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Mass Spectrometric Calibration Procedure for Real-Time Detection of Lighter Hydrocarbons

Makuachukwu F. Mbaegbu [1], Puspa L. Adhikari [2], Ipsita Gupta [2,*] and Mathew Rowe [3]

[1] Craft & Hawkins Department of Petroleum Engineering, Louisiana State University,
Baton Rouge, LA 70803, USA; mbaegbu16@gmail.com
[2] The Department of Marine and Earth Sciences, The Water School, Florida Gulf Coast University,
Fort Myers, FL 33965, USA; padhikari@fgcu.edu
[3] Halliburton Services, Houston, TX 77032, USA; Mathew.Rowe@halliburton.com
* Correspondence: igupta@lsu.edu

Abstract: Determining gas compositions from live well fluids on a drilling rig is critical for real time formation evaluation. Development and utilization of a reliable mass spectrometric method to accurately characterize these live well fluids are always challenging due to lack of a robust and effectively selective instrument and procedure. The methods currently utilized need better calibration for the characterization of light hydrocarbons (C_1–C_6) at lower concentrations. The primary goal of this research is to develop and optimize a powerful and reliable analytical method to characterize live well fluid using a quadruple mass spectrometer (MS). The mass spectrometers currently being used in the field have issues with detection, spectra deconvolution, and quantification of analytes at lower concentrations (10–500 ppm), particularly for the lighter (<30 *m/z*) hydrocarbons. The objectives of the present study are thus to identify the detection issues, develop and optimize a better method, calibrate and QA/QC the MS, and validate the MS method in lab settings. In this study, we used two mass spectrometers to develop a selective and precise method to quantitatively analyze low level lighter analytes (C_1–C_6 hydrocarbons) with masses <75 *m/z* at concentrations 10–500 ppm. Our results suggest that proper mass selection like using base peaks with *m/z* 15, 26, 41, 43, 73, and 87, respectively, for methane, ethane, propane, butane, pentane, and hexane can help detect and accurately quantify hydrocarbons from gas streams. This optimized method in quadrupole mass spectrometer (QMS) will be invaluable for early characterization of the fluid components from a live hydrocarbon well in the field in real time.

Keywords: mass spectrometric calibration; lighter hydrocarbons; fragmentation; base peaks

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1. Introduction

Real-time analyses of hydrocarbons and other gases on-site at oil and gas rigs allow 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, different methods and instruments have been used for characterizing the gases in live-well fluid. A mass spectrometric analysis is one of them, which has been recently used during drilling to establish the composition of the gases in the fluid. 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 [1]. 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 [1], and more importantly the

GC-based analytical units are not conveniently portable and don't work very well in tough drilling conditions. 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 [2]. Compositional variations, reservoir compartmentalization, porosity trends are also interpretable from MS data analyses.

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 specialists. The limitations experienced from current technologies such as the gas trap method and post analysis of the gases in the mud logging cabin [3] can be offset by the use of the MS. Real-time mass-spectrometric measurement is a proficient and immediate way to analyze the well fluids [4]. Implementing such a method can lead to a better understanding of the reservoir, its characteristics, and on-site safety.

The MS commonly used by operators and service companies in the oil and gas sector belongs to the class of quadrupole mass spectrometer (QMS) with a specific industrial name such as 'jumping mass spectrometer' [4]. It is called a jumping MS because of its ability to move from one mass peak to another during an analysis and, unlike most MS systems, it is robust enough to work in rocking boats in oilfields [4]. Unlike the commonly used gas chromatography-mass spectrometry (GC-MS), the jumping MS used in oilfields may not have the extra dimension to separate masses based on their molecular weight/volatility, which has led to a deconvolution and mass interference problems. The mass deconvolution and interference problems have limited the current on-site use of MS because it affects the accuracy and repeatability of MS to analyze lighter hydrocarbons (C_1–C_6) and other gases at lower concentrations. Consequently, the detection ability of the MS for lighter hydrocarbons are affected and need to be improved for real time analyses.

This study aims to resolve the deconvolution and mass interference issue by proper mass selection, calibration, and tuning, and improved resolution, position, and radiofrequency for the system. We developed and validated an analytical approach to characterize live-well fluids using two quadrupole mass-spectrometers (QMS) for lower-molecular-weight hydrocarbons otherwise known as the lighter/volatile hydrocarbons. The lower limit of detection was determined for both the MS systems, especially targeting accuracy for concentrations below or at 20 ppm, which has been challenging for live well gas analysis. The optimized MS method was also validated for its detection capabilities for those lighter hydrocarbons in complex mixtures at low concentrations. The successful calibration of the tools and results generated thereof are presented in this paper with the goal to help the improved analysis of fluid components from live hydrocarbon fluids in the field in real time.

2. Background

Mud gas analysis is the first breath of a well and a form of monitoring reservoir fluids in drilling fluids and has existed for about 80 years. In the past, gas monitoring was done by observing mud volume and bubble in returned drilling fluids. As times progressed, rig operations became more complex and hence the need for more sophisticated analyses. Mud gas analysis has developed from observation of mud volumes to uses of tools like gas chromatogram integrated with-flame ionization detector (GC-FID) or mass spectrometer (GC-MS), and independent mass spectrometer (MS). Tools like GC-MS and GC-FID require two components: separation instrumentation and the detecting component. In the case of GC-MS, GC is the separation mechanism, and MS is for detection. While these GC-FID or MS based systems provide separation of analytes, the main problem with these systems is their inability to work accurately in rough drilling environments. Moreover, the separation capability 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 [5].

Over the years, mass spectrometers have been used to study the behavior of hydrocarbons in petroleum industry. The MS is capable of detecting minute changes in intermolecular arrangements, isotopes, and ionization potential of pure gases [6]. The prospects and challenges of mass spectrometry in petroleum engineering and applied fields have been demonstrated for complex compounds and heavy molecules [7,8]. In laboratory settings, high resolution and accurate measurements are possible but detection and measurement on the rig can be operationally challenging.

During a drilling operation, the cuttings circulated through the annulus of the well emit signature gases (particular to the formation) [9]. 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 [1]. 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 [10].

The MS first ionizes the hydrocarbons using electron ionization (EI) and then uses specific mass-to-charge (m/z) ratio to select target analytes. Thus, on drilling sites, gases are commonly examined and quantified using daughter peaks in MS, formed after fragmentation of the parent mass via electron ionization. However, there are two significant challenges to the choice of peak after ionization/fragmentation: the deconvolution matrix of the gas standards and the quantitative validation of the gases by gas standards.

Lighter hydrocarbons (LHC) are volatile and would readily escape to the atmosphere unlike heavier hydrocarbon compounds. LHCs typically evolve from the drilling fluids at lower concentrations, 10–500 ppm. Due to the lightness and lower concentrations of some of the hydrocarbons, quantitative analysis of the gases remains a challenge. The corroboration of the LHCs against gas standards would solidify the knowledge of the MS response to the gases at varying concentrations.

