Characterization and quantitative determination of aromatics, nitrogen, sulfur and trace metals in fuel and hydrocarbon samples

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ABSTRACT

High resolution two- dimensional gas chromatography time- of- flight mass spectrometry (GC x GC TOFMS), inductively coupled plasma mass spectrometry (ICP-MS) and trace nitrogen/ sulfur analysis methods are used to analyze the fuel and hydrocarbon liquid samples. The high resolution two- dimensional gas chromatography (GC x GC) along with one dimensional gas chromatography are used to separate the complex samples and to report the identification of separated components provided by time- of- flight mass spectrometer (TOFMS). Traces of elements in gasoline, diesel fuel, pygas samples are determined by inductively coupled plasma mass spectrometry (ICP-MS). A lithium metaborate fusion method was used for sample preparation. As nitrogen/ sulfur are present in smaller concentrations in gasoline, diesel fuel and pygas samples, accurate determination of these nitrogen/ sulfur concentrations is important for quality control, to prevent engine deposits and to meet the regulatory requirements. For this a nitrogen/ sulfur instrument with an automatic quick furnace is used for selective and sensitive measurements of these elements.

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CHAPTER 1: Introduction

The determination of aromatic compounds in reformulated gasoline (RFG) is of importance to refiners because laws exist limiting the amount of emission of ozone forming and pollutant compounds [1]. The levels of aromatic compounds in gasoline are adjusted by refiners to comply with the environmental regulations and to improve the performance and properties of the fuels.

The environmental protection agency (EPA) has established that the determination of benzene, toluene and total aromatics should be done by gas chromatography mass spectrometry (GC-MS) [2]. EPA has also certified that a fuel complies with the standards for RFG only if it contains a minimum of 2.0 mass percent oxygen and maximum volume percent benzene. The emission performance of a fuel is based on a complex model which requires the input of a number of fuel parameters (chemical composition and physical properties), each of which must be measured by a specific test method designated by the EPA [3]. Such input parameters include the chemical composition and total aromatic content of the fuel. Due to the complex hydrocarbon matrix of the fuel, it is difficult to chromatographically separate all aromatic compounds from other non- aromatic hydrocarbons. To ensure the consistent implementation of the EPA method, the American Society for Testing and Materials (ASTM) has developed a standard test method that meets the requirement of the EPA. This standard test method (D5769) is used for the determination of total aromatics in finished gasoline samples by Gas Chromatography Mass Spectrometry. In this study, the analysis of fuel and hydrocarbon samples is complicated by a relatively large number of

volatile components, and GC x GC TOFMS has been investigated for the complete aromatic analysis and characterization of these samples.

The Pegasus 4D GC x GC TOFMS has several advantages over traditional GCMS systems. The Pegasus II provides a spectral collection rate up to 500 full- range mass spectra/ second to allow accurate measurement of the narrowest GC peaks. The analyte detectability can be increased by cryo- focusing the sample before separation by the secondary column. The automated peak find algorithm effectively locates the position of all the peaks in the chromatogram and reduces analysis time [4]. The unique features of the Pegasus II in fuel analysis were evaluated using a fast gas chromatographic method for rapid determination of total aromatics in finished gasoline [5].

Traces of elements in fuel and hydrocarbon samples are determined by inductively coupled plasma mass spectrometry (ICP- MS). A lithium metaborate fusion method for sample preparation and a standard multi- element calibration were used to quantify these samples.

Nitrogen and sulfur compounds exist in a wide variety of analytical samples like petroleum refinery, and environmental samples. The determination of these compounds in complex samples like gasoline, diesel fuel, and pygas samples is important for quality control. Due to the complex nature of the fuel and hydrocarbon samples and the low concentrations, an element specific method for nitrogen/ sulfur is required. To meet this challenge, a nitrogen/ sulfur analyzer that uses oxidative combustion followed by chemiluminescence detection for nitrogen and UV fluorescence detection for sulfur was utilized. The nitrogen/ sulfur analyzer is an example of simultaneous nitrogen/ sulfur detection and is known for its selectivity and sensitivity. The main goal of these studies is

to prepare a series of calibration standards and then quantify the gasoline samples using the calibrated standards.

1.1 Gasoline

Gasoline is a refined product of petroleum consisting of a mixture of hydrocarbons, additives and blending agents. The composition of gasoline depends on the crude oils used, the refinery processes available, and the product specifications. Gasoline is primarily divided into regular, plus and premium according to the different octane number. Gasoline primarily comes from petroleum cuts with boiling points ranging from 38^{o}C to 150- 205^{o}C and is blended with different components to improve the fuel properties.

Different grades of gasoline (regular, plus and premium) are obtained through blending of light straight runs, catalytic reformates, hydrocracked gasoline, catalytically cracked gasoline, alkylates, n- butane and oxygenates like Methyl Tertiary Butyl Ether(MTBE) [6].

The elimination of lead from gasoline made the refiners rely mostly on Methanol, Ethanol, oxygenates like Di Methyl Ether [DME], Methyl Tert- Butyl Ether (MTBE), Ethyl Tertiary Butyl Ether [ETBE], and Tetra Amyl Methyl Ether [TAME] to achieve acceptable octane levels [7].

1.2 Gasoline blending

Streams of gasoline blends are refined from crude oil or petroleum. The hydrocarbon molecules in the crude oil range from one to 50 or more carbon atom. Petroleum refining in general is distillation as well as chemical treatment. Catalyst and

pressure are the two factors which separate the hydrocarbon molecules and combine them into petroleum streams for commercial petroleum products. Gasoline is blended from various petroleum refinery streams by direct distillation of crude oil, hydrocracking, catalytic and thermal cracking, catalytic reforming, alkylation and polymerization.

Direct distillation of crude oil separates mixture of substances with a narrow difference in the boiling points and is one of the most important steps in the refining process. The crude oil contains various components having different sizes, weights and boiling temperatures. The components in the crude oil can be separated by fractional distillation because of different boiling temperatures. Hydrocracking is the process of catalytic cracking in the presence of elevated partial pressure of hydrogen which permits wide variations in the yields of gasoline by removing sulfur and nitrogen hetero- atoms. Hydrocracked stocks of gasoline lacks high octane olefin content present in catalytically cracked stocks, so they must be reformed [8]. The reforming process converts low octane olefins to higher octane liquid components in the gasoline. Catalytic reforming completely replaces thermal reforming. Most catalytic reforming catalysts contain platinum with another promoting metal such as rhenium [8, 9]. In gasoline refining, alkylation processes convert the refinery gases into gasoline range liquids, however this approach is expensive and not commonly used in gasoline production [8, 10].

Polymerization is a process of reacting or combining two or more low molecular weight olefins into higher molecular weight olefin liquids for gasoline blending [8]. The polymerization process is no longer used to produce gasoline blend streams [8, 10]. With the elimination of lead phase in gasoline, different options for increasing the octane have been explored [11]. Refining and blending of fuel components produce a fuel with

increased knock resistance [12]. Oxygenates like MTBE, ETBE, and DME are also added to gasoline to increase the overall octane number and to improve combustion efficiency [13].

1.3 Physical and chemical properties of gasoline

Table 1: Physical and chemical properties of gasoline

Property	Information	Reference
Molecular weight	108[a]	Anonymous 1989
Color	Colorless to pale brown or pink	Sax and Lewis 1989; Weiss 1986
Physical state	Liquid	Sax and Lewis 1989
Boiling point	Initially, 39^0C After 10% distilled, 60^0C	Budavari et al. 1989; OHM/TADS 1991;
Density	0.7-0.8 g/cm^3 [b]	IARC 1989
Odor	Gasoline odor	Weiss 1986
Odor threshold	0.025 ppm [c]	Weiss 1986
Solubility:		
Water at 20^0C	Insoluble	OHM/TADS 1991; Sax and Lewis 1989

Property	Information	Reference
Organic solvent	Absolute alcohol, ether, chloroform, benzene	Budavari et al. 1989; Sax and Lewis 1989
Partition coefficients:		
Log K_{ow}	2.13-4.87 [d]	Air Force 1989
Log K_{oc}	1.81-4.56 [d]	Air Force 1989
Vapor pressure:		
At 60^0C	465 mmHg	Weiss 1986
At 56^0C	518 mmHg	Weiss 1986
At 51^0C	593 mmHg	Weiss 1986
At 47^0C	698mmHg	Weiss 1986
At 41^0C	773mmHg	Weiss 1986

Property	Information	Reference
Henry's law constant; at 20^0C	$4.8*10^{-4}$- 3.3 m^3/ mol [e]	Air Force 1989
Auto ignition temperature	280-486^{0}C	NEPA 1986; Sax and Lewis 1989
Flammability limits	1.4-7.4%	Weiss 1986
Explosive limits	1.3-6.0%	Budavari et al. 1989; Sax and Lewis 1989

a. Average molecular weight.

b. Temperature not specify

c. Not specified whether data for air or water

d. ASTM has established guidelines on the compositions of gasoline that will permit satisfactory performance under a range of conditions. These guidelines define five volatility classes that vary by seasonal climatic changes. The values given for vapor pressure at the given temperatures are based on volatility classes

e. Since data are not available for gasoline, ranges are given indicating different values for the individual components.

Table 2- Major components of gasoline

Component	Percentage	Component
		Other possible components
C_5	3.0	Octane enhancers
C_6	11.6	Methyl t-butyl ether(MTBE)
C_7	1.2	t-butyl alcohol(TBA)
C_9	0.7	Ethanol
C_{10}- C_{13}	0.8	Methanol
Total of n-alkanes	17.3	Antioxidants
Branched alkanes		N,Ndialkylphenylenediamine
C_4	2.2	2,6-dialkyl and 2,4,6- trialkylphenols
C_5	15.1	Butylated methyl, ethyl and dimethyl phenols
C_6	8.0	Triethyene tetramine
C_7	1.9	Metal deactivators
C_8	1.8	N,N-disalicylidene-1,2ethanediamine
C_9	2.1	N,N-disalicylidene-propanediamine
C_{10} - C_{13}	1.0	N,N-disalicylidene-cyclohexanediamine
Total of branched	32.0	Disalicylidene-N-methyl-dipropylenetriamine
Cyclo alkanes		Ignition controllers
C_6	3.0	Tri-o-cresylphosphate(TOCP)
C_7	1.4	Icing inhibitors
C_8	0.6	Isopropyl alcohol
Total of cyclo	5.0	Detergents/dispersants
Olefins		Alkyl amine phosphates
C_6	1.8	Poly-isobutene amines
Total of olefins	1.8	Long chain alkyl phenols
Aromatics		Long chain alcohols
Benzene	3.2	Long chain carboxylic acids
Toluene	4.8	Long chain amines

Component	Percentage	Component
Xylenes	6.6	Corrosion inhibitors
Ethyl benzene	1.4	Carboxylic acids
C_3- benzene	4.2	Phosphoric acids
C_4- benzene	7.6	Sulfonic acids
Others	2.7	
Total aromatics	30.5	

[a] Adapted from Air Force 1989

[b] Percent by weight

CHAPTER 2: Instrumentation

2.1 GC x GC TOFMS

All the work has been performed on a PEGASUS 4D GC x GC TOFMS which has an Agilent Technologies 7890A GC system equipped with an Pegasus HT (High Throughput) TOFMS having a Micro channel plate detector. The auto sampler used is CTC Analytics Combi Pal System and the true signal deconvolution is done by Chroma TOF.

Basic principle of GC x GC:

GC x GC is an analytical technique that can be used to separate the volatile organic compounds in a gaseous mixture based on two different separation mechanisms. The Gas Chromatograph usually consists of two capillary columns with different stationary phases i.e., one in the main oven and the other in the secondary oven coupled in series. Between the two columns is a trapping and cooling device which is called the Thermal Modulator.

A schematic overview of a GC x GC system is shown in Figure 1.

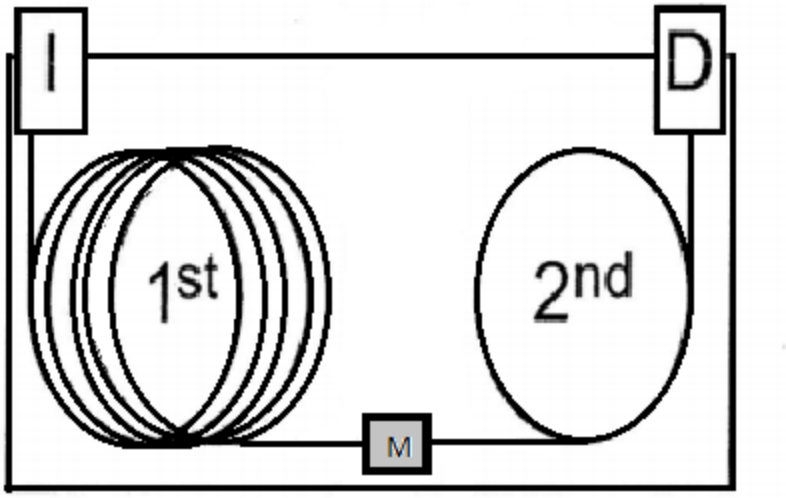

Figure 1: Gas chromatograph

I= Injector

M= Thermal Modulator

D= Detector

1^{st}= 1^{st} dimension column

2^{nd}= Secondary Oven

The first dimension column is a conventional GC- separation, with a normal GC-column length in an oven that will be temperature programmed. The one dimensional (1D) chromatogram which is obtained in a conventional GC separation shows a chromatogram in which the x- axis represents the retention time and the y- axis represents the intensity. In the two-dimensional chromatogram, the x- axis represents the retention time of the separation on the first dimension column and the y-axis represents the retention time on the secondary oven.

Pegasus 4D GC x GC TOFMS instrumentation in this project consists of:

1. Gas chromatograph

A. Carrier gas

B. Injector

C. Capillary column

D. Thermal modulator

E. Secondary oven

2. Transfer line

3. Mass spectrometer

A. Ion source

B. Mass analysis

C. Ion detection

4. Data processing and peak deconvolution

1. Gas chromatograph:

A. Carrier gas:

In gas chromatography, the carrier gas (mobile phase) that carries the analyte through the column should be light and inert. The most commonly used carrier gases or the mobile phase in GC x GC TOFMS are helium, hydrogen and nitrogen. In this work, helium is used as the carrier gas due to its inert nature. It is safer than hydrogen which can accumulate when the GC, mass spectrometer, or rough pump is shut down un-

intentionally or due to an internal or external power failure. The low molecular weight of helium allows faster analyses than nitrogen.

Martin and Synge proposed that the higher diffusivities of solutes in gas would result in faster partitioning of the analytes between two phases, more efficient columns, and shorter separation times [14]. The work demonstrated that the gas could be used as a mobile phase and was further supported by the work of James and Martin in 1952. In this paper, the use of passing an inert gas through a steel column packed with activated carbon in order to separate a homologous series of fatty acids was discussed [15]. The work of Martin, Synge, and James was further developed by Van Deemter who is credited with the development of "rate theory" [16]. The theory incorporates both kinetic and mass transfer effects with the "plate theory" developed by Craig [17]. Van Deemter proposed that the broadening of chromatographic peaks traveling through a column is dependent upon three factors: eddy diffusion (A- term), longitudinal diffusion (B- term), and the resistance to mass transfer (C- term) [16]. It should be noted that the resistance to mass transfer term includes the resistance to mass transfer in the stationary phase, C_s and in the mobile phase, C_m. Equation 1 shows the standard and extended forms of the van Deemter equation relating these three factors to the plate height H, and the average linear velocity $\bar{\mu}$.

$$H = 2\lambda d_p + \frac{2\gamma D_m}{\bar{\mu}} + \left[\frac{\omega d_c^2 \bar{\mu}}{D_m} + \frac{R d_f^2 \bar{\mu}}{D_s}\right] = A + \frac{B}{\bar{\mu}} + (C_s + C_m)\bar{\mu} \quad \text{.....Equation 1}$$

In the above equation

$$2\lambda d_p, \frac{2\gamma D_m}{\bar{\mu}}, \frac{\omega d_c^2 \bar{\mu}}{D_m}, \qquad \frac{R d_f^2 \bar{\mu}}{D_s} \; correspond\ to\ the\ A, \qquad \frac{B}{\bar{\mu}}, C_s\ and\ C_m\ terms$$

A= Eddy diffusion

$\frac{B}{\bar{\mu}}$ = longitudinal diffusion/ average linear velocity

C_s= Resistance to mass transfer in the stationary phase

C_m= Resistance to mass transfer in the mobile phase

A graphical representation of the Van Deemter equation is shown in Figure 2 for nitrogen, helium, and hydrogen. The optimal linear velocity of the column is located at the lowest point on the curve which often corresponds to the point at which each of the three factors are minimized [16, 18].

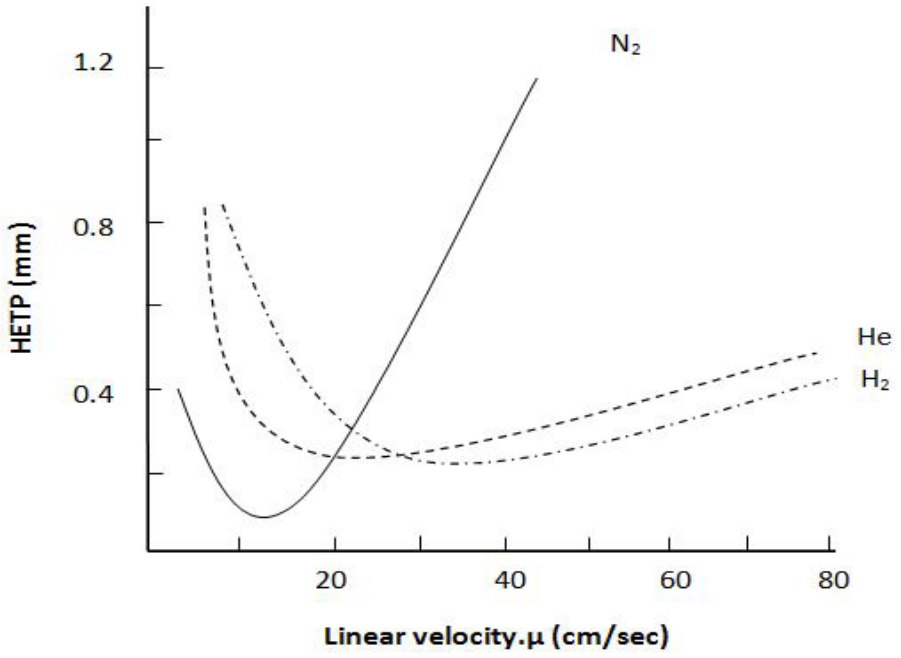

Figure 2: Typical van deemter plots for common carrier gases used in GC systems

B. Injector:

Sample introduction in gas chromatography is critical, in quantitative analysis since the amount of sample lost during the process is dependent on the sample introduction method. In this work, the sample is introduced by an auto sampler because of its better precision and accuracy when compared to that of manual sample injection.

Types of injection: split and splitless

The most common type of inlet system used in GC x GC is a split/ splitless inlet. A schematic diagram of the split/ splitless inlet system is shown in the figure 3. The purge valve attached to the inlet determines the type of injection whether it is split/ splitless. In a split injection, the purge valve opens allowing only a small fraction of the sample to be injected onto the capillary column. The split injections prevent the nonvolatile components or other contaminants from reading the capillary column and

produce sharp and narrow peaks [19- 21]. The main disadvantage is that it is less accurate than splitless injection for quantitation studies. The amount of sample that enters the capillary column is determined by the split ratio which is set by the user and is defined by the equation:

Split ratio = (S + C) / C

Where:

S= flow rate at the splitter vent

C= flow rate at the column outlet

In a splitless injection, the analyte sample that is vaporized goes into the capillary column and this type of injection is preferred in trace analysis where the sample contains very small amount of analyte. Figure 3 shows typical glass liners that are often used for splitless and split injections, respectively. In splitless injections, the glass liner doesn't contain any obstructions thereby allowing all the sample components into the column. In splitless injection, only the pure samples or solvent less samples are analyzed to prevent the damage to the capillary column. In split injections, a piece of glass wool in the glass liner traps the nonvolatile components and prevents them from entering into the capillary column [21, 22].

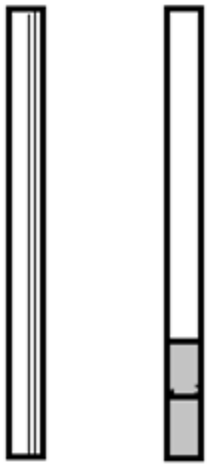

Figure 3: Split less and split liner

Heart cutting vs. comprehensive two dimensional GC:

The main difference between heart cutting and comprehensive two dimensional GC is the amount of sample or the effluent that is separated on the secondary column. In heart cutting, only selected portion of the effluent is analyzed on the secondary column. As opposed to heart cutting, in the comprehensive GC x GC all the effluent from the primary column passes through the secondary column. In other words in the comprehensive technique, the entire sample is separated on both the primary and the secondary columns.

C. Capillary column:

The sample that is injected into a heated injection port, gets vaporized, and carried into a capillary column by a carrier gas such as helium or hydrogen.

Column dimensions and stationary phase:

The columns used for a GC x GC TOFMS generally can vary in the length, internal diameters, and film thickness of the stationary phase. In general, the dimensions of the first column are typical of a column that is normally used with a single column GC or GC- MS system. The dimensions of the secondary column are usually much smaller. The second column usually has a length of 1- 2 meters and the internal diameter is about half the size of the first column [24- 28]. The main purpose of this secondary column is to perform a fast separation of compounds in the effluent from the primary column using a more polar stationary phase on the secondary column [24- 28]. A typical column set-up is that the primary column contains a polar stationary phase which separates the analytes based on polarity and the second column which separates the compounds based on their boiling points [23- 28].

Table 3: Column configuration

S. No	Type	Location	Length (M)	Internal Diameter(μ)	Film Thickness	Maximum Temperature
1	Capillary	GC Oven	10.000	180	0.20	340
2	Capillary	Secondary	0.790	100	0.10	320
3	Capillary	Transfer Line	0.210	100	0.10	320

In this work the capillary column used is a fused silica tube that is 10 m with a protective polyamide coating on the outside of surface for mechanical protection and the inner surface of the capillary column is coated with a specially formulated stationary phase. In this capillary column, the separation of the components of the mixture is done

with respect to time by their different migration rates through the column. Interaction of the sample molecules with the stationary phase as they move through the capillary column results in the retention of the sample molecules in the stationary phase and the duration of the retention depends on the type of analyte molecules, type of stationary phase, column temperature, flow rate and the type of carrier gas. The separation occurs through multiple events of retention and desorption during sample movement through the column in the carrier gas stream where the degree of this separation determines the chromatographic resolution.

Press fit connector:

The primary column and the secondary column are connected by a connector called the press fit which is made up of a fused silica tube which provides an inert pathway as the sample passes from primary to secondary column. The press fit is prone to leaks which may be due to uneven cuts of the column, or the use of a capillary column having a larger internal diameter than the primary column. In GC x GC TOFMS, the only way to the seal of the press fit is by performing a leak test for air on the instrument [27].

D. Thermal modulator and its functions:

The modulator serves to allow the chromatographic peak that elutes or emerges from the end of the primary column to be time-sampled into the second column. The modulator is often referred to as the heart of the GC x GC, since it is the one which generates the second dimension separation of the sample. There are several modulators available in the market for GC x GC systems and the most commonly used modulators are the Deans switch, thermal sweeper and the thermal modulator. The thermal modulator uses alternating jets of cold and hot nitrogen gas to perform peak modulation in a two

stage process [27]. The two cold jets focus the fraction of eluent to narrow the bandwidth which ultimately split the narrow peak forming slices of eluent fraction. The two hot jets keep the fraction of eluent moving through the modulator making the process continuous as well as preventing interference between the fractions. The nitrogen gas for the modulator is cooled by liquid nitrogen which enters the instrument from a small Dewar attached to the side of the GC oven. The Dewar is directly attached to a tank of liquid nitrogen. The flow of the liquid nitrogen into the Dewar is controlled by the data acquisition software or by the user [27]. In a thermal modulator, the length of time for the hot jacket is slightly shorter than that of the cold jacket and this time is determined by the modulation period which is controlled by the system software. This is critical for effective separation and for reducing the bandwidth of the sample. The software allows the user to change the modulation temperature, modulation period, and the time for the hot and cold jets. The modulator is also used to manipulate the retention of analytes on the second column by changing the modulation period and the pulse time for the two hot nitrogen jets in the modulator [27]. The modulation period depends on the complexity of the sample. The sample with the less complex mixture requires short modulation period and vice- versa. The final parameter of the thermal modulator that can be changed is its temperature which should be higher than the initial temperature of the secondary oven. However the modulator temperature does not interfere with the peak modulation process or the secondary column separation. The main reason behind the increase in modulator temperature is to reduce the overload of the sample on the secondary column.

Specifications for thermal modulator:

LN_2 modulator: Liquid nitrogen

Consumable- free Modulator: Immersion cooler

Minimum temperature: GC oven temperature + 3^{o}C above the GC oven temperature

For ambient- cooled GC ovens typical +30^{o}C

Maximum temperature: 400^{o}C

Maximum heating rate: 40^{o}C per minute

LN_2 modulator cold jet flow, gas pressure: ~6 Ipm/ 15 psi (1.03 bar), dry nitrogen (dew point < -50^{o}C) with periodic defrosting as needed

Consumable free modulator cold jet flow, gas pressure: ~10 Ipm/ 15 psi (1.03 bar), dry air (dewPoint < -50^{o}C) with periodic defrosting as needed

Hot jet low, gas pressure: ~20 Ipm/ 30 psi (2.03 bars), dry air

Modulation period: 1- 65 sec

Hot pulse: minimum, 100 ms; 400 ms typical

E. Secondary oven:

The secondary oven is mainly used to optimize of the second dimension chromatographic separation. The dimensions of secondary column in the secondary over are small in terms of the length or internal diameter when compared to that of primary column and result in higher linear velocities for analytes moving through this column. The main purpose of the second column is to perform rapid separation of the eluent from the primary column using a more polar stationary phase on the second column resulting a thorough separation of the volatile analytes [24- 28].

Specifications for the secondary oven:

Minimum temperature: GC oven temperature +5^{o}C, above ambient temperature

Maximum temperature: 400^{o}C

Heating rate, maximum: 40^{o}C per minute

Cooling gas, flow pressure: Air, ~ 40 Lpm/ 30 psi (2.07 bar)

2. Transfer line:

After the sample has been separated on both columns, it passes through a heated transfer line that serves to transfer the sample from the gas chromatograph to the mass spectrometer and also ensures that the sample remains in the gas phase when entering the ion source of the mass spectrometer [29- 31]. The temperature of the transfer line depends on the type of analyte in the sample and the temperature of the transfer line should be high enough to keep the sample in the vapor state, but low enough not to degrade any analyte in the sample.

3. Mass spectrometer:

In the mass spectrometer, the volatile analytes that is separated in the gas chromatograph are ionized, fragmented, analyzed, and identified based on their fragmentation pattern. A typical mass spectrometer has three main parts: the ion source, mass analyzer and the detector. The mass analyzer defines the sensitivity, resolution, and speed of the mass spectrometer. Common types of mass analyzers include double focusing, ion traps, quadrupoles, and time-of-flight analyzers. During this work, a time-of-flight mass analyzer is used.

