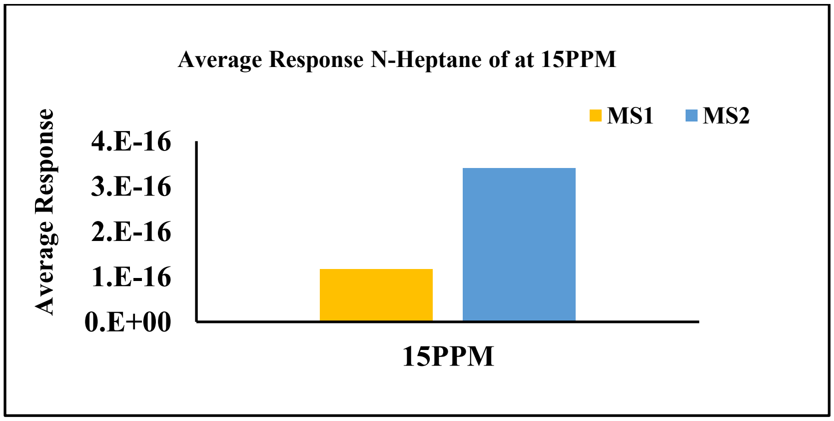


Figure 6. 26. Average Mass Spectrometer Response to N-Heptane

Figures 6.21 – 6.26 shows the average Mass Spectrometer response of the heavier hydrocarbon and nonhydrocarbons with orders of 10^{-16} – 10^{-13} for the gases in the mixed standard with the concentration of 15PPM.

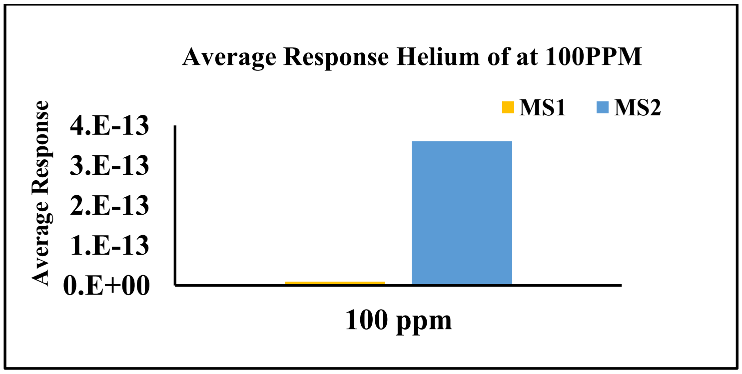


Figure 6. 27. Average Mass Spectrometer Response to Helium

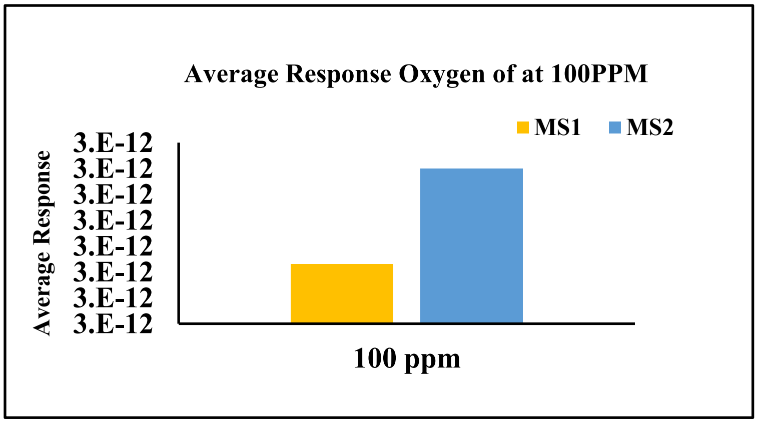


Figure 6. 28. Average Mass Spectrometer Response to Oxygen

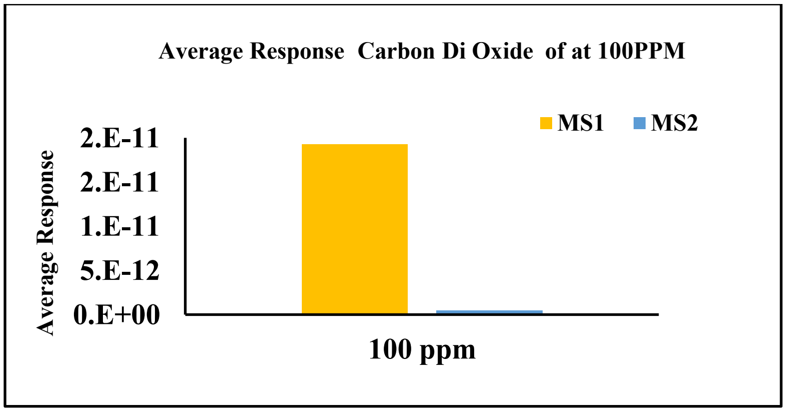


Figure 6. 29. Average Mass Spectrometer Response to Carbon Di Oxide

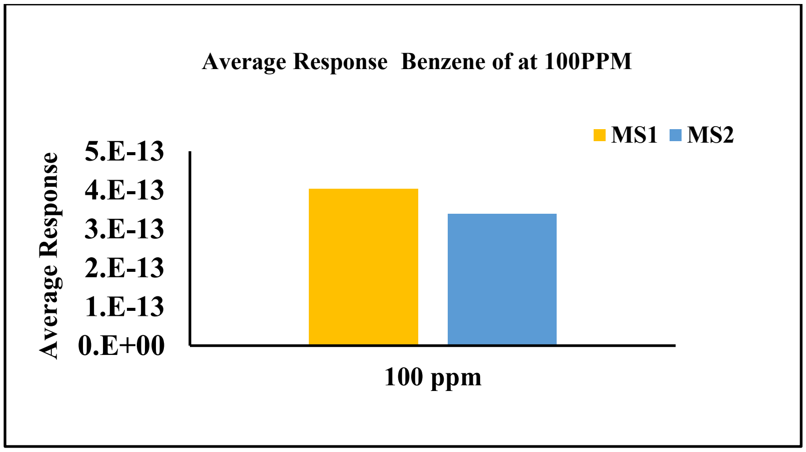


Figure 6. 30. Average Mass Spectrometer Response to Benzene

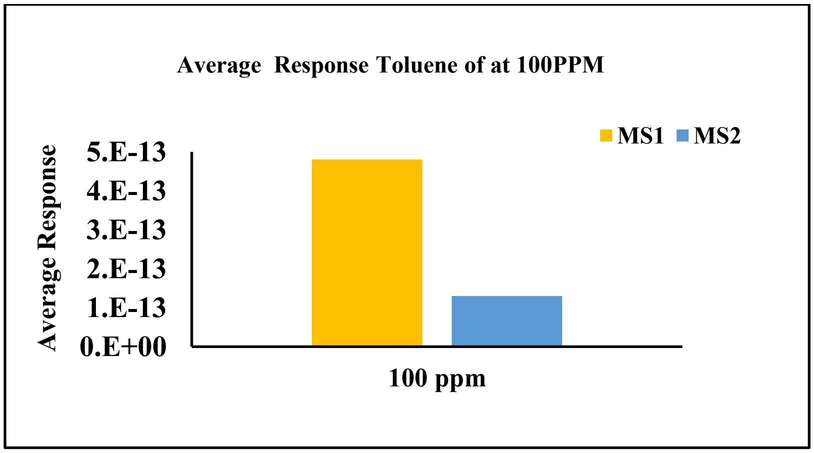


Figure 6. 31. Average Response Toluene in MS1 & MS2

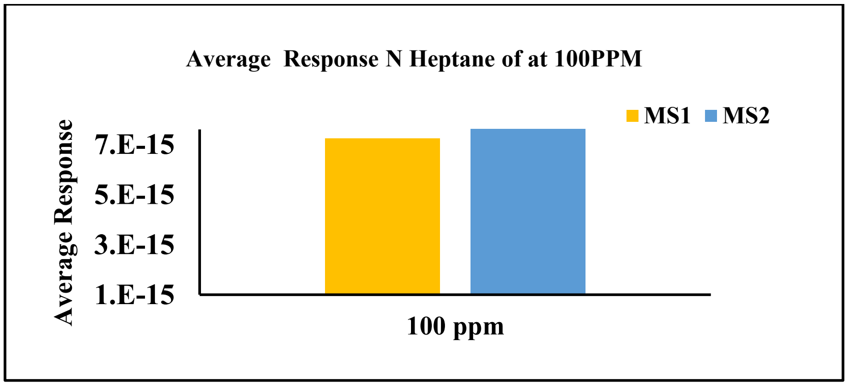


Figure 6. 32. Average Mass Spectrometer Response to N- Heptane

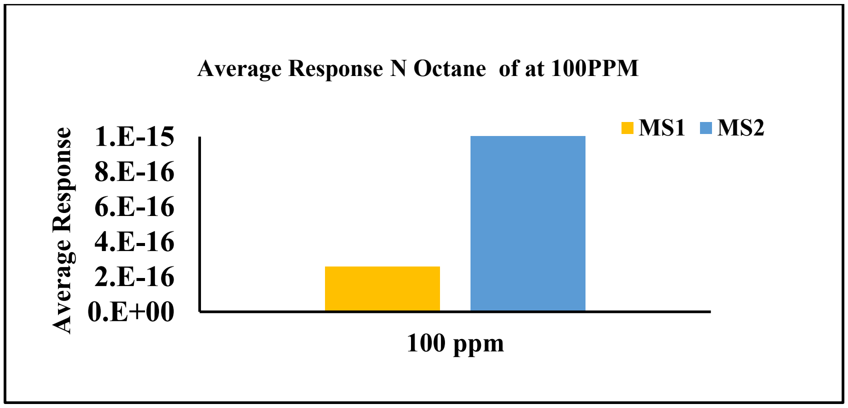


Figure 6. 33. Average Mass Spectrometer Response to N- Octane

Figure 6.27 – 6.33 shows a significant increase in the order (10^{-16} – 10^{-11}) of gases detected as the average mass spectrometer response with similarities in the responses of the gases to both mass spectrometers. Overall, the tools remain sensitive with slight difference for both nonhydrocarbons and the heavier hydrocarbons. The spectrum may seem exaggerated, but the y-axis marks the numbers, and for all the compounds analyzed, the order of magnitude does not change by more than one.