The mass spectrometer (MS) consists of three main components: an ion processing system, vacuum pumps, and control systems. The mass spectrometer operates on the principle of bombarding the gaseous component with low voltage electrons, which a filament emits as the temperature rises. The bombarded molecules ionize into positive ions and pass through a slit, which maintains a low negative potential. The ions are displayed as peaks, also called fragments. These peaks become representative of unknown mass (m) to charge (z) or 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 ions formed after ionization.

There are different 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. Among them, the quadrupole mass spectrometers (QMS) are the most common spectrometers because of simplicity, high sensitivity, and fast scanning. The QMS consists of four 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, a mass analyzer could be a tandem MS–mass spectrometer capable of multi-stage mass filtering/analysis, improving selectivity.

Considering the operating characteristics of the MS, it is a necessary tool for fieldwork in the oil and gas industry [6]. Possessing the added capabilities to serve multiple purposes and still provide reliable results concerned with detection and sensitivity [6] makes the tool and its operational use more reliable. However, there are challenges in detecting and quantifying lower concentrations of gases in live-well fluids. Instrumentation of the MS has existed for more than 70 years and has been used for many applications, but the limit of detection for mud gas analysis is ~20 ppm or greater.

Mud gas samples are complex mixtures of “overlapping hydrocarbon species” [11]. 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. In this study, we develop and test a robust calibration method for hydrocarbon gases, particularly the low molecular weight species or LHCs, and at lower concentrations, 10–500 ppm for application to real time analyses in the field.

3. Establishment of Methodology

The mass spectrometer used in this study is a commercially available quadrupole mass spectrometer (QMS). It consists of an ion source, 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, fragments. The gases are first ionized and then the ions (*m/z*) are accelerated through the ion accelerator and filtered by the four parallel poles (quadrupoles) with alternating electricity in the forms of alternating current (AC) and direct current (DC) [12].

Although the gases detected are selected based on their *m/z* ratio, a 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 important to understand that the MS detects ions formed after fragmentation due to the electron ionization, not the atomic masses of the gases. The quadrupoles are significant in the design of the QMS 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.

3.1. Binary and Mixed Standards

There are two types of standards used for this study for the method development/calibration and validation; mixed and binary standards balanced in either Nitrogen (N), Helium (He) or Argon (Ar). Mixed standards, also known as "Blend", is the compressed mixture of more than one gas balanced at varied concentrations (Table 1). 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 are typically inert and abundant in nature, ensuring the safety of compressed gases.

Table 1. List of blends used in this study at various concentrations.

Standard 1		Standard 2		Standard 3	
Component	**Concentration**	**Component**	**Concentration**	**Component**	**Concentration**
	(ppm)		**(ppm/%)**		**(ppm/%)**
1 Butene	10	Benzene	50	Methyl Cyclohexane	200
1 Pentene	10	ethylene	50	Benzene	500
1,3,Butadiene	10	Helium		Ethylene	500
Acetylene	10	Methylene	50	Helium	500
Benzene	10	propylene	50	N-Octane	500
Ethane	10	toluene	50	Propylene	500
Ethylbenzene	10	Argon	100	Toluene	500
Ethylene	10	ethane	100	Hexane	1000
Hexane	10	Hexane	100	N-Heptane	1000
Isobutene	10	N-Butane	100	CO_2	3000
Isoprene	10	N Heptane	100	Argon	5000
M Xylene	10	N Octane	100	Ethane	5000
Methane	10	N Pentane	100	N-Butane	5000
Methyl acetylene	10	Propane	100	N-Pentane	5000
N-Butane	10	CO_2	300	Propane	5000
N-Pentane	10	Methane	0.10%	Methane	1%
O-Xylene	10	Oxygen	1%	Oxygen	5.00%
P- Xylene	10	Nitrogen	98.76%	Nitrogen	90.68%

In this study, we used Airgas supplier of gases, a third party company guaranteeing purity measured at 99.99%. There are three sets of gas standards used in this experiment; named as standard 1 (ST1), standard 2 (ST2), standard 3 (ST3). ST1 (Table 1) 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. Analysis of the lighter hydrocarbons, C_1–C_6, was the main focus of this study.

3.2. Operational Conditions of Mass Spectrometer

The MS were operated at a fixed amount of voltage of about 70 eV in the filament and temperature at 80 degrees Fahrenheit. It also comes with a gas column with an operating pressure of 15–20 psi 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 by diminishing levels of uncertainties. This also offers the opportunity to adjust the dwell time and mass-to-charge ratio *(m/z)*. The dwell time was 200 ms and the *m/z* was from 2–200. The instrument was tuned daily prior to calibration.

3.3. Gas Standards and Fragmentation Pattern

Two types of gas standards were used in this study; sets of binary standards with known balance and a select gas to be analyzed for, and mixed standards with numbers of gases mixed together in a known balance (Table 1). The binary standards, as they have only one analyte mixed in known balance, were used to understand the fragmentation pattern of select gas analyte after electron ionization (EI) in MS. The fragmentation of hydrocarbon studied was C_1 through C_6 and Propylene. In order to understand in detail, the fragmentation patterns, the first step is to know the preferred theoretical peaks, at the molecular mass, 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. The fragmentation patterns was used for peak selection; to choose particular *m/z* with highest abundance and lowest interferences, which help improve the interpretation of lighter hydrocarbon constituents. The mass (*m/z*) selected after the fragmentation of the binary standards was termed as 'base peak' which helps ascertain the detection limits of the MS. Afterward, the selected peaks amongst the tested and analyzed hydrocarbons were QA/QC ed to ensure that there is minimal interference within the group of lighter hydrocarbons.

After analyzing the fragmentation patterns for all binary standards and finalizing the base peak for each analytes, mixed gas standards at various concentration (10, 15, 100, and 500 ppm) were passed through the MS system. The use of mixed gas standards simulates 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 99.99%, limiting any concerns of impurities existence in the gases.

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 this experiment, the addition of an extra valve served the purpose. The fact that we chose silicon as a connecting line is also important. The choice of copper tubes 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 [3]. For this reason, gases detected will present lower statistical uncertainties.

3.4. Base Peak Selection

Base peak is ions with higher intensity on the spectra or result (Figure 1). 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 (*m/z*) 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. The gas used for calibration had different concentrations levels (10, 15, 100, and 500 ppm) with different constituents in different balances. These gases generated peaks at specific *m/z* ratios. These resulting fragment peaks were 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 target hydrocarbon compound.