A. Ion source:

The main purpose of the ion source is to ionize and fragment the analyte in a given sample [30, 31]. The commonly used ionization in gas chromatography- mass spectrometry is Electron Impact Ionization (EI) and Chemical Ionization (CI). Electron Impact Ionization removes a valence electron from the atom with lowest ionization energy by bombarding the molecules with a beam of electrons resulting in the formation of a typically unstable radical- cation that undergoes rearrangement and/ or fragmentation [31, 32]. These mass fragments are unique and produce a characteristic mass spectrum for the analyte. In this work, only the electron impact ionization is used. The ion source usually has a heating block, filament and a repeller as shown in figure 4. The heating block maintains the analyte in the vapor state by maintain a constant temperature. The filament is generally held at 70 eV and generates high energy electrons capable of removing the valence electrons from the analyte. The analyte molecules fragment according to their structure and the type of functional groups present [32]. The fragmentation pattern (relative amount vs. mass/ charge ratio) is called a mass spectrum and is often unique to the molecule. The fragments in the ion source are pushed through a small opening to the mass analyzer by the repeller and the main purpose of the pumps is to remove the carrier gas, neutral and the negatively charged ions from the MS system and to slow down the analyte ions during fragmentation in the ion source.

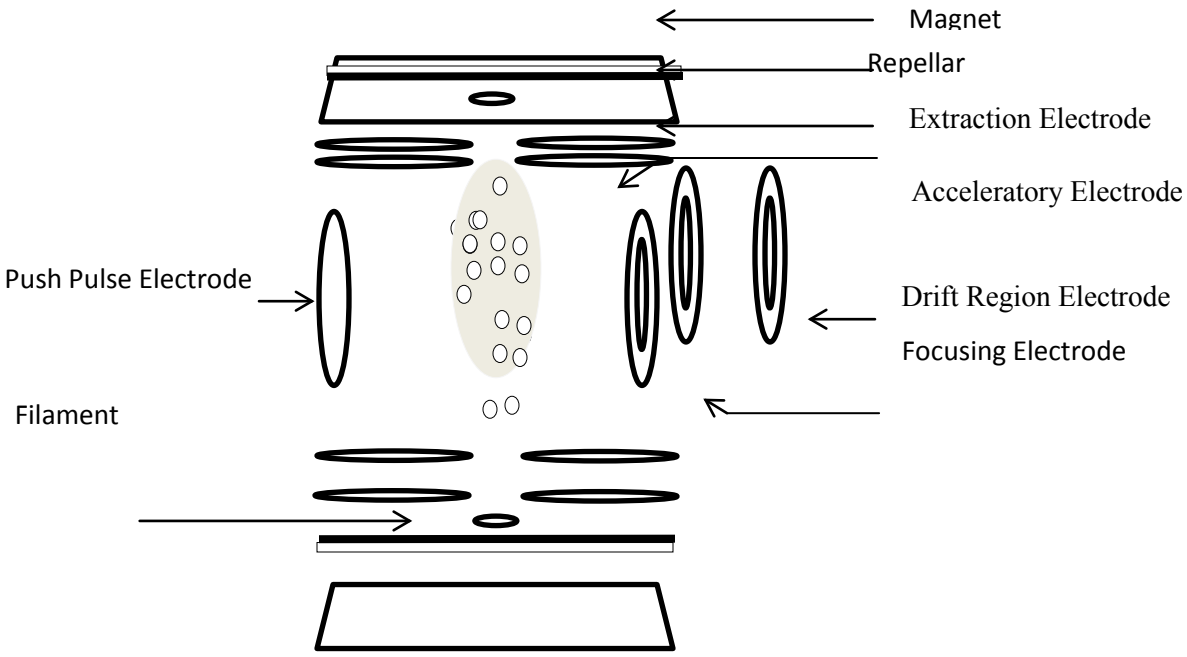

Figure 4: Ion source

B. Mass analyzer:

In this work, a time of flight mass analyzer is used. In general a time of flight systems are known for their high sensitivity, high resolution, and faster scan rates. In a time- of- flight mass spectrometer, the mass/ charge ratio of an ion is determined by measuring its travel time through the instrument starting from the ion source to the detector. All ions have the same kinetic energy. So the ion travels are proportional to their mass/ charge ratio. The smaller the ion, the faster its time- of- flight. Ions produced in the ion source are pushed out of it by applying an electrical pulse to the push pulse electrode as displayed in figure 6. The electrical force is created due to the difference in the electrical potential between the accelerating electron grid and push pulse electrode accelerates the positively charged ions into the flight tube. All of the ions having the same kinetic energy accelerate almost simultaneously and leave the ion source as displayed in figure 8. The ions from the ion source enter into a drift region where they

have a constant energy as displayed in figure 8. Since all the ions have the same kinetic energy, their mass- to charge ratio determines their velocity as shown in figure 9. For ions having the same m/z ratio but moving with different velocities, the ions travelling with higher velocity reach the positively charged reflectron and move deep farther into it compared to ions with lower velocity. All ions of the same m/z reach the detector at the same time.

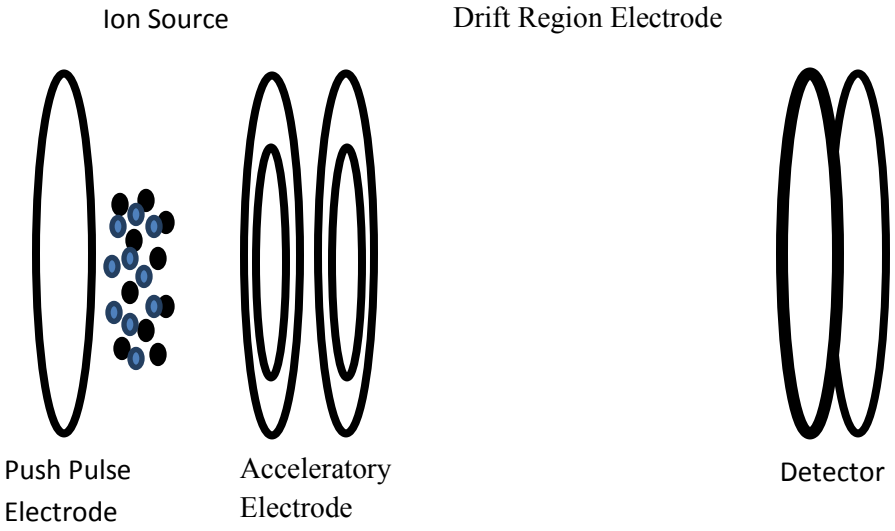

Figure 5: Ions pushed from ion source

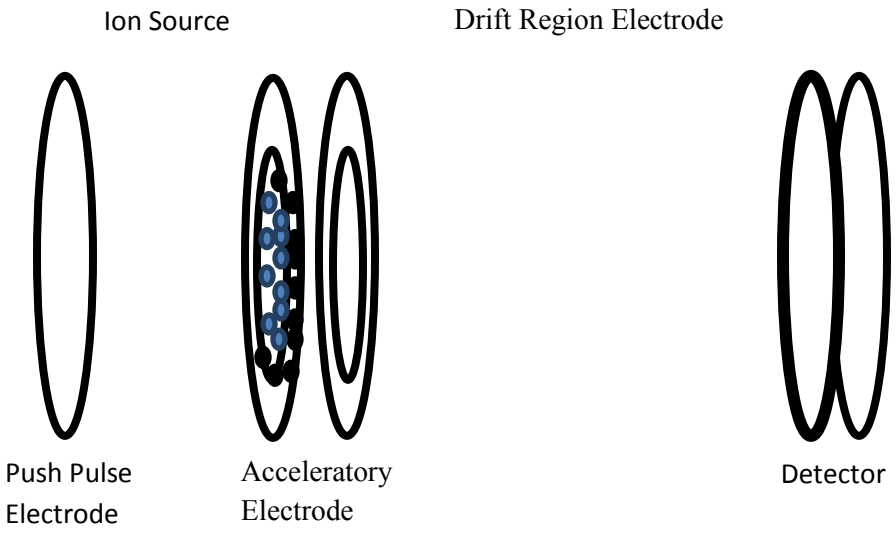

Figure 6: Ions acceleration

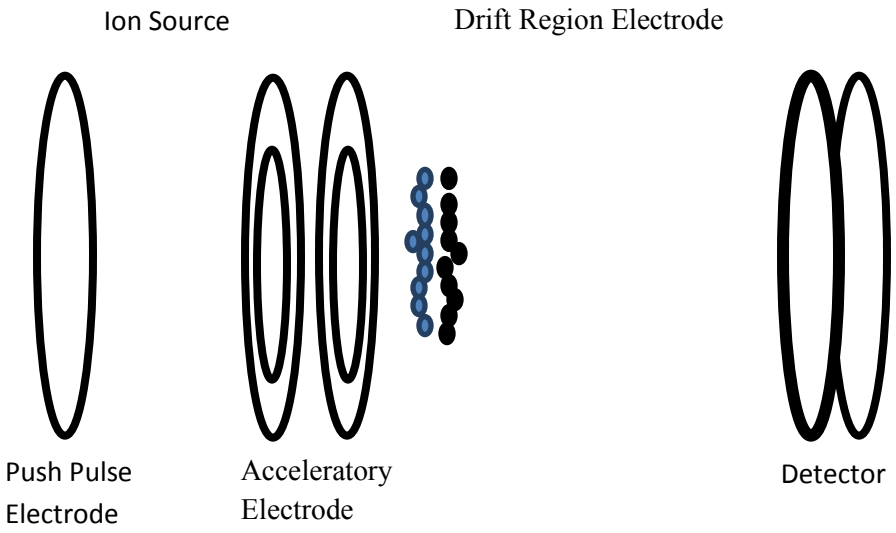

Figure 7: Ions in drift region

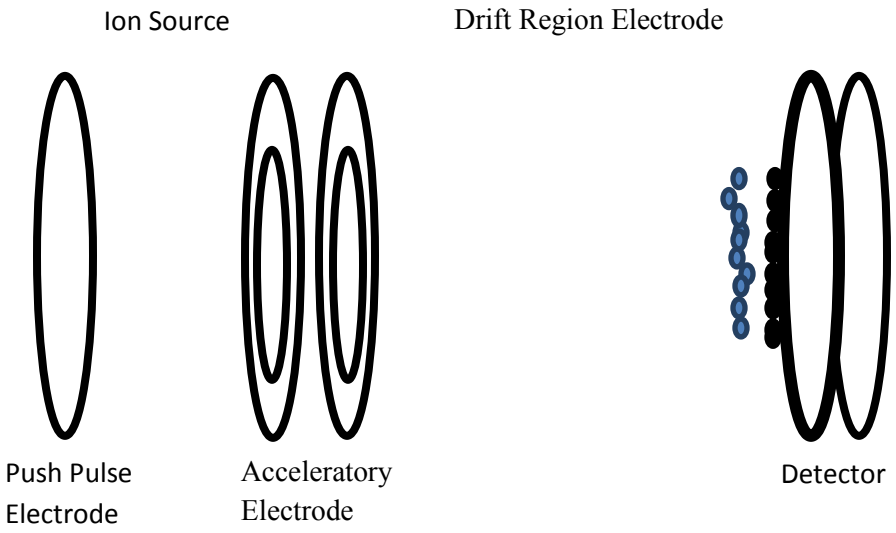

Figure 8: Ions mass/ charge ratio at detector

Ideally, all the ions pulsed from the ion source should have the same kinetic energy, but they actually have a range of kinetic energies depending on several factors. This causes differences in the time- of- flight even for ions having the same mass/ charge ratio and reduces the mass resolution of the mass spectrometer. In order to reduce these differences and improve the mass resolution, an electrostatic device called a reflectron/ ion mirror is placed in the drift region. One advantage of the reflectron is that it reduces the overall size of the mass spectrometer as shown in figure 9.

The mass/ charge ratio of each ion is determined by the equation

$t = \text{slope} * \sqrt{m/z} + \text{Offset}$

Slope and offset values are constant and are specific to a particular mass spectrometer for a given set of parameter values. The slope and offset values are determined using a mass calibration standard. This mass calibration standard is done automatically by the chromaTOF software. During the determination of the slope and

offset, the valve connecting the ion source chamber to the vial with a calibration compound, PFTBA is opened. The vapors of the PFTBA are introduced into the ion source and a mass spectrum is obtained. Since the mass calibration of PFTBA is known, the time- of- flight of each mass is measured. These measured values are then used to calculate the slope and offset values automatically by solving a set of linear equations by the chromaTOF software.

Since the probability of creating multiple charged ions by electron impact ionization with electrons of 70 eV energy, is low, almost all of the ions created are singly charged (z=1). Thus, the m/z values calculated from the time-of-flight equation give the masses of the ions directly. The time-of-flight is measured as the time between the moment when the push pulse is triggered and the moment when the signal maximum from the corresponding ion packet is detected. The time-of-flight of the heaviest ion possible for detection (m/z=1000) is approximately 170 μsec. This is the time required to acquire the complete mass spectrum of the sample ionized in the ion source. In addition, the complete mass spectrum is obtained by sampling all ions in the ion source simultaneously. These two important features, simultaneous sampling of all ions for each mass spectrum and a very short acquisition time for the mass spectrum, are the main advantages of that Time- of- Flight Mass Spectrometry.

Vacuum system:

Ions travel a long distance of more than one meter in the TOFMS. In order to survive during this period of travel to the detector, the ions must travel in a vacuum. To avoid ion loss due to scattering, or reactions, the average ion path until collision with a residual gas molecule, l (the mean free path), has to be much longer than the travel

distance L, shown as l>>L. This determines what vacuum level is required for the operation of the mass spectrometer. Optimal performance is achieved at residual gas pressure below 10^{-6}Torr. The pressure of the vacuum is kept at 10^{-7} torr for a time- of-flight mass spectrometer by two turbo molecular pumps.

The mass spectrometer is enclosed within a vacuum chamber and consists of two parts, the Ion Source Chamber and the Analyzer Chamber. The vacuum pumping system includes two high performance turbo molecular vacuum pumps, rough pump and turbulent pump specifically suited for pumping out the carrier gases such as helium or hydrogen. These turbo molecular pumps are backed by a mechanical rotary vane vacuum pump. The pumping speed of the turbo molecular pumps corresponds with the desired maximum carrier gas flow rate. The residual gas pressure is measured by a hot cathode gauge attached to the main analysis chamber.

C. Ion detection:

The ion detector used in this work is a micro channel plate and is common for most mass spectrometer systems. Approximately one million small pores each with a diameter of 10 μm penetrate the glass body of the micro channel plate creating one million single channel electron multipliers. Ions striking the internal surface of these channels knock out several electrons from the channel surface due to an effect called ion-electron emission. These created electrons, called secondary electrons, are accelerated by the electric field applied across the plate surfaces. Due to electron-electron emission, each of the accelerated secondary electrons has enough energy to knock out several electrons when it strikes the channel wall surface. This process is repeated many times creating an

avalanche of electrons. Thus, the signal from a single ion can be amplified, which makes it easier to detect ions and to electronically process the resulting signal.

The amount of amplification, also known as the detector gain, depends on the detector voltage applied across the micro- channel plate and the condition of the surface of the micro- channels. The ability to generate electrons can change due to surface degradation, ion and electron collisions, and moisture adsorption. The degree and rate of degradation, depends on detector usage conditions. In order to prevent exposing the ion detector to the highly abundant ions created from the carrier gas and residual gas, all undesirable ions are deflected by applying an electrical pulse to a set of deflection plates, located after the ion source. The electrical pulse has an appropriate delay and duration after each sampling of the ion source.

4. Data processing and peak deconvolution:

Peak deconvolution and data processing are the final points in mass spectrometer system to locate a specific mass/ charge ratio in the TIC (Total Ion Chromatogram). ChromaTOF has a peak deconvolution algorithm built in the data processing software making it possible to input multiple masses producing multiple EICs (Extracted Ion Chromatogram) on a single chromatogram. Due to the higher sensitivity of TOFMS system, the software produces EIC's with high S/N ratio, has a high mass spectral acquisition rate up to 500 Hz, and stable baseline spectra. In general the data processing for the acquired samples can be processed immediately or at a later time.

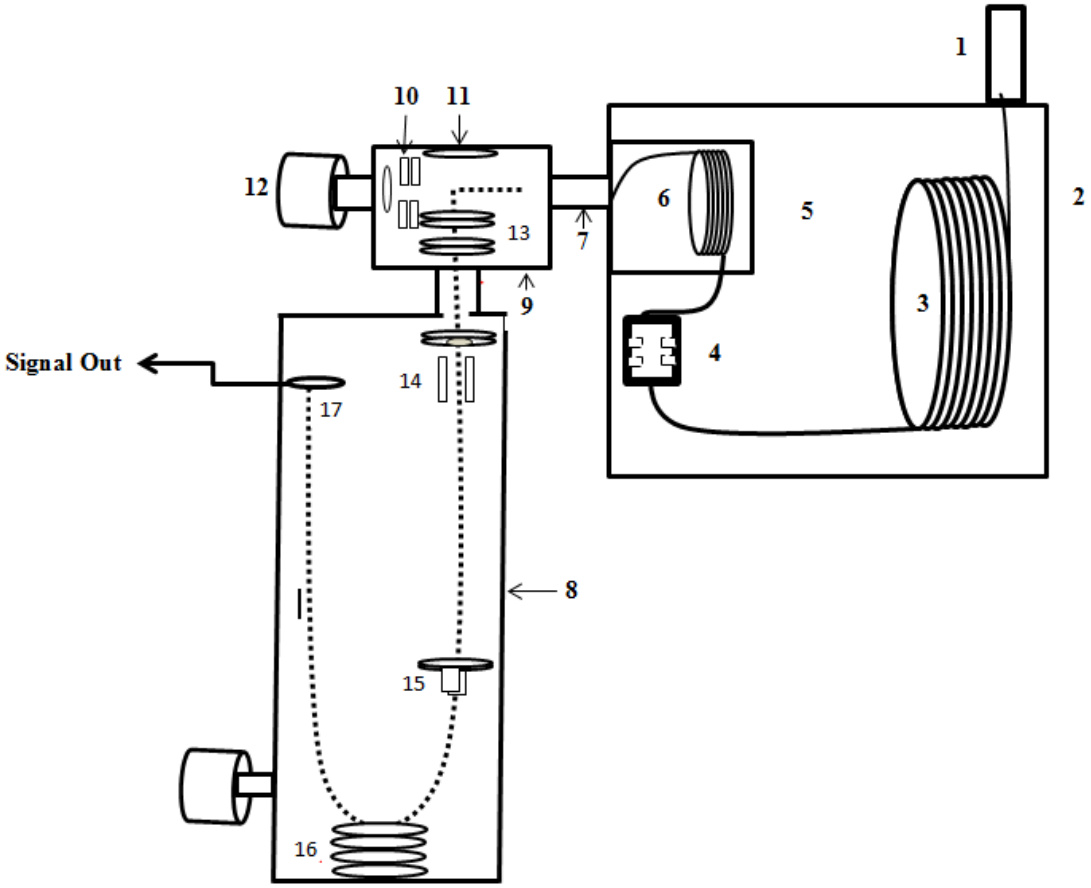

Figure 9: GC x GC TOFMS instrument

1. Sampling Inlet
2. Main Oven
3. 1st Dimension capillary column
4. Thermal modulator
5. Secondary oven
6. 2nd Dimension capillary column
7. Heated transfer line
8, 9. Main analysis chamber
10. electron focusing optics
11. push pulse plate
12. Turbo molecular pump
13. Ion focusing optics
14. Z- steering and deflection plates
15. Einzel lens and Y- steering plates
16. Reflectron
17. Detector

2.2 Inductively coupled plasma mass spectrometry (ICP- MS)

Principle:

The principle of ICP- MS is that the sample or analyte gets ionized by the application of high temperature plasma. These ionized atoms are then separated and identified according to their m/z (mass to charge ratio). A typical ICP- MS system consists of five sections:

1. Automated sample introduction system
2. Inductively coupled plasma (ICP)
3. Interface
4. Mass spectrometry
5. Data processing and display system

1. Automated sample introduction system:

The most common type of sample introduction is when the liquid sample is forced into a pneumatic nebulizer by a peristaltic pump. This pneumatic nebulizer converts the liquid sample into an aerosol, which is transferred to a spray chamber from which the aerosol is carried by a stream of argon gas to the plasma through the spray chamber.

2. Inductively coupled plasma:

Plasma which is a partially ionized gas with sufficiently high temperature atomizes and ionizes most of the elements in the periodic table and argon is used as a carrier gas since it produces pure form of ions because of its inert nature.

The following are the types of ionization processes that occur in the ICP:

$M + A^+ \longrightarrow M^+ + A^+ + e^-$ (ion- atom collision)

$M + A \longrightarrow M^+ + A + e^-$ (atom- atom collision)

$M + e^- \longrightarrow M^+ + 2e^-$ (electron impact)

$Ar^+ + X \longrightarrow Ar + X^+$ (charge transfer)

$Ar^m + X \longrightarrow Ar + X^+ + e^-$ (penning ionization)

Penning ionization happens when a meta- stable atom collide with a neutral atom and ionizes the neutral atom by the de- excitation of the meta- stable atom. In ICP, the plasma torch consists of three concentric silica quartz tubes each of which is open at the top.

A RF induction coil is wrapped around the top opening of the silica quartz tube. Auxiliary argon passes through the central tube and argon gas is passed through the middle or second tube. The sample in the form of dried aerosol passes through the central tube by argon carrier gas. The helical flow pattern of the argon plasma gas isolates the outer most quartz tube from the plasma. Ionization of argon gas is done by a spark from a tesla coil probe. These seeded free electrons absorb enough energy from the coil and maintain constant temperature of the plasma 6000- 10000K. Accelerated electrons collide with the atoms and transfer their energy to the entire gas. Coolant gas passes through the outer tube and protects the quartz torch from overheating. Ions produced in the plasma enter the mass spectrometer through the interface.

3. Interface:

The interface transfers the ions from the extremely hot plasma into the mass spectrometer. The mass spectrometer requires high vacuum to avoid the collisions between ions and with the gas molecules which diverts the ions from their trajectory. Also the mass spectrometer does not work at high temperatures. The temperature is reduced by a series of vacuum chambers held at low pressure. A water cooled nickel sampling cone with one mm diameter orifice is used to introduce gases into the mass spectrometer. A fraction of the plasma along with the analyte passes through the orifice and because of high vacuum pressure a gas expansion is formed which might take a form of a cone. Just behind this sample cone, another water cooled cone called a skimmer cone is placed with a small orifice. The ions passes through this skimmer as an ion beam into the mass spectrometer where the ions are separated according to their mass/ charge ratio. Several mass spectrometers are available for mass analysis but in this study, an iCAP Qc ICP MS, Thermo Scientific with a quadrupole mass filter is used.

4. Quadrupole mass spectrometer:

Quadrupole consists of four parallel rods where opposite rods are connected to radiofrequency and direct current which creates an electric field. The electric field in the quadrupole deflects or transmits ions of different masses. Only specified ions of same mass to charge are passed through the quadrupole and transferred to the ion detector. All other ions collide with the rods and are removed before reaching the detector. The detector then transfers the ion information to the data processor.

5. Data processing and display System:

The detector transfers the ion information to system control for data processing. Experiment controller software system converts the signals into graphical display with real time data. The software can not only detect all the elements in the periodic table but also their isotope and isobars.

2.3 Nitrogen/ sulfur analyzer [34, 35]

Principle:

The sample is introduced by a sample boat into furnace where it gets vaporized and carried by argon gas to a high temperature zone where it reacts with oxygen and gets converted to nitric oxide (NO). This NO reacts with ozone (O_3) and is converted to excited nitrogen dioxide (NO_2^*). The light emitted by this excited nitrogen dioxide when it decays is measured by a photo multiplier tube (PMT).

For sulfur, the sample is introduced by an automatic boat controller into furnace where it gets vaporized and carried to a high temperature zone where it is oxidized by oxygen and converted to sulfur dioxide which is then irradiated by ultraviolet rays to form excited sulfur dioxide (SO_2^*). This excited sulfur dioxide returns to the ground state with the emission of photon energy. This emitted fluorescence is measured by a photo multiplier tube (PMT).

Apparatus:

Microliter Syringe: A microliter syringe with a constant rate injector system, capable of delivering 5- 250 µl is used to inject samples into sample boat.

Sample inlet system: Direct injection and boat inlet system are the two types of sample inlet systems and the inlet system used with this instrument is a boat inlet system which facilitates analysis of samples that would react with the syringe needle. The boat inlet external to the furnace cools to room temperature to dissipate the heat from the boat when it is removed from the furnace. The boat is constructed of quartz.

Furnace: The electric furnace is maintained at a temperature (900- 1000^{o}C) sufficient to pyrolyze and combust the sample and oxidize sulfur to sulfur dioxide (SO_2) and organically bound nitrogen to nitric oxide (NO).

Combustion tube: A quartz combustion tube is used so that the inlet end of the tube is large enough to accommodate the sample boat.

Drier tube: The apparatus is equipped with a drier for the removal of water vapor produced during the oxidation reactions. The water vapor must be eliminated prior to the measurement by the chemiluminescence detector.

Chemiluminescent detector measures the light emitted from the reaction between nitrous oxide and ozone and the UV fluorescence detector measures the light emitted from the fluorescence of sulfur dioxide by UV light.

Vacuum system: The chemiluminescence detector is equipped with a vacuum system to maintain the reaction cell at reduced pressure (typically at 20- 25 mm hg) which improves the signal to noise ratio of the detector.

CHAPTER 3: Experimental section

Chemicals used:

3.1 GC x GC TOFMS:

The following aromatic compounds were analyzed: benzene, toluene, ethylbenzene, styrene, α- methylstyrene and cumene.

Table 4: List of aromatics for standard calibration

Aromatic compound	Purity	Supplier
Benzene	99.9 %	J. T. Baker
Toluene	99.97 %	Pharmco Aaper
Ethylbenzene	99.9 %	Fisher Scientific
Styrene	99 %	Sigma Aldrich
α- Methylstyrene	99 %	Aldrich
Cumene	98 %	Aldrich

All the reagents used in this study were of analytical grade or better. Calibration standards were freshly prepared by appropriate dilutions of the stock with 2, 2, and 4-trimethylpentane (Isooctane). The reagents that were used for GC x GC TOFMS are as follows: 2, 2, 4- trimethylpentane (Sigma Aldrich- Reagent grade ACS), ethanol (Fisher Scientific- 0.2 µ filtered), and methanol (Fisher Scientific- 0.2 µ filtered).

GC x GC TOF Analysis

All analysis was performed on an Agilent Technologies 7890A GC system equipped with a Pegasus HT High Throughput TOFMS. The GC was fitted with a capillary split/ splitless injection port. The mass spectrometer was fitted with Agilent Technologies high vacuum turbo pump V551 navigator. The auto- sampler used for this instrument is CTC Analytics CombiPAL System with a 10 µL syringe.