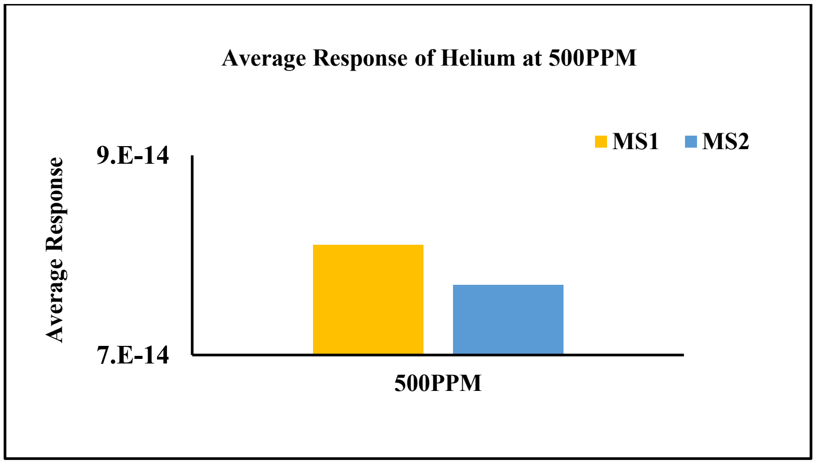


Figure 6. 34. Average Mass Spectrometer Response to Helium

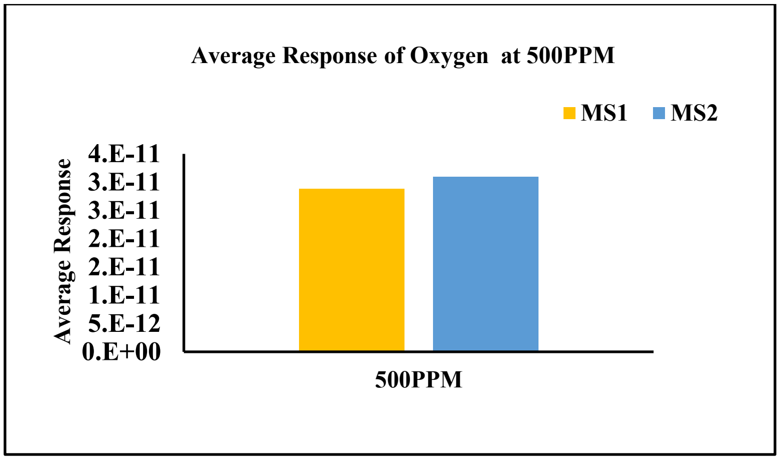


Figure 6. 35. Average Mass Spectrometer Response to Oxygen

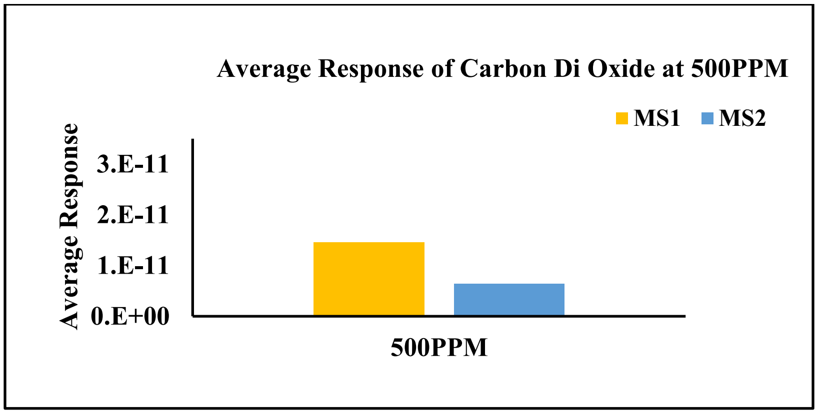


Figure 6. 36. Average Mass Spectrometer Response to Carbon di Oxide

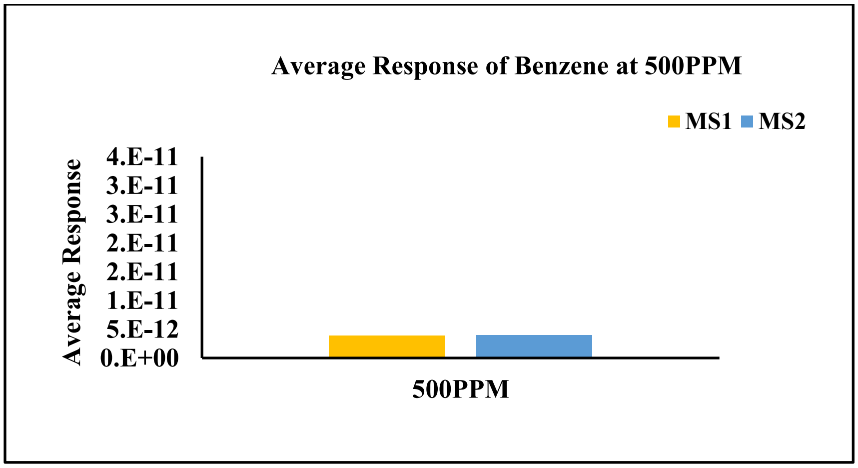


Figure 6. 37. Average Mass Spectrometer Response to Benzene

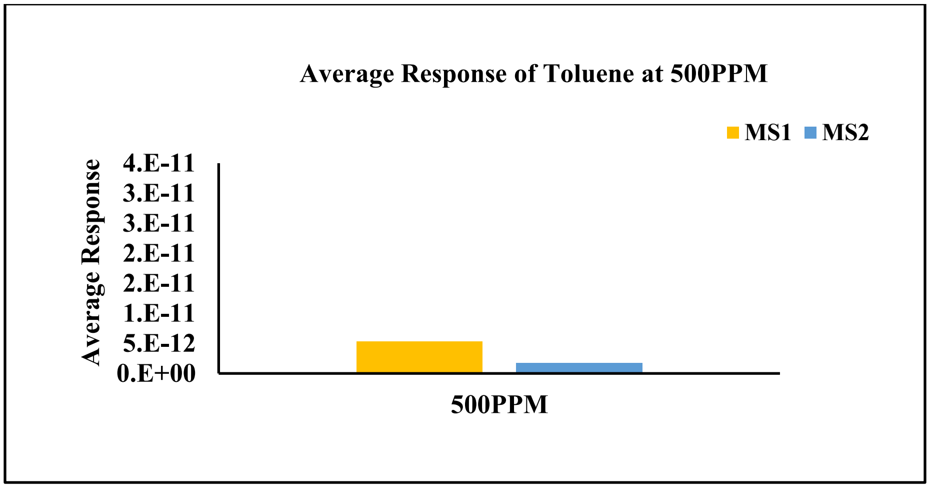


Figure 6. 38. Average Mass Spectrometer Response to Toluene

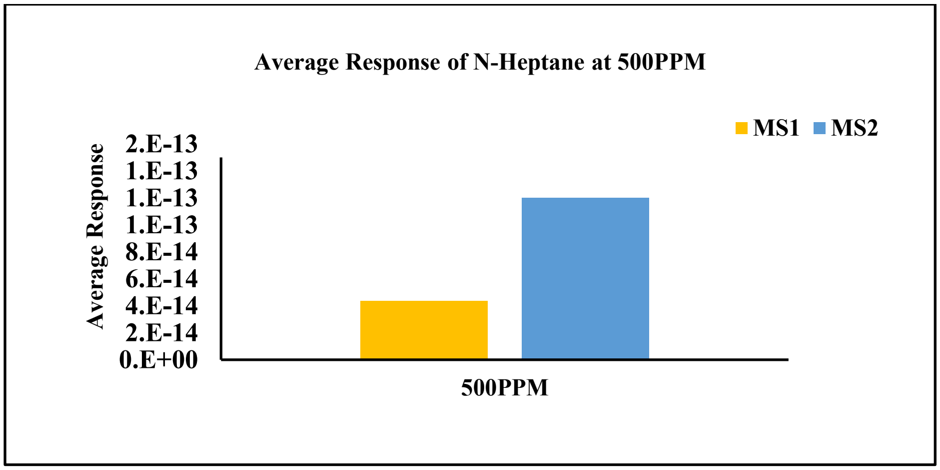


Figure 6. 39. Average Mass Spectrometer Response to N- Heptane

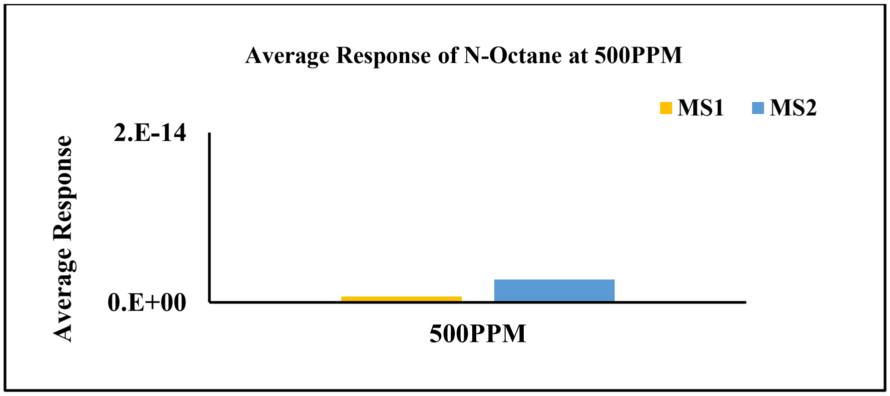


Figure 6. 40. Average Mass Spectrometer Response to N-Octane

Figures 6.34 – 6.40 represents the average mass spectrometer response to the gases at 500PPM. Like the response of the gas to the mass spectrometer at ~100PPM becomes closer in the order of response. The nonhydrocarbons and heavier hydrocarbon compounds detected are in the order of $10^{-14} – 10^{-11}$. Compared to the MS response at 100PPM, the order of magnitude of the MS detection increased by about four orders - evidence that the tool increased sensitivity to higher concentration gases.