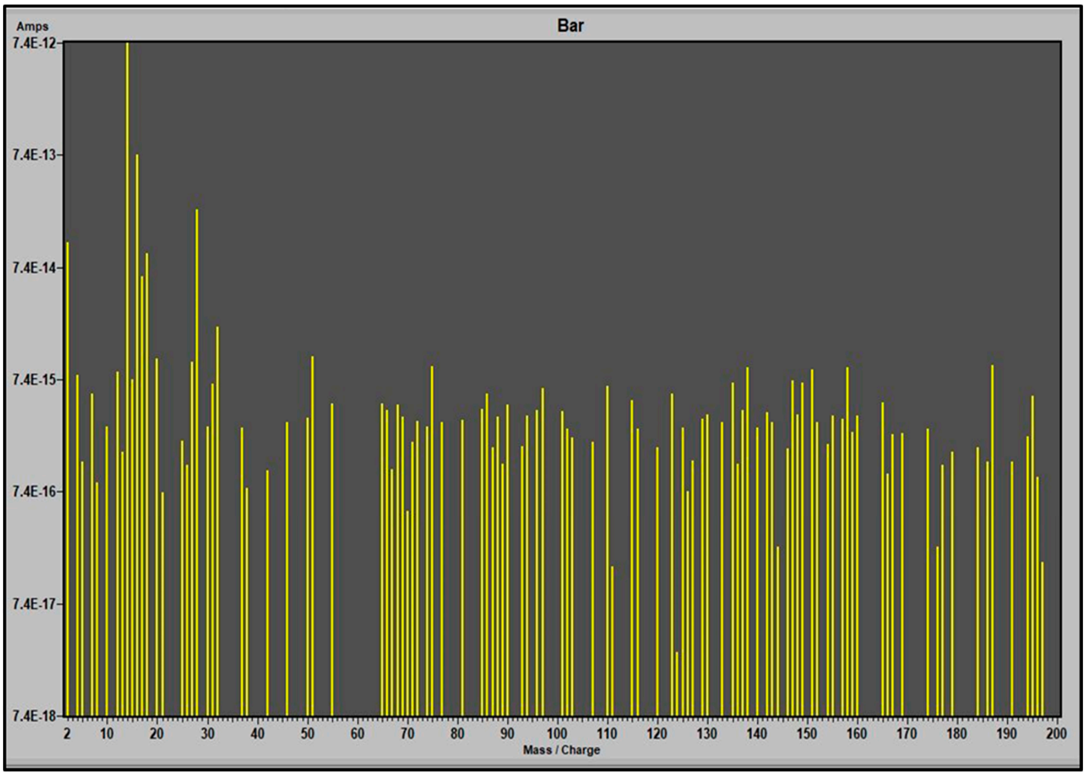


Figure 1. Sample reading of air for masses 2–200–an example spectrum.

3.5. *QA/QC of Fragmentation Pattern and Base Peak Selection*

The fragmentation pattern is representative of the structures/peaks of the daughter masses formed after electron ionization of the parent compound. The fragmentation ions are secondary ions of the parent–molecule ion. Typically, the signals corresponding to the concentrations of each *m/z* (including the daughter ions formed after fragmentations) are in millivolts. Thus, the signals are amplified and displayed as the spectra or fragment patterns. To achieve fragmentation of ions, we bombarded the molecules at 70 eV, which is the operational eV for both the QMS tested in this research. There are different types of ions produced after the ionization process.

The resulting fragment peaks after EI of target gas analytes were compared to preselected base peaks from the fragmentation process. As long as there is minimal interference and peaks match the selected peak, the *m/z* ratio becomes appropriate for the hydrocarbon compound. In addition, the most suitable peak "base peak" was queried statistically by calculating the %Relative Standard Deviation (%RSD). The peaks of choice, the sensitivity of the tool, and repeatability of the experiment 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 C_1 to C_6 components which can then be directly used and applied in the field for an improved analysis of fluid components from a live well.

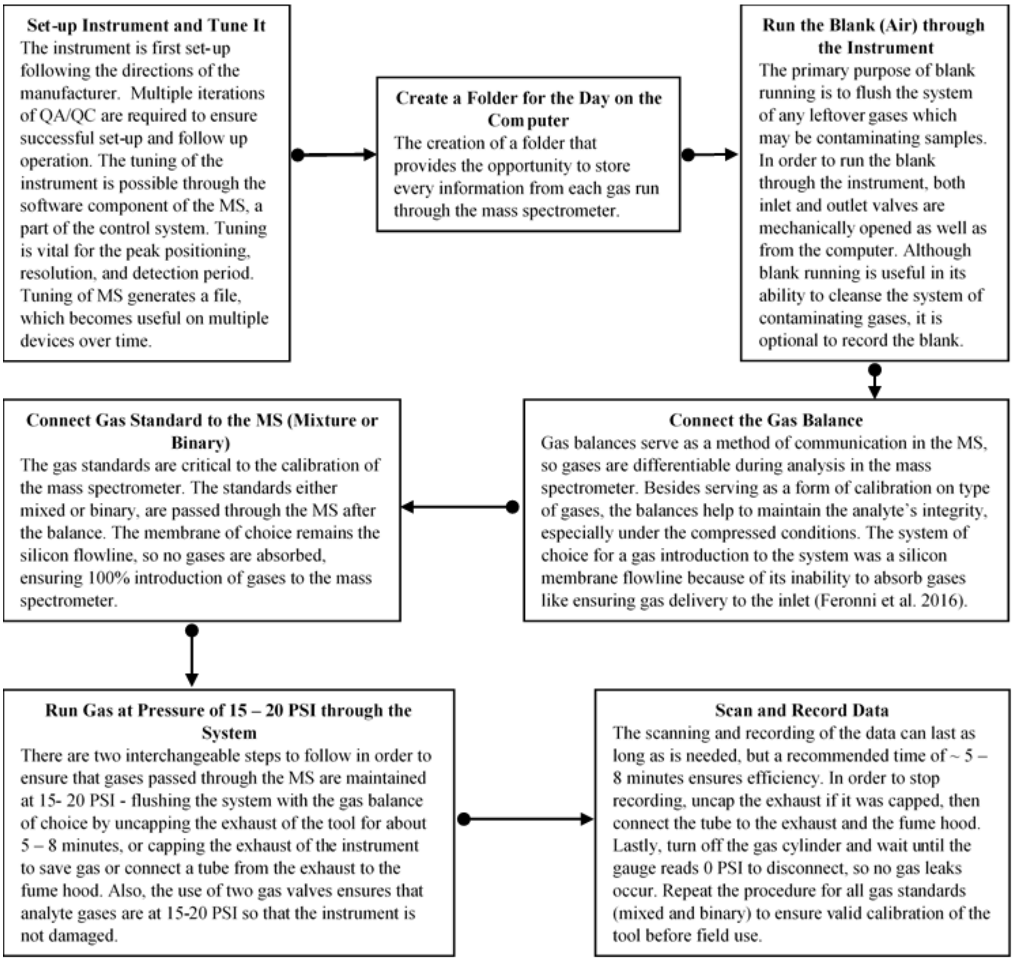
The peaks of choice, the sensitivity of the tool, and repeatability of the experiment are QA/ QC steps that improve the reliability of the tool as well as its operations. All these steps were adopted in this study for the calibration of the QMS, thus establishing a robust methodology that operators and service personnel can use onsite.