Table 5: Column configuration for GC oven

Type	Location	Length (m)	Internal diameter	Max Temp	Film thickness	Phase	Bleed masses
Inlet	Front						
Capillary	GC Oven	10.00	180.00	340.0	0.2	RTX- 5	74,
Capillary	Secondary	0.570	100.00	320.0	0.1	RXI- 17	74,
Capillary	Transfer	0.210	100.00	320.0	0.1	RXI- 17	74,
Detector	TOF						

Table 6: Experimental conditions

Component	Condition
GC	
Type	Agilent 7890A system equipped with a
Carrier gas	Helium at 1.00 ml/ min constant flow
Injection size	0.1 µL using a 1.2 µL syringe
Split ratio	500:1
Oven temperature programming	10^{o}C for 3 min, then to 100 ^{0}C at 10 ^{0}C/ min finally to 250 ^{0}C at 25^{o}C/ min
Modulation period(2D)	8.00 sec
Hot pulse time (2D)	0.4
Cool time between stages (2D)	3.6
GC- MS Interface	
Interface	Capillary direct
Temperature	280^{o}C
Equilibrium time	1 sec
MS	
Type	Time- of- flight
Acquisition voltage	1475
Ion source temperature	200^{o}C
Storage mass range	5- 1000 U
Acquisition rate	100 spectra/ sec
Ionization voltage	70 eV

Sample preparation:

Renewable energy solutions Polyflow (RES Polyflow):

The RES Polyflow process is robust and is designed to handle the types and percentages of polymers present including plastic waste, tires and carpets as reported by

EPA. The RES Polyflows technology thermally decomposes hydrocarbon based materials such as plastic and rubber and converts them into organic compounds that can be marketed as transportation fuels and new feed stocks for new polymer production. The end product generated by the RES Polyflow is a liquid known as pygas from which diesel fuel, octane enhancers and gasoline blend stocks can be yielded. The main purpose of this work is to analyze these different pygas samples, diesel fuel, gasoline.

Calibration curves:

A 7 g stock aromatic mix was prepared by adding the seven aromatic compounds in decreasing order of their weights to a 10 mL volumetric flask.

Table 7: Stock solution

Compound	Mass (g)	Mass percent (%)
Benzene	1.0	14.28
Toluene	1.0	14.28
Ethylbenzene	1.0	14.28
Styrene	2.0	28.57
α- Methylstyrene	1.0	14.28
Cumene	1.0	14.28

This stock aromatic mix was diluted using serial dilution by isooctane to produce different calibration standards. A 1 % calibration standard was prepared by adding 0.21 g of stock solution to 2.79 g of isooctane. A 2 % calibration standard was prepared by adding 0.42 g of stock solution to 2.58 g of isooctane. A 3 % calibration standard was prepared by adding 0.63 g of stock solution to 2.37 g of isooctane. A 4% calibration standard was prepared by adding 0.84 g of stock solution to 2.16 g of isooctane. A 5%

calibration standard was prepared by adding 1.05 g of stock solution to 1.95 g of isooctane. The mass percent of aromatic compounds in different calibration standards are as follows:

Table 8: Mass percent of aromatics in different calibration standards

Compound	1%	2%	3%	4%	5%
Benzene	1	2	3	4	5
Toluene	1	2	3	4	5
Ethylbenzene	1	2	3	4	5
Styrene	2	4	6	8	10
α- methylstyrene	1	2	3	4	5
Cumene	1	2	3	4	5

Internal standard:

For the reliable quantitative data, internal standards are required to correct the analytical and chemical losses during analysis. It was observed that the linearity with the benzene in calibrations standards was lost over a narrow concentration range and is not reproducible or the reproducibility is lost for the same set of calibration standards. This led to the conclusion that internal standards are needed which are structurally similar to that of the analytes and where the mass differences between the analytes and the internal standards are more than one mass unit. The deuterated components in the internal standard mix used for the analysis are shown in Table 9.

Table 9: Internal standards

Component	CAS number	Purity %	Weight	Mix Ratio
Benzene- d6	1076- 43- 3	97.1	16.70	2 ml
Ethylbenzene- d8	25837- 05- 2	97	16.80	2 ml
Naphthalene- d8	1146- 65- 2	100	8.84	1 g
Toluene- d8	2037- 26- 5	98.2	57.66	7 ml

Limit of detection (LOD):

The limit of detection or the detection limit (LOD) is the lowest quantity of a compound that can be distinguished from the absence of that compound. The calculation method is again based on the slope and the intercept of the calibration curve.

$S_{y/x} = [\sum (d_i^2) / N-2]^{1/2}$

$d_i = y_i - (m * x_i + b)$

$S_{y/x}$ = Limit of Detection

d_i = residuals

N = number of runs for each set of calibration standard

m = slope from equation of line

b = intercept from equation of line

The Carrier gas used for the GC x GC TOFMS is PRAXAIR BIP HE (Build In Purife Helium). PRAXAIR 22 PSI (cooling the oven) and 235 PSI (cold jets in Modulator) nitrogen refrigerated liquid are used.

3.2 Inductively coupled plasma mass spectrometry (ICP- MS)

The following elements were analyzed as per federal and state hazardous waste criteria: chromium, manganese, nickel, arsenic, selenium, silver, cadmium, mercury, lead, vanadium, cobalt, zinc and copper. All analysis was performed on iCAP Q ICP with a quadruple mass analyzer. All the standard solutions and samples were prepared using double distilled water. All the reagents used in this study were of analytical grade or better. Calibration standards were freshly prepared by appropriate dilutions of the stock with 3 % nitric acid.

Sample and standard preparation:

Gasoline and diesel samples:

Gasoline with super grade was obtained from Get GO Gas station. Diesel sample was obtained from two different places on different days. Gasoline with regular grade was obtained from the gas station on different days. All these samples were analyzed for chromium, manganese, nickel, arsenic, selenium, silver, cadmium, lead, vanadium, cobalt, zinc and copper on ICP- MS.

Renewable energy solutions polyflow (RES Polyflow Samples):

The RES Polyflow process is robust and is designed to handle the types and percentages of polymers present including plastic waste, tires and carpets as reported by EPA. The pygas samples were collected from the reactor at different days and at different times and are named according to them. The main purpose of this work is to characterize these different pygas samples. All these samples were analyzed for chromium,

manganese, nickel, arsenic, selenium, silver, cadmium, mercury, lead, vanadium, cobalt, zinc and copper on ICP- MS.

Gasoline, diesel and Polyflow samples are acid digested or solubilized by lithium metaborate fusion before analysis. In general metals will not dissolve in organic solvents or regular solvent, and acid digestion is a method of dissolving the metal into solution which can then be analyzed to determine the amount of element or metal present in the sample. Organic sample materials present in the sample are generally decomposed into carbon dioxide with nitric acid and reagent hydrogen peroxide.

Acid digestion procedure:

A. Half a gram (solid) or One gram (liquid) of the sample is weighed into a teflon beaker
B. Add 5 ml of nitric acid and 5 ml of water to the sample
C. Gently heat the solution mixture, avoid spattering
D. After about 5 min when the reaction slows down, add 2 ml of hydrogen peroxide
E. When all but about 3- 4 ml of solution left, add more 5 ml of nitric acid and water
F. After the reaction is complete, add 2 ml of hydrogen peroxide
G. Drive off all but about 3 ml
H. Cool, add 5 ml water and transfer to a 50 ml volumetric with distilled water.

Lithium metaborate fusion method:

A. Mix 0.1 g oven- dried sediment/ sample with 0.5 g lithium metaborate in a high purity graphite crucible
B. Heat in a muffle furnace for 15 min at 1000 ^{0}C

C. Remove crucible and pour melt into polypropylene wide- mouth bottle containing 3 % nitric acid
D. Cap bottle and shake until solution is complete
E. Add concentrated nitric acid in small (1 ml) aliquots to dissolve particulate/ turn solution clear if needed after shaking

Standard preparation:

A 10 ppm multi element analysis mixture was taken. An intermediate standard (500 ppb) was prepared to make a set of standards in parts per billion range. A 500 ppb calibration standard was prepared by adding 2.5 ml of 10 ppm multi- element standard diluting to 50 ml with distilled water. A 0.5 ppb, 1.0 ppb, 3.0 ppb, 10 ppb and 30 ppb calibration standards were prepared by adding 50 µL, 100 µL, 300 µL, 1 ml and 3 ml of intermediate standard (500 ppb) respectively and diluting to 50 ml with distilled water and a calibration standard was constructed using this set of standards.

3.3 Nitrogen/ sulfur analyzer

Nitrogen/ sulfur concentrations were analyzed on Mitsubishi Nitrogen/ sulfur analyzer which uses an oxidative combustion followed by chemiluminescence and fluorescence detection coupled with automatic boat controller (ABC 210) and automatic quick furnace (AQF 2100 H). All the reagents used in this study were of analytical grade or better. The reagents that were used for nitrogen sulfur determination are as follows: N, N- dimethylaniline (Acros organics), dibenzothiophene (Aldrich), toluene (Pharmco Aaper –UV reagent grade ACS). All the standard solutions and samples were prepared using toluene. Calibration standards were freshly prepared by appropriate dilutions of the stock with toluene.

Standard preparation:

The stock solution for nitrogen sulfur determination is prepared based on mass by taking N, N- dimethyl aniline (0.1 g) and dibenzothiophene (0.1 g) in toluene (99.8 g) which is 1000 ppm. Calibration standards of 10 ppm, 50 ppm, 100 ppm, 300 ppm, 500 ppm of N, N- dimethyl aniline and dibenzothiophene were prepared by adding 0.5 ml, 2.5 ml, 5 ml, 15 ml, 25 ml of stock solution (1000 ppm) to a 50 ml volumetric flask respectively and finally diluting to 50 ml with toluene.

Sample preparation:

All the gasoline and diesel fuel sample are directly analyzed for nitrogen/ sulfur content whereas the Polyflow samples are diluted to 1/ 10 in toluene.

Table 10: Experimental conditions for nitrogen/ sulfur analyzer

Sample volume	25 µL
Inlet heater temperature	900 ^{0}C
Outlet heater temperature	1000 ^{0}C
Argon flow	300 ml/ min
Oxygen flow	300 ml/ min

The carrier gas used in nitrogen/ sulfur analyzer is PRAXAIR ultra-high pure compressed argon and oxygen with 99.993 % pure is used for combustion of the sample.

CHAPTER 4: Results and discussion

4.1 GC x GC TOFMS

4.1.1 One dimensional gas chromatography

Qualitative and quantitative analyses of all the gasoline, diesel fuel, Pygas samples and distillation standard, D 86 were performed by both one dimensional and two dimensional gas chromatography. All the samples were analyzed twice by both one dimensional and two dimensional gas chromatography to evaluate the method and to check the reproducibility of the results.

4.1.1.1 Calibration of aromatic compounds (1D)

Set 1:

A set of calibration standards of 1 %, 2 %, 3 %, 4 % and 5 % each of benzene, toluene, ethylbenzene, cumene, α- methyl styrene and 2 %, 4 %, 6 %, 8 % and 10 % of styrene is made to which an internal standard is added. All the gasoline, diesel fuel, pygas samples and the distillation standard were taken into a 2.0 ml vial to which a known amount of internal standard is added and was qualitatively determined which is then quantified using the set 1 calibration standards.

In order to quantitatively determine the fuel and hydrocarbon samples, calibration curve measurements were performed and the typical calibration curves for benzene, toluene, ethylbenzene, styrene, cumene, α- methyl styrene are shown in figures 10 to 15. In the calibration curves, X- axis represents the concentration and the Y- axis represents the ratio of the area of analyte to that of internal standard

Benzene:

The calibration curve for benzene was constructed using the following concentrations: 1, 2, 3, 4, 5 %. Each standard was run in triplicate for reproducibility of the results. The calibration curve for benzene is shown in figure 10 and the linearity is good with a correlation coefficient (R^2= 0.99993). The internal standard used for benzene is benzene- d6 having a mass of 84+83 comes out at 72.77 sec.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Benzene	78	73.93	Y= +0.928628x + 0.0516181	0.99993

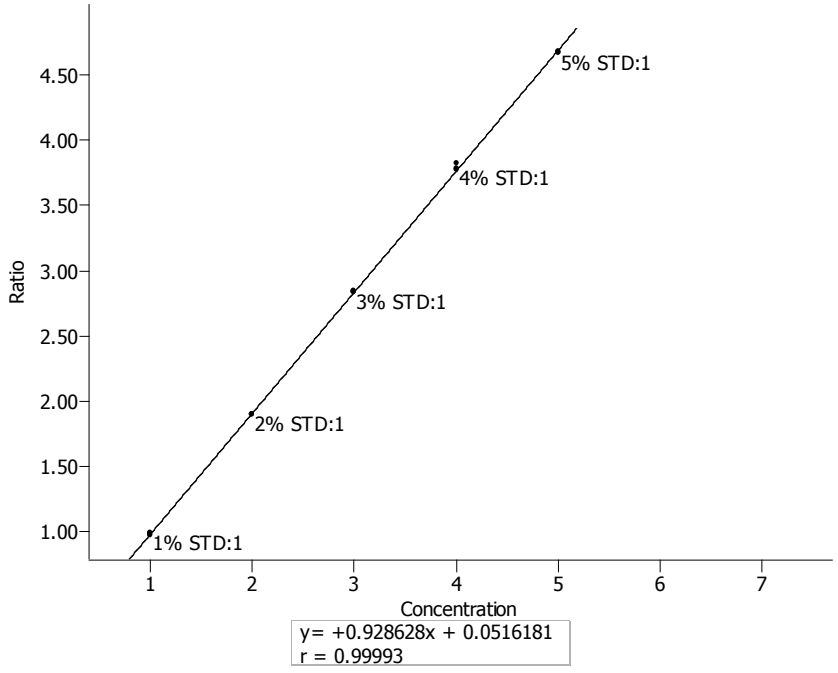

Figure 10: Calibration curve of benzene

Toluene

The calibration curve for toluene was constructed using the following concentrations: 1, 2, 3, 4, 5%. Each standard was run in triplicate for reproducibility of the results. The calibration curve for toluene is shown in figure 11 and the linearity is good with a correlation coefficient (R^2= 0.99991). The internal standard used for toluene is toluene- d_8 having a mass of 100 + 99 comes out at 186.32 sec.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Toluene	92	192.44	Y= + 0.283795x – 0.0148417	0.99991

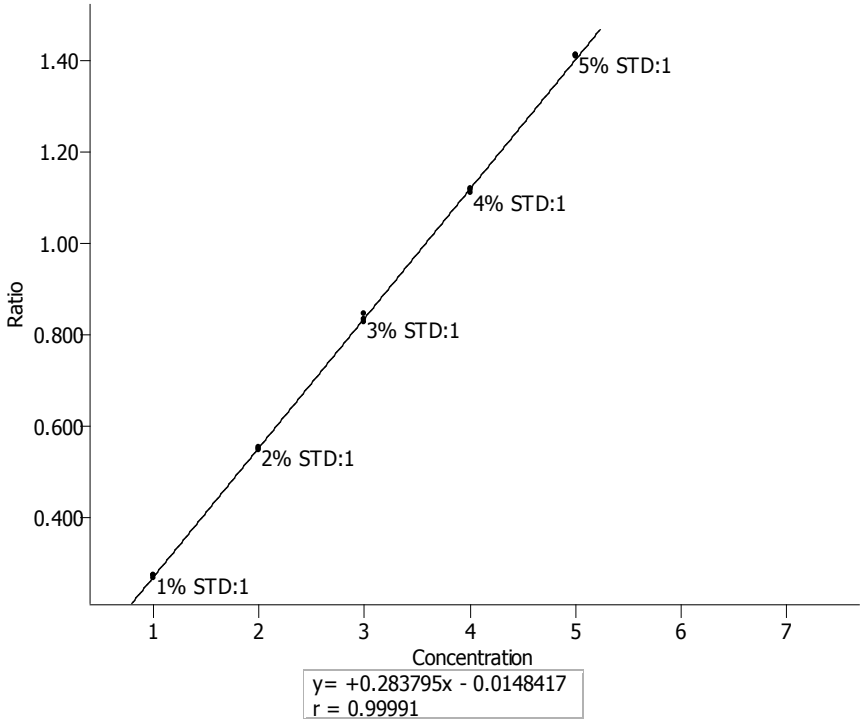

Figure 11: Calibration curve of toluene

Ethylbenzene:

The calibration curve for ethylbenzene was constructed using the following concentrations: 1, 2, 3, 4, 5%. Each standard was run in triplicate for reproducibility of the results. The calibration curve for ethylbenzene is shown in figure 12 and the linearity is good with a correlation coefficient (R^2= 0.99781). The internal standard used for ethylbenzene is ethylbenzene- d_8 having a mass of 116 + 115 comes out at 324.64 sec.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Ethylbenzene	106	331.0	Y= +1.50237X – 0.324424	0.99783

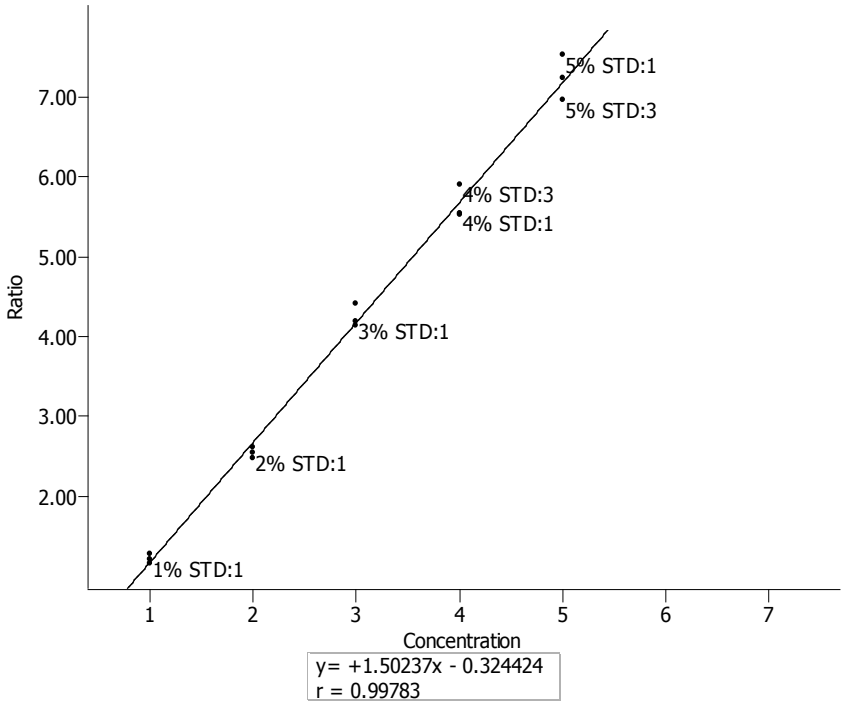

Figure 12: Calibration curve of ethylbenzene

Styrene:

The calibration curve for styrene was constructed using the following concentrations: 2, 4, 6, 8 10%. Each standard was run in triplicate for reproducibility of the results. The calibration curve for styrene is shown in figure 13 and the linearity is good with a correlation coefficient (R^2= 0.99698). The internal standard used for styrene is ethylbenzene- d_8 having a mass of 116 + 115 comes out at 324.64 sec.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Styrene	104	369.37	Y= + 2.761X - 1.12104	0.99787

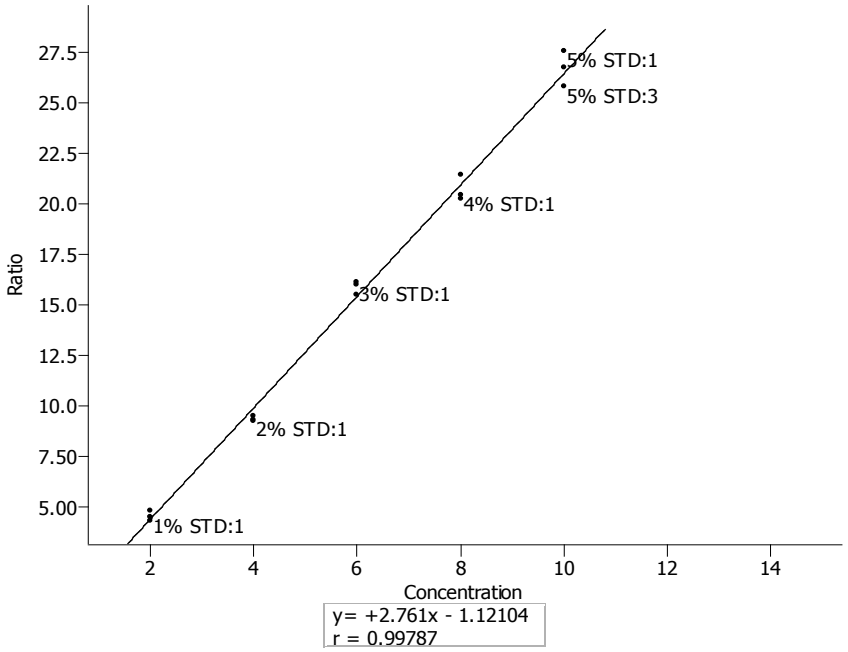

Figure 13: Calibration curve of styrene

Cumene:

The calibration curve for cumene was constructed using the following concentrations: 1, 2, 3, 4, 5%. Each standard was run in triplicate for reproducibility of

the results. The calibration curve for cumene is shown in figure 14 and the linearity is good with a correlation coefficient (R^2= 0.99753). The internal standard used for cumene is ethylbenzene- d_8 having a mass of 116 + 115 comes out at 324.64 sec.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Cumene	120	407.84	Y= + 1.07585X - 0.316722	0.99753

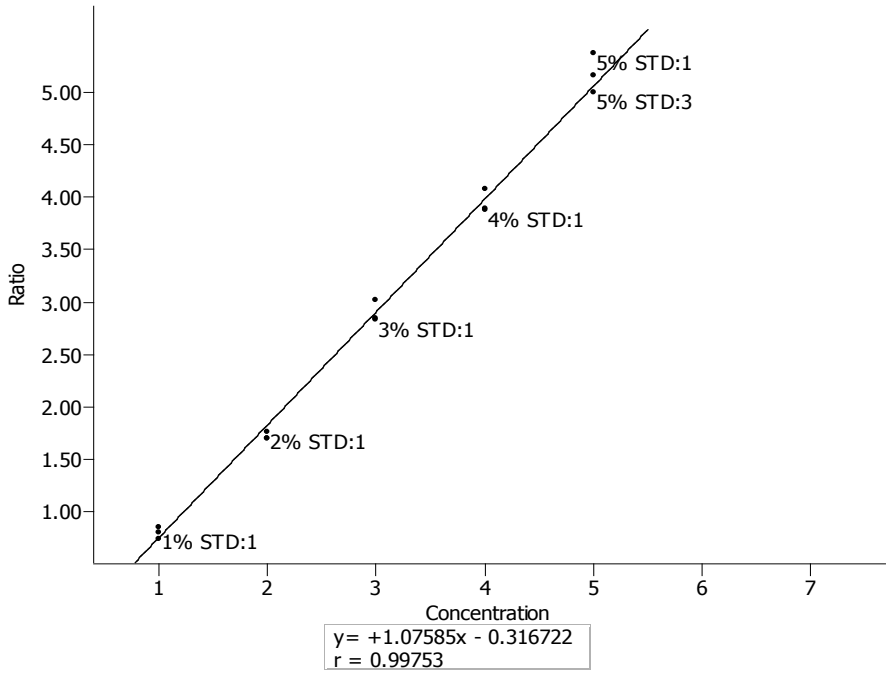

Figure 14: Calibration curve of cumene

α- Methylstyrene:

The calibration curve for α- methylstyrene was constructed using following concentrations: 1, 2, 3, 4, 5%. Each standard was run in triplicate for reproducibility of results. The calibration curve for α- methylstyrene is shown in figure 15 and the linearity is good with a correlation coefficient (R^2= 0.99692). The internal standard used for α-Methylstyrene is ethylbenzene- d_8 having a mass of 116 + 115 comes out at 324.64 sec.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
α- Methylstyrene	118	472.49	Y= + 1.46462x – 0.527142	0.99626

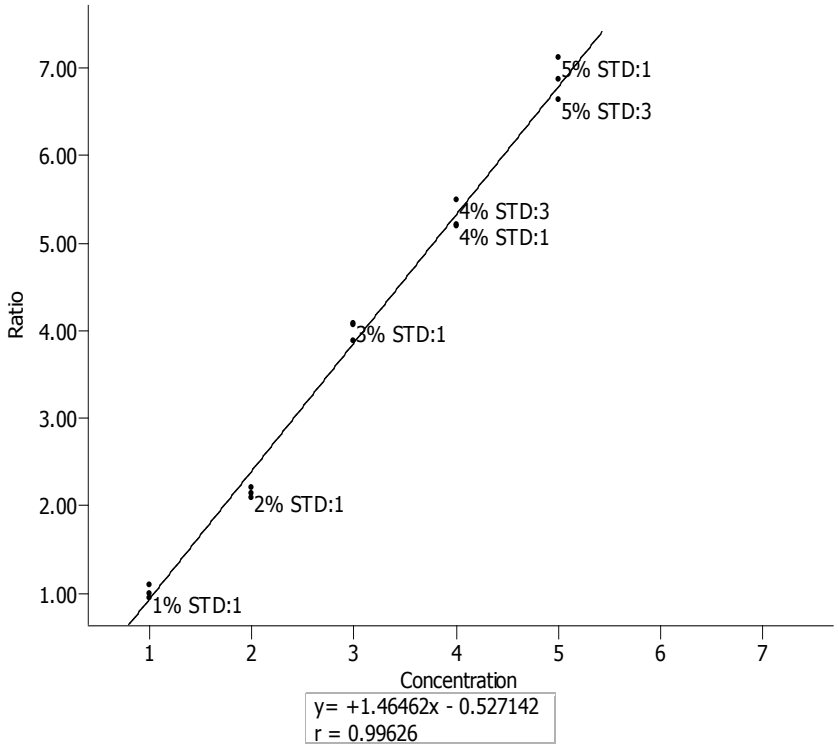

Figure 15: Calibration curve of α- methylstyrene

4.1.1.2 Limit of detection for aromatics in mass percent (1D)

The limit of detection or the detection limit (LOD) is the lowest quantity of a compound that can be distinguished from the absence of that compound. The calculation method is again based on the slope and the intercept of the calibration curve.

Table 11: Limit of detection for aromatics in mass percent

Compound	1D (Mass Percent)
Benzene	0.02
Toluene	0.007
Ethylbenzene	0.2
Styrene	0.6
Cumene	0.1
α- Methylstyrene	0.2

Different grades of gasoline, diesel, polyflow and distillation standard D86 were qualitatively determined and then quantified using the calibration set 1. The retention time, area and mass percent of each the aromatic compounds in different grades of gasoline, diesel and distillation standard D86 are tabulated below.

4.1.1.3 Distillation standard D 86 (1D)

The distillation standard D 86 was qualitatively determined and then quantified using the calibrated standards. Table 12 shows only the calibrated compounds, with their retention time, area and mass percent. D 86 contains only toluene and Cumene.