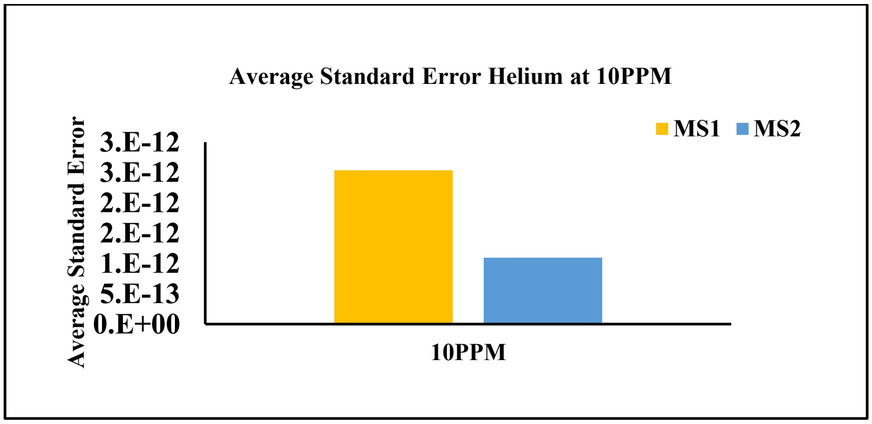


Figure 6. 41. Average Standard Error for Helium

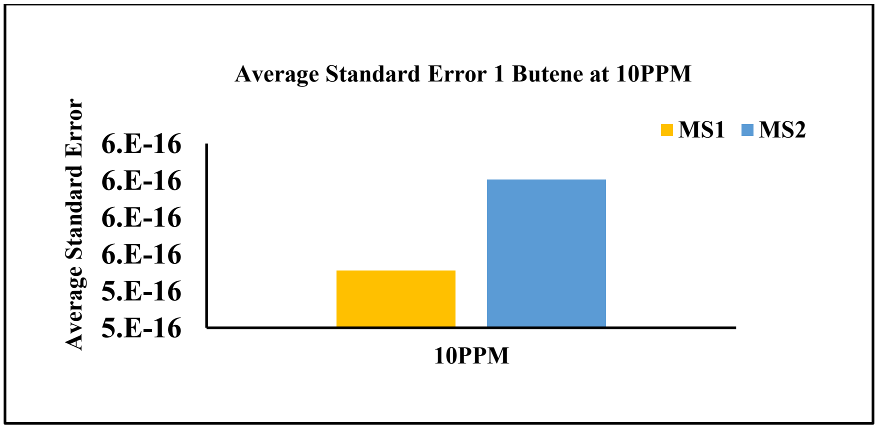


Figure 6. 42. Average Standard Error for 1 Butene

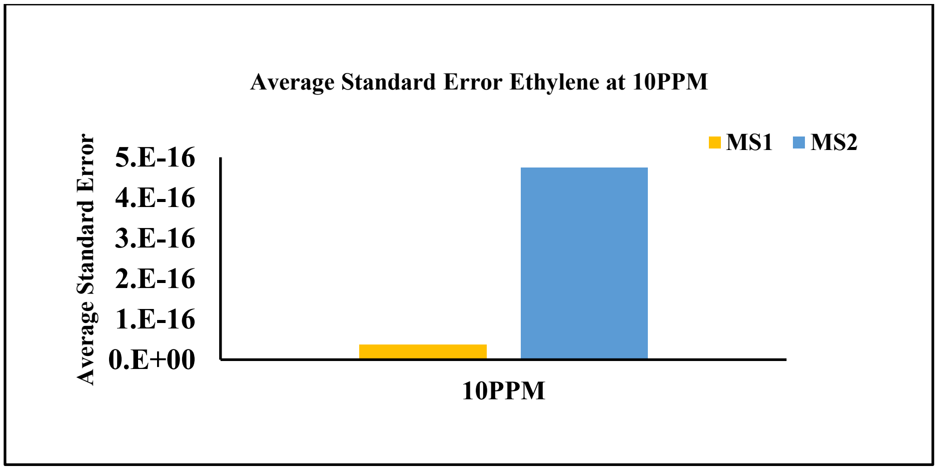


Figure 6. 43. Average Standard Error for Ethylene

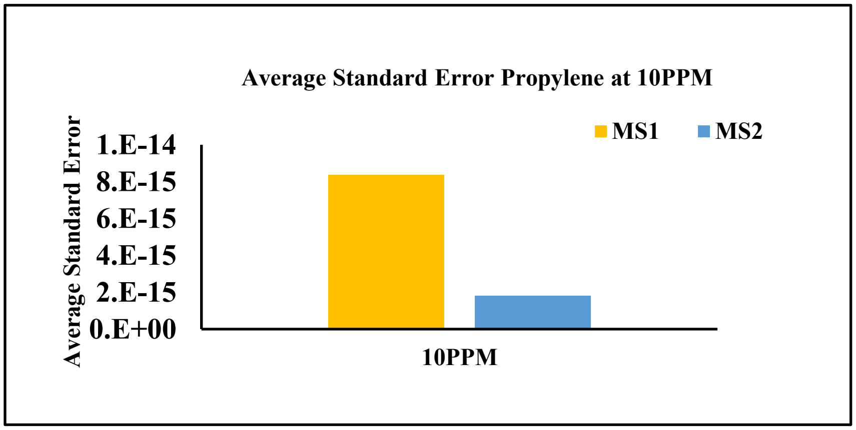


Figure 6. 44. Average Standard Error for Propylene

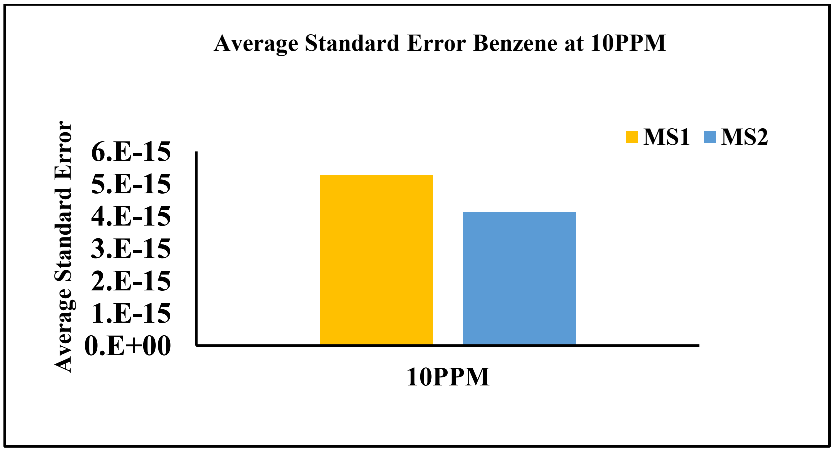


Figure 6. 45. Average Standard Error for Benzene

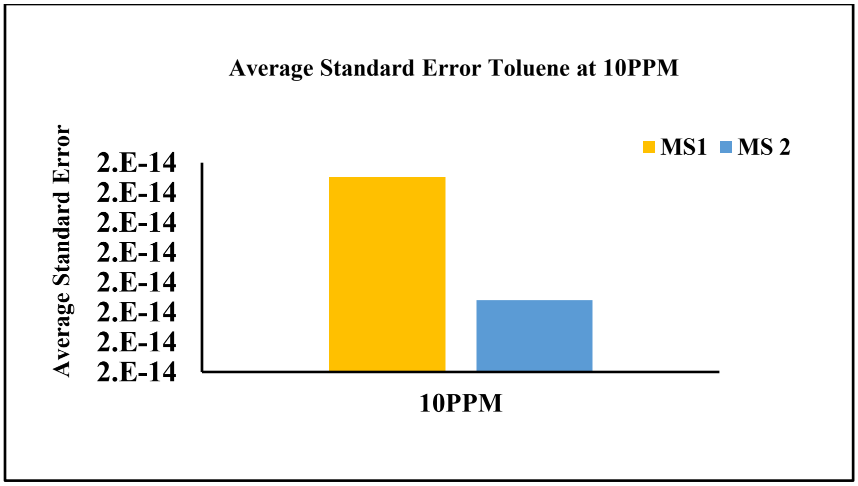


Figure 6. 46. Average Standard Error for Toluene

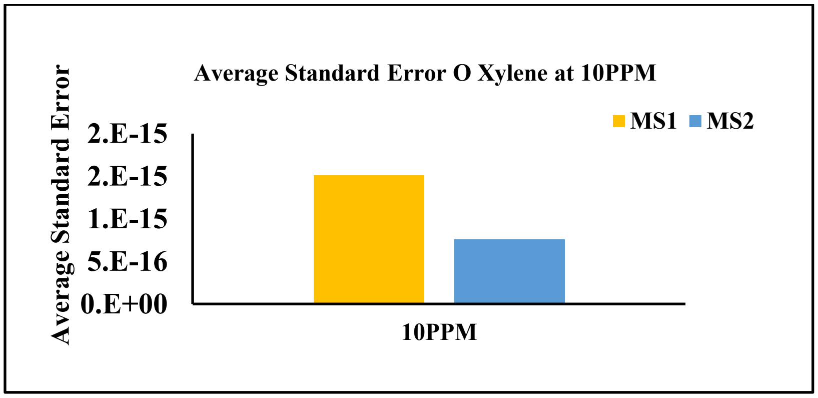


Figure 6. 47. Average Standard Error for O Xylene

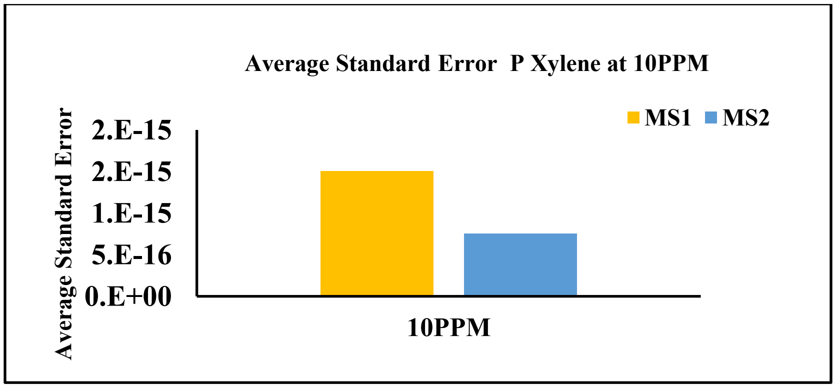


Figure 6. 48. Average Standard Error for Helium

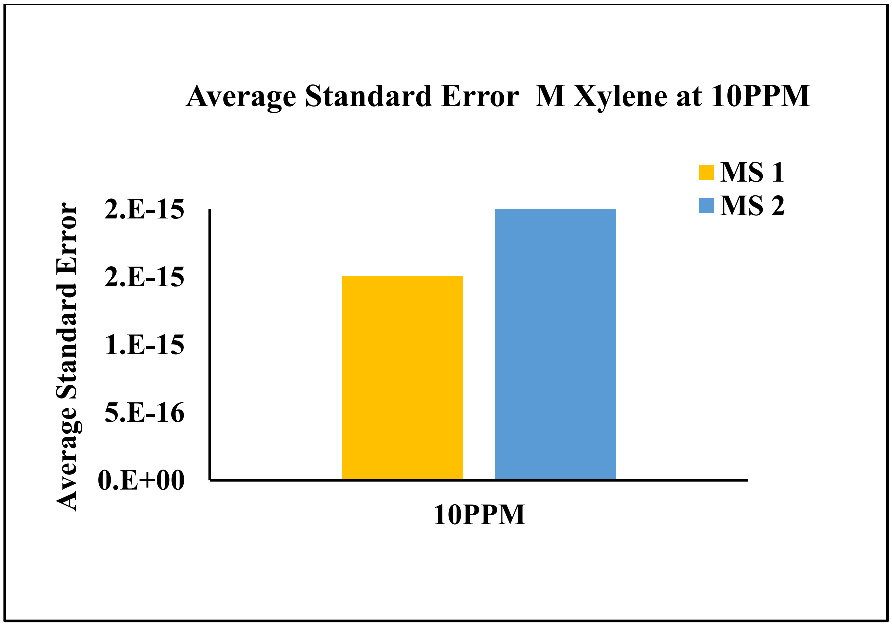


Figure 6. 49. Average Standard Error for M Xylene

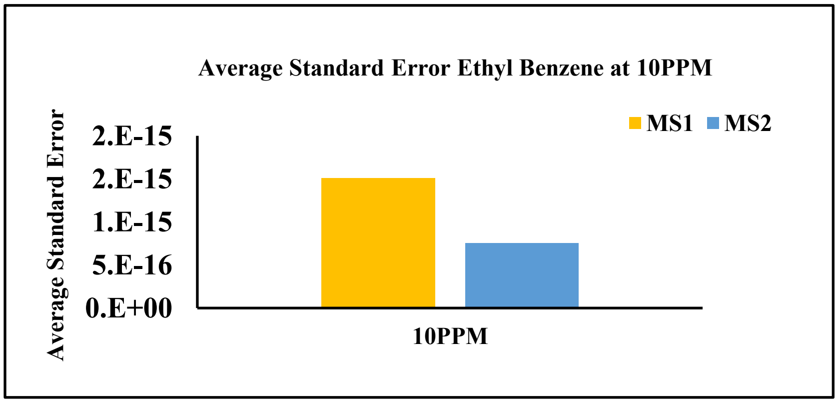


Figure 6. 50. Average Standard Error for Ethyl Benzene

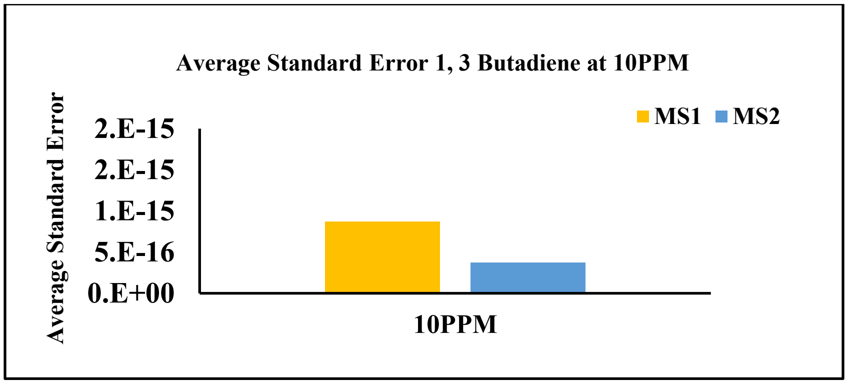


Figure 6. 51. Average Standard Error for 1,3 Butadiene

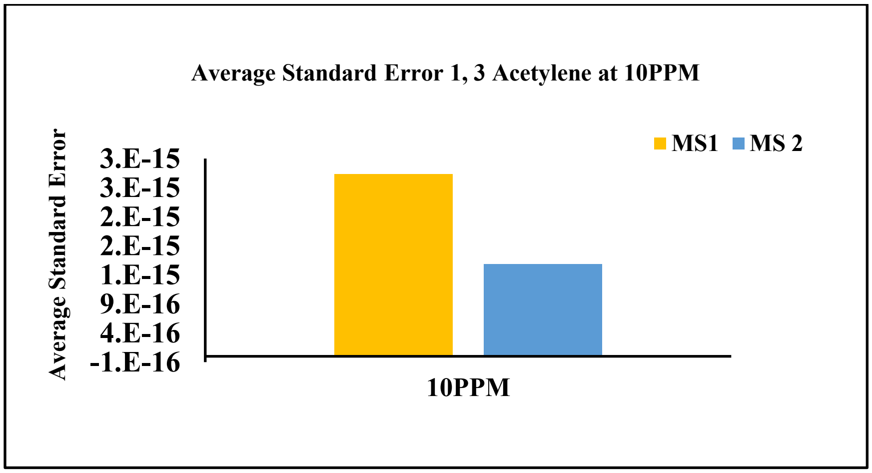


Figure 6. 52. Average Standard Error for 1, 3 Acetylene

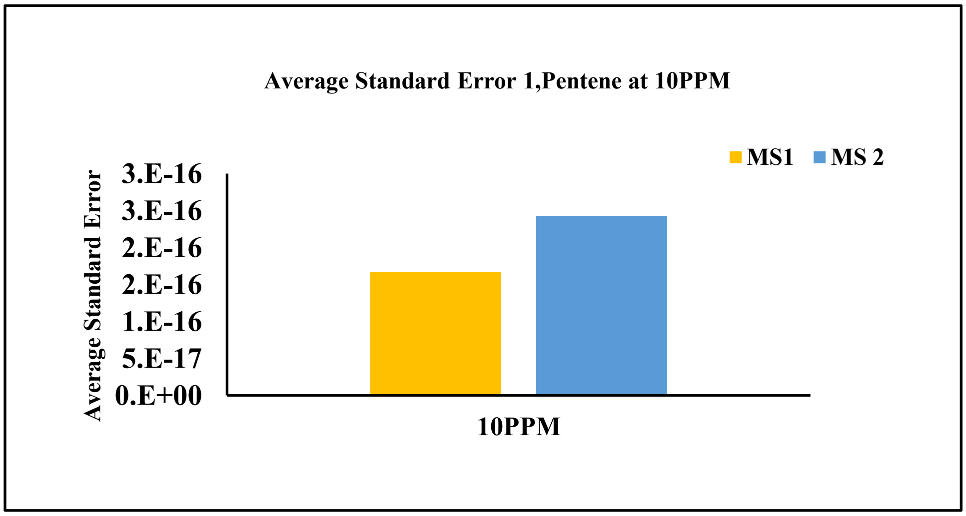


Figure 6. 53. Average Standard Error for 1, Pentene

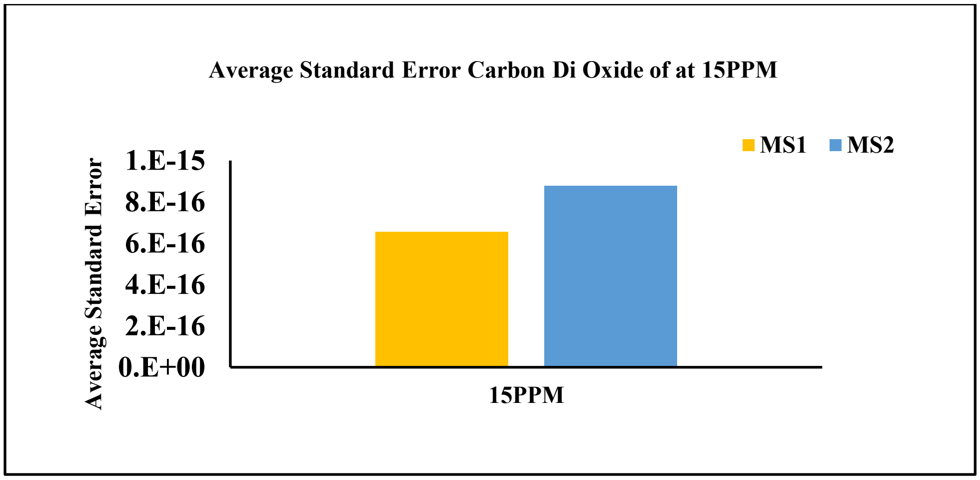


Figure 6. 54. Average Standard Error for Carbon Di Oxide

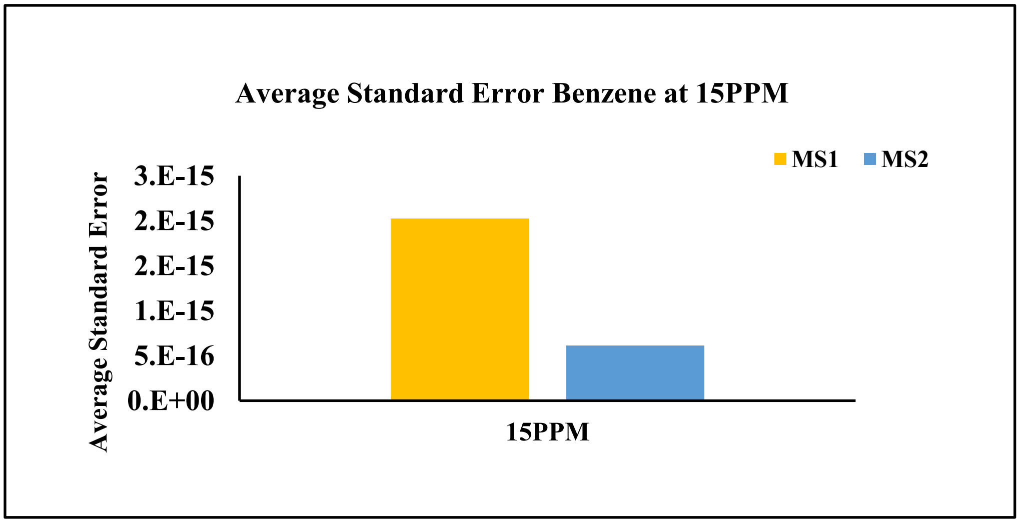


Figure 6. 55. Average Standard Error for Benzene

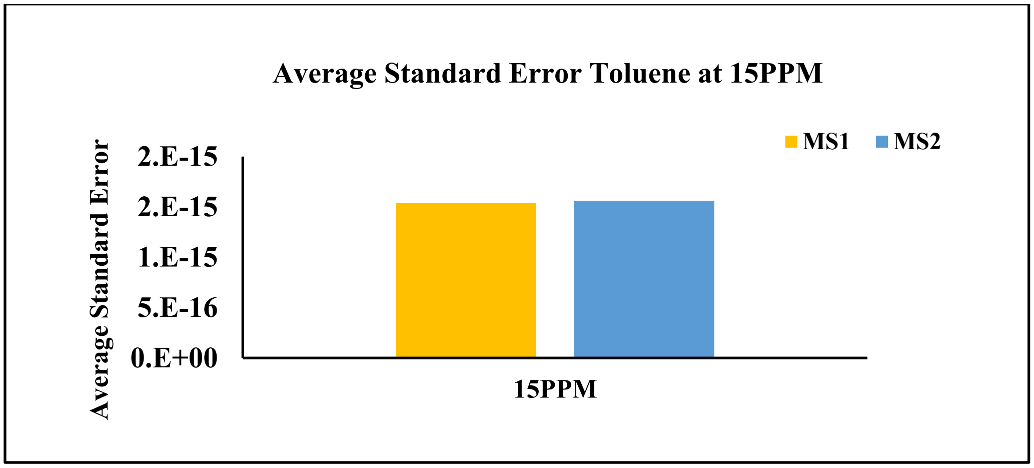


Figure 6. 56. Average Standard Error for Toluene

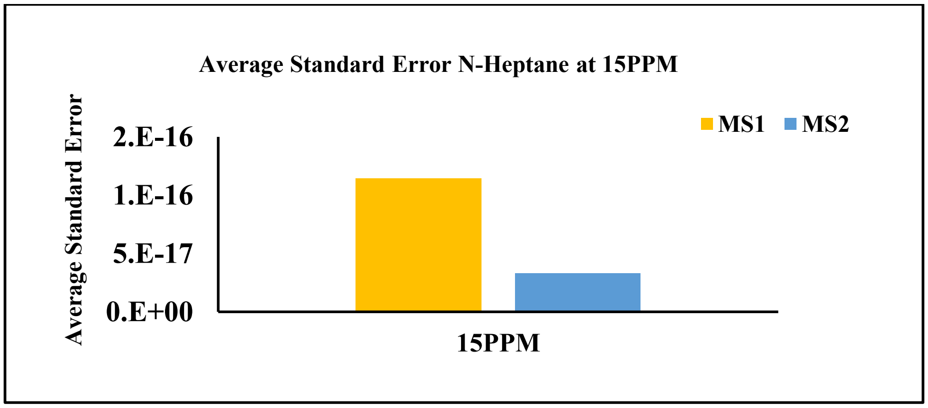


Figure 6. 57. Average Standard Error for N-Heptane