3.6. 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.

3.7. Statistical Analyses of Data

The testing of the mass spectrometer resulted in the creation of datasets 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, 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% for the analysis to be within acceptable criteria.



Set-up Instrument and Tune It
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.

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.

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

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 because of its inability to absorb gases like ensuring gas delivery to the inlet (Feronni et al. 2016).

Connect Gas Standard to the MS (Mixture or Binary)
The gas standards are critical 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 to the mass spectrometer.

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 - 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 ensures that analyte gases are at 15-20 PSI so that the instrument is not damaged.

Scan and Record Data
The scanning and recording of the data can last as long as is needed, but a recommended time of ~ 5 – 8 minutes ensures efficiency. 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.

Figure 2. Procedural Steps.

3.8. Procedural Steps

The steps below outline how the calibration process was achieved for the QMS under study (Figure 2).

In pursuing the 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 were studied, primarily focusing on hydrocarbons (C_1–C_6), on each instrument by using binary standards that contain lighter hydrocarbons balanced in either nitrogen or argon.

4. Results and Discussion

4.1. Fragmentation of Lighter Hydrocarbons

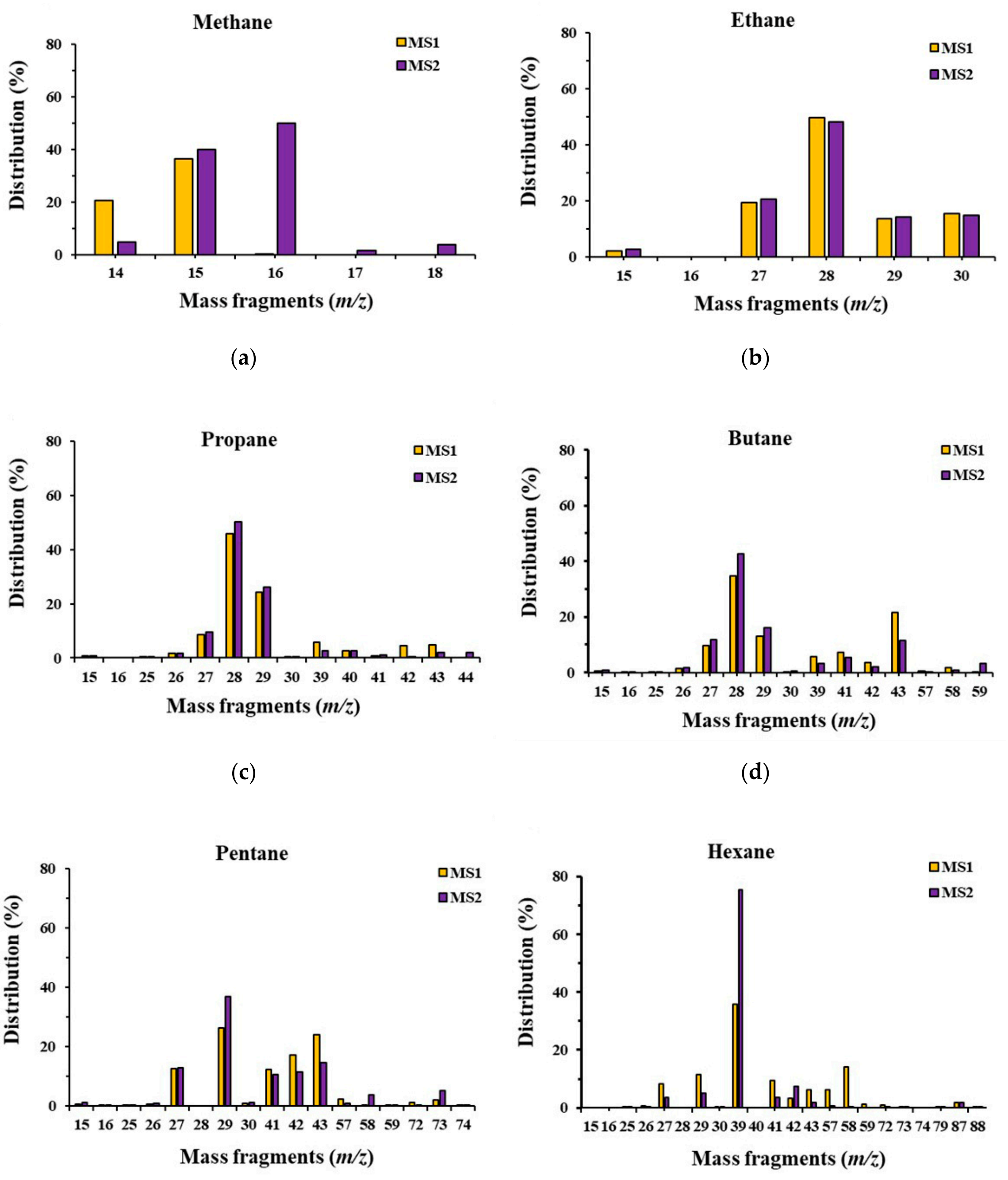
All gas standards, both binary and mixed standards were analyzed for best peak, average standard error (SE), percent relative standard deviation (%RSD), and calibrated masses of the gases. The fact that we were able to minimize the %RSD to acceptable values (<10%) imply that these instruments and the calibration procedures developed will be able to detect the lighter hydrocarbons at fairly low concentrations—a challenge that the oil and gas industry currently faces.

C_1–C_6: Methane, Ethane, Propane, Butane, Pentane and Hexane

The C_1–C_6 hydrocarbons, namely, methane (C_1–CH_4), ethane (C_2–C_2H_6), propane (C_3–C_3H_8), butane (C_4–C_4H_{10}), pentane (C_5–C_5H_{12}), and hexane (C_6–C_6H_{14}) are the six main components of hydrocarbon gases. Methane is the shortest alkane group with a molecular mass of 16 g/mol while hexane is the longest hydrocarbon with a molecular mass of 86.18 g/mol studied in this study. A major guiding factor for the peak selection was the compatibility of the gases passed through the mass spectrometers tested. Argon is used as a gas balance, except for pentane where nitrogen was used (based on availability). Argon is inert and therefore interference with the hydrocarbon gas components is minimized. Nitrogen does not interfere with pentane.

Methane fragmented into molecular masses 14, 15, and 16 amu. According to Figure 3, mass 16, 17, and 18 were detected by mass spectrometer 2 only, which automatically discredits the peaks at 16, 17, or 18, deductively guiding the fact that mass 15 is a good peak choice due to its relative abundance mass and response factors for both mass spectrometers MS1 and MS2. 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. Methane at mass 15 showed a robust peak and had lowest interferences from other masses from heavier hydrocarbons, thus making it an appropriate peak of choice, the base peak. 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 MS1 & MS2. This also establishes % mass difference as of the analytical methods to justify similarity between the mass spectrometers.