Table 12: Quantified aromatics in D 86 in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	73.05	234196	7.2
Toluene- d8	186.27	536014.6	7.2
Toluene	194.11	4355544	32.8
Ethylbenzene- d8	324.56	55481	7.2
Cumene	408.21	783143.3	13.4
Naphthalene- d8	656.28	91706	7.2

4.1.1.4 Gasoline samples (1D)

Different grades of gasoline like regular and super were collected from different places on different days. This gasoline sample was characterized and was quantified against standard calibration that contains six aromatic compounds. Each sample was run in triplicate to check the reproducibility of the method. All the gasoline samples were named according to their grade and the date they were collected and the format used in naming the samples is type, grade, the day it was collected (YY/ MM/ DD). All the aromatic compounds in the gasoline samples were listed below in mass percent.

Gasoline super (130611):

Gasoline super (130611) was qualitatively determined and then quantified using the calibrated standards. Table 13 shows only the calibrated compounds, with their retention time, area and mass percent. Gasoline super (130611) contains benzene, toluene, ethylbenzene and cumene which have 0.2, 12.0, 1.2 and 0.6 mass percent respectively of the six aromatic compounds.

Table 13: Quantified aromatics in gasoline super (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.91	561732.3	7.2
Benzene	74.32	138877.3	0.2
Toluene- d8	186.05	886809.7	7.2
Toluene	192.95	3018553	12.1
Ethylbenzene- d8	324.48	72569.33	7.2
Ethylbenzene	330.72	108332	1.2
Cumene	407.48	22399	0.6
Naphthalene- d8	656.34	113648.3	7.2

Gasoline regular (130611):

Gasoline regular (130611) was qualitatively determined and then quantified using the calibrated standards. Table 14 shows only the calibrated compounds, with their retention time, area and mass percent. Gasoline regular (130611) contains benzene, toluene, ethylbenzene and cumene which has 0.9, 6.5, 1.4 and 0.4 mass percent respectively of the six aromatic compounds

Table 14: Quantified aromatics in gasoline regular (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.89	538421.6	7.2
Benzene	74.16	502686.3	0.9
Toluene- d8	185.78	760428.3	7.2
Toluene	192.15	1396424.6	6.5
Ethylbenzene- d8	324.55	60151.3	7.2
Ethylbenzene	330.64	104507	1.4
Cumene	407.51	9290.7	0.4
Naphthalene-d8	656.35	92289.3	7.2

Gasoline regular (130522):

Gasoline regular (130522) was qualitatively determined and then quantified using the calibrated standards. Table 15 shows only the calibrated compounds, with their retention time, area and mass percent. Gasoline regular (130522) contains benzene, toluene, ethylbenzene and cumene which has 0.4, 4.5, 1.0 and 0.42 mass percent respectively of the six aromatic compounds.

Table 15: Quantified aromatics in gasoline regular (130522) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.96	517231.7	7.2
Benzene	74.31	216459	0.4
Toluene- d8	185.67	686292	7.2
Toluene	191.91	870442.3	4.5
Ethylbenzene- d8	324.52	57583.33	7.2
Ethylbenzene	330.83	65038	1.0
Cumene	407.52	7604.63	0.4
Naphthalene- d8	656.26	82324	7.2

Gasoline regular (130505):

Gasoline regular (130505) was qualitatively determined and then quantified using the calibrated standards. Table 16 shows only the calibrated compounds, with their retention time, area and mass percent. Gasoline super (130505) contains benzene, toluene, ethylbenzene and Cumene which has 0.3, 4.1, 1.2 and 0.4 mass percent respectively of the six aromatic compounds.

Table 16: Quantified aromatics in gasoline regular (130505) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.21	570382.66	7.2
Benzene	73.56	207907.33	0.3
Toluene- d8	185.15	859535	7.2
Toluene	191.45	988876.33	4.1
Ethylbenzene- d8	324.28	71690.67	7.2
Ethylbenzene	330.5	104094.33	1.2
Cumene	407.36	11371.1	0.4
Naphthalene- d8	656.23	107566.67	7.2

4.1.1.5 Diesel samples (1D)

Diesel samples were collected from different places on different days. These samples were characterized and were quantified against standard calibration that contains six aromatic compounds to check the reproducibility of the method. All the diesel samples were named according to their grade and the dates they were collected and the format of the date for the samples is yy/mm/dd. All the diesel samples were qualitatively determined and is then quantified using the calibration standard. All the diesel samples do not contain any aromatic content in them. Most of the diesel samples had decane derivatives in it when quantified. The complete peak table of diesel is shown in the table 17.

Table 17: Peak table of diesel collected on different days

Compound	Retention Time(sec)	Area	Mass Percent
Benzene	-	-	-
Toluene	-	-	-
Ethylbenzene	-	-	-
Styrene	-	-	-
Cumene	-	-	-
à-Methylstyrene	-	-	-
Benzene- d6	73.48	181157	7.2
Toluene- d8	186.07	434284	7.2
Ethylbenzene- d8	324.81	33099	7.2
Naphthalene- d8	656.32	53138	7.2
Unknown 1	587.44	26399	Not quantified
Undecane	675.57	72942	Not quantified
Tridecane	752.47	75592	Not quantified
Hexadecane	801.52	16618	Not quantified
Tridecane	838.9	69614	Not quantified
Decane, 2,9-dimethyl	870.82	22817	Not quantified

4.1.1.6 Polyflow samples

The end product generated by the RES Polyflow process is a liquid known as pygas from which diesel fuel, octane enhancers and gasoline blend stocks can be produced. The pygas samples were collected from the reactor at different days and at different times and are named according to them. All the pygas samples were qualitatively determined and then quantified using the calibrated standards. All the quantified pygas samples, with their retention time, area and mass percent are shown in their respective tables.

130417 Post Scrub:

Table 18: Quantified aromatics in 130417 post scrub in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72.94	687776.5	7.2
Benzene	74.16	791077.5	1.2
Toluene- d8	185.87	1141726.5	7.2
Toluene	192.38	2484210.5	7.7
Ethylbenzene- d8	324.38	103799	7.2
Ethylbenzene	330.57	334169.5	2.4
Styrene	368.22	894330.5	3.6
Cumene	407.54	5367.95	0.3
à-Methylstyrene	471.96	17610.5	0.5
Naphthalene-D8	656.19	131376	7.2

130313 post scrub:

Table 19: Quantified aromatics in 130313 post scrub in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72.63	555038.7	7.2
Benzene	73.82	1550722	2.9
Toluene- d8	185.37	801934	7.2
Toluene	191.66	923829	4.1
Ethylbenzene- d8	324.26	66800	7.2
Ethylbenzene	330.57	67365.3	0.9
Styrene	367.96	172631	1.3
Naphthalene- d8	656.12	91574.5	7.2

130313 pyrogas scrub:

Table 20: Quantified aromatics in 130313 pyrogas scrub in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	73.19	588892.3	7.2
Benzene	74.44	709632.7	1.2
Toluene- d8	185.99	958630.7	7.2
Toluene	192.15	766540.3	2.9
Ethylbenzene- d8	324.42	88094.67	7.2
Ethylbenzene	330.52	165896.7	1.5
Styrene	368.05	368054.3	1.9
Cumene	407.42	9060.7	0.4
à-Methylstyrene	471.87	17829	0.5
Naphthalene- d8	656.21	124778	7.2

Hydro treated gasoline fraction:

Table 21: Quantified aromatics in hydro treated gasoline fraction in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.45	583422.3	7.2
Benzene	73.73	383447	0.7
Toluene- d8	185.46	973335.3	7.2
Toluene	192.27	2418040	8.8
Ethylbenzene- d8	324.45	87961.3	7.2
Ethylbenzene	331.49	1395190	10.8
Styrene	369.77	4020901	17.0
Cumene	407.13	106681.3	1.4
à-Methylstyrene	471.77	273235.7	2.5
Naphthalene- d8	656.17	156481.3	7.2

111005 Dr- 1 heated 2x:

Table 22: Quantified aromatics in 111005 Dr- 1 heated 2X in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	73.11	528779	7.2
Benzene	74.41	366199.3	0.7
Toluene- d8	185.86	866701	7.2
Toluene	192.45	2362865	9.7
Ethylbenzene- d8	324.54	75155	7.2
Ethylbenzene	331.35	1332289	12.0
Styrene	369.61	3901744	19.2
Cumene	407.17	103168.3	1.6
à-Methylstyrene	471.76	265254.7	2.8
Naphthalene- d8	655.99	132827	7.2

Set 2:

Calibration and quantitation of aromatic compounds (1D):

A set of Calibration standards were freshly made on a different day and the qualitative, quantitative analysis of the gasoline, diesel and distillation standard D86 was determined to check the reproducibility of the results. The compound mass, retention time, equation of the line and the correlation coefficient of each of the calibrated compounds are shown in the table. Benzene- d6 was used as an internal standard for benzene, toluene- d8 was used as an internal standard for toluene and Ethylbenzene- d8 was used as an internal standard for ethylbenzene, styrene, cumene and à-Methylstyrene.

Table 23: Equation of line and correlation coefficient of calibrated aromatics

Compound	Mass	Retention Time(sec)	Equation of Line	Correlation Coefficient
Benzene	78	73.62	Y= + 0.954137x - 0.0221691	0.99903
Toluene	92	191.19	Y= + 0.291794x - 0.0425493	0.99885
Ethylbenzene	106	330.25	Y= + 1.46861x - 1.15141	0.99749
Styrene	104	368.29	Y= + 2.66367x - 1.15141	0.99581
Cumene	120	407.13	Y= + 1.10755x - 0.381265	0.99708
à-Methylstyrene	118	471.75	Y= + 1.43772x - 0.529426	0.99593

The limit of detection or the detection limit (LOD) is the lowest quantity of a compound that can be distinguished from the absence of that compound. The calculation method is again based on the slope and the intercept of the calibration curve.

Table 24: Limit of detection for aromatics in mass percent

Compound	1D (Mass Percent)
Benzene	0.02
Toluene	0.006
Ethylbenzene	0.2
Styrene	0.6
Cumene	0.1
Methyl styrene	0.2

All the samples were qualitatively determined and then quantified using their respective calibration curves. The retention time, quant mass, area and mass percent of the aromaticcompounds in different grades of gasoline, diesel and distillation standard D86 are tabulated below.

Distillation standard D 86:

The distillation standard D 86 was qualitatively determined and then quantified using the calibrated standards. Table 25 shows only the calibrated compounds, with their retention time, area and mass percent. The quantified distillation standard D 86 contains only toluene and cumene in 32.3 and 13.2 mass % respectively of the six aromatic compounds.

Table 25: Quantified aromatics in distillation standard D 86 in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	73.05	256717	7.2
Toluene- d8	185.32	638363.3	7.4
Toluene	193.09	5434350	32.3
Ethylbenzene- d8	324.13	53025.67	7.4
Cumene	407.66	751443.7	13.2
Naphthalene- d8	655.93	84779.33	7.4

Gasoline samples:

Different grades of gasoline like regular and super were collected from different places on different days. This gasoline sample was characterized and was quantified against standard calibration that contains six aromatic compounds to check the reproducibility of the method. All the gasoline samples were listed with their quantified aromatic content with their retention time, area and mass percent.

Gasoline super (130611):

Table 26: Quantified aromatics in gasoline super (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.05	690706	7.4
Benzene	73.41	164162.7	0.3
Toluene- d8	185.1	1123784	7.4
Toluene	192.35	3526120	10.9
Ethylbenzene- d8	323.85	99155.33	7.4
Ethylbenzene	330.01	134816.7	1.1
Cumene	406.99	29232	0.6
Naphthalene- d8	655.97	158181	7.4

Gasoline regular (130611):

Table 27: Quantified aromatics in gasoline regular (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	71.96	715313.7	7.4
Benzene	73.22	671810.7	1.0
Toluene- d8	184.67	1142053	7.4
Toluene	191.3	1883875	5.8
Ethylbenzene- d8	323.78	99067.67	7.4
Ethylbenzene	330.04	150518.7	1.3
Cumene	407	12673.17	0.5
Naphthalene-d8	656.05	151409.7	7.4

Gasoline regular (130522):

Table 28: Quantified aromatics in gasoline regular (130522) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.43	609090.3	7.4
Benzene	73.78	257123.3	0.5
Toluene- d8	185.07	873386	7.4
Toluene	191.32	1045274	4.2
Ethylbenzene- d8	323.98	78162	7.4
Ethylbenzene	330.26	82614	0.9
Cumene	407.14	9765.23	0.5
Naphthalene- d8	655.97	122436.3	7.4

Gasoline Regular (130505):

Table 29: Quantified aromatics in gasoline regular (130505) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72	687245.7	7.4
Benzene	73.32	218200	0.4
Toluene- d8	184.97	1093153	7.4
Toluene	191.24	1081919	3.5
Ethylbenzene- d8	323.87	94348.67	7.4
Ethylbenzene	330.09	126295	1.1
Cumene	406.91	17528	0.5
Naphthalene- d8	656.18	171664.3	7.4

Diesel samples:

Diesel samples were collected from different places on different days. These samples were characterized and quantified against standard calibration that contains six aromatic compounds to check the reproducibility of the method. All the aromatic compounds in the gasoline samples were listed below in mass percent. Diesel samples collected on 130611, 130505 do not contain the six aromatic compounds present in the set of calibration standards. Most of the diesel samples had decane derivatives in it when quantified. The complete peak table of diesel is shown in the table 30.

Table 30: Peak table of diesel collected on different days in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene	-	-	-
Toluene	-	-	-
Ethylbenzene	-	-	-
Styrene	-	-	-
Cumene	-	-	-
à-Methylstyrene	-	-	-
Benzene-d6	73.25	256261	7.4
Toluene-d8	185.53	586943	7.4
Ethylbenzene- d8	324.19	43564	7.4
Naphthalene-D8	656.08	84925	7.4
Unknown 1	587.16	31207	Not Quantified
Hexadecane	675.22	101224	Not Quantified
Unknown 2	752.23	118185	Not Quantified
Decane, 2,5,9-trimethyl-	801.41	60680	Not Quantified
Hexadecane	838.8	51768	Not Quantified
Hexadecane	870.63	22483	Not Quantified
Decane, 6-ethyl-2-methyl-	899.25	45296	Not Quantified

Polyflow samples:

The end product generated by the RES Polyflow process is pygas from which diesel fuel, octane enhancers and gasoline blend stocks are produced. The pygas samples were collected from the reactor at different days and at different times and are named according to them. All the quantified aromatic compounds in the pygas samples are listed below in mass percent with their retention time and area.

130417 post scrub:

Table 31: Quantified aromatics in 130417 post scrub in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72.05	773645.7	7.4
Benzene	73.25	1004229	1.4
Toluene- d8	185.1	1308338	7.4
Toluene	192.23	3160319	8.4
Ethylbenzene- d10	323.95	121685.3	7.4
Ethylbenzene	330.26	430962.3	2.6
Styrene	368.16	1190324	4.1
Cumene	407.06	10553.7	0.4
à-Methylstyrene	471.42	24889	0.5
Naphthalene-D8	655.93	169313.7	7.4

130313 post scrub:

Table 32: Quantified aromatics in 130313 post scrub in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72.53	605018.7	7.4
Benzene	73.72	1720457	3.0
Toluene- d8	184.99	879665.3	7.4
Toluene	191.23	1049827	4.2
Ethylbenzene- d10	323.93	76982.67	7.4
Ethylbenzene	330.14	79336.67	0.9
Styrene	367.64	210649	1.5
Naphthalene- d8	655.95	101290.3	7.4

130313 pyrogas scrub:

Table 33: Quantified aromatics in 130313 pyrogas Scrub in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.19	597873.7	7.4
Benzene	73.42	741893.3	1.3
Toluene- d8	184.52	982413	7.4
Toluene	190.89	796359.7	2.9
Ethylbenzene- d10	323.9	92381.67	7.4
Ethylbenzene	330.01	175429	1.5
Styrene	367.64	394935.3	2.0
Cumene	407	9358.767	0.4
à-Methylstyrene	471.55	20542	0.5
Naphthalene- d8	656.02	134896	7.4

Hydro treated gasoline fraction:

Table 34: Quantified aromatics in hydro treated gasoline fraction in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.87	542846.3	7.4
Benzene	74.15	356061.7	0.7
Toluene- d8	185.26	903415.3	7.4
Toluene	192.02	2234195	8.6
Ethylbenzene- d10	324.27	83385.67	7.4
Ethylbenzene	331.19	1252491	10.5
Styrene	369.54	3687290	17.0
Cumene	406.88	104627.3	1.5
à-Methylstyrene	471.58	256728.7	2.5
Naphthalene- d8	656.05	145533.7	7.4

111005 Dr- 1 heated 2X:

Table 35: Quantified aromatics in 111005 Dr- 1 heated 2X in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72.27	447732.7	7.4
Benzene	73.54	312112.7	0.7
Toluene- d8	184.91	741600	7.4
Toluene	191.5	1994131	9.3
Ethylbenzene- d10	324.1	67861	7.4
Ethylbenzene	331.04	1123544	11.5
Styrene	369.47	3279778	18.6
Cumene	406.94	93674	1.6
à-Methylstyrene	471.59	225396	2.7
Naphthalene- d8	655.91	124769.3	7.4

4.1.2 Two dimensional gas chromatography

GC x GC, combined with the Pegasus high throughput TOFMS, has the potential to allow a significant reduction in chromatographic analysis time. The GC X GC thermal modulation system traps the higher volatility aliphatic and aromatics commonly found in all the volatile samples and a secondary column type with different conditions provides greater separation. The modulator placed between the columns, consists of a quad- jet system that creates two distinct trapping zones that traps and focuses all the effluent from the primary column before it is released into the secondary column. Qualitative and quantitative analysis of all the gasoline, diesel and Polyflow samples were conducted by GC x GC TOFMS.

Set 1:

4.1.2.1 Calibration and quantitation of aromatic compounds (2D)

In order to quantitatively determine the fuel and hydrocarbon samples, calibration curve measurements were performed and the typical calibration curves for benzene, toluene, ethylbenzene, styrene, cumene, α- methyl styrene are shown in figures 16 to 21. In the calibration curves, X- axis represents retention time of the separation on the first dimension column and the y-axis represents the retention time on the secondary oven.

Benzene:

The calibration curve for benzene was constructed using the following concentrations: 1, 2, 3, 4, 5 %. Each standard was run in triplicate for reproducibility of the results. The calibration curve for benzene is shown in figure 16 and the linearity is good with a correlation coefficient (R^2= 0.99990). The internal standard used for benzene is benzene- d6 having a mass of 84+83 comes out at 72, 2.920 secs. The first retention time is the separation on the first dimension column and the second retention time represents the retention time on the secondary oven.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Benzene	78	72, 2.970	Y= + 0.868726x + 0.140604	0.99990

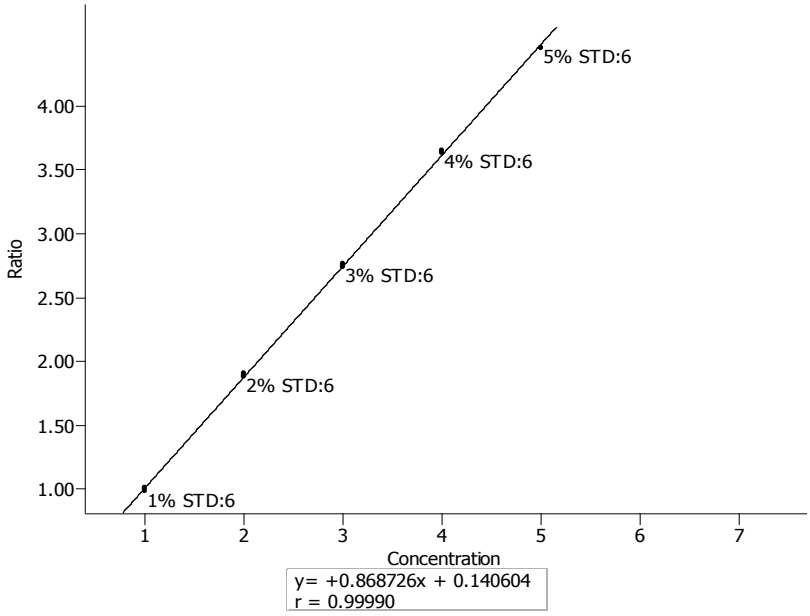

Figure 16: Calibration curve of benzene

Toluene

The calibration curve for toluene was constructed using the following concentrations: 1, 2, 3, 4, 5%. Each standard was run in triplicate for reproducibility of the results. The calibration curve for toluene is shown in figure 8 and the linearity is good with a correlation coefficient (R^2= 0.99993). The internal standard used for toluene is toluene- d_8 having a mass of 100 + 99 comes out at 184, 5.290 secs.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Toluene	92	192, 5.150	Y= + 0.24661x + 0.0312776	0.99993

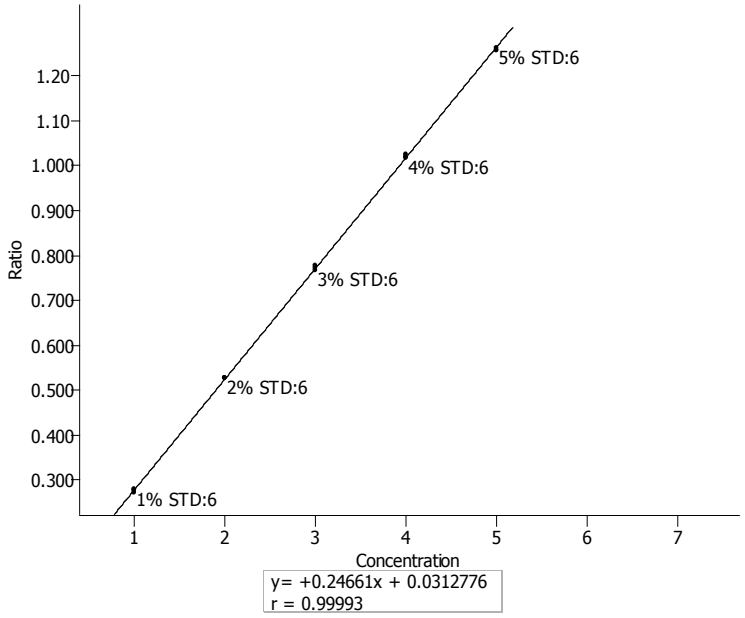

Figure 17: Calibration curve of toluene

Ethylbenzene:

The calibration curve for ethylbenzene was constructed using the following concentrations: 1, 2, 3, 4, 5%. Each standard was run in triplicate for reproducibility of the results. The calibration curve for ethylbenzene is shown in figure 9 and the linearity is good with a correlation coefficient (R^2= 0.99660). The internal standard used for ethylbenzene is ethylbenzene- d_8 having a mass of 116 + 115 comes out at 328, 4.240 secs.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Ethylbenzene	106	328, 4.430	Y= + 1.17374x + 0.108833	0.99660

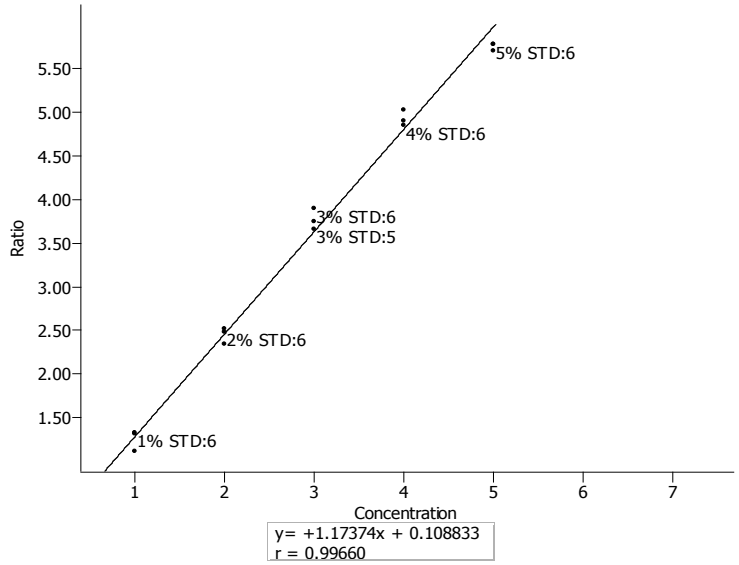

Figure 18: Calibration curve of ethylbenzene

Styrene:

The calibration curve for styrene was constructed using the following concentrations: 2, 4, 6, 8 10%. Each standard was run in triplicate for reproducibility of the results. The calibration curve for styrene is shown in figure 10 and the linearity is good with a correlation coefficient (R^2= 0.99925). The internal standard used for styrene is ethylbenzene- d_8 having a mass of 116 + 115 comes out at 328, 4.240 secs.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Styrene	104	368, 4.8	Y= + 2.27666x - 0.0183661	0.99925

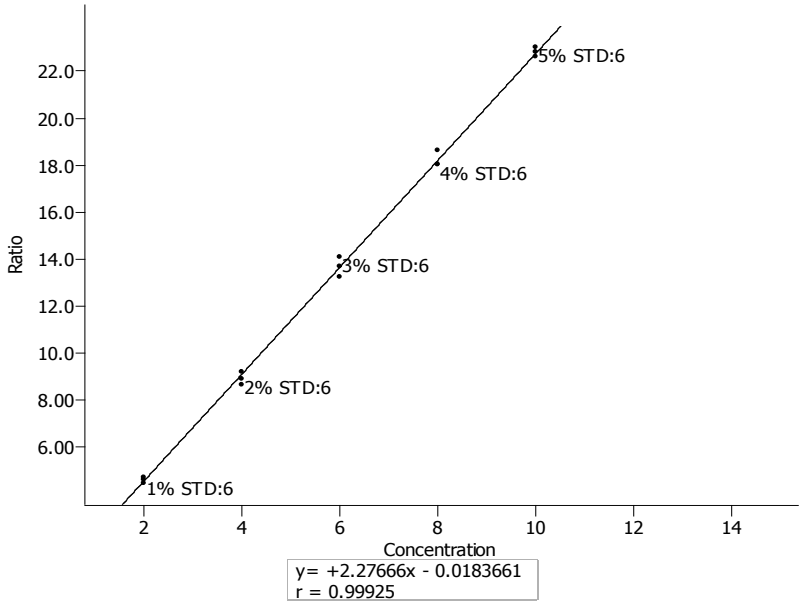

Figure 19: Calibration curve of styrene

Cumene:

The calibration curve for cumene was constructed using the following concentrations: 1, 2, 3, 4, 5%. Each standard was run in triplicate for reproducibility of the results. The calibration curve for cumene is shown in figure 11 and the linearity is good with a correlation coefficient (R^2= 0.99913). The internal standard used for cumene is ethylbenzene- d_8 having a mass of 116 + 115 comes out at 328, 4.240 secs.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
Cumene	120	408, 4.07	Y= + 0.949077x - 0.0350854	0.99913

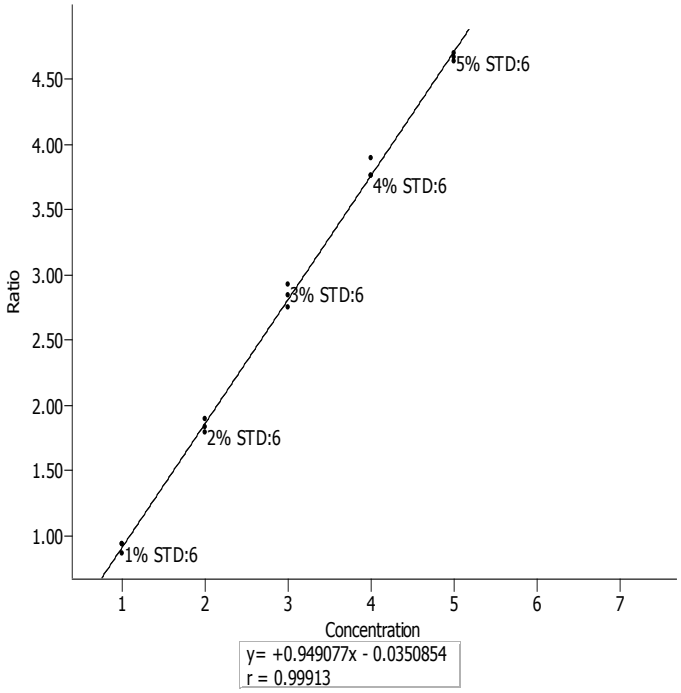

Figure 20: Calibration curve of cumene

α- Methylstyrene:

The calibration curve for α- methylstyrene was constructed using the following concentrations: 1, 2, 3, 4, 5%. Each standard was run in triplicate for reproducibility of the results. The calibration curve for α- methylstyrene is shown in figure 12 and the linearity is good with a correlation coefficient (R^2= 0.99868). The internal standard used for cumene is ethylbenzene- d_8 having a mass of 116 + 115 comes out at 328, 4.240 secs.