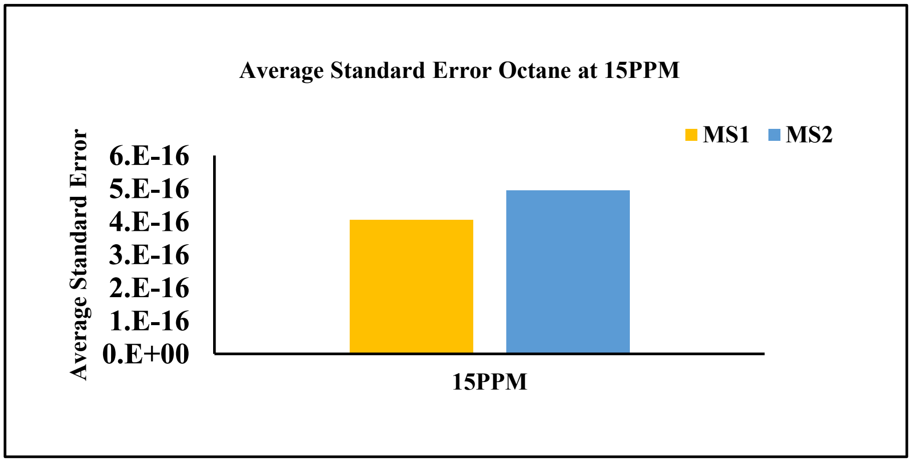


Figure 6. 58. Average Standard Error for Octane

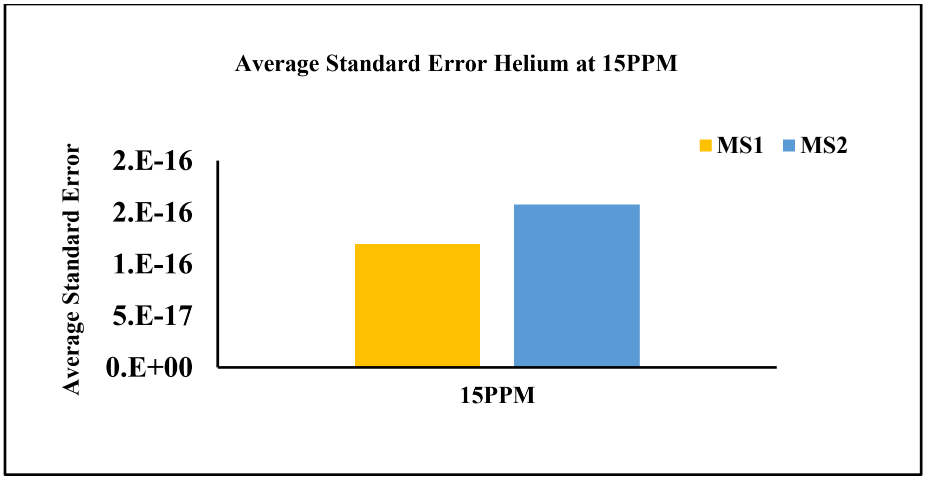


Figure 6. 59. Average Standard Error for Helium

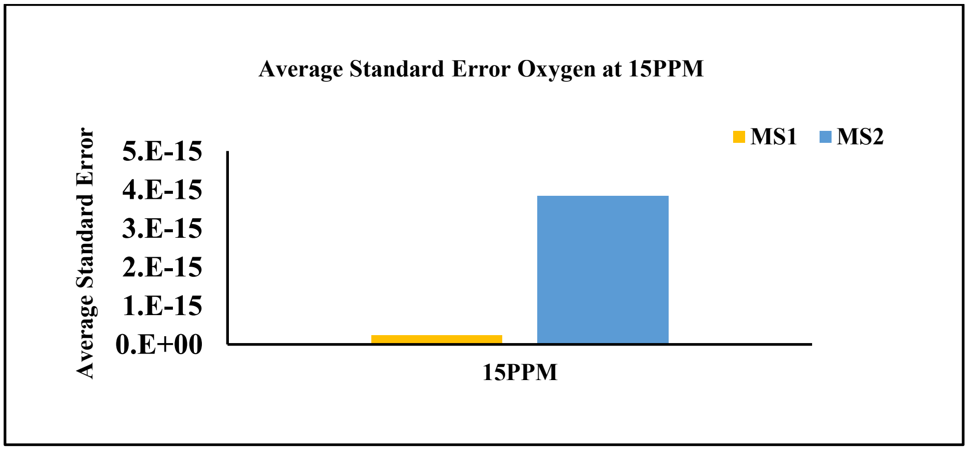


Figure 6. 60. Average Standard Error for Oxygen

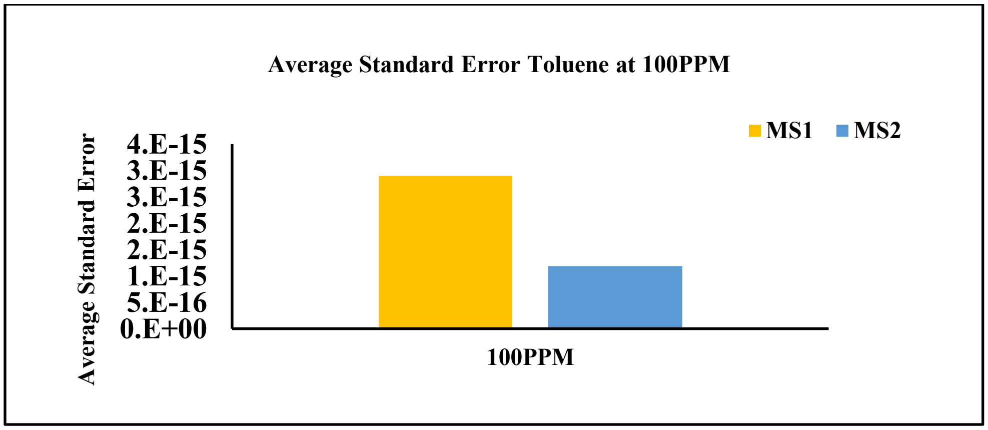


Figure 6. 61. Average Standard Error for Toluene

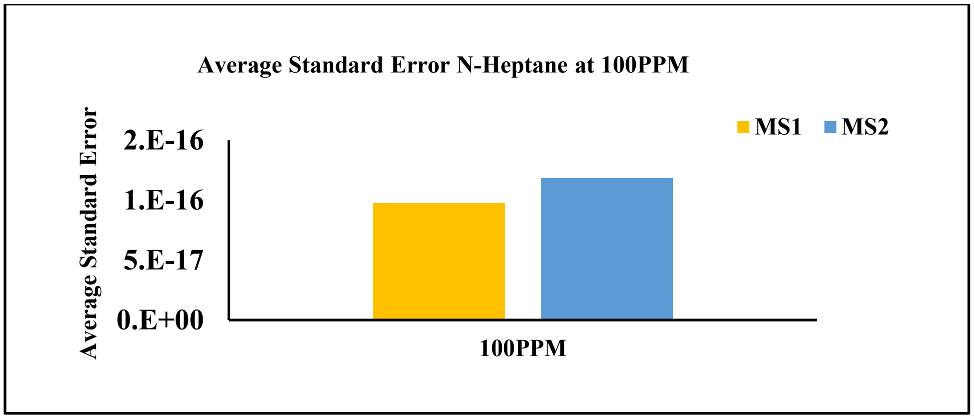


Figure 6. 62. Average Standard Error for N- Heptane

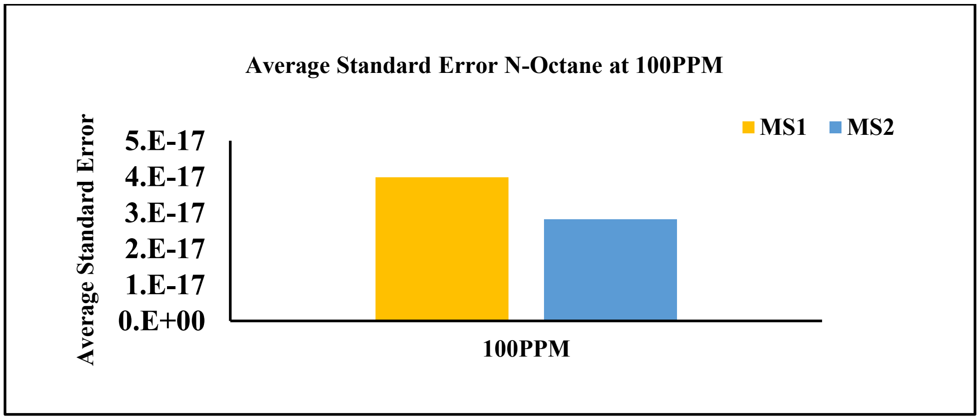


Figure 6. 63. Average Standard Error for N-Octane

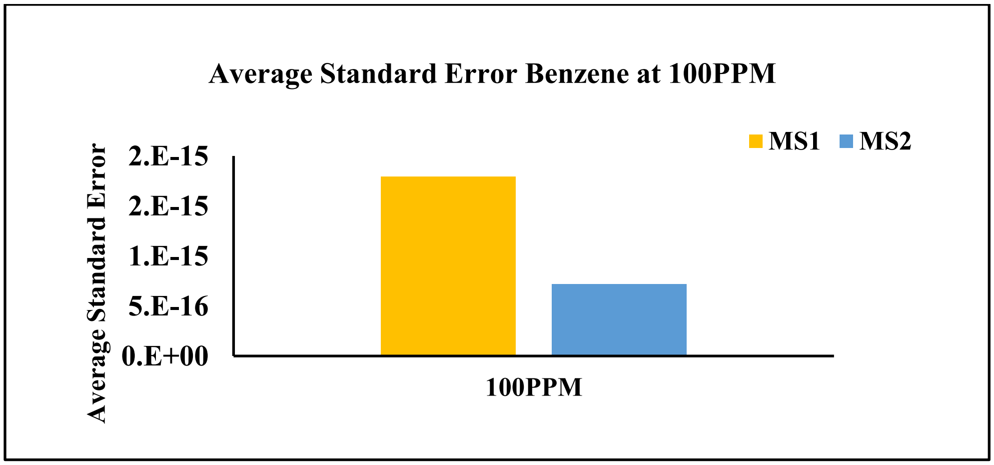


Figure 6. 64. Average Standard Error for Benzene

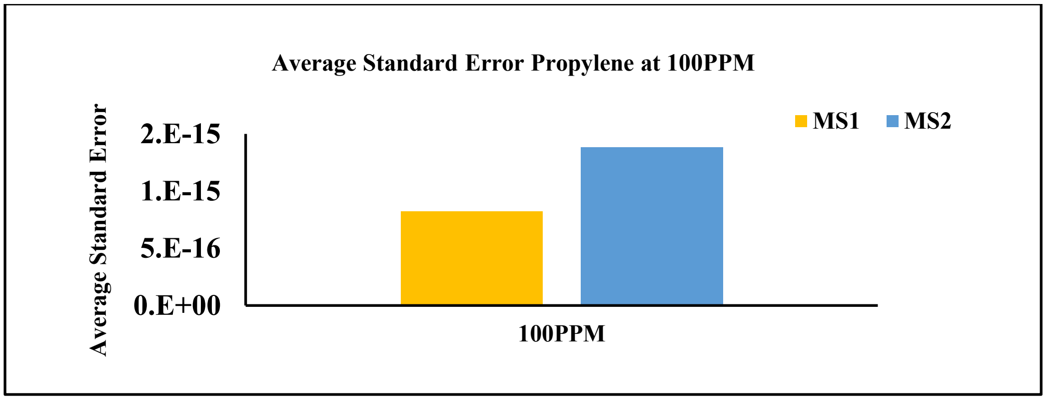


Figure 6. 65. Average Standard Error for Propylene

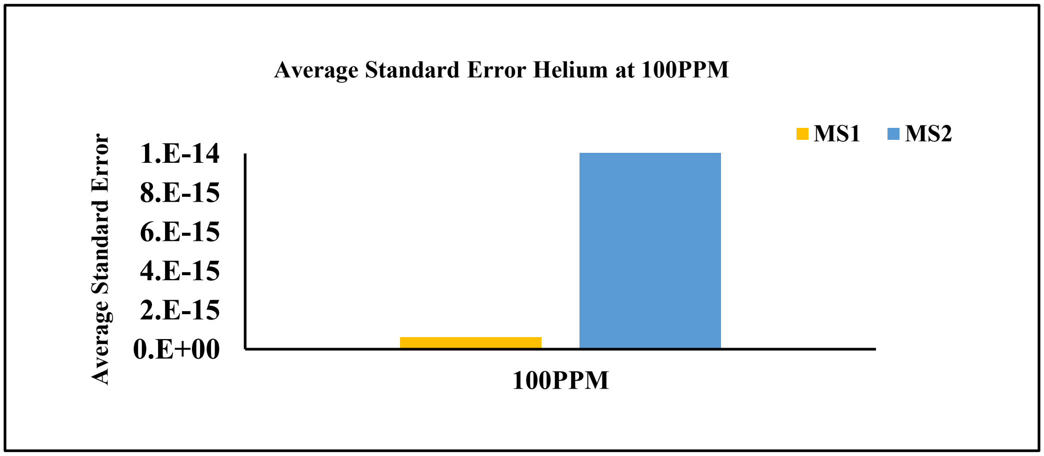


Figure 6. 66. Average Standard Error for Helium

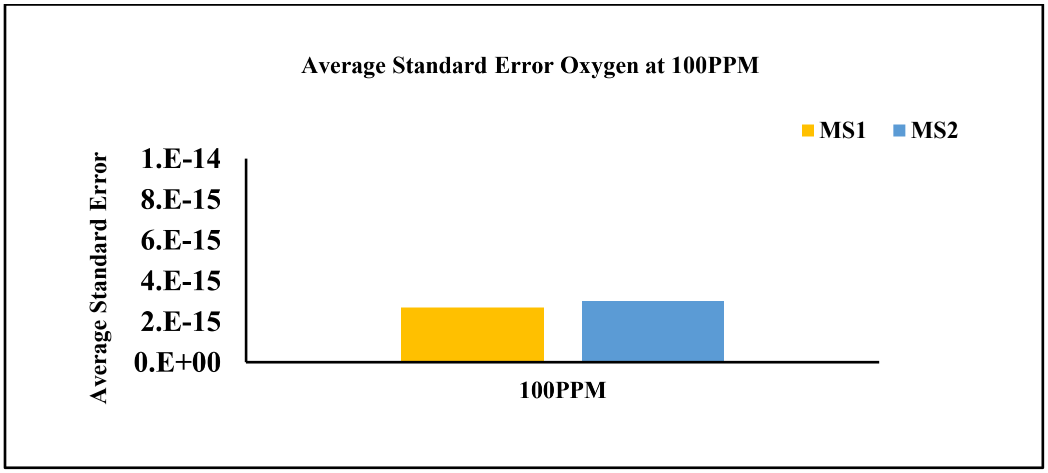


Figure 6. 67. Average Standard Error for Oxygen

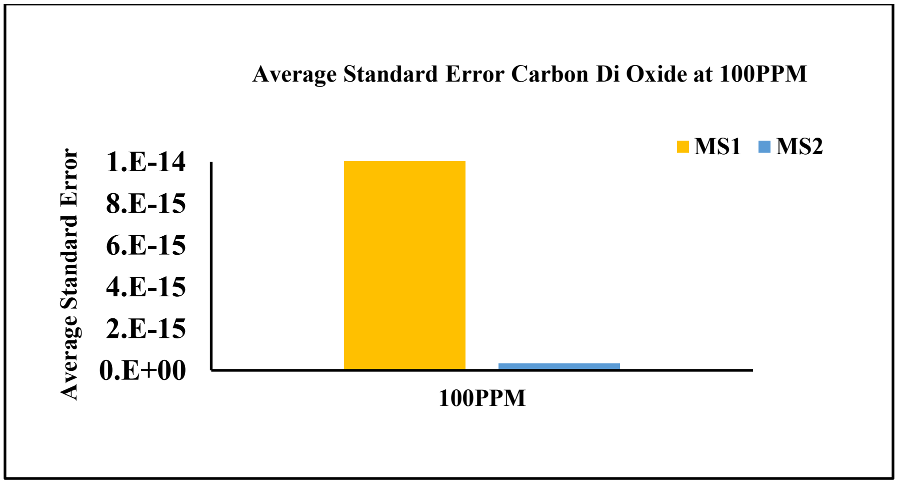


Figure 6. 68. Average Standard Error for Carbon Di Oxide

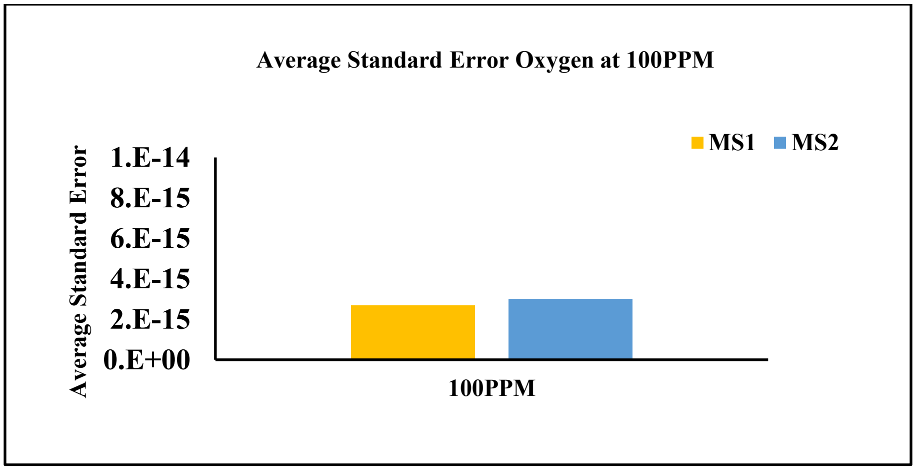


Figure 6. 69. Average Standard Error for Oxygen

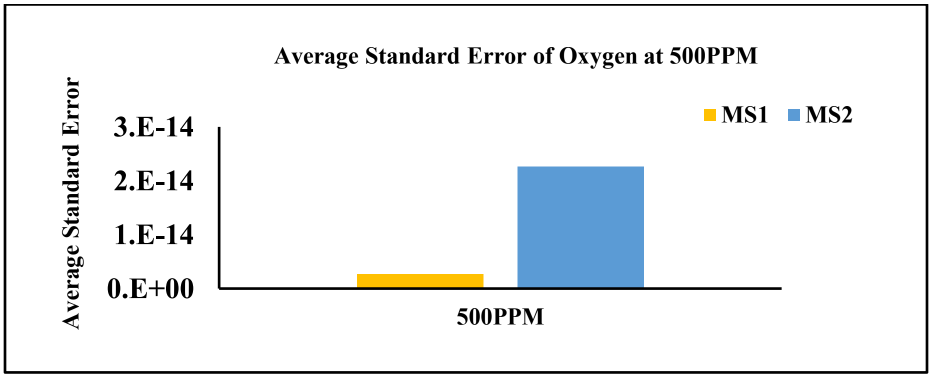


Figure 6. 70. Average Standard Error for Oxygen

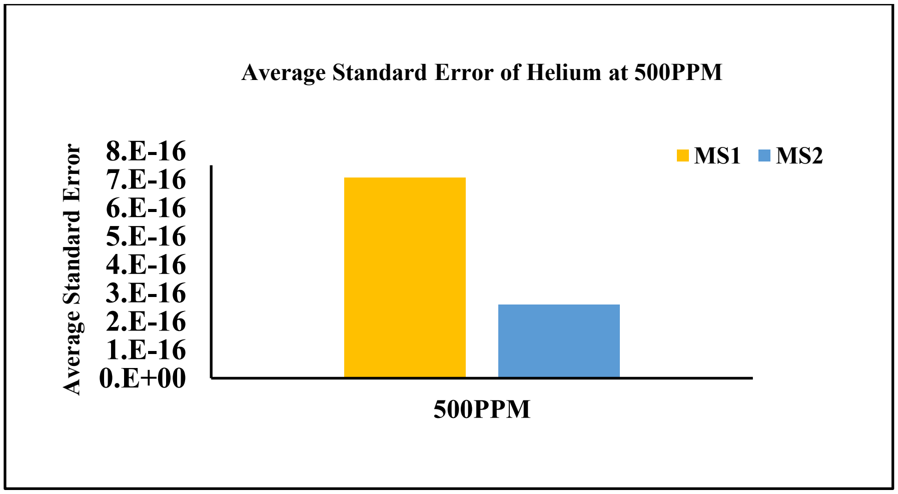


Figure 6. 71. Average Standard Error for Helium

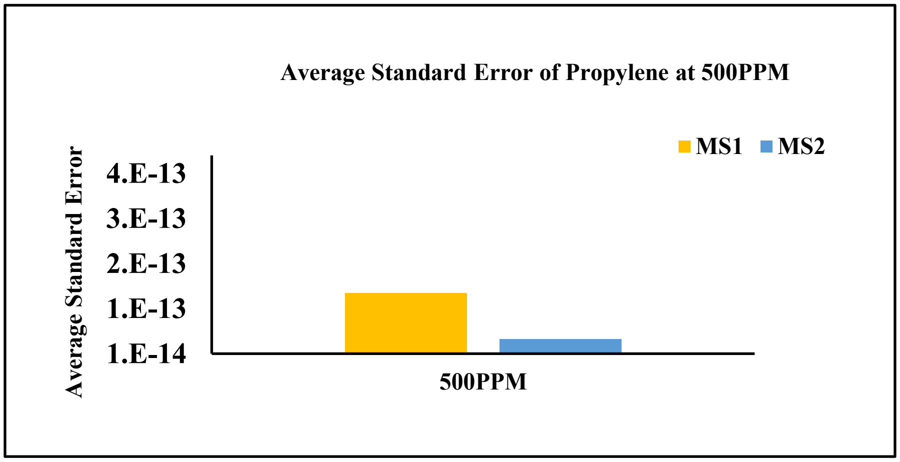


Figure 6. 72. Average Standard Error for Propylene

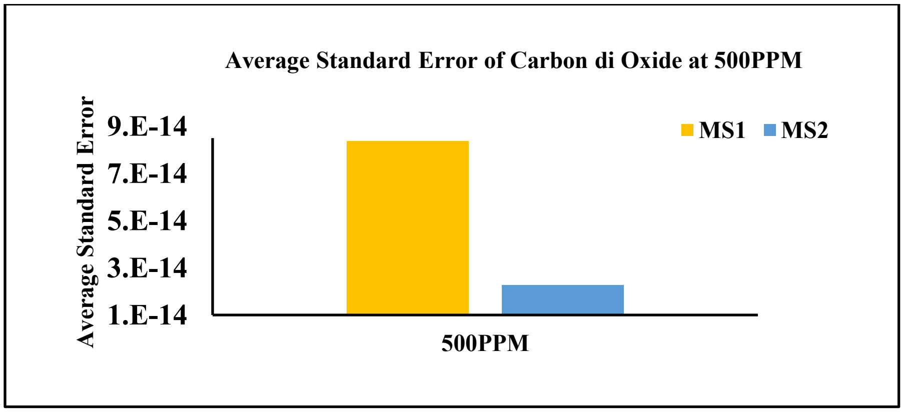


Figure 6. 73. Average Standard Error for Carbon Di Oxide

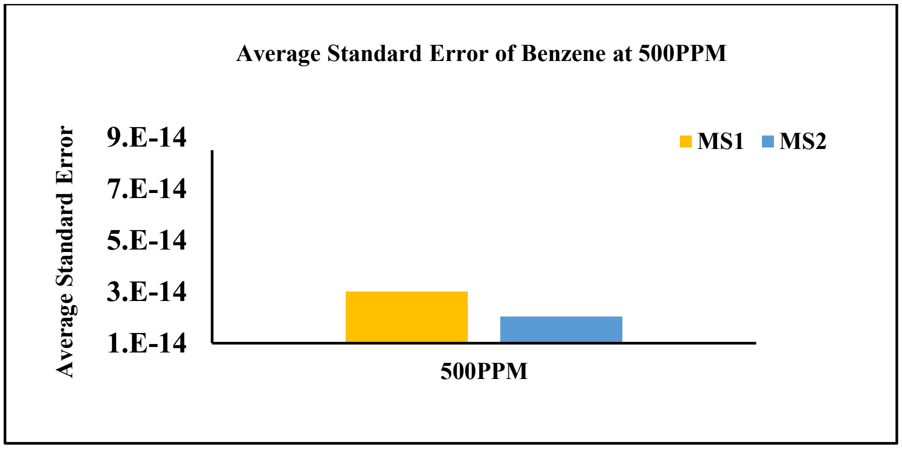


Figure 6. 74. Average Standard Error for Benzene