Ethane is detectable from masses 25, 26, 27, 29, and 30. The mass spectrometers' responses (Figure 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. 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 and 30 were favorable to avoid interference from nitrogen should it be present in the gas stream, given its abundance in air. 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.



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 3. The product ion spectra and their relative distribution (%) for C_1–C_6 formed after ionization of binary standards in each MS; (**a**) Methane balanced in Argon, (**b**) Ethane balanced in Argon, (**c**) Propane balanced in Argon, (**d**) Butane balanced in Argon, (**e**) Pentane balanced in Nitrogen, and (**f**) Hexane balanced in Argon.

Propane fragments into 15, 16, 25, 26, 27, 30, 39, 40, 41, 42, 43, and 44 (Figure 3). Considering the response from both MS and potential interferences from other anlytes, we decide to select mass 41 for propane as base mass. In the case of propane, the peaks are less abundant compared to the other compounds analyzed, with masses at 40, 41, 42, 43, and 44. 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 determined to be the most reliable peak.

Butane follows the trend of the other alkanes by fragmenting from 15 through 59 but selected mass 43 as the N-butane peak. We selected mass 43 for butane (Figure 3), for MS1

& MS2 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 MS1 and MS2 is independent of the tool's functions in gas detection.

Pentane is the second-longest chain studied in this experiment. Although the theoretical mass of pentane exists at 72.15, the experimental deduction for this study uses 73 g/mol for identification of pentane. At 72, pentane is not detected by MS2 (Figure 3), but at 73 both MS1 and MS2 detected the five-chain hydrocarbon. Thus, 73 is chosen as the base mass of pentane (Figure 3). The selection of pentane is guided and reinforced by the detections of the gas by both MS1 and MS2-a significant indicator for higher confidence on the chosen base peak.

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 3), there are no fragments within the range of 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.

4.2. Using Fragmentation for Calibration

Fragmentation of binary standards is an essential first 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 base mass selected for the analysis using the binary standards were used to develop the method for the analysis of mixed standards which are similar to the real time environmental samples–with a number of gases mixed together. 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 study.

One of the major challenges faced in MS analyses of live fluids is that of deconvolution, which occurs when base masses overlap due to fragmentation of components. In gas mixtures this generates a problem, viz. which base mass represents what component, and how much of that component? For example, if propane fragments into masses similar to 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 C_1–C_6 components irrespective of deconvolution. Our results suggest that using methane 15, ethane 26, propane 41, butane 43, pentane 73, and hexane 87 base masses minimizes such matrix inteferences and can help detect true hydrocarbon components from gas streams in live well fluids (Figure 3). 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 (Figure 4).

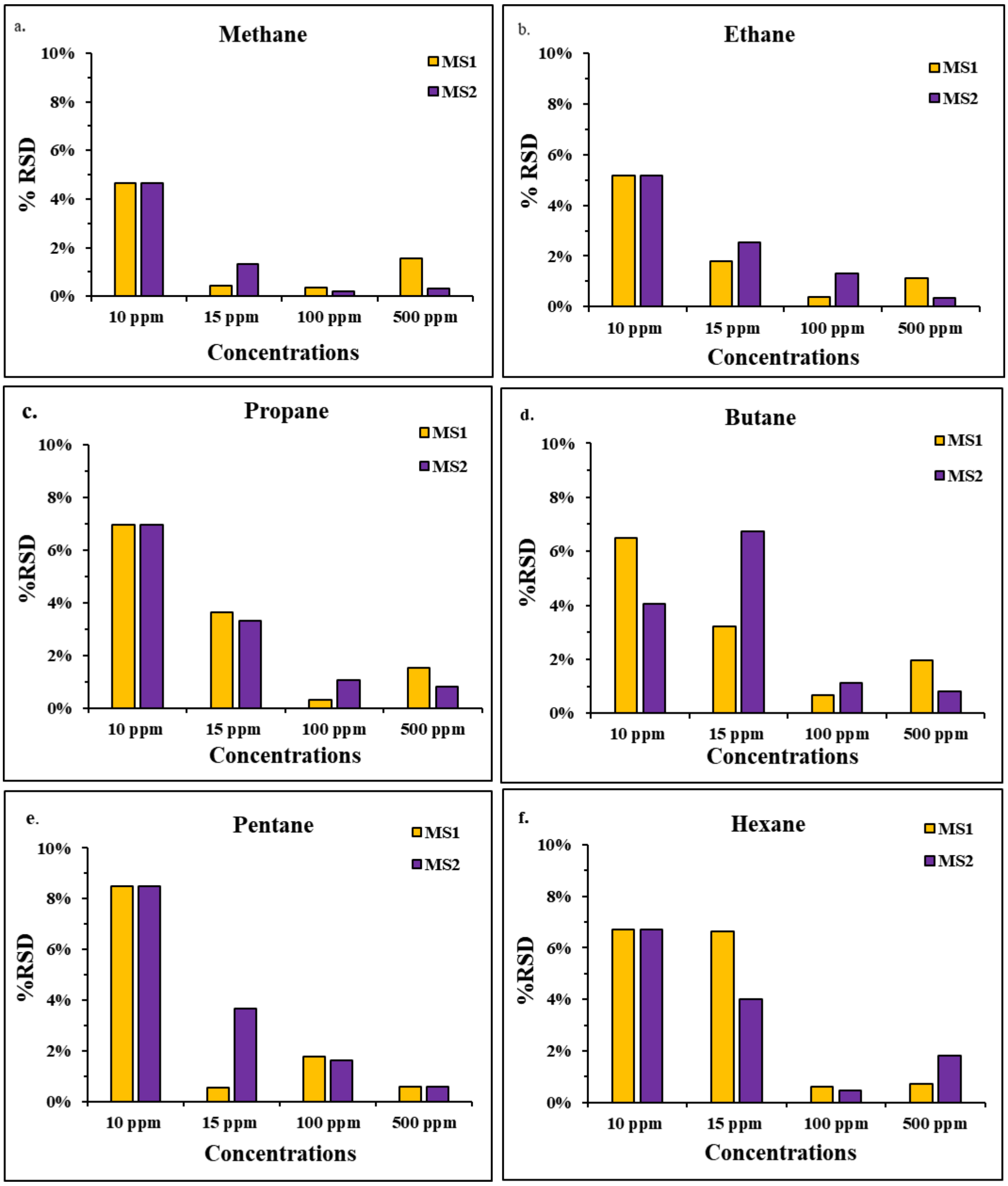


Figure 4. % Relative Standard Deviation (%RSD) of average response for different concentrations (10, 15, 100, and 500 ppm) of C_1–C_6 (**a**). methane, (**b**). ethane, (**c**). propane, (**d**). butane, (**e**). pentane, (**f**). hexane) for each mass spectrometer (MS).