Name	Mass	Absolute R. T (Sec)	Equation	Correlation Coefficient
α- Methylstyrene	118	472, 4.540	Y= + 1.23089x - 0.106699	0.99868

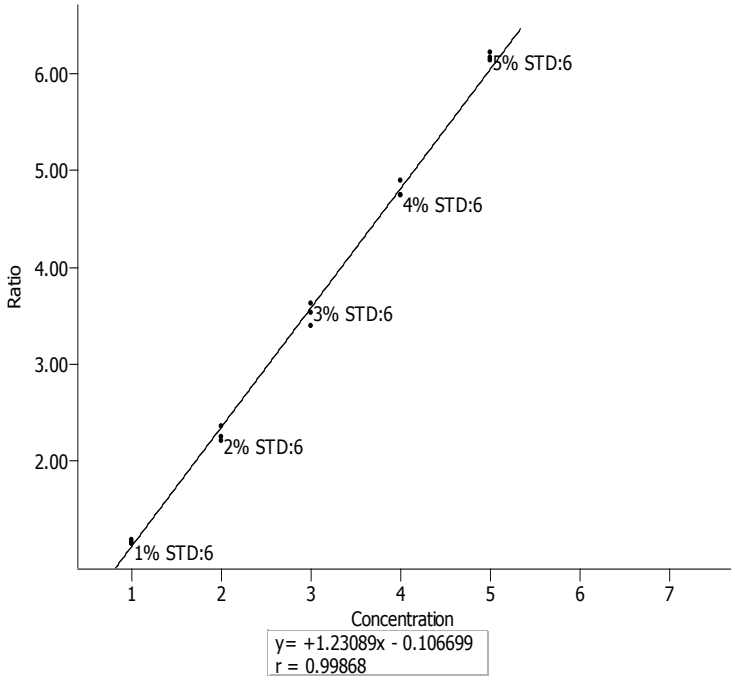

Figure 21: Calibration curve of α- methyl styrene

4.1.2.2 Limit of detection for aromatics in mass percent (2D)

The limit of detection or the detection limit (LOD) is the lowest quantity of a compound that can be distinguished from the absence of that compound. The calculation method is again based on the slope and the intercept of the calibration curve.

Table 36: Limit of detection for aromatics in mass percent

Compound	2D (Mass Percent)
Benzene	0.02
Toluene	0.005
Ethylbenzene	0.2
Styrene	0.5
Cumene	0.2
Metstyrene	0.2

Different grades of gasoline, diesel, polyflow and distillation standard D86 were qualitatively determined and then quantified using the calibration set 1. The retention time, quant mass, area and mass percent of the aromatic compounds in different grades of gasoline, diesel and distillation standard D86 are tabulated below.

4.1.2.3 Distillation standard D 86

The distillation standard D 86 was qualitatively determined and then quantified using the calibrated standards. Table 37 shows only the calibrated compounds, with their retention time (primary column followed by secondary column), area and mass percent. The quantified distillation standard D 86 contains only toluene and cumene in 28.98 and 11.71 mass % respectively of the six aromatic compounds.

Table 37: Quantified aromatics in distillation standard D 86 in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72 , 2.920	778167	7.2
Toluene- d8	184 , 5.290	1273751	7.2
Toluene	192 , 5.370	9143276	29.0
Ethylbenzene- d8	328 , 4.230	124116	7.2
Cumene	408 , 4.130	1374799	11.7
Naphthalene-D8	656 , 6.120	196841.7	7.2

4.1.2.4 Gasoline samples

Different grades of gasoline like regular and super were collected from different places on different days. This gasoline sample was characterized and was quantified against standard calibration that contains six aromatic compounds to check the reproducibility of the method. All the aromatic compounds in the gasoline samples were

listed below in mass percent. The quantified gasoline samples with their retention time (primary column followed by secondary column), area and mass percent were listed in their respective tables.

Gasoline super (130611):

Table 38: Quantified aromatics in gasoline super (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.970	1019042	7.2
Benzene	72 , 3.020	282627.3	0.3
Toluene- d8	184 , 5.280	1797112	7.2
Toluene	192 , 5.210	5263786	11.8
Ethylbenzne- d8	328 , 4.240	152410.7	7.2
Ethylbenzene	328 , 4.420	233138	1.2
Cumene	408 , 4.050	59225.33	0.5
Naphthalene- d8	656 , 6.120	266794	7.2

Gasoline regular (130611):

Table 39: Quantified aromatics in gasoline regular (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.990	964932.3	7.2
Benzene	72 , 3.050	1037752	1.1
Toluene- d8	184 , 5.280	1686046	7.2
Toluene	192 , 5.160	2825337	6.7
Ethylbenzne- d8	328 , 4.250	150868.7	7.2
Ethylbenzene	328 , 4.430	240412.3	1.3
Cumene	408 , 4.040	31926.33	0.4
Naphthalene- d8	656 , 6.130	251053.7	7.2

Gasoline regular (130522):

Table 40: Quantified aromatics in gasoline regular (130522) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.960	721356.7	7.2
Benzene	72 , 3.020	388909.7	0.5
Toluene- d8	184 , 5.250	1173270	7.2
Toluene	192 , 5.110	1492085	4.4
Ethylbenzne- d8	328 , 4.240	112321.7	7.2
Ethylbenzene	328 , 4.420	131537	0.9
Cumene	408 , 4.050	21890.33	0.3
Naphthalene- d8	656 , 6.130	191031.7	7.2

Gasoline regular (130505):

Table 41: Quantified aromatics in gasoline regular (130505) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.970	732802.7	7.2
Benzene	72 , 3.030	302162.7	0.3
Toluene- d8	184 , 5.270	1230088	7.2
Toluene	192 , 5.130	1376990	3.4
Ethylbenzne- d8	328 , 4.230	109790.7	7.2
Ethylbenzene	328 , 4.410	184347	1.0
Cumene	408 , 4.040	26132	0.6
Naphthalene- d8	656 , 6.120	191591.7	7.2

4.1.2.5 Diesel samples:

Diesel samples were collected from different places on different days. Diesel samples were characterized and were quantified against standard calibration that contains six aromatic compounds to check the reproducibility of the method. All the aromatic compounds in the diesel samples were listed below in mass percent. diesel samples collected on 130611, 130505 do not contain the six aromatic compounds present in the set of calibration standards. Most of the diesel samples had decane derivatives.

Diesel Marathon (130611):

Table 42: Quantified aromatics in diesel marathon (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.950	108638	7.2
Toluene- d8	184 , 5.190	194416	7.2
Toluene	192 , 5.020	5232.4	0
Ethylbenzne- d8	328 , 4.190	21214	7.2
Naphthalene-D8	656 , 6.100	24048	7.2

Diesel pilot (130611):

Table 43: Quantified aromatics in diesel pilot (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.940	346254	7.2
Toluene- d8	184 , 5.240	493696	7.2
Toluene	192 , 5.080	6849.833	0.0
Ethylbenzne- d8	328 , 4.240	53721.33	7.2
Ethylbenzene	328 , 4.430	1337.467	0.0
Naphthalene- d8	656 , 6.140	88707.33	7.2

Diesel (130505):

Table 44: Quantified aromatics in diesel (130505) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.960	423049.6667	7.2
Toluene- d8	184 , 5.260	606754	7.2
Toluene	192 , 5.100	10226.03333	0.0
Ethylbenzne- d8	328 , 4.250	66510	7.2
Ethylbenzene	328 , 4.460	1643.233333	0.0
Naphthalene- d8	656 , 6.170	109770	7.2

4.1.2.6 Polyflow samples:

The end product generated by the RES Polyflow process is pygas from which diesel fuel, octane enhancers and gasoline blend stocks are produced. The pygas samples were collected from the reactor at different days and at different times and are named according to them. The main purpose of this work is to characterize these different pygas samples and quantify them with the calibration standards by two dimensional gas chromatography using a thermal modulator.

130417 post scrub:

Table 45: Quantified aromatics in 130417 post scrub in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72 , 3.020	862955.7	7.2
Benzene	72 , 3.080	999185.7	1.2
Toluene- d8	184 , 5.290	1443342	7.2
Toluene	192 , 5.190	3094072	8.6
Ethylbenzne- d8	328 , 4.270	142831.3	7.2
Ethylbenzene	328 , 4.460	365217	2.1
Styrene	368 , 4.840	1171710	3.6
Cumene	408 , 4.070	13047	0.4
à-Methylstyrene	472 , 4.540	30942.67	0.5
Naphthalene- d8	656 , 6.170	195703.7	7.2

130313 Post scrub:

Table 46: Quantified aromatics in 130313 post scrub in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72 , 3.040	713056	7.2
Benzene	72 , 3.100	2144589.3	3.3
Toluene- d8	184 , 5.300	1173097	7.2
Toluene	192 , 5.160	1358289	4.6
Ethylbenzne- d8	328 , 4.270	118429.3	7.2
Ethylbenzene	328 , 4.450	92896	1.0
Styrene	368 , 4.810	290432.7	1.6
Cumene	408 , 4.070	3984.2	0.3
à-Methylstyrene	472 , 4.540	7118.0	0.4
Naphthalene- d8	656 , 6.190	159615.6	7.2

130313 Pyrogas scrub:

Table 47: Quantified aromatics in 130313 pyrogas scrub in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 3.020	728225	7.2
Benzene	72 , 3.070	937176	1.3
Toluene- d8	184 , 5.300	1193479.3	7.2
Toluene	192 , 5.160	996132	3.3
Ethylbenzne- d8	328 , 4.270	129901.6	7.2
Ethylbenzene	328 , 4.460	151300.3	1.6
Styrene	368 , 4.820	496621.6	2.0
Cumene	408 , 4.070	17623.3	0.5
à-Methylstyrene	472 , 4.540	31517.6	0.6
Naphthalene- d8	656 , 6.180	191103.6	7.2

Hydro treated gasoline fraction:

Table 48: Quantified aromatics in hydro treated gasoline fraction in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.970	801458	7.2
Benzene	72 , 3.030	509488.7	0.6
Toluene- d8	184 , 5.310	1320768	7.2
Toluene	192 , 5.210	3199752	9.7
Ethylbenzne- d8	328 , 4.280	156968	7.2
Ethylbenzene	328 , 4.470	526902.7	10.8
Styrene	368 , 4.950	4549218	12.8
Cumene	408 , 4.090	178861.3	1.2
à-Methylstyrene	472 , 4.580	414013.7	2.2
Naphthalene- d8	656 , 6.200	256383.7	7.2

111005 Dr- 1 Heated 2X:

Table 49: Quantified aromatics in 111005 Dr- 1 heated 2X in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 3.020	729611	7.2
Benzene	72 , 3.070	535404.3	0.7
Toluene- d8	184 , 5.310	1225945	7.2
Toluene	192 , 5.220	3311649	10.8
Ethylbenzne- d8	328 , 4.290	144501	7.2
Ethylbenzene	328 , 4.480	590791	11.5
Styrene	368 , 4.960	4779006	18.6
Cumene	408 , 4.100	184475.3	1.4
à-Methylstyrene	472 , 4.580	421419	2.5
Naphthalene- d8	656 , 6.210	230253	7.2

Set 2:

Calibration and quantitation of aromatic compounds(2D):

Another set of calibration standards was freshly made on a different day and the qualitative, quantitative analysis of the gasoline, diesel and distillation standard D86 was determined to check the reproducibility of the results. The compound mass, retention time, equation of the line and the correlation coefficient of each of the calibrated compounds are shown in the table. Benzene- d6 was used as an internal standard for benzene, toluene- d8 was used as an internal standard for toluene and ethylbenzene d8 was used as an internal standard for ethylbenzene, styrene, cumene and à-Methylstyrene.

Table 50: Equation of Line and Correlation Coefficient for aromatic compounds

Compound	Mass	Retention Time(sec)	Equation of Line	Correlation Coefficient
Benzene	78	72, 3.030	Y= + 0.967116x - 0.0333183	0.99966
Toluene	92	192, 5.15	Y= + 0.280284x - 0.0195039	0.99970
Ethylbenzene	106	328, 4.45	Y= + 1.94329x + 0.582849	0.99057
Styrene	104	368, 4.86	Y= + 3.54404x + 1.04438	0.99295
Cumene	120	408, 4.08	Y= + 1.47025x + 0.262839	0.99209
à-Methylstyrene	118	472, 4.540	Y= + 1.96333x + 0.0729557	0.99447

The limit of detection or the detection limit (LOD) is the lowest quantity of a compound that can be distinguished from the absence of that compound. The calculation method is again based on the slope and the intercept of the calibration curve.

Table 51: Limit of detection for aromatics in mass percent

Compound	Limit of Detection (Mass Percent)
Benzene	0.03
Toluene	0.006
Ethylbenzene	0.2
Styrene	0.5
Cumene	0.2
Metstyrene	0.2

All the samples were qualitatively determined and then quantified using their respective calibration curves. The retention time, quant mass, area and mass percent of the aromaticcompounds in different grades of gasoline, diesel and distillation standard D86 are tabulated below.

Distillation standard D 86:

The quantified distillation standard D 86 contains only toluene and cumene in 31.8 and 12.6 mass % respectively of the six aromatic compounds.

Table 52: Quantified aromatics in distillation standard D 86 in mass percent

Compound	Retention Time (sec)	Area	Mass percent
Benzene- d6	72 , 2.950	320209	7.4
Toluene- d8	184 , 5.300	535097.3	7.4
Toluene	192 , 5.270	4541254	31.8
Ethylbenzene- d8	328 , 4.260	36677	7.4
Cumene	408 , 4.130	578080.7	12.6
Naphthalene-D8	656 , 6.180	67981.67	7.4

Gasoline samples:

Different grades of gasoline like regular and super were collected from different places on different days. These gasoline samples were characterized and was quantified against standard calibration that contains six aromatic compounds to check the reproducibility of the method. All the aromatic compounds in the gasoline samples were listed below in mass percent.

Gasoline super (130611):

Table 53: Quantified aromatics in gasoline super (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.970	459747.7	7.4
Benzene	72 , 3.020	112774.3	0.3
Toluene- d8	184 , 5.320	781793.7	7.4
Toluene	192 , 5.220	2348810	11.3
Ethylbenzne- d8	328 , 4.270	52089.33	7.4
Ethylbenzene	328 , 4.450	113881.7	1.5
Cumene	408 , 4.090	22932.67	0.5
Naphthalene- d8	656 , 6.190	108671.3	7.4

Gasoline regular (130611):

Table 54: Quantified aromatics in gasoline regular (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 3.020	452644.3	7.4
Benzene	72 , 3.080	450617.7	1.0
Toluene- d8	184 , 5.310	755981	7.4
Toluene	192 , 5.190	1198146	6.0
Ethylbenzne- d8	328 , 4.280	57543.67	7.4
Ethylbenzene	328 , 4.470	98849	1.3
Cumene	408 , 4.090	10954.33	0.4
Naphthalene- d8	656 , 6.210	95261	7.4

Gasoline regular (130522):

Table 55: Quantified aromatics in gasoline regular (130522) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 3.010	435055.3	7.4
Benzene	72 , 3.060	205395.3	0.5
Toluene- d8	184 , 5.320	727211.7	7.4
Toluene	192 , 5.190	850162	4.4
Ethylbenzne- d8	328 , 4.300	60527.33	7.4
Ethylbenzene	328 , 4.480	65365.67	1.0
Cumene	408 , 4.110	9927.2	0.3
Naphthalene- d8	656 , 6.230	100574.7	7.4

Gasoline regular (130505):

Table 56: Quantified aromatics in gasoline regular (130505) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 3.000	456770	7.4
Benzene	72 , 3.060	146634	0.3
Toluene- d8	184 , 5.320	759108.7	7.4
Toluene	192 , 5.180	740321.7	3.7
Ethylbenzne- d8	328 , 4.300	63669.33	7.4
Ethylbenzene	328 , 4.480	70471.67	1.0
Cumene	408 , 4.110	13124.67	0.4
Naphthalene- d8	656 , 6.230	102470.3	7.4

Diesel samples:

Diesel samples were collected from different places on different days. These samples were characterized and was quantified against standard calibration that contains six aromatic compounds to check the reproducibility of the method. All the aromatic compounds in the diesel samples were listed below in mass percent. Diesel samples collected on 130611, 130505 do not contain the six aromatic compounds present in the set of calibration standards. The qualitative determination of the diesel samples had many decane derivatives in it.

Diesel marathon (130611):

Table 57: Quantified aromatics in diesel marathon (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.990	279305	7.4
Toluene- d8	184 , 5.300	415569.7	7.4
Toluene	192 , 5.140	7919.433	0.1
Ethylbenzne- d8	328 , 4.300	40990.67	7.4
Ethylbenzene	328 , 4.480	1080.83	03
Naphthalene-D8	656 , 6.260	62841.33	7.4

Diesel pilot (130611):

Table 58: Quantified aromatics in diesel pilot (130611) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 3.000	99649.67	7.4
Toluene- d8	184 , 5.310	148316.7	7.4
Toluene	192 , 5.140	1782.267	0.1
Ethylbenzne- d8	328 , 4.310	14305.67	7.4
Ethylbenzene	328 , 4.500	372.5333	0.3
Naphthalene- d8	656 , 6.280	22801.33	7.4

Diesel (130505):

Table 59: Quantified aromatics in diesel (130505) in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.970	317896	7.4
Toluene- d8	184 , 5.330	473785	7.4
Toluene	192 , 5.140	6155.8	0.1
Ethylbenzne- d8	328 , 4.310	45777	7.4
Ethylbenzene	328 , 4.520	1045.18	0.3
Naphthalene- d8	656 , 6.300	71670	7.4

Polyflow samples:

The end product generated by the RES Polyflow process is pygas from which diesel fuel, octane enhancers and gasoline blend stocks are produced. The pygas samples were collected from the reactor at different days and at different times and are named according to them.

130417 Post scrub:

Table 60: Quantified aromatics in 130417 post scrub in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72 , 3.070	644083	7.4
Benzene	72 , 3.120	853477.7	1.4
Toluene- d8	184 , 5.370	1096559	7.4
Toluene	192 , 5.270	2555852	8.8
Ethylbenzne- d8	328 , 4.340	95402.67	7.4
Ethylbenzene	328 , 4.530	319523.7	2.7
Styrene	368 , 4.920	981317.7	4.6
Cumene	408 , 4.140	9830.4	0.3
à-Methylstyrene	472 , 4.630	24066.67	0.5
Naphthalene- d8	656 , 6.360	108790	7.4

130313 Post scrub:

Table 61: Quantified aromatics in 130313 post scrub in mass percent

Compound	Retention Time (sec)	Area	Mass Percent
Benzene- d6	72 , 3.090	511712.7	7.4
Benzene	72 , 3.140	1655737	3.4
Toluene- d8	184 , 5.360	866180	7.4
Toluene	192 , 5.220	1001862	4.3
Ethylbenzne- d8	328 , 4.340	72040	7.4
Ethylbenzene	328 , 4.530	76379.33	1.0
Styrene	368 , 4.900	217621.7	1.6
Cumene	408 , 4.140	2748.4	0.2
à-Methylstyrene	472 , 4.630	4520.3	0.3
Naphthalene- d8	656 , 6.360	77445.6	7.4

130313 Pyrogas scrub:

Table 62: Quantified aromatics in 130313 pyrogas scrub in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 3.060	682718.7	7.4
Benzene	72 , 3.110	862174	1.33
Toluene- d8	184 , 5.370	1146006	7.4
Toluene	192 , 5.220	899509	2.97
Ethylbenzne- d8	328 , 4.350	62110.33	7.4
Ethylbenzene	328 , 4.540	226514.3	1.91
Styrene	368 , 4.910	484289	2.39
Cumene	408 , 4.160	16829.33	0.36
à-Methylstyrene	472 , 4.650	30904.33	0.49
Naphthalene- d8	656 , 6.400	119236	7.4

Hydro treated gasoline fraction:

Table 63: Quantified aromatics in hydro treated gasoline fraction in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.940	628202.3	7.4
Benzene	72 , 2.990	436037.3	0.7
Toluene- d8	184 , 5.320	1131187	7.4
Toluene	192 , 5.220	2635501	8.8
Ethylbenzne- d8	328 , 4.260	69066	7.4
Ethylbenzene	328 , 4.510	1433116	10.9
Styrene	368 , 4.940	4129093	17.8
Cumene	408 , 4.090	148100.3	1.7
à-Methylstyrene	472 , 4.570	342562	3.0
Naphthalene- d8	656 , 6.180	197075.3	7.4

111005 Dr- 1 heated 2X:

Table 64: Quantified aromatics in 111005 Dr- 1 heated 2X in mass percent

Compound	Retention Time(sec)	Area	Mass Percent
Benzene- d6	72 , 2.940	542792.3	7.4
Benzene	72 , 3.000	394880.7	0.8
Toluene- d8	184 , 5.320	963692.3	7.4
Toluene	192 , 5.210	2404326	9.4
Ethylbenzne- d8	328 , 4.270	65472.67	7.4
Ethylbenzene	328 , 4.500	1308891	11.7
Styrene	368 , 4.920	3673365	18.5
Cumene	408 , 4.080	131314.3	1.8
à-Methylstyrene	472 , 4.560	290748.7	3.0
Naphthalene- d8	656 , 6.180	157398.3	7.4

Following is a summary of the tabular data for quantified aromatic compounds in the distillation standard, gasoline, diesel fuel and pygas samples by two dimensional gas chromatoraphy. The concentrations are given in mass percent.

Set 1 (2D):

Table 65: 2D data for samples in mass percent

Compound	Distillation standard	Gasoline Super(130611)	Regular (130611)	Regular 130522	Regular 130505	Diesel Marathon (130611)	Diesel Pilot (130611)
Benzene	0	0.3	1.0	0.5	0.3	0	0
Toluene	31.8	11.3	6.0	4.4	3.7	0	0
Ethylbenzene	0	1.5	1.3	1	1.0	0	0
Styrene	0	0	0	0	0	0	0
Cumene	12.6	0.5	0.4	0.3	0.4	0	0
α- methyl styrene	0	0	0	0	0	0	0

	Diesel (130505)	130417 Post Scrub	130313 Post Scrub	130313 Pyrogas Scrub	Hydro Treated Gasoline Fraction	111005 Dr- 1 Heated 2X
Benzene	0	1.4	3.4	1.3	0.7	0.8
Toluene	0	8.8	4.4	3.0	8.7	9.4
Ethylbenzene	0	2.7	1.0	1.9	10.9	11.7
Styrene	0	4.6	1.6	2.4	17.8	18.5
Cumene	0	0.3	0.2	0.4	1.7	1.8
α- methyl styrene	0	0.4	0.3	0.5	3.0	3.0

Set 2 (2D):

Table 66: 2D data for samples in mass percent

Compound	Distillation standard	Gasoline Super(130611)	Regular (130611)	Regular 130522	Regular 130505	Diesel Marathon (130611)	Diesel Pilot (130611)
Benzene	0	0.3	1.1	0.4	0.3	0	0
Toluene	29.0	11.8	6.7	4.4	3.4	0	0
Ethylbenzene	1.6	1.2	1.3	0.9	1.0	0	0
Styrene	0	0	0	0	0	0	0
Cumene	11.7	0.5	0.4	0.3	0.6	0	0
α- methyl styrene	0	0	0	0	0	0	0

Compound	Diesel (130505)	130417 Post Scrub	130313 Post Scrub	130313 Pyrogas Scrub	Hydro Treated Gasoline Fraction	111005 Dr- 1 Heated 2X
Benzene	0	1.2	3.3	1.3	0.6	0.6
Toluene	0	8.6	4.6	3.3	9.7	10.8
Ethylbenzene	0	2.1	1.0	1.6	10.8	11.5
Styrene	0	3.6	1.6	2.0	12.8	18.6
Cumene	0	0.4	0.3	0.5	1.2	1.4
α- methyl styrene	0	0.5	0.4	0.6	2.2	2.4

Following is a summary of the tabular data for quantified aromatic compounds in the distillation standard, gasoline, diesel fuel and pugas samples by one dimensional gas chromatoraphy. The concentrations are given in mass percent.

Table 67: 1D data for sample in mass percent

Compound	Distillation standard	Gasoline Super(130611)	Regular (130611)	Regular 130522	Regular 130505	Diesel Marathon (130611)	Diesel Pilot (130611)
Benzene	0	0.2	1.0	0.4	0.3	0	0
Toluene	32.8	12.0	6.5	4.5	4.1	0	0
Ethylbenzene	0	1.2	1.4	1.0	1.2	0	0
Styrene	0	0	0	0	0	0	0
Cumene	13.4	0.6	0.4	0.4	0.4	0	0
α- methyl styrene	0	0	0	0	0	0	0

Compound	Diesel (130505)	130417 Post Scrub	130313 Post Scrub	130313 Pyrogas Scrub	Hydro Treated Gasoline Fraction	111005 Dr- 1 Heated 2X
Benzene	0	1.2	3.0	1.2	0.6	0.7
Toluene	0	7.7	4.1	2.9	8.8	9.6
Ethylbenzene	0	2.4	0.9	1.5	10.7	12.0
Styrene	0	3.5	1.3	1.9	16.9	19.1
Cumene	0	0.3	0	0.4	1.4	1.7
α- methyl styrene	0	0.5	0	0.5	2.5	2.8

Table 68: 1D data for all samples in mass percent

Compound	Distillation standard	Gasoline Super(130611)	Regular (130611)	Regular (130522)	Regular (130505)	Diesel Marathon (130611)	Diesel Pilot (130611)
Benzene	0	0.3	1.0	0.5	0.3	0	0
Toluene	32.3	10.9	5.8	4.2	3.5	0	0
Ethylbenzene	0	1.1	1.3	0.9	1.1	0	0
Styrene	0	0	0	0	0	0	0
Cumene	13.1	0.6	0.5	0.4	0.5	0	0
α- methyl styrene	0	0	0	0	0	0	0

	Diesel (130505)	130417 Post Scrub	130313 Post Scrub	130313 Pyrogas Scrub	Hydro Treated Gasoline Fraction	111005 Dr- 1 Heated 2X
Benzene	0	1.4	3.0	1.3	0.7	0.7
Toluene	0	8.4	4.2	2.9	8.6	9.3
Ethylbenzene	0	2.6	0.9	1.5	10.5	11.5
Styrene	0	4.1	1.5	2.0	17.0	18.5
Cumene	0	0.42	0	0.43	1.47	1.58
Metstyrene	0	0.5	0	0.5	2.5	2.7

4.1.3 Qualitative characterization and quantitation of gasoline, diesel fuel and pygas samples

The chromaTOF deconvolution software package processes the data and gives a complete sample assay which has peak table, hit table, mass spectra of each ion, a 3D image and total ion chromatogram of each sample. In other words, qualitative characterization of the sample and quantitative data for specific analyte of interest are provided by the software.