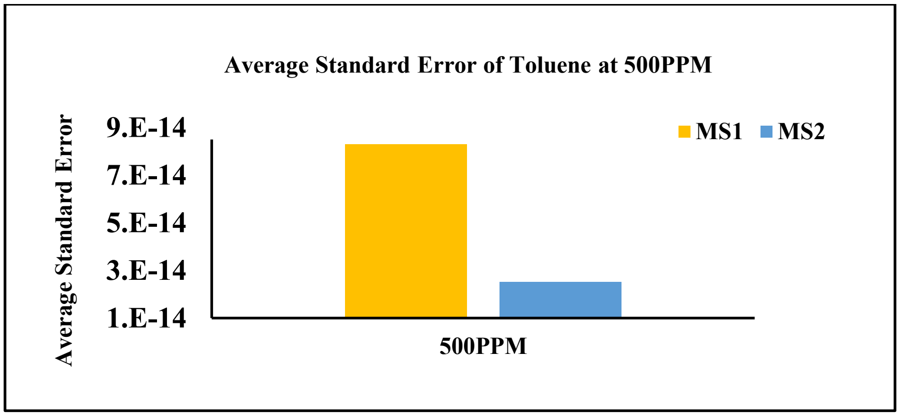


Figure 6. 75. Average Standard Error for Toluene

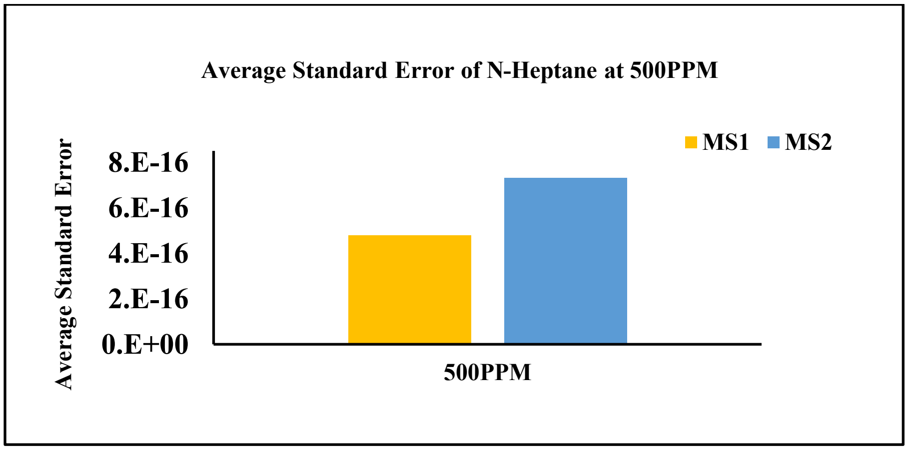


Figure 6. 76. Average Standard Error for N- Heptane

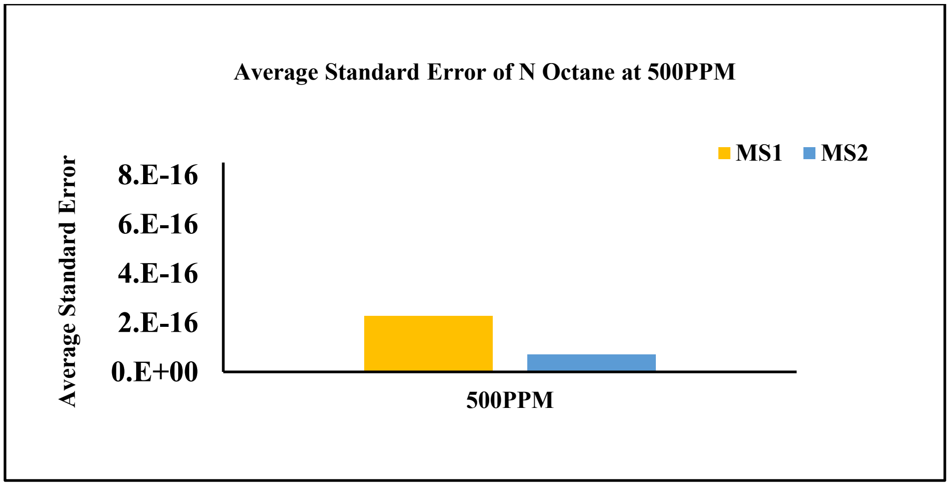


Figure 6. 77. Average Standard Error for N-Octane

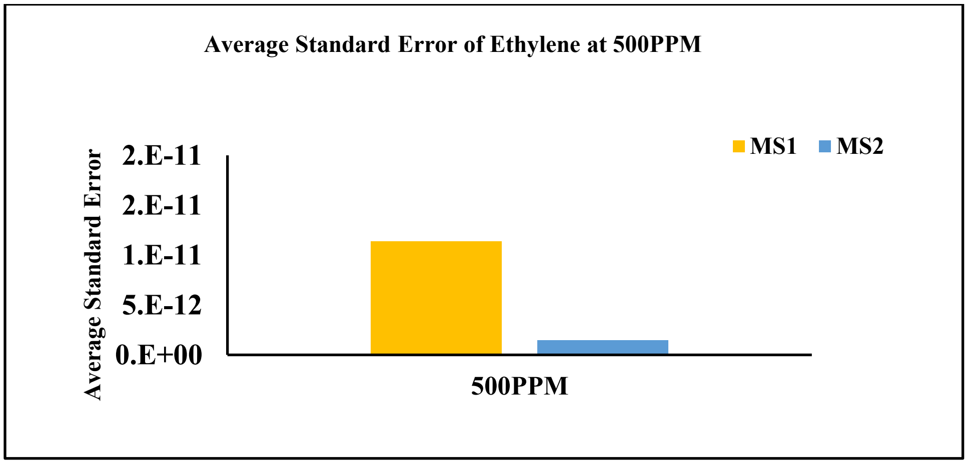


Figure 6. 78. Average Standard Error for Ethylene

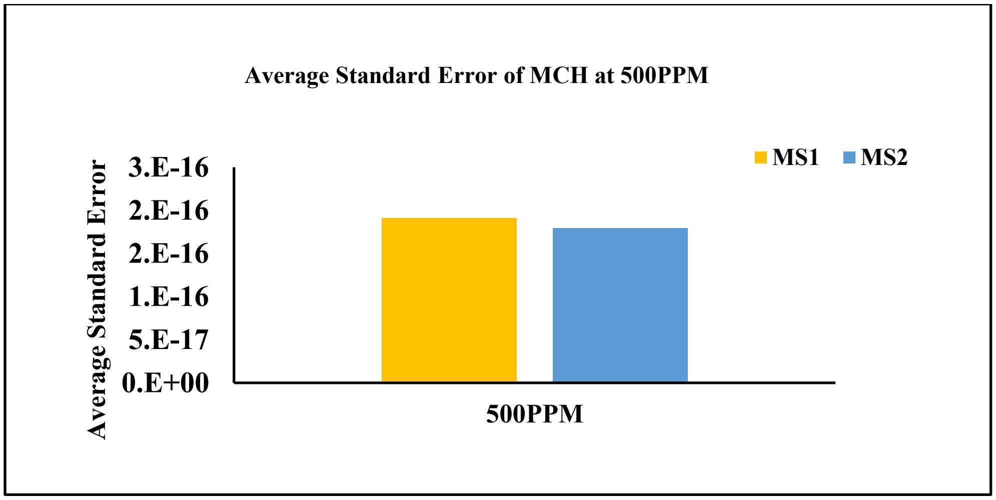


Figure 6. 79. Average Standard Error for MCH

Figures 6.41 – 6.79, represent the average standard error at 10,15,100 and 500PPM, all associated with the detection capability, sample size and standard deviation of the experiments. The standard error remains in the order of 10^{-13} – 10^{-16}, where the errors of order 10^{-13} - 10^{-15} are associated with errors in detections from gas mixed standards measured at ~ 10 – 15 PPM. The order of magnitude of standardized error for the lower concentrations is expected from the gases because the gas availability for ionization is not as abundant as in higher concentration gas standards. In the case of the gases with ~100PPM – 500PPM concentration the order of magnitude is 10^{-13} – 10^{-12} for the standardized error. Overall, these errors remain minimal and almost insignificant to the results of the mass spectrometric analysis for both tools.

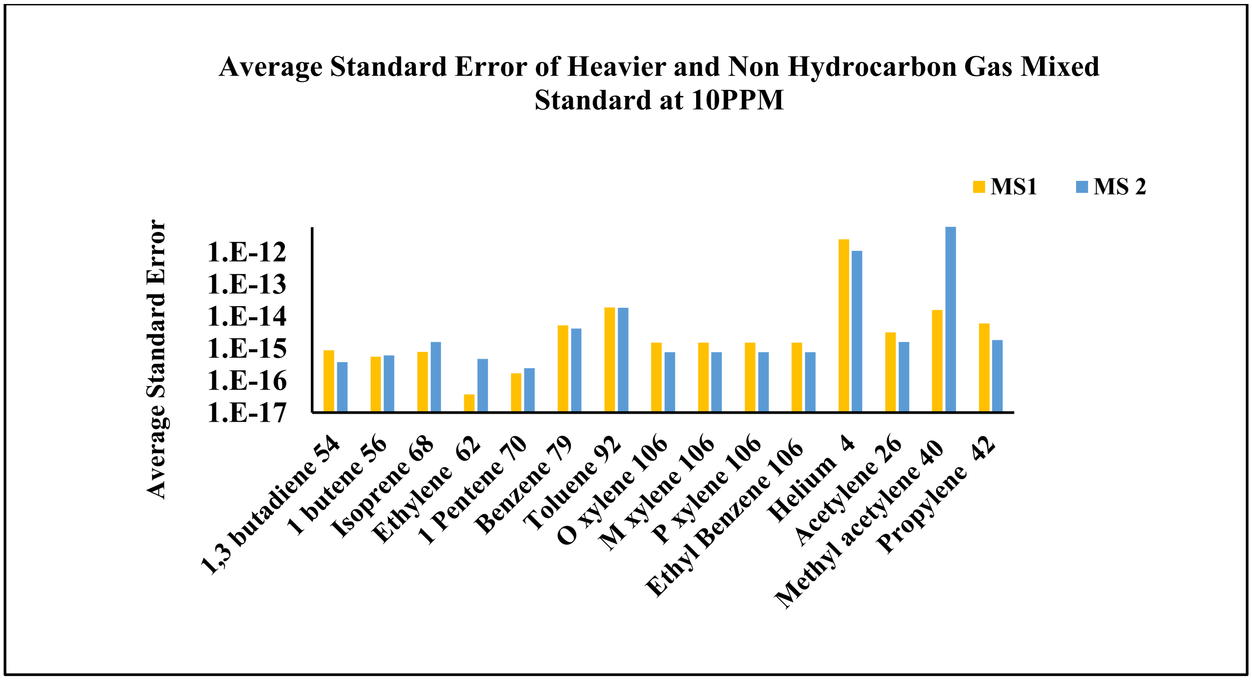


Figure 6. 80. Cumulative Average Standard Error for Heavier and Non-Hydrocarbons at 10PPM

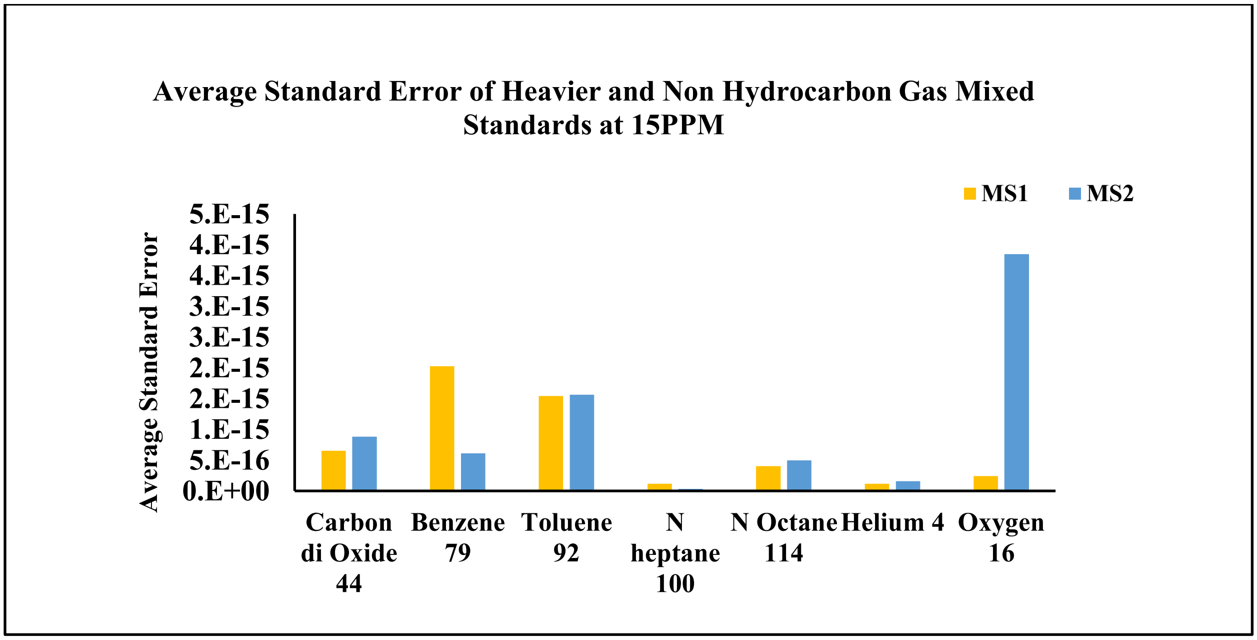


Figure 6. 81. Cumulative Average Standard Error for Heavier and Non-Hydrocarbons at 15PPM