Besides the deconvolution problem, the limit of detection of the gases was a challenge as well. It is a critical contributor for the method development using a 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 with a range of concentrations (10, 15, 100, and 500 ppm) ran in the MS. The primary focus was to validate the ability of the MS method to accurately detect and quantify the gases at lower concentrations (i.e., 10 and 15 ppm). The % relative standard deviation (%RSD) versus the concentrations were determined (Figure 4) as the main criteria for method validation. As expected, 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 concentrations, 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.

4.3. Response to Binary Gas Standards for MS1 and MS2

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 (Figure 5). 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.

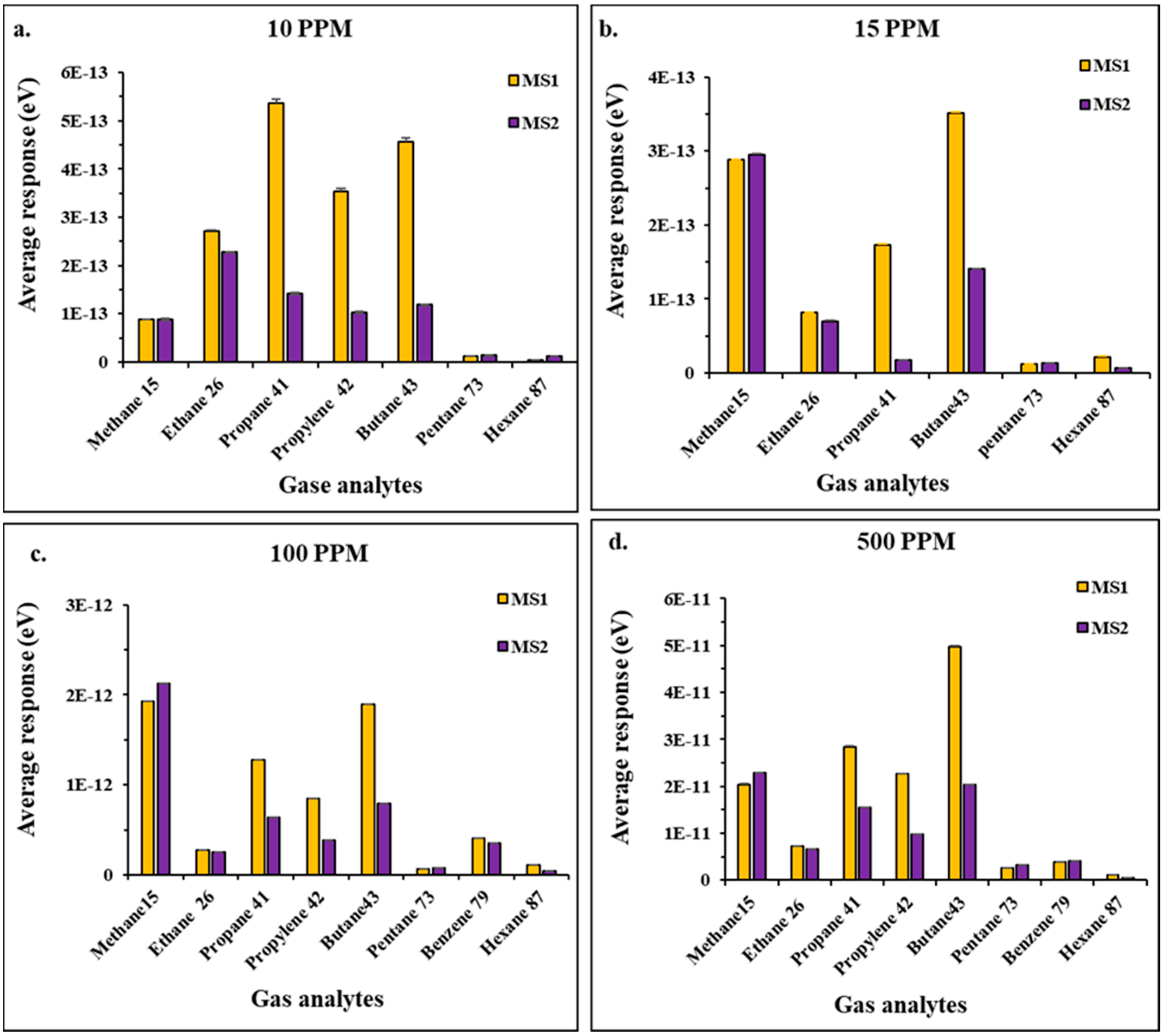
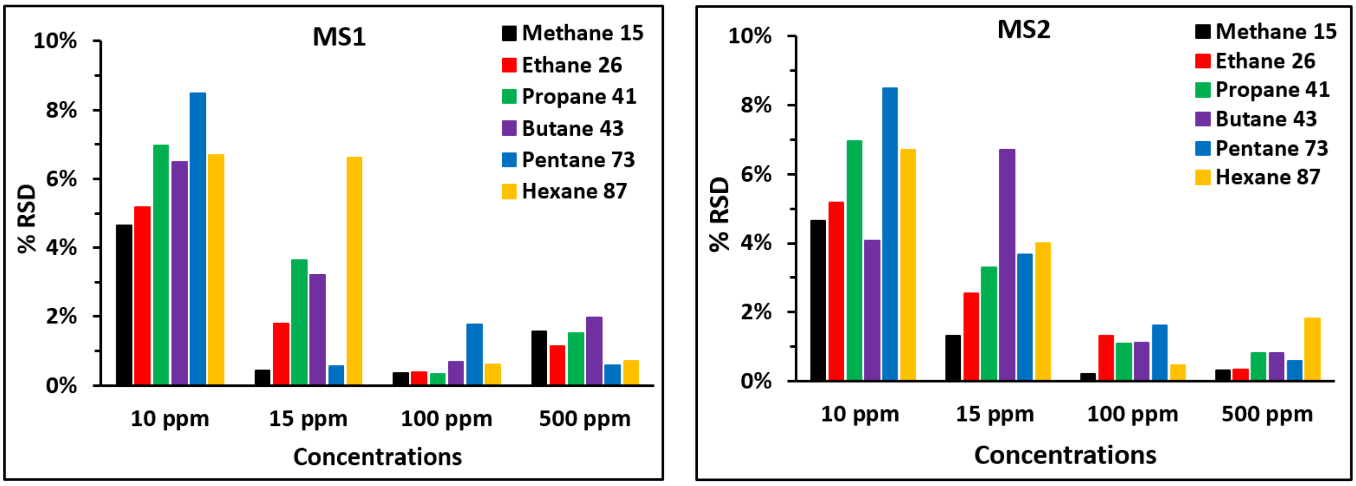


Figure 5. Average MS Response for Mixed Standards at various Concentrations. (**a**) 10 ppm, (**b**) 15 ppm, (**c**) 100 ppm, and (**d**) 500 ppm.