Gasoline Super (130611):

The complete characterization of gasoline regular was shown with their peak table, total ion chromatogram, 3D image. Peak table shows all the compounds that are present in the Gasoline regular which is a qualitative determination. Each compound in the

sample was given with their type, retention time, quant mass, concentration, area and quantitation.

Table 69: Peak table of gasoline super (130611)

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Styrene/20130716 2d	Not Found		104	-	-
à-Methylstyrene/20130716 2d	Not Found		118	-	-
Benzene-D6	Quantified	72 , 2.910	84+83	7.2	1123589
Benzene	Quantified	72 , 2.960	78	0.16	312011
Toluene-D8	Quantified	184 , 5.300	100+99	7.2	1968065
Toluene	Quantified	192 , 5.230	92	11.35	5571729
1,4-Di(methyl-d3)benzene-d4	Quantified	320 , 4.480	116+115	7.2	20973
1,4-Di(methyl-d3)benzene-d4:2	Quantified	328 , 4.240	116+115	7.2	161050
Ethylbenzene	Quantified	328 , 4.420	106	1.23	249666
Ethylbenzene:2	Quantified	336 , 4.290	106	4.21	72249
Benzene, (1-methylethyl)-	Quantified	408 , 4.050	120	0.44	61391
Naphthalene-D8	Quantified	656 , 6.140	136+135	7.2	275127
Acetone	Unknown	16 , 3.570	50	-	58945
Butane, 1-chloro-2-methyl-	Unknown	16 , 3.990	57	-	39502
Butane, 2-methyl-	Unknown	24 , 1.160	57	-	1450108
Ethanol	Unknown	24 , 1.390	45	-	3110400
Butane, 2,2-dimethyl-	Unknown	32 , 1.190	72	-	46848
Pentane, 2-methyl-	Unknown	32 , 1.250	55	-	463256

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Butane, 2,3-dimethyl-	Unknown	40 , 1.330	71	-	775030
1-Hexene, 4-methyl-	Unknown	40 , 1.380	56	-	974144
n-Hexane	Unknown	48 , 1.430	57	-	523883
2-Hexene, (Z)-	Unknown	48 , 1.500	55	-	142235
2-Pentene, 4-methyl-	Unknown	48 , 1.560	69	-	79144
Pentane, 2,4-dimethyl-	Unknown	56 , 1.520	57	-	1717663
Cyclopentane, methyl-	Unknown	56 , 1.680	69	-	282686
Unknown 1	Unknown	72 , 1.660	71	-	21069
Cyclohexane	Unknown	72 , 2.030	56	-	116130
Pentane, 2,3-dimethyl-	Unknown	80 , 1.800	56	-	2766959
3-Hexene, 2-methyl-, (E)-	Unknown	88 , 2.010	69	-	91921
Pentane, 2,2,4-trimethyl-	Unknown	96 , 1.840	57	-	15090043
Heptane, 3-methylene-	Unknown	96 , 2.080	70	-	76313
Heptane	Unknown	104 , 2.030	57	-	146036
Unknown 2	Unknown	104 , 2.490	81	-	20918
3-Hexene, 3-methyl-, (E)-	Unknown	112 , 2.340	69	-	34475
2-Butyn-1-ol	Unknown	120 , 2.500	69	-	29415
Cyclohexane, methyl-	Unknown	120 , 2.600	55	-	155424
Azetidine	Unknown	128 , 2.140	57	-	48514
Hexane, 2,4-dimethyl-	Unknown	144 , 2.300	57	-	1890691
Pentane, 2,3,4-trimethyl-	Unknown	160 , 2.650	71	-	1660565

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Heptane, 2,2,3,3,5,6,6-heptamethyl-	Unknown	160 , 2.810	84	-	13909
Pentane, 2,3,3-trimethyl-	Unknown	168 , 2.700	70	-	655643
Hexane, 2,3-dimethyl-	Unknown	184 , 2.610	70	-	590264
Unknown 3	Unknown	184 , 2.650	69	-	25705
Heptane, 2-methyl-	Unknown	192 , 2.590	57	-	172602
Unknown 4	Unknown	192 , 2.660	56	-	47773
Toluene-D8	Unknown	192 , 4.910	98	-	46493
Heptane, 2-methyl-	Unknown	200 , 2.450	57	-	256993
2(3H)-Furanone, dihydro-5-methyl-	Unknown	200 , 2.530	56	-	170883
Heptane, 3-methyl-	Unknown	208 , 2.480	57	-	261839
Cyclohexane, 1,3-dimethyl-, cis-	Unknown	208 , 2.820	97	-	15379
Hexane, 2,2,4-trimethyl-	Unknown	224 , 2.310	57	-	1146625
Cyclopentane, 1-ethyl-3-methyl-	Unknown	232 , 2.750	55	-	67462
Octane	Unknown	248 , 2.450	57	-	146230
3-Ethyl-2-hexene	Unknown	256 , 2.690	83	-	12943
Hexane, 2,3,5-trimethyl-	Unknown	272 , 2.320	85	-	56676
Heptane, 2,2-dimethyl-	Unknown	280 , 2.270	57	-	45070
Heptane, 2,6-dimethyl-	Unknown	296 , 2.240	57	-	61067
Heptane, 2,5-dimethyl-	Unknown	304 , 2.280	57	-	216298
4-Nonene, 3-methyl-, (Z)-	Unknown	312 , 2.540	55	-	25330
Unknown 5	Unknown	328 , 2.360	84	-	17362

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Heptane, 3,4-dimethyl-	Unknown	328 , 2.390	57	-	68318
Decane, 5-methyl-	Unknown	336 , 2.310	57	-	34137
Unknown 6	Unknown	336 , 4.330	105	-	21940
Octane, 2-methyl-	Unknown	344 , 2.280	71	-	68484
o-Xylene	Unknown	344 , 4.130	91	-	2981637
Pentane, 3-ethyl-3-methyl-	Unknown	352 , 2.230	85	-	22499
Octane, 3-methyl-	Unknown	352 , 2.290	57	-	1053920
Cyclopentane, 1-methyl-2-propyl-	Unknown	360 , 2.620	55	-	26925
o-Xylene	Unknown	368 , 4.400	91	-	1254075
Heptane, 3,3,5-trimethyl-	Unknown	376 , 2.290	71	-	133849
Nonane	Unknown	384 , 2.320	57	-	115050
Heptane, 2,3,6-trimethyl-	Unknown	400 , 2.300	57	-	227302
2-Pyrrolidinone	Unknown	408 , 2.230	85	-	8785.7
Decane, 2,5,9-trimethyl-	Unknown	416 , 2.230	57	-	68279
Octane, 3,6-dimethyl-	Unknown	424 , 2.270	57	-	39934
Heptane, 2,5-dimethyl-	Unknown	432 , 2.280	57	-	15846
Benzene, propyl-	Unknown	440 , 4.000	91	-	350720
2,2,7,7-Tetramethyloctane	Unknown	448 , 2.280	57	-	614952
Benzene, 1-ethyl-2-methyl-	Unknown	448 , 4.060	105	-	1090053
Benzene, 1,2,3-trimethyl-	Unknown	456 , 3.930	105	-	317954
Heptane, 2,2,4,6,6-pentamethyl-	Unknown	464 , 2.300	57	-	481318

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Benzene, 1-ethyl-2-methyl-	Unknown	464 , 4.320	105	-	163376
Nonane, 2,6-dimethyl-	Unknown	480 , 2.390	57	-	156930
Benzene, 1,2,3-trimethyl-	Unknown	480 , 4.130	105	-	1271155
Benzene, (2-methylpropyl)-	Unknown	496 , 3.800	91	-	36000
Benzene acetaldehyde, à-methyl-	Unknown	496 , 3.980	105	-	28762
o-Cymene	Unknown	512 , 3.900	119	-	53920
Benzene, 1,2,3-trimethyl-	Unknown	512 , 4.330	105	-	259351
Azetidine	Unknown	520 , 2.230	57	-	356060
Pentane, 3,3-dimethyl-	Unknown	520 , 2.390	71	-	52894
Benzene, 2-propenyl-	Unknown	520 , 4.940	117	-	67219
Decane, 2,5,9-trimethyl-	Unknown	528 , 2.320	57	-	41876
Benzene, 1,4-diethyl-	Unknown	536 , 4.070	105	-	36019
Pentane, 3-ethyl-2,2-dimethyl-	Unknown	544 , 2.400	57	-	241953
Benzene, 1-methyl-4-propyl-	Unknown	544 , 3.860	105	-	294176
Benzene, butyl-	Unknown	544 , 3.930	91	-	122867
Benzene, 1-methyl-3-(1-methylethyl)-	Unknown	544 , 4.030	119	-	47554
o-Cymene	Unknown	552 , 3.860	119	-	95006
Benzene, 1-methyl-4-propyl-	Unknown	552 , 4.130	105	-	92846
Methane, isocyanato-	Unknown	560 , 2.350	57	-	48435
Hexane, 3,3,4,4-tetramethyl-	Unknown	560 , 2.430	71	-	26721
Pentane, 2,2,3,4-tetramethyl-	Unknown	568 , 2.360	57	-	53158

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Benzene, 1-methyl-3-(1-methylethyl)-	Unknown	568 , 4.040	119	-	196393
Undecane, 4-methyl-	Unknown	576 , 2.420	57	-	22000
Benzene, 1-methyl-3-(1-methylethyl)-	Unknown	576 , 4.050	119	-	121426
Benzene, 1-ethenyl-4-ethyl-	Unknown	576 , 4.520	117	-	9480.5
Undecane, 4-methyl-	Unknown	584 , 2.430	57	-	30784
Benzene, 1-methyl-4-butyl	Unknown	592 , 3.780	105	-	21592
Benzene, (1,1-dimethylpropyl)-	Unknown	592 , 3.840	119	-	15738
Benzene, 2-ethyl-1,4-dimethyl-	Unknown	592 , 4.370	119	-	30517
o-Cymene	Unknown	600 , 4.190	117	-	12632
Heptane, 4-ethyl-2,2,6,6-tetramethyl-	Unknown	608 , 2.320	57	-	77778
2,2,7,7-Tetramethyloctane	Unknown	616 , 2.340	57	-	14315
Indan, 1-methyl-	Unknown	616 , 4.830	117	-	12978
Hexadecane	Unknown	624 , 2.380	57	-	9680.4
Benzene, (1,1-dimethylpropyl)-	Unknown	632 , 3.820	119	-	40433
Benzenepropanal, á-methyl-	Unknown	632 , 3.940	105	-	28642
Benzene, 1-methyl-3-(1-methylethyl)-	Unknown	632 , 4.500	119	-	30861
1H-Indene, 2,3-dihydro-4-methyl-	Unknown	632 , 4.820	117	-	33475
Benzene, (1,1-dimethylpropyl)-	Unknown	640 , 4.000	119	-	37065
Octane, 2,6-dimethyl-	Unknown	648 , 2.330	57	-	85000
Benzene, (1-methylbutyl)-	Unknown	648 , 4.010	105	-	10578
Benzene, 1-methyl-4-(1-methylpropyl)-	Unknown	656 , 4.030	119	-	24921

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Azulene	Unknown	656 , 6.250	128	-	92586
Benzene, 1,4-diethyl-2-methyl-	Unknown	672 , 4.270	133	-	19659
Octane, 2,4,6-trimethyl-	Unknown	680 , 2.430	57	-	14205
Decane, 2,2,7-trimethyl-	Unknown	696 , 2.390	57	-	29108
Decane, 2,5,9-trimethyl-	Unknown	728 , 2.280	57	-	10016
Naphthalene, 2-methyl-	Unknown	744 , 4.740	142	-	9397.5
1H-Indene, 1-ethylidene-	Unknown	752 , 4.330	142	-	16363
1H-Indene, 1-ethylidene-	Unknown	760 , 4.440	142	-	16091

The hit table shows the possibility of all the compounds that are present with a given mass to charge ratio and at a particular retention time. Each compound was given with their similarity, type of library, ID of that compound, formula, molar mass and the contributor of the reference data.

Table 70: Hit table of benzene in gasoline regular (130611)

Name	Similarity	Library	Id	Formula	Weight	Contributor
Benzene	954	mainlib	43787	C6H6	78	NIST Mass Spectrometry Data Center, 1990.
Benzene	923	mainlib	43787	C6H6	78	NIST Mass Spectrometry Data Center, 1990.
Benzene	923	replib	10366	C6H6	78	Chemical Concepts
Benzene	915	replib	10364	C6H6	78	
Benzene	906	replib	10367	C6H6	78	Japan AIST/NIMC Database-Spectrum MS-NW- 75
1,5-Hexadien-3-yne	897	mainlib	43770	C6H6	78	
1,5-Hexadiyne	892	replib	699	C6H6	78	
1,5-Hexadiyne	883	mainlib	1692	C6H6	78	Japan AIST/NIMC Database-Spectrum MS-NW-4647
2,4-Hexadiyne	860	mainlib	43743	C6H6	78	
2,4-Hexadiyne	853	replib	10356	C6H6	78	NIST Mass Spectrometry Data Center, 1990.
2,4-Hexadiyne	851	replib	10357	C6H6	78	Chemical Concepts

The spectra compare the peak true spectra (compound spectra) with that of reference spectra before it assigns a particular chemical name to the compound. The spectrum of benzene is shown in the figure 22.

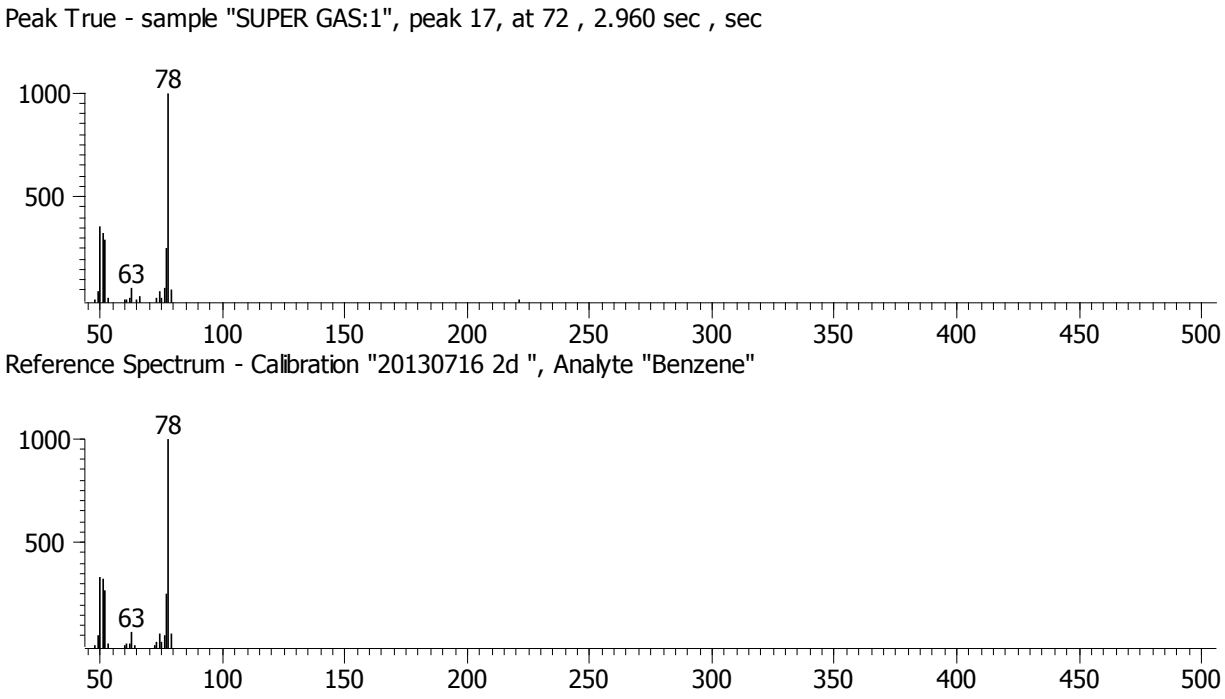

Figure 22: Spectra of benzene in gasoline regular (130611)

The 3D image of the Gasoline super is shown in the figure 23. The x- axis represents the time on primary column and y- axis represents the retention time on secondary column.

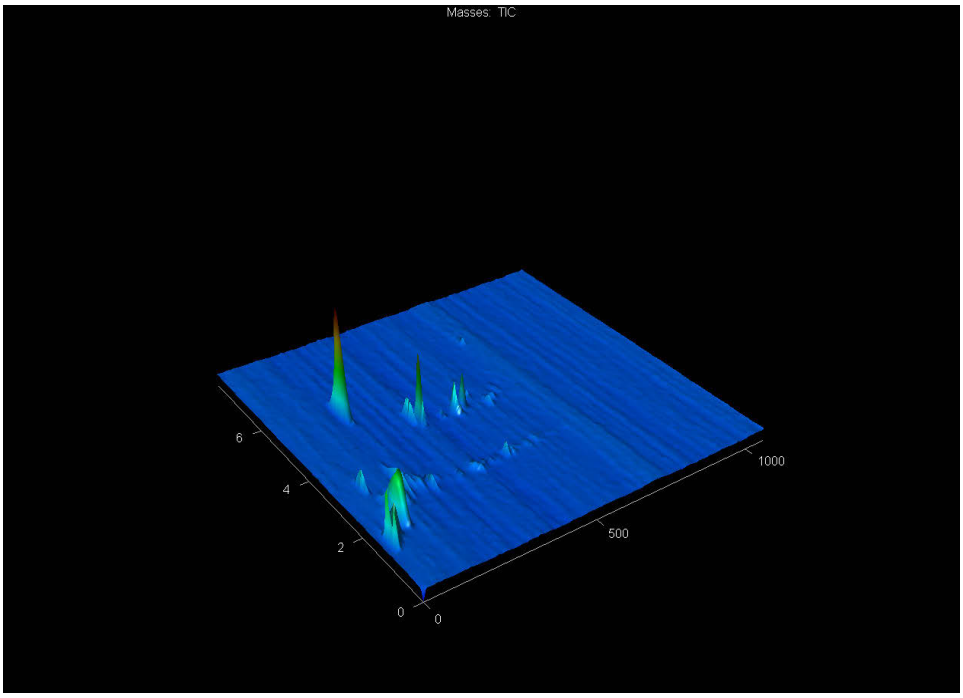

Figure 23: 3D Image of gasoline super (130611)

The total Ion chromatogram of the gasoline regular was shown in the figure 24. Each peak in the chromatogram represents a compound. The x- axis in the chromatogram represents the retention time and y- axis represents the intensity.

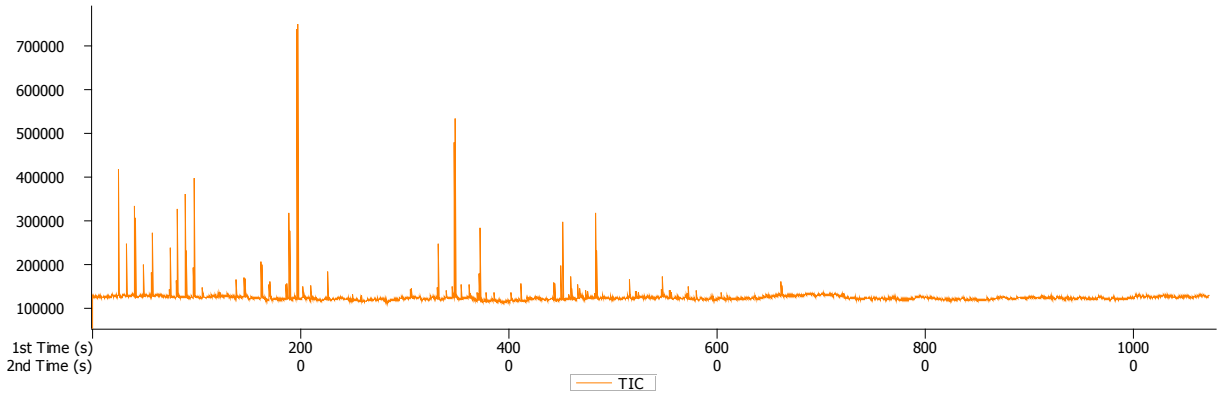

Figure 24: Total ion chromatogram of gasoline super (130611)

Diesel pilot (130611):

The complete characterization of diesel pilot is shown with their peak table, total ion chromatogram, 3D image. The peak table shows all the compounds that are present in the diesel pilot which is a qualitative determination. Each compound in the sample is given with their type, retention time, quant mass, concentration, area and quantitation.

Table 71: Peak table of diesel pilot (130611)

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Benzene/20130716 2d	Not Found		78	-	-
1,4-Di(methyl-d3)benzene-d4/20130716 2d	Not Found		116+115	-	-
Styrene/20130716 2d	Not Found		104	-	-
Benzene, (1-methylethyl)-/20130716 2d	Not Found		120	-	-
à-Methylstyrene/20130716 2d	Not Found		118	-	-
Benzene-D6	Quantified	72 , 2.940	84+83	7.2	296383
Toluene-D8	Quantified	184 , 5.240	100+99	7.2	410644
Toluene	Quantified	192 , 5.080	92	-0.07	5881.9
1,4-Di(methyl-d3)benzene-d4:2	Quantified	328 , 4.240	116+115	7.2	44817
Ethylbenzene	Quantified	328 , 4.430	106	-0.06	1773.7
Ethylbenzene:2	Quantified	336 , 4.200	106	0.47	994.02
Naphthalene-D8	Quantified	656 , 6.140	136+135	7.2	70503
Toluene-D8	Unknown	192 , 4.900	98	-	106039
Cyclohexane, 1,3-dimethyl-	Unknown	208 , 2.810	55	-	16615
Cyclohexane, ethyl-	Unknown	288 , 2.930	55	-	15445

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Octane, 2-methyl-	Unknown	344 , 2.260	57	-	14403
o-Xylene	Unknown	344 , 4.080	91	-	28285
Octane, 3-methyl-	Unknown	352 , 2.290	57	-	23755
1-Ethyl-4-methylcyclohexane	Unknown	360 , 2.690	55	-	32660
p-Xylene	Unknown	368 , 4.360	91	-	11534
Nonane	Unknown	384 , 2.320	57	-	45601
Cyclohexane, 1-ethyl-4-methyl-, cis-	Unknown	384 , 2.800	55	-	16078
Cyclohexane, (1-methylethyl)-	Unknown	408 , 2.840	55	-	20676
Pentane, 2,2,3,3-tetramethyl-	Unknown	416 , 2.250	57	-	27761
Octane, 3,6-dimethyl-	Unknown	424 , 2.260	57	-	22886
Octane, 2,3-dimethyl-	Unknown	432 , 2.310	57	-	12883
Benzene, 1-ethyl-4-methyl-	Unknown	448 , 4.060	105	-	24014
Hexane, 4-ethyl-2-methyl-	Unknown	456 , 2.300	57	-	73688
Cyclohexane, 1-methyl-3-(1-methylethyl)-	Unknown	456 , 2.770	55	-	18685
Nonane, 3-methyl-	Unknown	464 , 2.320	57	-	28740
Cyclohexane, 1-methyl-2-propyl-	Unknown	472 , 2.650	55	-	46066
4-Decene, 4-methyl-, (E)-	Unknown	480 , 2.800	55	-	30906
Benzene, 1,2,3-trimethyl-	Unknown	480 , 4.120	105	-	42606
Decane	Unknown	496 , 2.340	57	-	162025
Decane, 2,6,7-trimethyl-	Unknown	512 , 2.330	57	-	61185
Cyclohexane, 1,4-dimethyl-2-octadecyl-	Unknown	520 , 2.620	69	-	56188

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Cyclohexane, butyl-	Unknown	520 , 2.840	83	-	17477
Nonane, 3,7-dimethyl-	Unknown	528 , 2.370	57	-	26534
Cyclohexane, 2-ethyl-1,3-dimethyl-	Unknown	536 , 2.660	55	-	29613
1,1'-Bicyclopentyl	Unknown	536 , 3.420	67	-	14794
Benzene, 1-methyl-4-propyl-	Unknown	544 , 3.870	105	-	25558
Benzene, butyl-	Unknown	544 , 3.940	91	-	10470
Decane, 4-methyl-	Unknown	552 , 2.360	57	-	69580
2,3,4-Trimethyl-hex-3-enal	Unknown	552 , 2.760	69	-	13302
o-Cymene	Unknown	552 , 3.880	119	-	10844
Decane, 3-methyl-	Unknown	560 , 2.390	57	-	44468
Cyclohexane, 1-isopropyl-1-methyl-	Unknown	568 , 2.750	55	-	74720
1,3,8-p-Menthatriene	Unknown	568 , 4.050	119	-	13624
Cyclohexane, 1,4-dimethyl-2-octadecyl-	Unknown	576 , 2.740	69	-	16291
1,3,8-p-Menthatriene	Unknown	576 , 4.070	119	-	10538
1-Nonylcycloheptane	Unknown	584 , 2.810	55	-	23458
Undecane	Unknown	592 , 2.410	69	-	17613
cis-Decalin, 2-syn-methyl-	Unknown	592 , 3.230	67	-	21107
Decane	Unknown	608 , 2.360	57	-	47470
1-Methyldecahydronaphthalene	Unknown	608 , 3.340	67	-	14321
p-Cymene	Unknown	608 , 4.170	119	-	8641.6
Undecane, 2,8-dimethyl-	Unknown	616 , 2.400	57	-	21284

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Cyclohexane, (1-methylethyl)-	Unknown	616 , 2.910	83	-	14246
Cyclooctane, methyl-	Unknown	624 , 2.760	55	-	39679
Indan, 1-methyl-	Unknown	632 , 4.840	117	-	9528.6
Undecane, 4,6-dimethyl-	Unknown	640 , 2.430	57	-	133317
Naphthalene, 1,2,3,4-tetrahydro-	Unknown	640 , 5.220	104	-	14292
Naphthalene, decahydro-1,6-dimethyl-	Unknown	656 , 3.190	81	-	17917
Cyclohexane, 1-methyl-4-(1-methylbutyl)-	Unknown	664 , 2.780	55	-	31066
Cyclohexane, 1-(cyclohexylmethyl)-3-methyl-, cis-	Unknown	672 , 2.900	55	-	20410
Dodecane	Unknown	680 , 2.480	55	-	61244
Naphthalene, 1,2,3,4-tetrahydro-2-methyl-	Unknown	688 , 4.810	104	-	10402
Tridecane	Unknown	696 , 2.460	57	-	19115
Octane, 2,7-dimethyl-	Unknown	704 , 2.470	57	-	14828
(E)-Hex-3-enyl (E)-2-methylbut-2-enoate	Unknown	704 , 3.000	83	-	12234
Cyclopentane, (2-methylpropyl)-	Unknown	712 , 2.840	55	-	20561
Undecane, 2,8-dimethyl-	Unknown	728 , 2.320	57	-	73505
Cyclopentane, 2-isopropyl-1,3-dimethyl-	Unknown	728 , 2.600	69	-	45349
Naphthalene, 1,2,3,4-tetrahydro-5-methyl-	Unknown	728 , 4.510	118	-	9858.8
Dodecane, 4,6-dimethyl-	Unknown	736 , 2.210	57	-	71841
Tridecane	Unknown	752 , 2.170	57	-	77509
Cyclooctane, 1,4-dimethyl-, cis-	Unknown	752 , 2.350	83	-	26658
Tridecane	Unknown	760 , 2.060	57	-	144685