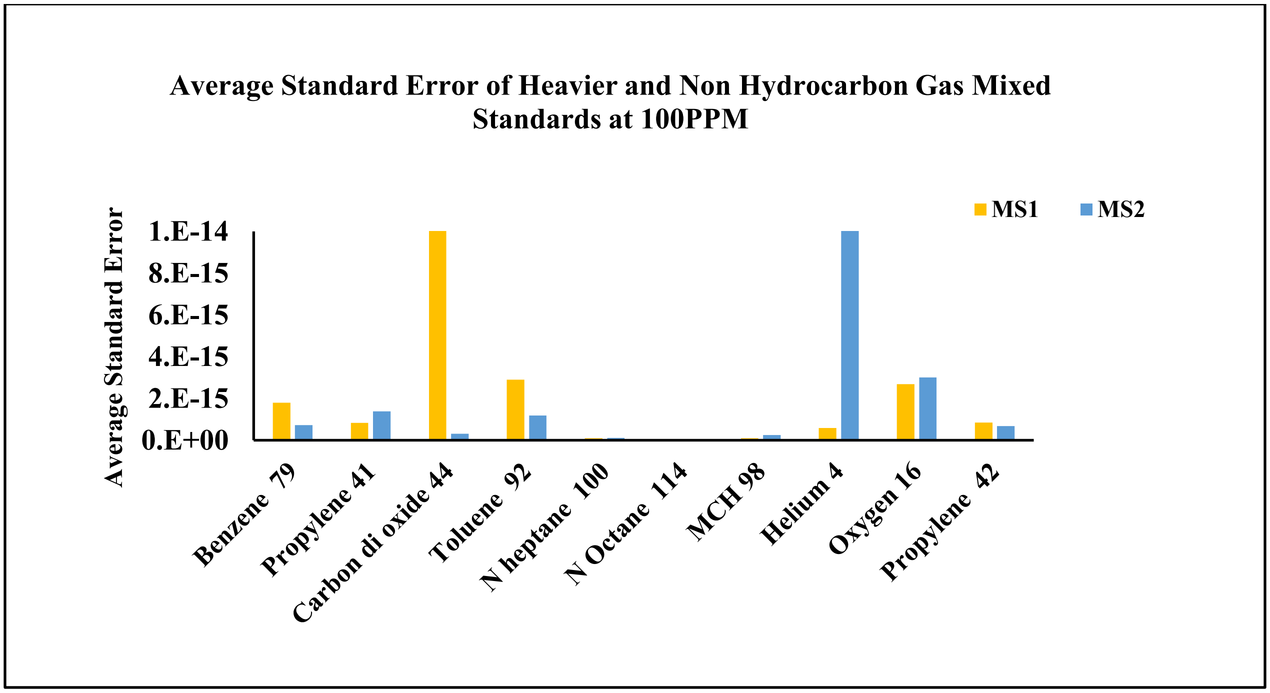


Figure 6. 82. Cumulative Average Standard Error for Heavier and Non-Hydrocarbons at 100PPM

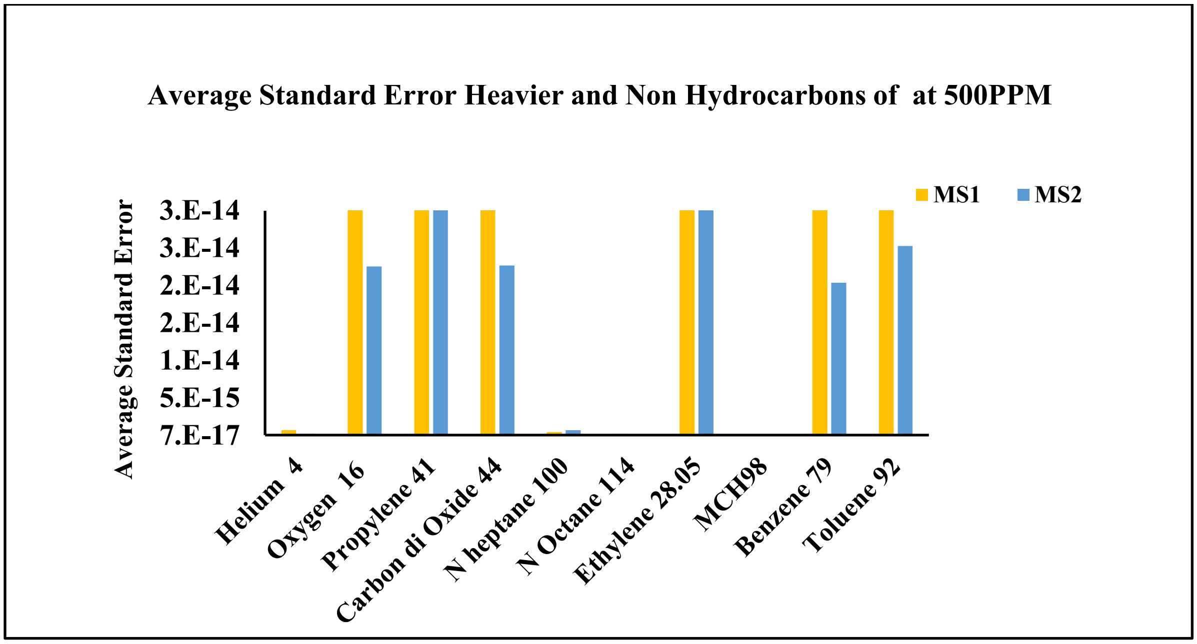


Figure 6. 83. Cumulative Average Standard Error for Heavier and Non-Hydrocarbons at 500PPM

CHAPTER 7. CONCLUSIONS AND RECOMMENDATIONS

Two quadrupole mass spectrometers (QMS) used on rig sites were calibrated successfully for C1- C6 and both MS can detect hydrocarbons at low (~10 – 15 PPM) and high concentrations (100-500PPM). Two different QMS of similar type and manufacturer were used to test repeatability of the calibration method developed in this study. Quantitative analysis is possible because the deconvolution problem was resolved through binary and mixed gas standard resolutions, base peaks selections, and statistical analyses of the data output for uncertainty management. The calibration method developed resulted in errors that were insignificant (for both mass spectrometers) for the lighter hydrocarbons. Also, the method of operation of the mass spectrometers was improved ensuring that similar results will be reproduced on the rig. Our results suggest that using methane 15, ethane 26, propane 41, butane 43, pentane 73 and hexane 87 base masses can help detect these hydrocarbon components from gas streams in live well fluids. The %RSD provides the opportunity to quantify the response of the tools to the binary gas standards, which serve as a foundation for the mixed gas standard calibration process. The deconvolution problem also occurred due to the lack of an additional dimension for proper mass selection, unlike GS/MS-based instruments. The lack of a time dimension could be a significant issue for the tool in the field setting considering it is supposed to measure well fluids in real-time. In the lab, the problem was controlled by plotting preceding masses up to the selected base peak of interest – fragmentation of binary standards. However, this method may be time-consuming for an instrument supposed to expect to operate in real-time.

One of the motivations of this study lay in improving the detection for lighter hydrocarbons which have a tendency to escape and thus not detected especially if present in low amounts. It is a critical contributor to development of the calibration process of the mass spectrometer because of the trace quantities of gases measured on the field. In order to account for the variability, all gas mixed standards containing the tested binary compounds focused on upper bounds of concentration values. The concentrations were 10, 15, 100, and 500 PPM. Estimating the %RSD values for different ranges of gas concentration helps determine a metric for uncertainty, given that lower concentrations of lighter hydrocarbons can have higher uncertainty in measurements. Through the calibration process developed in this study, the limit of detection especially for lower hydrocarbon blends improved significantly, the metric being the %RSD values (Tables 1 & 2 for ~ 10-15PPM). % RSD values ranges from 2% (for higher concentrations) to 10% (for lower concentrations). For lower concentrations, the balance of hydrocarbons could suppress signatures, and thus it is critical, particularly for field settings, to take extra precaution tracking. In the laboratory, we manually removed the balances to enhance the signatures from the peak masses and ran the lower concentration of hydrocarbon blends the longest (up to 50 mins) in order to obtain robust %RSD for the compounds. In the field, this process could be adopted, particularly for lower concentrations, but it will increase analysis time.

Unlike the lighter hydrocarbons, the heavier hydrocarbons and nonhydrocarbons were not analyzed using a binary gas standard because of the inability of the suppliers to meet the request. As a result the focus of the nonhydrocarbons and heavier hydrocarbons were solely on the qualitative detection of the gases as well as the analysis of the error associated with the output. Like lighter hydrocarbons, the tools MS 1 and 2 could be used to analyze unknown gases using the calibration procedures above. We were able to detect complex hydrocarbons like butadiene, butene, benzene, heptane, toluene, octane, p-xylene, o-xylene and m-xylene, propylene, acetylene, pentene, ethylene, methyl-cyclohexene, and ethyl-benzene, as well as non-hydrocarbons like helium, carbon-dioxide, and oxygen using both the QMS.

The development of the calibration process in this study and subsequent testing of different components underscores the importance of developing suitable binary standards and choosing appropriate balances for the QMS. The run and scanning times were improved with the methodology adopted in this study. Fragmentation will occur, and can lead to challenges in determining appropriate peaks for use. Additionally, complex mixture of gases will generate interference – and a known calibration method will help characterize fluids better.

Recommendations:

MS systems break down long chains into shorter constituents. It is pertinent that this method of reservoir fluid characterization is combined with other characterization methods so that results obtained are understood appropriately and validated through different methods. The ability of the tool to detect early, and start fragmentation process simultaneously could lead to poor compositional analysis of the fluids (chemical makeup of the fluid analyzed) from the well but would be excellent in determining the components (singular gases present). High voltage has proved to lead to faster and earlier fragmentation processes (Adhikari et al., 2017) and this tool operates at 70 eV, which is fixed and high. To facilitate a more permanent solution, creating the possibility of having adjustable voltage during the tuning could help with the deconvolution problem. It provides an opportunity to measure the hydrocarbons at its corresponding or near molecular weight, and the lighter hydrocarbons will have fewer interferences from the fragments coming from the heavier hydrocarbons. Generally, the tool is simple to use and has the potential of reducing time spent on the rig as well as providing safer rigs. The calibration method, as currently employed, is adequate and robust.

Some other recommendations that can be made are:

a. Using a combination of the real-time mass-spectrometric method with other characterization methods, like sonic, neutron and density logging and well logging methods, although the latter is more for the type of reservoir fluid and the MS for the composition of the fluid.
b. Using and applying the Gas Chromatography Mass Spectrometer for real time detection.
c. Enhancing the operational capability for soft ionization with controlled supply of voltage.
d. Implementing the use of electron multiplier to achieve better detection limit in the QMS.

APPENDIX: PROCESSED DATA SAMPLES FROM CALIBRATION TESTS

MS1,10PPM									
	Masses	Test 1	Test 2	Test 3	Average	Stdev.P	Standard Error	%RSD	Variance
Methane	15	9.112E-14	8.22933E-14	9.07748E-14	8.80642E-14	4.08314E-15	9.13E-16	4.64%	1.667E-29
Ethane	26	2.816E-13	2.50719E-13	2.7905E-13	2.70459E-13	1.39971E-14	3.13E-15	5.18%	1.959E-28
Propane	41	5.668E-13	4.8426E-13	5.59839E-13	5.36974E-13	3.73836E-14	8.36E-15	6.96%	1.398E-27
Propylene	42	3.732E-13	3.15039E-13	3.71137E-13	3.53109E-13	2.69321E-14	6.02E-15	7.63%	7.253E-28
N butane	43	4.821E-13	4.15438E-13	4.74117E-13	4.57217E-13	2.97211E-14	6.65E-15	6.50%	8.833E-28
N pentane	73	1.435E-14	1.16662E-14	1.28614E-14	1.296E-14	1.09885E-15	2.46E-16	8.48%	1.207E-30
Hexane	87	4.86E-15	4.77573E-15	4.16779E-15	4.60102E-15	3.08249E-16	6.89E-17	6.70%	9.502E-32
Helium	4	1.388E-10	1.16644E-10	1.42148E-10	1.32515E-10	1.13077E-11	2.53E-12	8.53%	1.279E-22
1 butene	56.11	4.029E-14	3.56305E-14	4.12866E-14	3.90684E-14	2.46491E-15	5.51E-16	6.31%	6.076E-30
N butane	58	2.979E-14	2.55687E-14	2.84066E-14	2.79215E-14	1.75677E-15	3.93E-16	6.29%	3.086E-30
Iso butane	58.078	2.979E-14	2.55687E-14	2.84066E-14	2.79215E-14	1.75677E-15	3.93E-16	6.29%	3.086E-30
N butane	59	5.929E-15	4.92483E-15	4.7938E-15	5.21577E-15	5.06931E-16	1.13E-16	9.72%	2.57E-31
Ethylene	62.037	6.142E-15	6.39612E-15	6.5394E-15	6.35922E-15	1.64268E-16	3.67E-17	2.58%	2.698E-32
Isoprene	68.063	5.395E-14	4.54211E-14	4.95397E-14	4.96385E-14	3.48452E-15	7.79E-16	7.02%	1.214E-29
1 Pentene	70	5.713E-15	3.94424E-15	4.44907E-15	4.70195E-15	7.43721E-16	1.66E-16	15.82%	5.531E-31
Propylene	41	5.668E-13	4.8426E-13	5.59839E-13	5.36974E-13	3.73836E-14	8.36E-15	6.96%	1.398E-27
Benzene	79	3.481E-13	2.91733E-13	3.304E-13	3.23397E-13	2.35215E-14	5.26E-15	7.27%	5.533E-28
Toluene	92.14	1.324E-12	1.12919E-12	1.29207E-12	1.24855E-12	8.54224E-14	1.91E-14	6.84%	7.297E-27
O xylene	106	8.205E-14	6.60905E-14	7.76886E-14	7.52774E-14	6.736E-15	1.51E-15	8.95%	4.537E-29
P xylene	106	8.205E-14	6.60905E-14	7.76886E-14	7.52774E-14	6.736E-15	1.51E-15	8.95%	4.537E-29
Ethyl Benze	106.17	8.205E-14	6.60905E-14	7.76886E-14	7.52774E-14	6.736E-15	1.51E-15	8.95%	4.537E-29
M xylene	106.16	8.205E-14	6.60905E-14	7.76886E-14	7.52774E-14	6.736E-15	1.51E-15	8.95%	4.537E-29
Ethane	27	5.92E-13	5.14356E-13	5.85568E-13	5.63967E-13	3.51774E-14	7.87E-15	6.24%	1.237E-27
Ethane	28	0	4.20845E-12	0	1.40282E-12	1.98388E-12	4.44E-13	141.42%	3.936E-24
Ethane	29	4.022E-13	4.06227E-13	3.99468E-13	4.02648E-13	2.77376E-15	6.20E-16	0.69%	7.694E-30
Ethane	30	3.705E-14	3.42133E-14	3.18926E-14	3.4386E-14	2.1099E-15	4.72E-16	6.14%	4.452E-30
Propane	39	5.771E-13	4.88222E-13	5.72253E-13	5.45859E-13	4.08038E-14	9.12E-15	7.48%	1.665E-27
Propane	40	2.141E-13	1.34482E-13	4.15844E-14	1.30072E-13	7.05185E-14	1.58E-14	54.21%	4.973E-27
Methyl acety	40	2.141E-13	1.34482E-13	4.15844E-14	1.30072E-13	7.05185E-14	1.58E-14	54.21%	4.973E-27
1,3 butadien	54.09	3.198E-14	2.31638E-14	3.07616E-14	2.86352E-14	3.90068E-15	8.72E-16	13.62%	1.522E-29
Propane	44	2.461E-13	3.10452E-13	2.31887E-13	2.62798E-13	3.41895E-14	7.64E-15	13.01%	1.169E-27
Methane	16	8.606E-14	2.30306E-13	9.72964E-14	1.37886E-13	6.55117E-14	1.46E-14	47.51%	4.292E-27
Acetylene	26.04	2.816E-13	2.50719E-13	2.7905E-13	2.70459E-13	1.39971E-14	3.13E-15	5.18%	1.959E-28
Ethane	25	4.436E-14	3.99033E-14	4.4029E-14	4.27648E-14	2.02802E-15	4.53E-16	4.74%	4.113E-30

table cont'd.