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 (%RSD). The limits 10% and 5 % serve as a guide for higher and lower concentrations. Lower concentrations of gases were difficult to detect and thus a higher error margin is used. Lighter hydrocarbons at rig sites could occur in trace elements, ~10–15 ppm. At such concentrations, detection of gases becomes a challenge. For this reason, the sensitivity of the MS is prioritized and validated using % RSD.

Another conclusion of this testing and calibration process is that the base peak selections from the binary standards facilitated the analyses from the mixed standards. The combination of knowledge from binary fragmentation and base peak selections improved confidence in the representative masses selected for calibration and for analysis of those gases in the field at the selected mass. 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 % RSD served as a decision guide for testing sensitivity, and whether the best peak is indeed the best. As shown in the Figure 5, 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. Figure 6 demonstrates that the MS instruments are highly responsive and sensitive irrespective of the concentrations of the blend.



(**a**) (**b**)

Figure 6. % Relative Standard Deviation (%RSD) for different concentrations (10, 15, 100, and 500 ppm) of Gas Mixed Standards, (**a**) for MS1 and (**b**) for MS2.

4.4. Relative Standard Deviation Versus Concentration

Figure 6 represents the cumulative responses of the mass spectrometers individually analyzed as MS1 and MS2. The plots (%RSD versus Concentration) showed that higher concentrations had lower variation from the average MS response, which the cumulative plots above reinforce. The cumulative responses of each class of concentration 10, 15, 100, and 500 ppm are normal in distribution reflecting natural composition/population of data. However, fitting the entire plots projects the data as skewed to the right, indicating that gas component detection is greatly affected by concentration.

4.5. Standard Error for Lighter Hydrocarbons in the Mixed Standards

Figure 7 shows the average standard error (SE) 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 10 ppm from a mixed gas in the laboratory is reliable. Compared to the concentrations at 10 ppm, there is an improvement in average standard error for 15 ppm, confirming the initial hypothesis of higher concentration leads to better detection. For concentrations of 100 ppm, and 500 ppm, the error order of magnitude ranges from 10^{-15}–10^{-17} of the response (eV) (Figure 7), which is minimal to insignificant considering the concentration of gases passed through the mass spectrometer—another indicator of the reliability of both mass spectrometers used. 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 became 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 500 ppm, the mass spectrometer one and two used to deliver different types of average standard error values. In the case of hexane at 500 ppm, MS2 is more accurate in its measurement. However, the differences observed from MS1 to MS2 do not distort the results at lower and higher concentrations.

4.6. Comparison, Validation, and Reliability of MS1 and MS2

Based on the binary and mixed gas standard information above, both MS are similar to each other with minimal differences. Both MS 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.

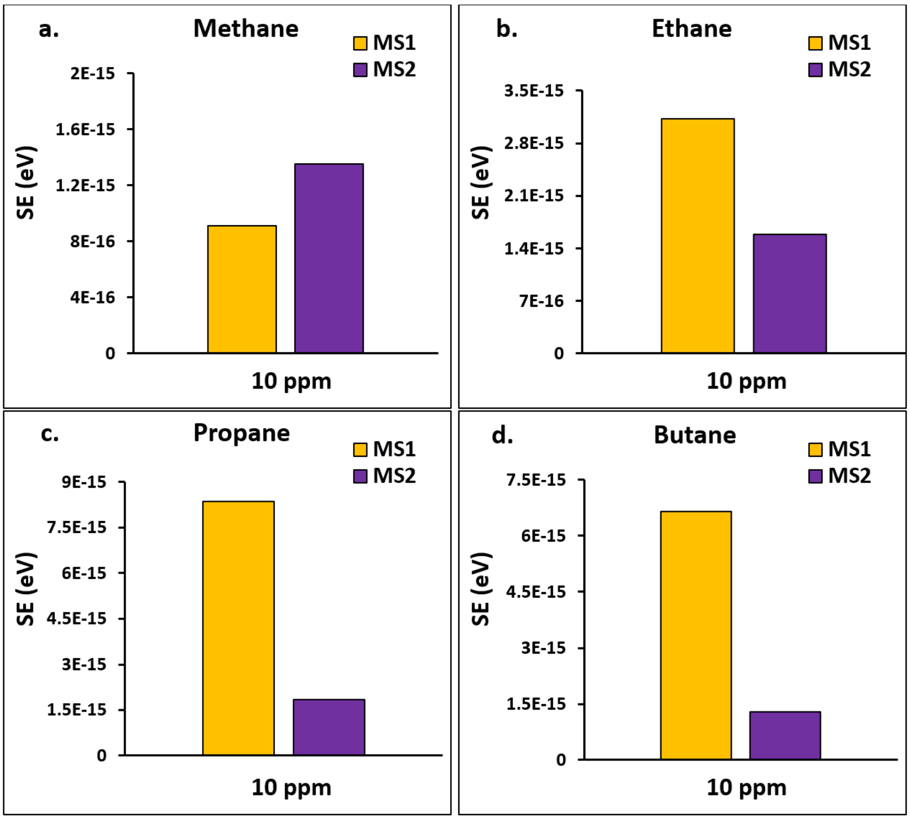


Figure 7. *Cont.*

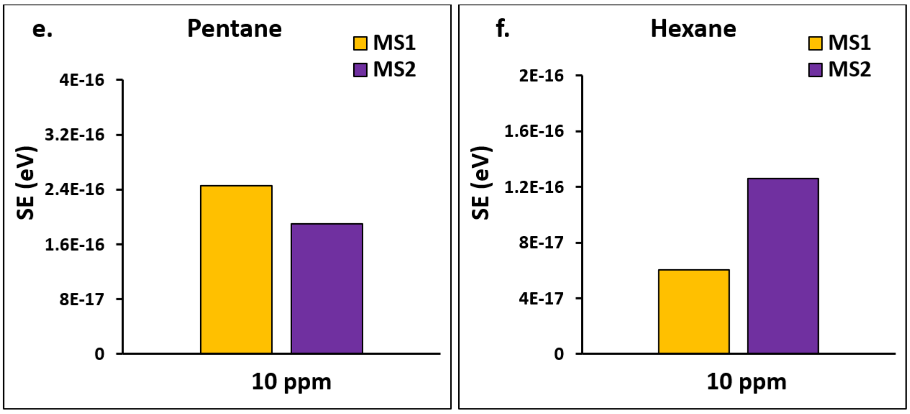


Figure 7. Average Standard Error (SE) of responses (eV) for C_1–C_6 ((**a**). methane, (**b**). ethane, (**c**). propane, (**d**). butane, (**e**). pentane, (**f**). hexane) at 10 ppm concentration, both MS.