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Naphthalene, 1,2,3,4-tetrahydro-1,1-dimethyl-	Unknown	768 , 3.520	145	-	23536
Cyclopentane, 1-butyl-2-propyl-	Unknown	776 , 2.260	69	-	21688
Cyclohexane, 2-propenyl-	Unknown	776 , 2.320	55	-	44502
Dodecane, 2,7,10-trimethyl-	Unknown	792 , 1.960	57	-	111144
Cyclopentane, 1-methyl-3-(2-methylpropyl)-	Unknown	800 , 2.150	55	-	241198
Naphthalene, 1,2,3,4-tetrahydro-5,7-dimethyl-	Unknown	800 , 3.390	145	-	10970
Tetradecane	Unknown	808 , 1.930	57	-	192030
Undecane, 2,8-dimethyl-	Unknown	832 , 1.880	57	-	108749
Hexadecane	Unknown	840 , 1.940	57	-	146991
Cyclopentane, 1-pentyl-2-propyl-	Unknown	840 , 2.060	83	-	41988
Cyclohexane, 1-methyl-3-propyl-	Unknown	848 , 2.080	55	-	82330
Hexadecane	Unknown	864 , 1.880	57	-	73146
Cyclohexane, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-	Unknown	864 , 2.050	69	-	38317
Hexadecane	Unknown	872 , 1.930	57	-	112472
Cyclooctane, 1,4-dimethyl-, cis-	Unknown	872 , 1.940	55	-	51249
Undecane	Unknown	888 , 1.890	57	-	73067
2,2-Dimethyl-3-heptene trans	Unknown	888 , 2.050	69	-	34368
Cyclohexane, 1-ethyl-1,3-dimethyl-, trans-	Unknown	896 , 2.060	55	-	26836
Hexadecane	Unknown	904 , 1.910	57	-	94114
Cyclohexane, 1,4-dimethyl-2-octadecyl-	Unknown	904 , 1.920	69	-	21755
Cyclohexane, 1-methyl-4-(1-methylbutyl)-	Unknown	912 , 2.050	55	-	23540

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Hexadecane	Unknown	920 , 1.910	57	-	43234
Cyclohexane, 1,1'-(1,2-dimethyl-1,2-ethanediyl)bis-, (R*,R*)-(ñ)-	Unknown	920 , 2.100	55	-	25635
Dodecane, 2-methyl-	Unknown	928 , 1.950	57	-	71307
2-Octene, 4-ethyl-, (E)-	Unknown	928 , 1.960	55	-	28670
Borane, [1,2-bis(1-methylethyl)butyl]bis(1-methylethyl)-	Unknown	936 , 2.070	55	-	64557
Hexadecane	Unknown	944 , 1.930	57	-	17410
Octane, 2,7-dimethyl-	Unknown	952 , 1.980	57	-	49983
Decane, 2,5,9-trimethyl-	Unknown	968 , 1.950	57	-	12453
Hexadecane	Unknown	976 , 2.000	57	-	41443
Sulfurous acid, 2-ethylhexyl isohexyl ester	Unknown	1000 , 2.010	57	-	19049

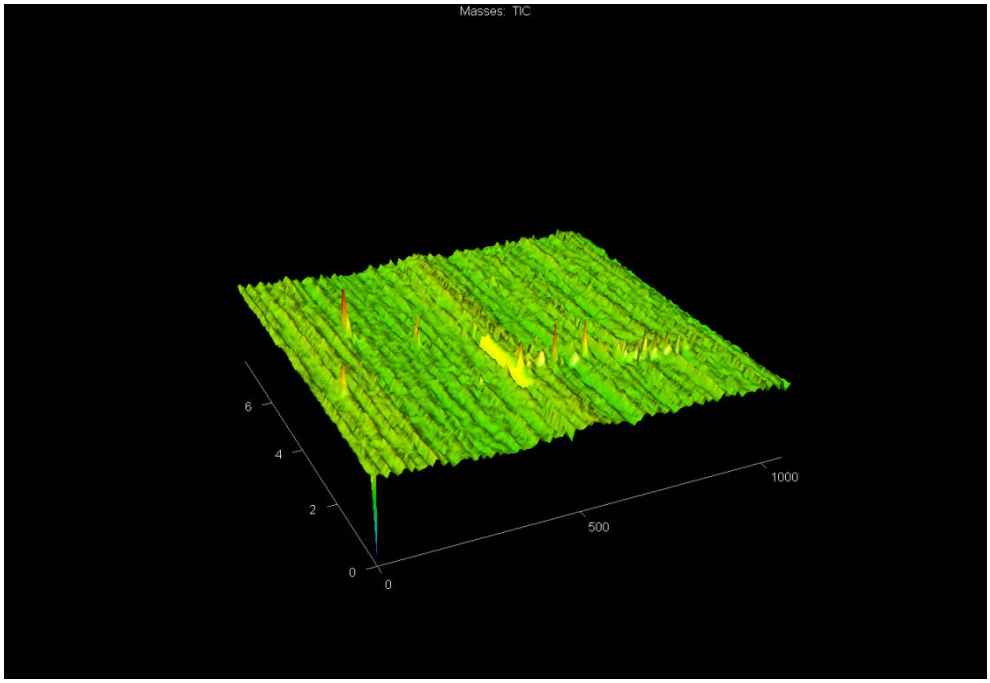

Figure 25: 3D Image of diesel pilot (130611)

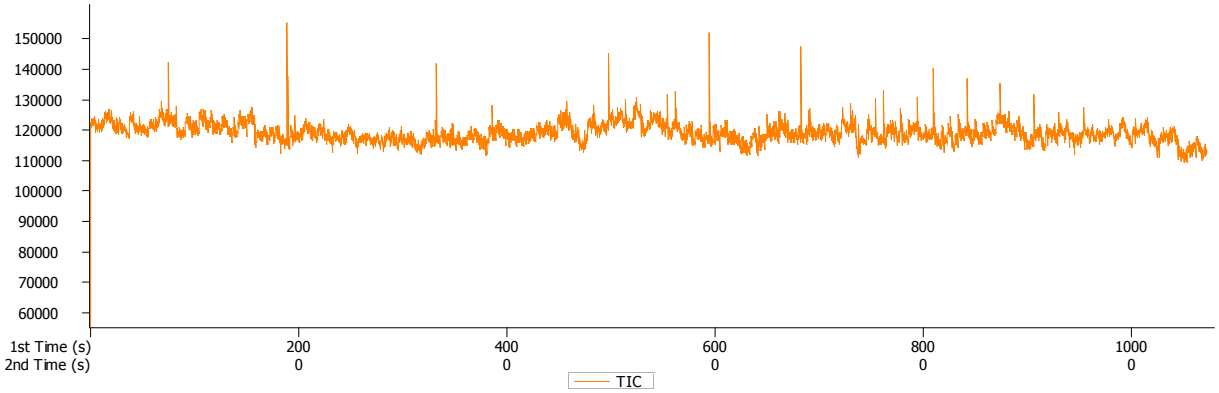

Figure 26: Total ion chromatogram of diesel pilot (130611)

Distillation standard D 86:

The complete characterization of Distillation Standard D 86 is shown with their peak table, total ion chromatogram, and 3D image. The peak table shows all the

compounds that are present in the Distillation Standard D 86 which is a qualitative determination. Each compound in the sample is given with their type, retention time, quant mass, concentration, area and quantitation.

Table 72: Peak table of distillation standard D 86

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Benzene/20130716 2d	Not Found		78		
Ethylbenzene/20130716 2d	Not Found		106		
Styrene/20130716 2d	Not Found		104		
à-Methylstyrene/20130716 2d	Not Found		118		
Benzene-D6	Quantified	72 , 2.920	84+83	7.2	804034
Toluene-D8	Quantified	184 , 5.280	100+99	7.2	1307310
Toluene	Quantified	192 , 5.360	92	28.86	9344674
1,4-Di(methyl-d3)benzene-d4	Quantified	320 , 4.490	116+115	7.2	10724
1,4-Di(methyl-d3)benzene-d4:2	Quantified	328 , 4.230	116+115	7.2	129697
Ethylbenzene:2	Quantified	336 , 4.340	106	1.39	16491
Benzene, (1-methylethyl)-	Quantified	408 , 4.140	120	11.56	1418051
Naphthalene-D8	Quantified	656 , 6.110	136+135	7.2	205554
Dimethyl ether	Unknown	24 , 1.320	45		22633
Pentane	Unknown	24 , 1.590	55		170367
Pentane	Unknown	32 , 1.200	49		2698.4
n-Hexane	Unknown	48 , 1.450	57		1929120
Cyclobutane, ethyl-	Unknown	56 , 1.690	56		11941

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Cyclohexane	Unknown	72 , 2.110	56		7505338
Methane, isocyanato-	Unknown	96 , 1.790	57		228750
Heptane	Unknown	104 , 2.110	71		2674657
Toluene-D8	Unknown	192 , 4.930	98		215397
Toluene	Unknown	200 , 4.830	91		1348690
o-Xylene	Unknown	344 , 4.160	91		4459654
o-Xylene	Unknown	368 , 4.420	91		2409482
Naphthalene, decahydro-, trans-	Unknown	536 , 3.470	67		1655249
Spiro[4.5]decane	Unknown	576 , 3.800	67		1207418
Spiro[4.5]decane	Unknown	584 , 3.620	67		63764

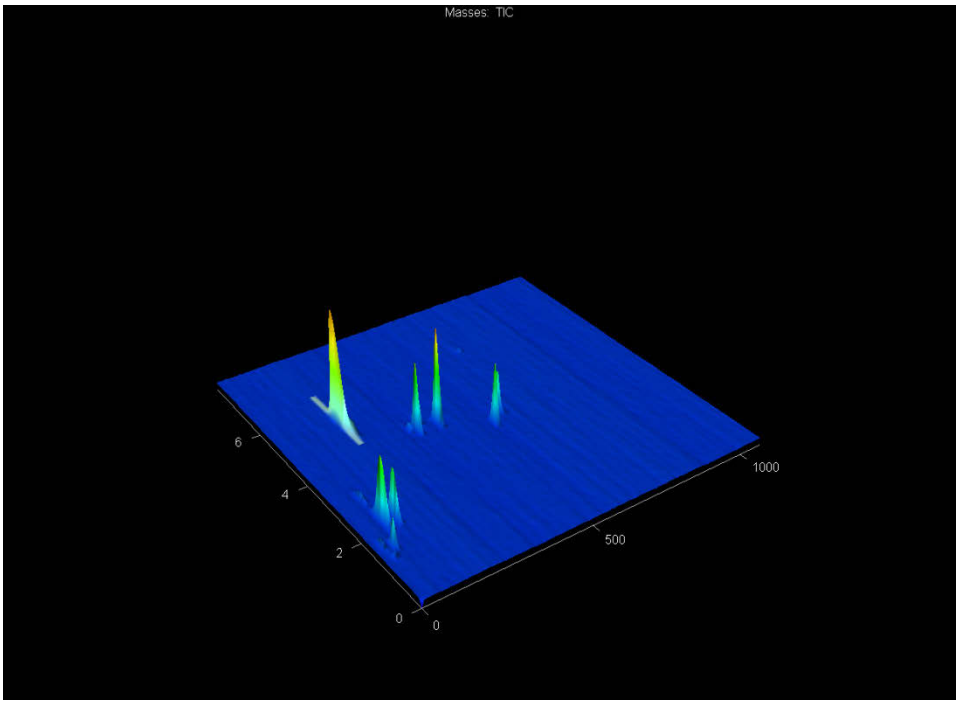

Figure 27: 3D Image of distillation standard D 86

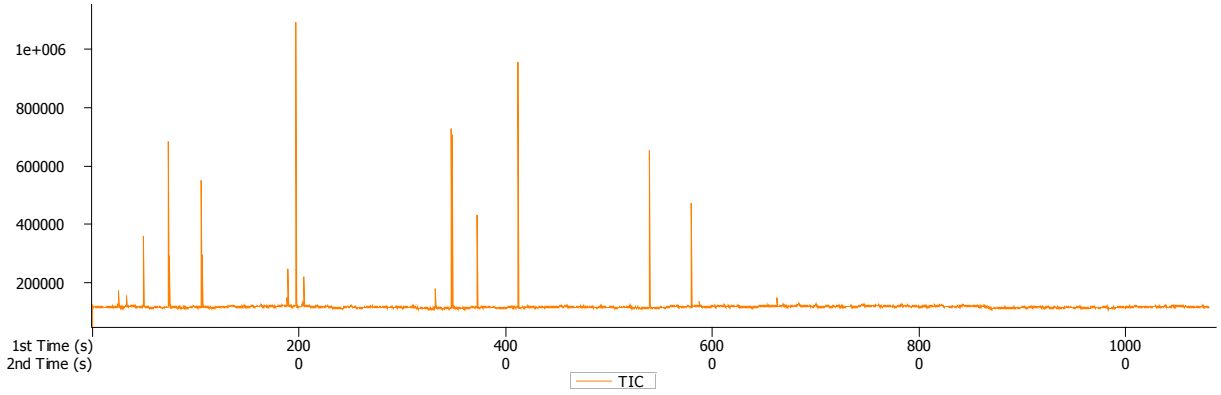

Figure 28: Total ion chromatogram of distillation standard D 86

130417 Post scrub:

The complete characterization of 130417 Post Scrub was shown with their peak table, total ion chromatogram, and 3D image. The peak table shows all the compounds that are present in the 130417 Post Scrub which is a qualitative determination. Each

compound in the sample is given with their type, retention time, quant mass, concentration, area and quantitation.

Table 73: Peak table of 130417 post scrub

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Benzene-D6	Quantified	72 , 3.020	84+83	7.2	965237
Benzene	Quantified	72 , 3.080	78	1.12	1070912
Toluene-D8	Quantified	184 , 5.290	100+99	7.2	1631630
Toluene	Quantified	192 , 5.190	92	8.52	3478796
1,4-Di(methyl-d3)benzene-d4	Quantified	320 , 4.500	116+115	7.2	15304
1,4-Di(methyl-d3)benzene-d4:2	Quantified	328 , 4.270	116+115	7.2	161991
Ethylbenzene	Quantified	328 , 4.460	106	2.03	404487
Ethylbenzene:2	Quantified	336 , 4.230	106	5.69	99946
Styrene	Quantified	368 , 4.840	104	3.64	1340127
Benzene, (1-methylethyl)-	Quantified	408 , 4.070	120	0.14	15305
à-Methylstyrene	Quantified	472 , 4.540	118	0.27	35666
Naphthalene-D8	Quantified	656 , 6.170	136+135	7.2	224483
1-Propene, 2-methyl-	Unknown	16 , 2.560	50		132438
Cyclopropane, ethyl-	Unknown	24 , 1.240	55		2283846
Unknown 1	Unknown	24 , 1.360	45		11220
2-Pentene, (E)-	Unknown	32 , 1.280	54		60981
1,4-Pentadiene	Unknown	32 , 1.390	68		197084
Unknown 2	Unknown	32 , 1.510	66		55632

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Pentane, 2-methyl-	Unknown	40 , 1.360	71		295565
Cyclopentane, bromo-	Unknown	40 , 1.490	67		244419
1-Pentene, 2-methyl-	Unknown	40 , 1.540	84		590842
1H-Tetrazole, 5-methyl-	Unknown	48 , 1.530	56		2957711
2-Pentene, 3-methyl-, (E)-	Unknown	48 , 1.620	69		1368003
Cyclopentene, 3-methyl-	Unknown	48 , 1.760	82		55119
5H-Tetrazol-5-amine	Unknown	56 , 1.670	57		59902
2-Hexene, (E)-	Unknown	56 , 1.690	55		316788
Cyclopentane, methyl-	Unknown	56 , 1.740	56		612828
Cyclopropane, (1-methylethylidene)-	Unknown	56 , 1.840	67		169268
1-Pentene, 2,4-dimethyl-	Unknown	64 , 1.800	56		606363
1,3-Pentadiene, 2-methyl-, (E)-	Unknown	64 , 2.030	67		398328
1,3-Cyclopentadiene, 1-methyl-	Unknown	64 , 2.260	80		73238
Methyl propargyl ether	Unknown	72 , 1.840	70		41793
6-Oxabicyclo[3.1.0]hexane	Unknown	72 , 1.890	55		383598
Ethanone, 1-(1-methyl-2-cyclopenten-1-yl)-	Unknown	72 , 2.040	81		456879
(Z),(Z)-2,4-Hexadiene	Unknown	72 , 2.110	67		1113021
1H-Tetrazol-5-amine	Unknown	80 , 1.810	85		27678
1-Hexene, 5-methyl-	Unknown	80 , 1.920	56		171581
2,3-Dimethyl-1,4-pentadiene	Unknown	80 , 2.050	81		40689
Cyclopropane, (1-methylethylidene)-	Unknown	80 , 2.420	67		73766

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
3-Hexen-1-yne	Unknown	80 , 2.730	79		80277
Butanoic acid, 1,1-dimethylethyl ester	Unknown	88 , 1.910	57		29539
Cyclopentane, 1,3-dimethyl-, cis-	Unknown	88 , 2.110	70		88195
Aminoacetonitrile	Unknown	88 , 2.160	55		124549
Pyridine, 2-chloro-6-(2-furanylmethoxy)-4-(trichloromethyl)	Unknown	88 , 2.300	81		37023
Cyclohexene	Unknown	88 , 2.590	67		278301
1-Heptene	Unknown	96 , 2.250	56		2224603
Borane, ethylisopropylmethyl-	Unknown	96 , 2.400	81		302744
Heptane	Unknown	104 , 2.140	57		913157
1,4-Hexadiene, 4-methyl-	Unknown	104 , 2.600	81		286056
(Z)-3-Heptene	Unknown	112 , 2.450	56		241356
1,3-Pentadiene, 2,3-dimethyl-	Unknown	112 , 2.780	81		236117
1-Heptene	Unknown	120 , 2.700	55		534632
1,5-Pentanediol, O,O'-di(3-methylbut-2-enoyl)-	Unknown	120 , 2.780	82		46745
3-Heptyne	Unknown	120 , 2.950	81		166155
Vinylcyclopentane	Unknown	128 , 3.010	67		91348
Methyl methacrylate	Unknown	128 , 4.470	69		117985
Cyclopentane, ethyl-	Unknown	136 , 2.870	69		85994
1,1'-Bicyclopropyl	Unknown	136 , 3.090	54		26520
Butane, 2-cyclopropyl-	Unknown	144 , 2.660	55		36034
Cyclohexene, 4-methyl-	Unknown	144 , 3.420	81		129853

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Bicyclo[4.1.0]heptane	Unknown	152 , 3.600	81		40353
1-Methylcyclohexa-2,4-diene	Unknown	152 , 3.900	79		36990
Isopropylcyclobutane	Unknown	160 , 2.800	55		27338
1-Methylcyclohexa-2,4-diene	Unknown	160 , 4.090	79		26807
2-Octene, (Z)-	Unknown	168 , 2.920	56		53720
2,3-Dimethyl-1,4-pentadiene	Unknown	168 , 3.700	81		62346
1,3,5-Hexatriene, 3-methyl-, (E)-	Unknown	168 , 4.270	77		18486
Cyclohexene, 4-bromo-	Unknown	176 , 3.590	81		94717
1-Ethylcyclopentene	Unknown	176 , 3.650	67		271623
1-Hexene, 3,3-dimethyl-	Unknown	184 , 2.850	69		164418
1-Methylcyclohexa-1,3-diene	Unknown	184 , 4.410	79		21119
Heptane, 2,5-dimethyl-	Unknown	192 , 2.580	57		54241
Cyclohexene, 3-methyl-	Unknown	192 , 3.830	81		190793
Toluene-D8	Unknown	192 , 4.910	98		91723
Heptane, 4-methyl-	Unknown	200 , 2.490	70		431065
3-Heptyne	Unknown	200 , 3.590	81		111053
Toluene	Unknown	200 , 4.810	91		21205
Unknown 3	Unknown	208 , 2.480	57		37091
Unknown 4	Unknown	208 , 2.820	55		60585
Spiropentane, propyl-	Unknown	216 , 3.060	67		17747
1,3-Pentadiene, 2,3-dimethyl-	Unknown	216 , 3.600	81		25348

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
1-Methylcyclohexa-2,4-diene	Unknown	216 , 4.060	79		22948
Cyclooctene, (Z)-	Unknown	224 , 3.060	67		21686
Cyclobutane, 1,2,3,4-tetramethyl-	Unknown	232 , 2.740	56		204536
1-Octene	Unknown	240 , 2.700	55		749880
Cyclopentene, 1,2,3-trimethyl-	Unknown	240 , 3.140	95		29148
Cyclopentanone	Unknown	240 , 6.970	55		35561
Octane	Unknown	248 , 2.480	57		288176
5,5-Dimethyl-1,3-hexadiene	Unknown	248 , 2.930	95		35881
3-Octene, (Z)-	Unknown	256 , 2.670	69		101379
2-Octene, (Z)-	Unknown	264 , 2.690	55		63359
Bicyclo[2.1.0]pentane, 1,4-dimethyl-	Unknown	264 , 2.970	81		37306
Cyclopentene, 1,2,3-trimethyl-	Unknown	264 , 3.020	95		18547
1-Hexene, 3,3,5-trimethyl-	Unknown	272 , 2.490	69		23936
1-Heptene, 3-methyl-	Unknown	272 , 2.740	56		19310
1-Propylcyclopentene	Unknown	272 , 3.110	67		35521
Hexane, 2,3,4-trimethyl-	Unknown	280 , 2.330	57		29678
Unknown 5	Unknown	280 , 3.140	55		30204
Cyclohexene, 1,6-dimethyl-	Unknown	280 , 3.180	67		81626
Cyclohexane, 1,3,5-trimethyl-, (1à,3à,5à)-	Unknown	288 , 2.580	69		120666
Cyclohexane, ethyl-	Unknown	288 , 2.940	83		36707
4-Decyne	Unknown	288 , 3.000	67		28892

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
2,3-Dimethyl-2-heptene	Unknown	304 , 2.520	55		134904
1-Ethyl-5-methylcyclopentene	Unknown	304 , 3.040	81		19260
2,4-Dimethyl-1-heptene	Unknown	312 , 2.560	55		711356
Cyclopentene, 3-propyl-	Unknown	312 , 3.160	67		28151
4-Ethylcyclohexene	Unknown	312 , 3.340	81		14089
Cyclohexane, 1,3,5-trimethyl-	Unknown	320 , 2.670	69		125971
Cyclopropane, 1,2-dimethyl-3-pentyl-	Unknown	328 , 2.560	55		14220
Cyclohexene, 3,3,5-trimethyl-	Unknown	344 , 2.860	109		11005
Cyclohexene, 3-ethyl-	Unknown	344 , 3.250	81		33401
o-Xylene	Unknown	344 , 4.100	91		47835
Octane, 3-methyl-	Unknown	352 , 2.300	57		15200
2(5H)-Furanone, 5-(2-methyl-2-propenyl)-	Unknown	352 , 2.860	55		15914
Cyclohexene, 3,3,5-trimethyl-	Unknown	352 , 2.920	67		31531
Cycloheptane, methyl-	Unknown	360 , 2.610	55		16469
Unknown 6	Unknown	368 , 2.560	56		15398
Unknown 7	Unknown	368 , 2.630	55		26264
p-Xylene	Unknown	368 , 4.430	91		16785
1-Nonene	Unknown	376 , 2.520	56		105906
Nonane	Unknown	384 , 2.340	57		96054
Benzene, propyl-	Unknown	440 , 4.030	91		20249
Cyclopropane, 1-heptyl-2-methyl-	Unknown	488 , 2.510	55		54155

Name	Type	R.T. (s)	Quant Masses	Concentration	Area
Decane	Unknown	496 , 2.350	56		12393
3-Octene, 2,6-dimethyl-	Unknown	568 , 2.530	69		20446
Cyclopropane, 1-heptyl-2-methyl-	Unknown	584 , 2.580	69		22771
Undecane	Unknown	592 , 2.410	57		31578
Bicyclo[2.2.2]oct-2-ene	Unknown	656 , 4.370	80		14337
Cyclopropane, 1-heptyl-2-methyl-	Unknown	672 , 2.640	55		17821
Undecane	Unknown	680 , 2.480	70		3068.8
Unknown 8	Unknown	752 , 2.200	57		18077
Cyclooctane, 1,4-dimethyl-, cis-	Unknown	752 , 2.230	55		19644
Oxalic acid, allyl tridecyl ester	Unknown	760 , 2.120	55		32826
6-Tridecene	Unknown	800 , 2.070	55		22250
Tridecane	Unknown	808 , 1.930	57		14622
Decane, 2,5,9-trimethyl-	Unknown	840 , 1.960	57		16889
5-Dodecene, (E)-	Unknown	840 , 1.990	55		28671
Hexadecane	Unknown	872 , 1.950	57		13271
1-Trifluoroacetoxy-10-undecene	Unknown	872 , 1.990	55		19411
Oxalic acid, allyl hexadecyl ester	Unknown	904 , 1.930	57		8442.1
Unknown 9	Unknown	912 , 3.400	91		13611
Oxalic acid, allyl tridecyl ester	Unknown	928 , 1.980	57		7625.8

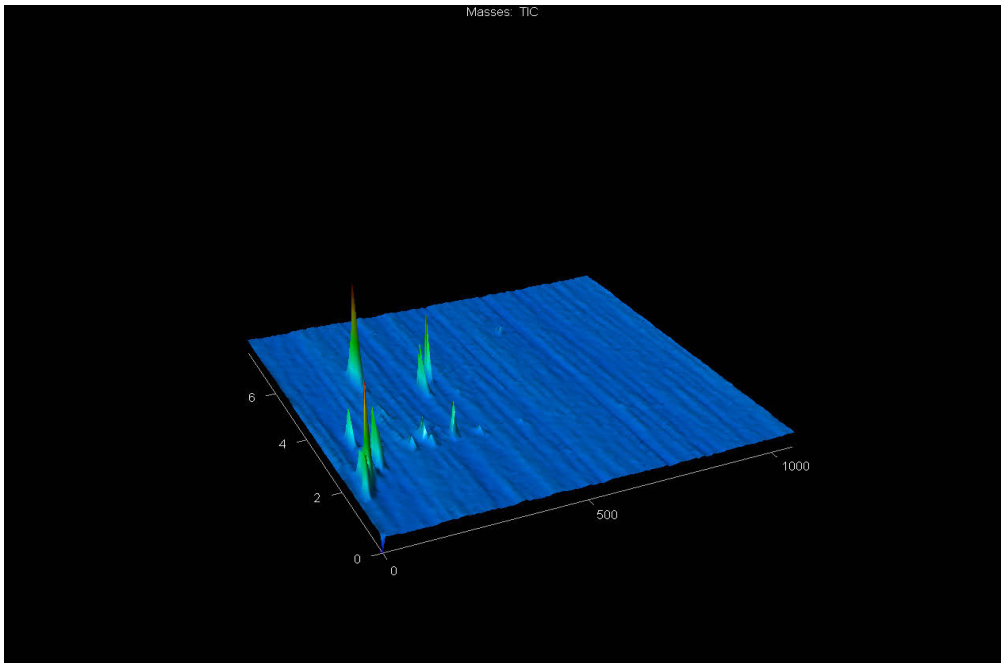

Figure 29: 3D Image of 130417 post scrub

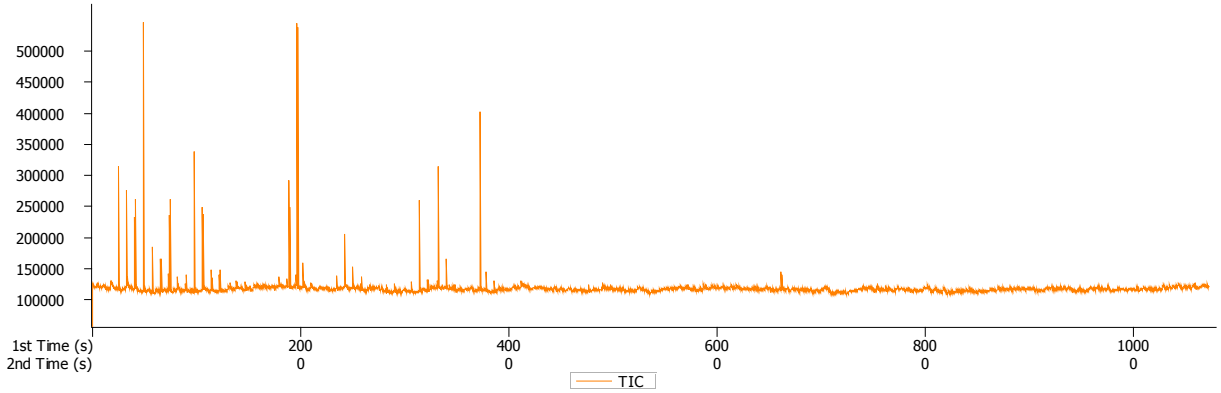

Figure 30: Total ion chromatogram of 130417 post scrub

The combination of fast GC technique with faster temperature programming, fast acquisition rate, and unique deconvolution algorithm allows accurate analysis of the samples. The total time for the analysis of samples is 18 min. The quantitation of the aromatics after the qualitative characterization is determined using the calibration standards.