MS2,10PPM									
Components	Mass Numbe	Test1	Test2	Test 3	Average	Stdev.P	Standard Error	Variance	%RSD
Methane	15	7.918E-14	9.23745E-14	9.44714E-14	8.86761E-14	6.76741E-15	1.35348E-15	6.87E-29	7.63%
Ethane	26	2.162E-13	2.32925E-13	2.33182E-13	2.2743E-13	7.95334E-15	1.59067E-15	9.488E-29	3.50%
Propane	41	1.3E-13	1.52589E-13	1.40548E-13	1.41052E-13	9.22122E-15	1.84424E-15	1.275E-28	6.54%
Propylene	42	8.989E-14	1.10309E-13	1.07353E-13	1.02516E-13	9.01227E-15	1.80245E-15	1.218E-28	8.79%
Butane	58	1.036E-13	1.16364E-13	1.17918E-13	1.12612E-13	6.43605E-15	1.28721E-15	6.213E-29	5.72%
Pentane	73	1.203E-14	1.36227E-14	1.48176E-14	1.34896E-14	1.14257E-15	2.28514E-16	1.958E-30	8.47%
Hexane	87	1.07E-14	1.20316E-14	1.20311E-14	1.15859E-14	6.29965E-16	1.25993E-16	5.953E-31	5.44%
Propane	44	6.421E-14	5.93143E-14	5.78855E-14	6.04686E-14	2.70632E-15	5.41264E-16	1.099E-29	4.48%
1,3 butadiene	54	2.521E-14	2.62918E-14	2.95989E-14	2.70328E-14	1.8677E-15	3.73541E-16	5.232E-30	6.91%
1 butene	56	3.054E-14	3.67419E-14	3.70617E-14	3.47806E-14	3.00262E-15	6.00524E-16	1.352E-29	8.63%
Iso butane	58	1.036E-13	1.16364E-13	1.17918E-13	1.12612E-13	6.43605E-15	1.28721E-15	6.213E-29	5.72%
Ethylene	62	3.305E-15	8.83456E-15	7.61753E-15	6.58554E-15	2.37263E-15	4.74526E-16	8.444E-30	36.03%
Isoprene	68	6.331E-14	8.08952E-14	7.9094E-14	7.44316E-14	7.90157E-15	1.58031E-15	9.365E-29	10.62%
1 Pentene	70	4.177E-15	7.0579E-15	4.97493E-15	5.40315E-15	1.21463E-15	2.42925E-16	2.213E-30	22.48%
Benzene	79	2.002E-13	2.49354E-13	2.34365E-13	2.27967E-13	2.05787E-14	4.11575E-15	6.352E-28	9.03%
Toluene	92.14	1.702E-13	3.80357E-13	3.41987E-13	2.97499E-13	9.14004E-14	1.82801E-14	1.253E-26	30.72%
O xylene	106	5.431E-15	1.41769E-14	1.23957E-14	1.06678E-14	3.77388E-15	7.54775E-16	2.136E-29	35.38%
P xylene	106	5.431E-15	1.41769E-14	1.23957E-14	1.06678E-14	3.77388E-15	7.54775E-16	2.136E-29	35.38%
Ethyl Benzene	106.17	5.431E-15	1.41769E-14	1.23957E-14	1.06678E-14	3.77388E-15	7.54775E-16	2.136E-29	35.38%
M xylene	106.16	5.431E-15	1.41769E-14	1.23957E-14	1.06678E-14	3.77388E-15	7.54775E-16	2.136E-29	35.38%
Helium	4	1.101E-10	1.1981E-10	1.22881E-10	1.17596E-10	5.44803E-12	1.08961E-12	4.452E-23	4.63%
Methane	16	2.954E-13	7.61626E-14	1.20477E-13	1.64018E-13	9.46554E-14	1.89311E-14	1.344E-26	57.71%
Acetylene	26	2.162E-13	2.32925E-13	2.33182E-13	2.2743E-13	7.95334E-15	1.59067E-15	9.488E-29	3.50%
Ethane	25	2.838E-14	3.83783E-14	3.66713E-14	3.44773E-14	4.36577E-15	8.73154E-16	2.859E-29	12.66%
Ethane	27	3.793E-13	4.91934E-13	4.88812E-13	4.53362E-13	5.23563E-14	1.04713E-14	4.112E-27	11.55%
Ethane	28	8.406E-13	0	0	2.80205E-13	3.9627E-13	7.9254E-14	2.355E-25	141.42%
Ethane	29	2.447E-13	2.23014E-13	2.31207E-13	2.32981E-13	8.95045E-15	1.79009E-15	1.202E-28	3.84%
Ethane	30	2.072E-14	1.78008E-14	1.76323E-14	1.87167E-14	1.41606E-15	2.83212E-16	3.008E-30	7.57%
Propane	39	2.178E-13	3.11911E-13	2.99095E-13	2.76264E-13	4.16797E-14	8.33595E-15	2.606E-27	15.09%
Propane	40	6.745E-11	7.35814E-14	0	2.25071E-11	3.17778E-11	6.35555E-12	1.515E-21	141.19%
Methyl acetylene	40	6.745E-11	7.35814E-14	0	2.25071E-11	3.17778E-11	6.35555E-12	1.515E-21	141.19%
Propylene	41	1.3E-13	1.52589E-13	1.40548E-13	1.41052E-13	9.22122E-15	1.84424E-15	1.275E-28	6.54%

table cont'd.

MS1, 15PPM									
	Mass Number	Test1	Test2	Test3	Average	Stdev.P	Standard Error	%RSD	Variance
Methane	15	2.9051E-13	2.94798E-13	3.00078E-13	2.95129E-13	3.91E-15	9.22E-16	1.33%	1.5311E-29
Ethane	26	6.75904E-14	7.13709E-14	7.14095E-14	7.01236E-14	1.79131E-15	4.22E-16	2.55%	3.2088E-30
Propane	41	1.36637E-14	1.92041E-14	1.94076E-14	1.74252E-14	2.66103E-15	6.27E-16	15.27%	7.0811E-30
Butane	43	1.27076E-13	1.45333E-13	1.48459E-13	1.40289E-13	9.42962E-15	2.22E-15	6.72%	8.8918E-29
Pentane	73	1.33082E-14	1.36158E-14	1.45047E-14	1.38096E-14	5.07303E-16	1.20E-16	3.67%	2.5736E-31
Hexane	87	7.18786E-15	7.37684E-15	6.70176E-15	7.08882E-15	2.84357E-16	6.70E-17	4.01%	8.0859E-32
Carbon Di Oxide	44	3.70013E-13	3.67491E-13	3.63288E-13	3.66931E-13	2.77392E-15	6.54E-16	0.76%	7.6946E-30
Propane	39	0	0	0	0	0	0.00E+00	0.00%	0
Propane	40	0	0	0	0	0	0.00E+00	0.00%	0
N- Butane	59	1.06646E-14	9.13615E-15	1.20426E-14	1.06145E-14	1.18708E-15	2.80E-16	11.18%	1.4092E-30
Benzene	79	1.12564E-13	1.25776E-13	1.33352E-13	1.23897E-13	8.5897E-15	2.02E-15	6.93%	7.3783E-29
Hexane	88	0	1.47486E-15	0	4.9162E-16	6.95256E-16	1.64E-16	141.42%	4.8338E-31
Toluene	92	3.78218E-14	5.04266E-14	5.26909E-14	4.69798E-14	6.54133E-15	1.54E-15	13.92%	4.2789E-29
N heptane	100	0	0	1.03045E-15	3.43485E-16	4.85761E-16	1.14E-16	141.42%	2.3596E-31
N Octane	114	0	0	3.64212E-15	1.21404E-15	1.71691E-15	4.05E-16	141.42%	2.9478E-30
Helium	4	7.13004E-15	7.98806E-15	6.78686E-15	7.30165E-15	5.05178E-16	1.19E-16	6.92%	2.552E-31
Oxygen	16	7.01656E-13	7.04094E-13	7.02447E-13	7.02732E-13	1.0155E-15	2.39E-16	0.14%	1.0312E-30
Methane	16	7.04094E-13	7.02447E-13	7.02447E-13	7.02996E-13	7.76141E-16	1.83E-16	0.11%	6.024E-31
Argon	20	0	0	0	0	0	0.00E+00	0.00%	0
Ethane	25	7.40267E-15	7.44172E-15	1.20619E-14	8.96877E-15	2.18724E-15	5.16E-16	24.39%	4.784E-30
Ethane	27	1.63645E-12	1.74895E-12	1.76129E-12	1.71557E-12	5.61681E-14	1.32E-14	3.27%	3.1549E-27
Ethane	28	3.30872E-09	3.44946E-09	3.45855E-09		6.85916E-11	1.62E-11	0.00%	4.7048E-21
Ethane	29	1.66011E-11	1.7433E-11	1.74892E-11	1.71744E-11	4.06077E-13	9.57E-14	2.36%	1.649E-25
Ethane	30	8.03396E-13	8.61839E-13	8.64049E-13	8.43094E-13	2.80854E-14	6.62E-15	3.33%	7.8879E-28

table cont'd.

MS2, 15PPM									
	Mass Number	Test1	Test2	Test3	Average	Stdev.P	Standard Error	%RSD	Variance
Methane	15	2.86345E-13	2.89094E-13	2.88934E-13	2.88124E-13	1.25985E-15	2.55574E-16	0.44%	1.58723E-30
Ethane	26	8.08691E-14	8.10141E-14	8.40129E-14	8.19654E-14	1.449E-15	2.93945E-16	1.77%	2.09961E-30
Propane	41	1.6434E-13	1.75454E-13	1.78903E-13	1.72899E-13	6.21394E-15	1.26056E-15	3.59%	3.86131E-29
N- Butane	43	3.35075E-13	3.54829E-13	3.6175E-13	3.50551E-13	1.13021E-14	2.29276E-15	3.22%	1.27739E-28
N pentane	73	1.20429E-14	1.21243E-14	1.19602E-14	1.20425E-14	6.6981E-17	1.35878E-17	0.56%	4.48646E-33
Hexane	87	2.10337E-14	2.11551E-14	2.42867E-14	2.21585E-14	1.50567E-15	3.0544E-16	6.79%	2.26704E-30
Carbon di Oxide	44	7.79757E-13	7.79908E-13	7.89027E-13	7.82897E-13	4.33482E-15	8.79362E-16	0.55%	1.87906E-29
Helium	4	5.46569E-15	4.67756E-15	6.57039E-15	5.57121E-15	7.76337E-16	1.57488E-16	13.93%	6.02699E-31
N- Butane	59	1.71965E-17	6.60891E-16	1.12521E-15	6.01099E-16	4.54316E-16	9.21627E-17	75.58%	2.06403E-31
Benzene	79	1.14277E-13	1.16577E-13	1.21499E-13	1.17451E-13	3.01253E-15	6.11122E-16	2.56%	9.07531E-30
Hexane	88	1.64719E-15	4.15477E-15	3.76161E-15	3.18786E-15	1.10118E-15	2.23385E-16	34.54%	1.21259E-30
Toluene	92	1.79815E-13	1.78968E-13	1.95712E-13	1.84832E-13	7.70102E-15	1.56223E-15	4.17%	5.93057E-29
N heptane	100	3.03708E-16	0	3.79391E-16	2.277E-16	1.63946E-16	3.32581E-17	72.00%	2.68782E-32
N Octane	114	7.25111E-16	5.52467E-15	3.91754E-17	2.09632E-15	2.44033E-15	4.95046E-16	116.41%	5.95521E-30
Propane	39	0	0	0	0	0	0	0.00%	0
Propane	40	0	0	0	0	0	0	0.00%	0
Oxygen	16	6.73782E-13	6.32943E-13	6.3421E-13	6.46978E-13	1.896E-14	3.84623E-15	2.93%	3.59482E-28
Methane	16	6.32943E-13	6.3421E-13	6.3421E-13	6.33788E-13	5.97636E-16	1.21237E-16	0.09%	3.57169E-31
Argon	20	0	0	0	0	0	0	0.00%	0
Ethane	25	1.12936E-14	8.82096E-15	9.19421E-15	9.76958E-15	1.08834E-15	2.20781E-16	11.14%	1.18448E-30
Ethane	27	4.12861E-12	4.21837E-12	4.39478E-12	4.24725E-12	1.10567E-13	2.24296E-14	2.60%	1.22251E-26
Ethane	28	3.39881E-09	3.43465E-09	3.467E-09		2.78524E-11	5.65014E-12	0.00%	7.75754E-22
Ethane	29	1.96533E-11	1.99715E-11	2.02503E-11	1.99584E-11	2.43894E-13	4.94763E-14	1.22%	5.94841E-26
Ethane	30	1.09547E-12	1.10914E-12	1.11658E-12	1.10707E-12	8.74362E-15	1.77373E-15	0.79%	7.6451E-29

table cont'd.