5. Conclusions and Recommendations

Two quadrupole mass spectrometers (QMS) used on rig sites were used to successfully develop and calibrate a method to analyze C_1–C_6 in live well fluid, and both MS can detect hydrocarbons as low as 10–15 ppm with higher selectivity, accuracy, and repeatability. The two QMS used in this study were of similar type and manufacturer, they were used to test repeatability of the method developed and calibrated/validated it. Quantitative analysis is possible because the deconvolution problem was resolved through proper mass (base peak) selection binary and mixed gas standard resolutions, and statistical analyses of the data output for uncertainty management. Our results suggest that using methane 15, ethane 26, propane 41, butane 43, pentane 73, and hexane 87 as base masses can help detect these hydrocarbon components from gas streams in live well fluids. These selected masses for each hydrocarbon minimize interferences and make quantitative analysis more accurate. The method developed resulted in errors that were insignificant and were acceptable (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. The %RSD provides the opportunity to quantify the response of the MS to the binary gas standards, which serve as a foundation for the mixed gas standard calibration/validation process. The deconvolution problem also occurred due to the lack of an additional dimension for proper mass selection, unlike GC-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 expected 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 are, therefore, not easily detected especially when present in low amounts. All gas mixed standards containing the tested binary compounds focused on upper bounds of concentration values; 10, 15, 100, and 500 ppm. Estimating the %RSD values for different ranges of gas concentrations 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 2 and 3 for ~10–15 ppm). The % RSD values ranges from 2% (for higher concentrations) to 10% (for lower concentrations) (Figures 5 and 7). 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 min) 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.

Table 2. Statistical values for Mass Spectrometer 1 (MS1); average response, standard deviation, variance and percent relative standard deviation (%RSD) for selected base mass at different concentrations.

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%

Table 3. Statistical values for Mass Spectrometer 2 (MS2); average response, standard deviation, variance and percent relative standard deviation (%RSD) for selected base mass at different concentrations.

MASS SPECTROMETER 2																	
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	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%

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. Fragmentation will occur, and can lead to challenges in determining appropriate peaks for use. Additionally, a complex mixture of gases will generate interference, and a known calibration method will help characterize fluids better.

6. Recommendations

The electron ionization (EI) in MS systems break down long chain hydrocarbon compounds into shorter constituents, consequently causing potential interferences/deconvolution issues while analyzing lighter hydrocarbons. Thus, 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 the 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 [13] 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 their corresponding or near molecular weight, and the lighter hydrocarbons will have fewer interferences from the fragments coming from the heavier hydrocarbons. As an additional QA/QC measure, select gas standards with known concentrations should be run at regular intervals to determine %RSD. 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 as follows:

- 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 used to study the type of reservoir fluid, and the MS the composition of the fluid.
- Using a Gas Chromatography Mass Spectrometer (GC-MS) in addition to this MS for real time detection, to validate, cross-check and confirm such analysis.
- Enhancing the operational capability for soft ionization with controlled supply of voltage.
- Implementing the use of electron multiplier to achieve better detection limit in the QMS.

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Nomenclature

MS–Mass Spectrometer; LHC–Lighter Hydro-carbon; QMS–Quadrupole Mass Spectrometer; Calibration; Fragmentation.

Highlights

- Lighter hydrocarbons (C_1–C_6) are hard to detect due to interferences from heavier compounds.
- A powerful and reliable analytical method was developed and validated in lab settings.
- Hydrocarbons with molecular masses <75 were detected at concentrations of 10–500 ppm.
- Base *m/z* of 15, 26, 41, 43, 73 and 87 are recommnded respectively for methane, ethane, propane, butane, pentane and hexane.

References

1. Nair, A.V.; Kurawle, I.B.; Kaul, M.; Mahalle, N.A.; Thomas, T.; Shivanikar, A.V.; Carvalho, V.H. Mud Gas Isotope Logging Using Mass Spectrometry. In Proceedings of the Asia Pacific Oil and Gas Conference & Exhibition, Jakarta, Indonesia, 4–6 August 2009. Society of Petroleum Engineers. [CrossRef]
2. Wicker, T.; Warren, B. Maximize Mass Spectrometer Mud Gas Data-Experienced Analysis Matters. Available online: http://www.searchanddiscovery.com/documents/2015/41623wicker/ndx_wicker.pdf (accessed on 10 April 2021).
3. Ferroni, G. Deep-Spectrum Gaschromatography and Carbon Isotopes Analysis While Drilling Enhance Value of Real-Time Formation Evaluation, Reducing Interpretation Uncertainty. In Proceedings of the International Petroleum Technology Conference, Bangkok, Thailand, 14–16 November 2016. [CrossRef]
4. Rowe, M.; Splapikas, T. Jumping Mass Spectrometer. In Proceedings of the SPE Kingdom of Saudi Arabia Annual Technical Symposium and Exhibition, Dammam, Saudi Arabia, 24–27 April 2017. [CrossRef]
5. Niyonsaba, E.; Manheim, J.M.; Yerabolu, R.; Kenttämaa, H.I. Recent advances in petroleum analysis by mass spectrometry. *Anal. Chem.* **2019**, *91*, 156–177. [CrossRef] [PubMed]
6. Hoover, H., Jr.; Washburn, H. Analysis of hydrocarbon gas mixtures by mass spectrometry. *Calif. Oil World* **1941**, *34*, 21–22.
7. Marshall, A.G.; Rodgers, R.P. Petroleomics: The next grand challenge for chemical analysis. *Acc. Chem. Res.* **2004**, *37*, 53–59. [CrossRef] [PubMed]
8. Hsu, C.S.; Shi, Q. Prospects for petroleum mass spectrometry and chromatography. *Sci. China Chem.* **2013**, *56*, 833–839. [CrossRef]
9. Espitalié, J.; Marquis, F.; Barsony, I. 9-GEOCHEMICAL LOGGING. In *Analytical Pyrolysis*; Voorhees, K.J., Ed.; Butterworth-Heinemann: Oxford, UK, 1984; pp. 276–304. [CrossRef]
10. Larter, S.R.; Aplin, A.C.; Corbett, P.W.; Ementon, N.; Chen, M.; Taylor, P.N. Reservoir geochemistry: A link between reservoir geology and engineering? *SPE Reserv. Eng.* **1997**, *12*, 12–17. [CrossRef]
11. Turner, R.E.; Overton, E.B.; Meyer, B.M.; Miles, M.S.; Hooper-Bui, L. Changes in the concentration and relative abundance of alkanes and PAHs from the Deepwater Horizon oiling of coastal marshes. *Mar. Pollut. Bull.* **2014**, *86*, 291–297. [CrossRef] [PubMed]
12. March, R.E. An introduction to quadrupole ion trap mass spectrometry. *J. Mass Spectrom.* **1997**, *32*, 351–369. [CrossRef]
13. Adhikari, P.L.; Wong, R.L.; Overton, E.B. Application of enhanced gas chromatography/triple quadrupole mass spectrometry for monitoring petroleum weathering and forensic source fingerprinting in samples impacted by the Deepwater Horizon oil spill. *Chemosphere* **2017**, *184*, 939–950. [CrossRef] [PubMed]