MS1, 100PPM									
	Mass number	Test 1	Test 2	Test 3	Average	Stdev.P	Standard Error	%RSD	Variance
Methane	15	1.92223E-12	1.92894E-12	1.93888E-12	1.93002E-12	6.84232E-15	1.35075E-15	0.35%	7.0226E-29
Ethane	26	2.7775E-13	2.75156E-13	2.765E-13	2.76469E-13	1.05911E-15	2.0908E-16	0.38%	1.6826E-30
Propane	41	1.27475E-12	1.26698E-12	1.27663E-12	1.27279E-12	4.17568E-15	8.24326E-16	0.33%	2.6154E-29
Propylene	42	8.44706E-13	8.42407E-13	8.52466E-13	8.46527E-13	4.30341E-15	8.4954E-16	0.51%	2.7779E-29
Butane	43	1.89484E-12	1.87137E-12	1.9013E-12	1.88917E-12	1.2859E-14	2.53851E-15	0.68%	2.4803E-28
Pentane	73	7.10613E-14	6.80619E-14	6.92249E-14	6.94494E-14	1.23475E-15	2.43753E-16	1.78%	2.2869E-30
Hexane	87	1.12192E-13	1.10514E-13	1.11443E-13	1.11383E-13	6.86549E-16	1.35532E-16	0.62%	7.0703E-31
N butane	58	1.58393E-13	1.63878E-13	1.52136E-13	1.58136E-13	4.79735E-15	9.4705E-16	3.03%	3.4522E-29
N- Butane	59	1.31501E-14	1.38315E-14	1.32833E-14	1.34217E-14	2.94871E-16	5.82108E-17	2.20%	1.3042E-31
Hexane	88	7.3869E-15	8.80195E-15	7.04838E-15	7.74574E-15	7.59531E-16	1.4994E-16	9.81%	8.6533E-31
Methane	16	3.12206E-12	3.12707E-12	3.12707E-12	3.1254E-12	2.36233E-15	4.66349E-16	0.08%	8.3709E-30
Argon	20	0	0	0	0	0	0	0.00%	0
Ethane	25	3.1572E-14	3.09998E-14	3.0916E-14	3.11626E-14	2.9148E-16	5.75413E-17	0.94%	1.2744E-31
Ethane	27	4.24251E-12	4.20109E-12	4.23167E-12	4.22509E-12	1.75382E-14	3.46223E-15	0.42%	4.6138E-28
Ethane	28	2.83556E-09	2.84064E-09	2.85401E-09		7.78302E-12	1.53645E-12	0.00%	9.0863E-23
Ethane	29	1.77804E-11	1.79294E-11	1.80519E-11	1.79206E-11	1.11001E-13	2.19128E-14	0.62%	1.8482E-26
Ethane	30	9.81178E-13	1.0002E-12	1.00624E-12	9.95873E-13	1.06803E-14	2.10841E-15	1.07%	1.711E-28
Propane	39	0	0	0	0	0	0	0.00%	0
Propane	40	0	0	0	0	0	0	0.00%	0
Benzene	79	4.09348E-13	4.10073E-13	3.90476E-13	4.03299E-13	9.07188E-15	1.79089E-15	2.25%	1.2345E-28
Propylene	41	1.27475E-12	1.26698E-12	1.27663E-12	1.27279E-12	4.17568E-15	8.24326E-16	0.33%	2.6154E-29
carbon di oxide	44	1.9089E-11	1.9419E-11	1.94082E-11	1.93054E-11	1.53077E-13	3.02191E-14	0.79%	3.5149E-26
Toluene	92	4.99946E-13	4.66345E-13	4.72048E-13	4.79446E-13	1.46814E-14	2.89827E-15	3.06%	3.2332E-28
N heptane	100	7.93051E-15	8.04383E-15	6.94442E-15	7.63959E-15	4.93731E-16	9.74679E-17	6.46%	3.6565E-31
N Octane	114	2.78898E-16	0	4.94189E-16	2.57696E-16	2.02308E-16	3.99379E-17	78.51%	6.1393E-32
MCH	98	4.33609E-15	5.42455E-15	4.63392E-15	4.79819E-15	4.59293E-16	9.06696E-17	9.57%	3.1643E-31
Helium	4	1.30806E-14	1.04603E-14	5.82554E-15	9.78883E-15	2.99969E-15	5.92173E-16	30.64%	1.3497E-29
Oxygen	16	3.09598E-12	3.12206E-12	3.12707E-12	3.11504E-12	1.36314E-14	2.691E-15	0.44%	2.7872E-28

table cont'd.

MS2 , 100PPM									
Composition	Mass Number	Test 1	Test 2	Test 3	Average	Stdev.P	%RSD	Standard Error	Variance
Methane	15	2.12893E-12	2.11768E-12	2.12336E-12	2.12332E-12	4.59643E-15	0.22%	9.19286E-16	3.16908E-29
Ethane	26	2.61718E-13	2.55019E-13	2.54005E-13	2.56914E-13	3.42186E-15	1.33%	6.84373E-16	1.75637E-29
Propane	41	6.47402E-13	6.31153E-13	6.43433E-13	6.40663E-13	6.91698E-15	1.08%	1.3834E-15	7.17669E-29
Propylene	42	3.89132E-13	3.83028E-13	3.91027E-13	3.87729E-13	3.41296E-15	0.88%	6.82591E-16	1.74724E-29
Butane	43	7.97035E-13	7.76701E-13	7.93032E-13	7.88923E-13	8.7955E-15	1.11%	1.7591E-15	1.16041E-28
Pentane	73	8.26835E-14	7.98721E-14	7.99723E-14	8.08426E-14	1.3023E-15	1.61%	2.60459E-16	2.54396E-30
Hexane	87	4.44626E-14	4.48618E-14	4.49353E-14	4.47532E-14	2.07672E-16	0.46%	4.15344E-17	6.46916E-32
Methane	16	3.38161E-12	3.35304E-12	3.35304E-12	3.36256E-12	1.34699E-14	0.40%	2.69397E-15	2.72156E-28
Argon	20	0	0	0	0	0	0.00%	0	0
Ethane	25	2.89441E-14	2.89071E-14	2.68936E-14	2.82482E-14	9.58031E-16	3.39%	1.91606E-16	1.37674E-30
Ethane	27	2.37356E-12	2.28694E-12	2.28122E-12	2.31391E-12	4.22422E-14	1.83%	8.44844E-15	2.6766E-27
Ethane	28	2.82254E-09	2.81919E-09	2.8189E-09		1.65026E-12	0.00%	3.30052E-13	4.08504E-24
Ethane	29	1.5893E-11	1.59713E-11	1.61173E-11	1.59939E-11	9.29528E-14	0.58%	1.85906E-14	1.29603E-26
Ethane	30	7.94125E-13	8.0678E-13	8.0639E-13	8.02432E-13	5.87575E-15	0.73%	1.17515E-15	5.17866E-29
Propane	39	0	0	0	0	0	0.00%	0	0
Propane	40	0	0	0	0	0	0.00%	0	0
N- Butane	59	7.42566E-14	7.31389E-14	7.07148E-14	7.27034E-14	1.47835E-15	2.03%	2.9567E-16	3.27827E-30
Hexane	88	0	3.07972E-15	2.13931E-15	1.73968E-15	1.28866E-15	74.07%	2.57731E-16	2.49095E-30
Toluene	92	1.445E-13	1.32797E-13	1.31247E-13	1.36182E-13	5.91602E-15	4.34%	1.1832E-15	5.2499E-29
N heptane	100	2.51076E-14	2.65156E-14	2.60948E-14	2.5906E-14	5.90108E-16	2.28%	1.18022E-16	5.22341E-31
N Octane	114	1.3114E-15	1.46491E-15	1.65625E-15	1.47752E-15	1.41068E-16	9.55%	2.82135E-17	2.98501E-32
MCH	98	2.82791E-15	4.9486E-16	0	1.10759E-15	1.23311E-15	111.33%	2.46622E-16	2.28084E-30
Benzene	79	3.45654E-13	3.53769E-13	3.46792E-13	3.48739E-13	3.58746E-15	1.03%	7.17491E-16	1.93048E-29
Propylene	41	6.47402E-13	6.31153E-13	6.43433E-13	6.40663E-13	6.91698E-15	1.08%	1.3834E-15	7.17669E-29
Helium	4	1.03872E-12	6.23339E-14	0	3.67018E-13	4.75646E-13	129.60%	9.51293E-14	3.39359E-25
Carbon di oxide	44	4.86735E-13	4.82955E-13	4.85575E-13	4.85088E-13	1.58089E-15	0.33%	3.16179E-16	3.74883E-30
Oxygen	16	3.38736E-12	3.38161E-12	3.35304E-12	3.374E-12	1.50099E-14	0.44%	3.00199E-15	3.37947E-28

table cont'd.

MS1 500PPM									
Component	Mass Number	Test 1	Test 2	Test 3	Average	Stdev.P	%RSD	Standard Error	Variance
Methane	15	2.018E-11	2.03029E-11	2.09112E-11	2.04647E-11	3.19677E-13	1.56%	1.06559E-13	1.5329E-25
Ethane	26	7.16097E-12	7.20557E-12	7.35248E-12	7.23967E-12	8.18189E-14	1.13%	2.7273E-14	1.00415E-26
Propane	41	2.79429E-11	2.82488E-11	2.89771E-11	2.83896E-11	4.33783E-13	1.53%	1.44594E-13	2.82252E-25
Propylene	42	2.23041E-11	2.24808E-11	2.31834E-11	2.26561E-11	3.79766E-13	1.68%	1.26589E-13	2.16334E-25
Butane	43	4.8797E-11	4.92143E-11	5.10551E-11	4.96888E-11	9.81002E-13	1.97%	3.27001E-13	1.44355E-24
Pentane	73	2.69214E-12	2.66018E-12	2.69513E-12	2.68248E-12	1.58215E-14	0.59%	5.27384E-15	3.75481E-28
Hexane	87	1.08944E-12	1.10868E-12	1.09968E-12	1.09927E-12	7.86251E-15	0.72%	2.62084E-15	9.27285E-29
Helium	4	7.90639E-14	8.01E-14	8.40007E-14	8.10619E-14	2.12241E-15	2.62%	7.07471E-16	6.75695E-30
Methane	16	2.85414E-11	2.94471E-11	2.94471E-11	2.91452E-11	4.26977E-13	1.47%	1.42326E-13	2.73464E-25
Oxygen	16	2.84324E-11	2.85414E-11	2.94471E-11	2.88069E-11	4.5485E-13	1.58%	1.51617E-13	3.10332E-25
Argon	20	0	0	0	0	0	0.00%		0
Ethane	25	7.30753E-13	7.39159E-13	7.50351E-13	7.40087E-13	8.02786E-15	1.08%	2.67595E-15	9.66699E-29
Ethane	27	3.36741E-11	3.40616E-11	3.47099E-11	3.41485E-11	4.27333E-13	1.25%	1.42444E-13	2.7392E-25
Ethane	28	2.87445E-09	2.88118E-09	2.94995E-09	2.90186E-09	3.41144E-11	1.18%	1.13715E-11	1.74569E-21
Ethane	29	5.75449E-11	5.8326E-11	5.94224E-11	5.84311E-11	7.70106E-13	1.32%	2.56702E-13	8.89595E-25
Ethane	30	5.66461E-12	5.74082E-12	5.83847E-12	5.74797E-12	7.11569E-14	1.24%	2.3719E-14	7.59495E-27
Propane	39	7.62431E-12	7.74886E-12	7.94597E-12	7.77304E-12	1.32427E-13	1.70%	4.41422E-14	2.63052E-26
Propane	40	0	0	0	0	0	0.00%	0	0
Propylene	41	2.79429E-11	2.82488E-11	2.89771E-11	2.83896E-11	4.33783E-13	1.53%	1.44594E-13	2.82252E-25
Propane	44	1.43802E-11	1.4406E-11	1.49258E-11	1.45707E-11	2.51364E-13	1.73%	8.3788E-14	9.47759E-26
carbon di oxide	44	1.43802E-11	1.4406E-11	1.49258E-11	1.45707E-11	2.51364E-13	1.73%	8.3788E-14	9.47759E-26
N butane	58	2.53869E-12	2.56565E-12	2.65804E-12	2.58746E-12	5.1108E-14	1.98%	1.7036E-14	3.91805E-27
N- Butane	59	4.04865E-13	3.96174E-13	4.23561E-13	4.082E-13	1.14265E-14	2.80%	3.80883E-15	1.95847E-28
Benzene	79	3.75243E-12	3.86795E-12	3.97362E-12	3.86467E-12	9.03292E-14	2.34%	3.01097E-14	1.2239E-26
Hexane	88	8.51853E-14	8.48217E-14	8.78825E-14	8.59632E-14	1.36528E-15	1.59%	4.55095E-16	2.796E-30
Toluene	92	4.95074E-12	5.53454E-12	5.39837E-12	5.29455E-12	2.49388E-13	4.71%	8.31292E-14	9.32913E-26
N heptane	100	4.42114E-14	4.50111E-14	4.16373E-14	4.36199E-14	1.43946E-15	3.30%	4.79818E-16	3.10805E-30
N Octane	114	0	1.60639E-15	4.29941E-16	6.78777E-16	6.79E-16	100.03%	2.26333E-16	6.91562E-31
Ethylene	28.05	2.87445E-09	2.88118E-09	2.94995E-09	2.90186E-09	3.41144E-11	1.18%	1.13715E-11	1.74569E-21
MCH	98	2.79424E-14	2.84905E-14	2.93359E-14	2.85896E-14	5.73206E-16	2.00%	1.91069E-16	4.92848E-31

table cont'd.

MS2, 500PPM									
Component	Mass Number	Test 1	Test 2	Test 3	Average	Stdev.P	%RSD	Standard Error	Variance
Methane15	15	2.27256E-11	2.28919E-11	2.28499E-11	2.28225E-11	7.06098E-14	0.31%	2.35366E-14	7.47861E-27
Ethane 26	26	6.66962E-12	6.71637E-12	6.71849E-12	6.70149E-12	2.25525E-14	0.34%	7.5175E-15	7.62923E-28
Propane 41	41	1.5376E-11	1.56493E-11	1.56376E-11	1.55543E-11	1.26147E-13	0.81%	4.2049E-14	2.38696E-26
Propylene 42	42	9.68407E-12	9.84371E-12	9.84627E-12	9.79135E-12	7.58673E-14	0.77%	2.52891E-14	8.63378E-27
Butane43	43	2.00395E-11	2.04012E-11	2.03738E-11	2.02715E-11	1.64441E-13	0.81%	5.48138E-14	4.05615E-26
Pentane 73	73	3.13151E-12	3.17175E-12	3.16912E-12	3.15746E-12	1.83798E-14	0.58%	6.12659E-15	5.06724E-28
Hexane 87	87	4.33391E-13	4.49807E-13	4.51362E-13	4.44853E-13	8.12976E-15	1.83%	2.70992E-15	9.91395E-29
Methane - 16	16	3.14435E-11	3.13683E-11	3.13683E-11	3.13934E-11	3.54266E-14	0.11%	1.18089E-14	1.88256E-27
Oxygen - 16	16	3.1278E-11	3.14435E-11	3.13683E-11	3.13633E-11	6.764E-14	0.22%	2.25467E-14	6.86276E-27
Helium -4	4	7.87281E-14	7.69678E-14	7.72085E-14	7.76348E-14	7.79312E-16	1.00%	2.59771E-16	9.1099E-31
Argon - 20	20	0	0	0	0	0	0.00%	0	0
Ethane - 25	25	6.89965E-13	6.95298E-13	6.98033E-13	6.94432E-13	3.34996E-15	0.48%	1.11665E-15	1.68334E-29
Ethane 27	27	2.82907E-11	2.86082E-11	2.86459E-11	2.8515E-11	1.59292E-13	0.56%	5.30972E-14	3.80608E-26
Ethane - 28	28	2.9328E-09	2.94366E-09	2.93842E-09		4.43524E-12	0.00%	1.47841E-12	2.9507E-23
Ethane 29	29	4.99017E-11	5.05529E-11	5.05997E-11	5.03514E-11	3.18607E-13	0.63%	1.06202E-13	1.52266E-25
Ethane30	30	4.66369E-12	4.70786E-12	4.71423E-12	4.69526E-12	2.24736E-14	0.48%	7.49118E-15	7.57591E-28
Propane 39	39	5.54653E-12	5.64316E-12	5.65154E-12	5.61374E-12	4.7648E-14	0.85%	1.58827E-14	3.4055E-27
Propane 40	40	0	0	0	0	0	0.00%	0	0
Propylene 41	41	1.5376E-11	1.56493E-11	1.56376E-11	1.55543E-11	1.26147E-13	0.81%	4.2049E-14	2.38696E-26
carbon di oxide 44	44	6.33223E-12	6.47179E-12	6.48113E-12	6.42838E-12	6.80967E-14	1.06%	2.26989E-14	6.95573E-27
N- Butane 59	59	2.57743E-12	2.56276E-12	2.54851E-12	2.5629E-12	1.18043E-14	0.46%	3.93476E-15	2.09012E-28
Benzene 79	79	3.93422E-12	4.05553E-12	4.07088E-12	4.02021E-12	6.1127E-14	1.52%	2.03757E-14	5.60477E-27
Hexane 88	88	3.4105E-14	3.68248E-14	3.88339E-14	3.65879E-14	1.9378E-15	5.30%	6.45934E-16	5.63262E-30
Toluene 92	92	1.61537E-12	1.76119E-12	1.78802E-12	1.72153E-12	7.5862E-14	4.41%	2.52873E-14	8.63255E-27
N heptane 100	100	1.23116E-13	1.21151E-13	1.17802E-13	1.2069E-13	2.19377E-15	1.82%	7.31257E-16	7.21895E-30
N Octane 114	114	2.97536E-15	2.51596E-15	2.52717E-15	2.67283E-15	2.13968E-16	8.01%	7.13226E-17	6.86733E-32
MCH98	98	2.0097E-15	3.28355E-15	2.93478E-15	2.74268E-15	5.37495E-16	19.60%	1.79165E-16	4.33351E-31
Ethylene 28.05	28.05	2.9328E-09	2.94366E-09	2.93842E-09	2.93829E-09	4.43524E-12	0.15%	1.47841E-12	2.9507E-23

table cont'd.

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