By reviewing the results, the reproducibility of the quantified aromatic data in fuel and hydrocarbon samples was good within each method and the data were comparable by two methods, one dimensional and two dimensional gas chromatography. In 1D there was not a good separation of the deuterated compounds from their respective analytes even though they were identified based on their m/z ratio, but in 2D there was a distinct separation of the deuterated compounds from their respective analytes on secondary column by reducing the width and increasing the height of the peaks and moreover the linearity with the calibrated compounds and the reproducibility of the data appear to be better by 2D GC method than the 1D GC method.

From the data, we observed that the gasoline with different grades collected on different days contains benzene, toluene, ethylbenzene, cumene but does not have any styrene, or α- methylstyrene. The data were comparable by both the methods and are reproducible when they are analyzed on different days except in benzene. The difference in mass percent of benzene might be due to the collection of the samples from different places or it might be due to the evaporation of benzene which is highly volatile (samples were more than 30 days old).

Diesel does not contain any of the six aromatic compounds in it. Most of it has alkane and alkene derivatives in it especially decane and decene derivatives when analyzed qualitatively.

Pygas samples contain all the six aromatic compounds, even the styrene and α-methylstyrene which are not seen in gasoline. The presence of styrene derivatives in pygas samples might be due to their starting materials plastic, rubber from which they were made.

4.2 Inductively Coupled Plasma Mass Spectrometry (ICP- MS)

The results and discussion are made on the basis of gasoline and diesel samples. A calibration curve for was constructed using the following concentrations: 0.5, 1.0, 3.0, 10.0, 30.0 ppb in 3 % nitric acid. Five calibration standards of known concentration along with a blank were analyzed which generated a calibration curve for each element. The R^2 (correlation coefficient) value represents the correlation of data points on a straight line. A correlation of 1.000 represents that all the data points lie on the same straight line. Any deviation of the value from the equation of the line decreases the value significantly.

In the Calibration Curves, the Y- axis represents the ICP signal in counts per second and the X- axis represents the concentration of individual elements. Calibration curves for vanadium, chromium, cobalt, and lead were prepared using the multi- element analysis mixture. The correlation coefficient and the equation of the line of each element were shown along with their respective calibration curves.

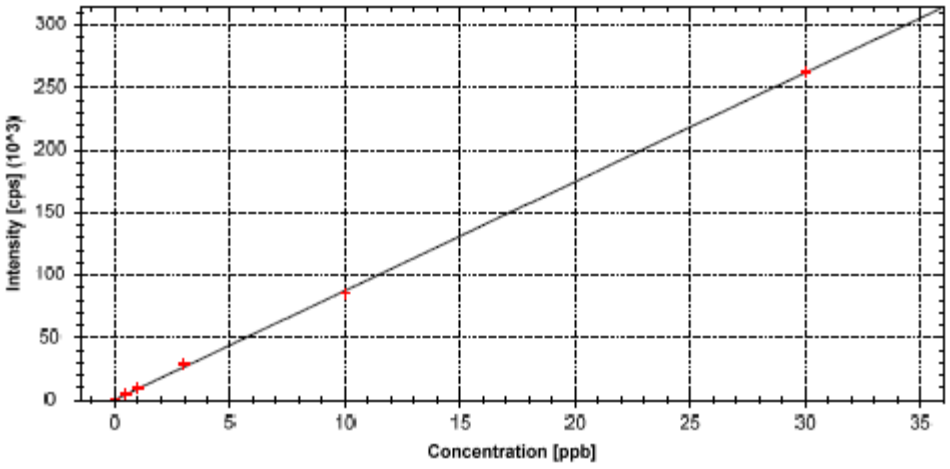

Figure 31: Calibration curve of vanadium

\f(x) = 8718.230*x + 60.000

r = 1.000

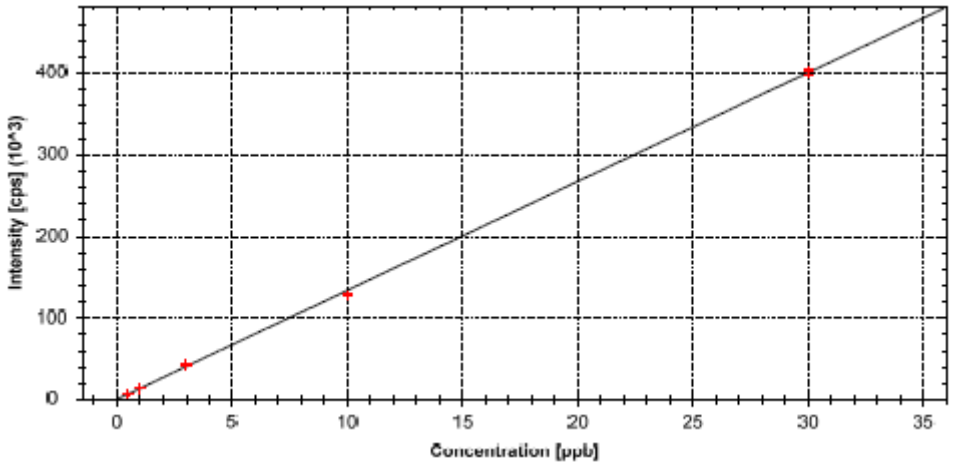

Figure 32: Calibration curve of chromium

f(x) = 13324.307*x + 570.014

r = 1.000

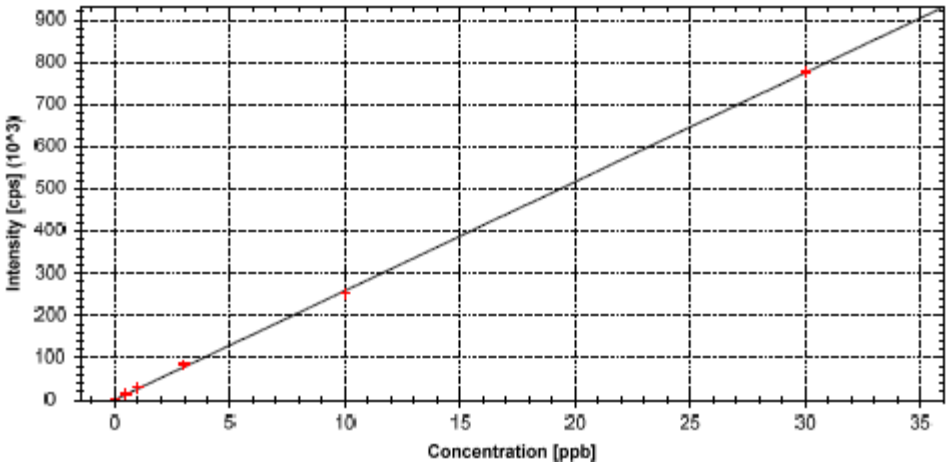

Figure 33: Calibration curve of cobalt

f(x) = 25812.914*x + 40.000

r = 1.000

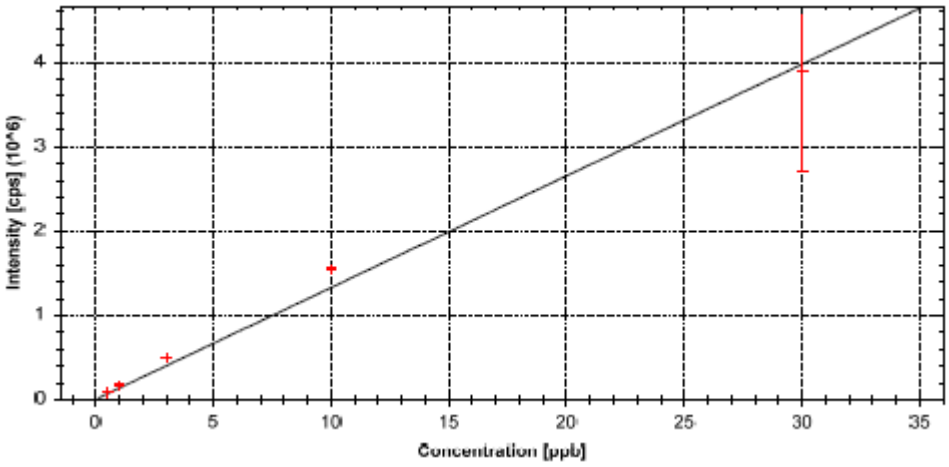

Figure 34: Calibration curve of lead

f(x) = 132275.793*x + 3495.509

r = 0.997

4.2.1 Elemental analysis of gasoline, diesel and pygas samples

A number of acid digestion procedures like nitric acid with hydrogen peroxide, sulfuric acid with hydrogen peroxide, nitric acid sulfuric acid mixture (1:3) with hydrogen peroxide, nitric acid hydrochloric acid mixture (1:3) with hydrogen peroxide and lithium metaborate fusion method were performed in order to dissolve the fuel and hydrocarbon samples. Of these, the lithium metaborate procedure is convenient and does not require the use of large amounts of strong acids and was selected as the method for preparation of the fuel samples. Elemental analysis of the dissolved fuel and hydrocarbon samples were performed using the calibration curves of their respective elements. Table 74 shows the calculated concentration of the elements in gasoline, diesel and pygas samples in parts per million (PPM). The data obtained from ICP- MS is in parts per billion (ppb). To convert to content in the original sample, the values that are obtained are

blank subtracted and multiplied with the total volume that it was diluted (50) and then divided with the amount of sample that was digested (i. e., 0.5 g). The value that obtained was finally divided with 1000 to convert the parts per billion (PPB) to parts per million (PPM).

4.2.2 Elemental analysis of gasoline, diesel and pygas samples

Qualitative and quantitative determination of chromium, lead, vanadium, cobalt, zinc and copper in Polyflow, gasoline and diesel samples were performed using the calibration curves of their respective elements. Table 76 shows the calculated concentration of the elements in gasoline and diesel samples in Parts per million (ppm).

The data obtained from the ICP- MS is in ppb. The concentration obtained for the samples are blank subtracted and multiplied with the total volume that it was diluted (50) and then divided with the amount of sample that was digested (i. e., 0.5 g). The value that were obtained were finally divided with 1000 to convert the PPB to PPM.

Gasoline samples contain chromium, vanadium and cobalt of all the elements that it was quantified. Diesel samples collected from two different places contain chromium, cadmium, lead, vanadium and cobalt in common when quantified against their respective standards. All the pygas samples contain chromium, lead, vanadium, cobalt in common but the Pygas samples, 130417 post scrub, 130313 post scrub, 130313 pyrogas scrub, 130712- 1 3:00 PM, 130712- 2 4:25 PM and 130712 treated contains zinc in addition to the above mentioned elements. All the elements in gasoline, diesel and pygas samples were listed in table 76 along with their concentrations in PPM.

Table 74: Elements in different grades of gasoline, diesel and pygas samples (PPM)

Analyte	Gasoline super	Gasoline Regular	Marathon diesel	Diesel pilot	130417 Post scrub	130313 Post scrub	130313 Pyrogas scrub
Chromium	0.31647	0.39468	0.565343	0.567006	0.735834	0.746404	0.836187
Manganese	0	0	0	0	0	0	0
Nickel	0	0	0	0	0	0	0
Arsenic	0	0	0	0	0	0	0
Selenium	0	0	0	0	0	0	0
Silver	0	0	0	0	0	0	0
Cadmium	0	0	0.000286	0.000297	0	0	0
Lead	0	0	0.326776	0.328944	0.16731	0.158789	0.160489
Vanadium	0.004917	0.00396	0.005676	0.004917	0.005511	0.005475	0.005234
Cobalt	0.00132	0.00363	0.004523	0.004158	0.006567	0.006561	0.006963
Zinc	0	0	0	0	0.087582	0.089334	0.08052
Copper	0	0	0	0	0	0	0

Analyte	130712-1 3:00	130712-2 4:25	130719 11;00	130719 12:30	130719 1:45 pm	130712 Treated
Chromium	0.899283	1.078506	1.153317	1.283898	1.383096	1.444311
Manganese	0	0	0	0	0	0
Nickel	0	0	0	0	0	0
Arsenic	0	0	0	0	0	0
Selenium	0	0	0	0	0	0
Silver	0	0	0	0	0	0
Cadmium	0	0	0	0	0	0
Lead	1.193593	1.206942	1.043922	0.969243	0.976414	1.030161
Vanadium	0.006831	0.005676	0.007194	0.009471	0.00759	0.007953
Cobalt	0.004158	0.006402	0.008382	0.009273	0.009273	0.009834
Zinc	0.344784	0.357905	0	0	0	0.086196
Copper	0	0	0	0	0	0

NOTE: Concentrations shown in table are in PPM

4.3 Nitrogen/ sulfur analyzer

The stock solution for nitrogen sulfur determination is prepared based on mass by taking N, N- dimethyl aniline (0.1 g) and dibenzothiophene (0.1 g) in toluene (99.8 g) which is 1000 ppm. Calibration standards of 10 ppm, 50 ppm, 100 ppm, 300 ppm, 500 ppm of N, N- dimethyl aniline and dibenzothiophene were prepared by adding 0.5 ml, 2.5 ml, 5 ml, 15 ml, 25 ml of stock solution (1000 ppm) to a 50 ml volumetric flask respectively and finally diluting to 50 ml with toluene. The concentrations of nitrogen and sulfur in the diluted standards are listed in the table.

Table 75: Nitrogen and sulfur concentrations in standards

Stock dibenzothiophene and	Nitrogen (PPM)	Sulfur (PPM)
10 PPM	1.155	1.740
50 PPM	5.775	8.7
100 PPM	11.55	17.40
300 PPM	34.65	52.20
500 PPM	57.75	87

4.3.1 Nitrogen

The calibration curve for nitrogen was constructed using the following concentrations: 10, 50, 100, 300 and 500 ppm. Each standard was run in triplicate for reproducibility of the results. The calibration curve for nitrogen was shown in figure and the linearity is good with a correlation coefficient (R^2= 0.999510). A calibration curve for nitrogen was plotted by taking the nitrogen volume (amount of sample injected times the concentration) on x- axis and area on y- axis.

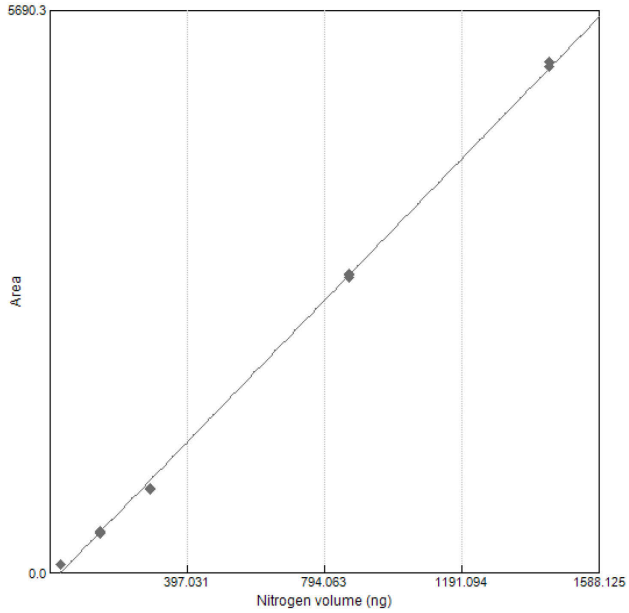

Figure 35: Calibration curve of nitrogen

Equation of the line Y = 3625.8741x – 108.6783

Correlation coefficient- 0.999510

All the calibration standards including the blank were run in triplicate and the signal traces for the calibration standard are shown in figure 53. The traces correspond to three repetitive injections of a refine toluene sample that contained about 10, 50, 100, 300 and 500 ppm N, N dimethyl aniline. The chromatogram demonstrates excellent sensitivity and selectivity.

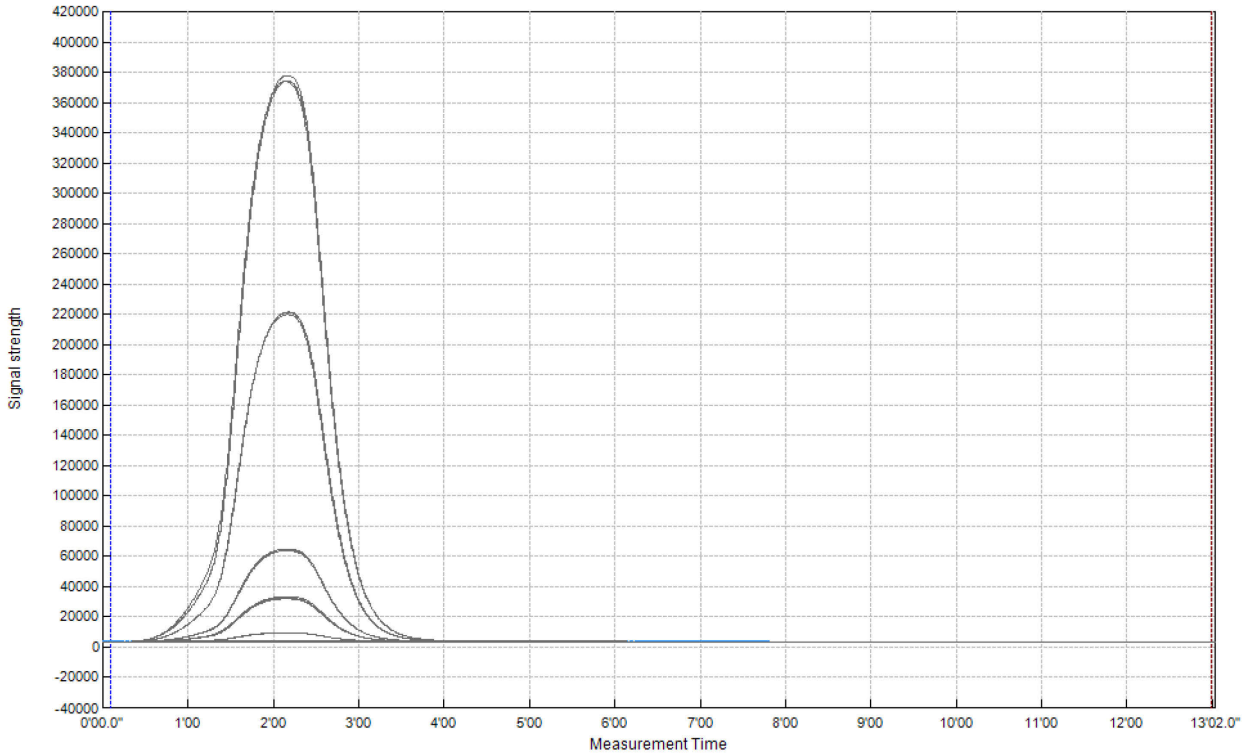

Figure 36: Signal traces for samples containing different concentrations of nitrogen

4.3.2 Sulfur:

The calibration curve for sulfur was constructed using the following concentrations: 10, 50, 100, 300 and 500 ppm. Each standard was run in triplicate for reproducibility of the results. The calibration curve for nitrogen was shown in figure and the linearity is good with a correlation coefficient (R^2= 0.999988). A calibration curve for sulfur was plotted by taking the nitrogen volume (amount of sample injected times the concentration) on x- axis and area on y- axis.

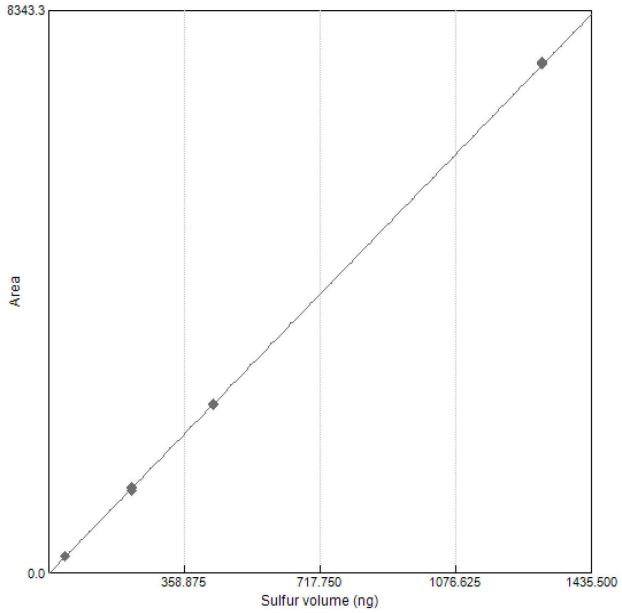

Figure 37: Calibration curve of sulfur

Equation of line Y = 5806.3238x – 13.5898

Correlation Coefficient- 0.999988

All the calibration standards including the blank were run in triplicate and the signal traces for the calibration standard are shown in figure 55. The traces correspond to three repetitive injections of a refine toluene sample that contained about 10, 50, 100, 300 and 500 ppm dibenzothiophene. The chromatogram demonstrates excellent sensitivity and selectivity.

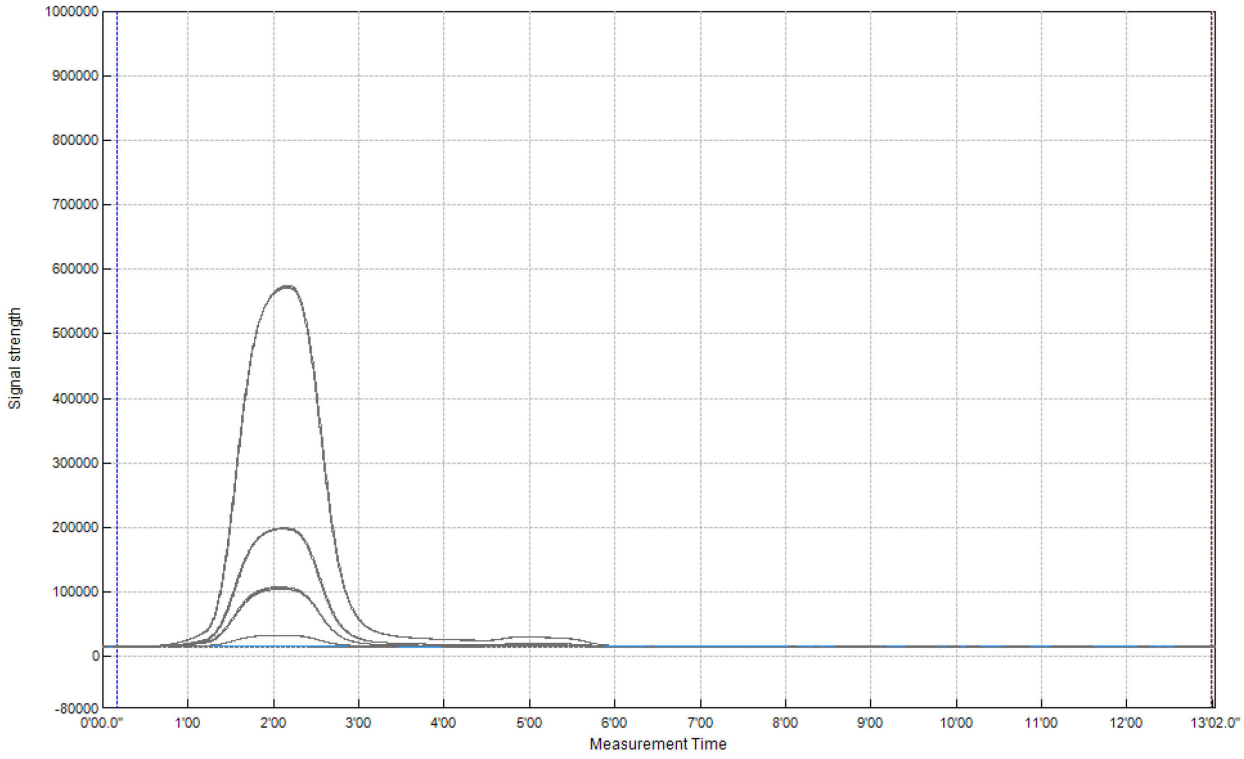

Figure 38: Signal traces for samples containing different concentrations of sulfur

Sample Preparation:

All gasoline and diesel fuel sample are directly analyzed for nitrogen/ sulfur content whereas the Polyflow samples are diluted to 1/ 10 in toluene. Nitrogen and sulfur concentration were quantified with their respective calibration standards. The concentrations along with their relative standard deviation percentage in each of the samples were listed in the table. From the results listed in table 78, we can conclude that the pygas samples contain large amount of nitrogen and sulfur when compared to that of gasoline and diesel samples. Because of the presence of large amount of nitrogen and sulfur in pygas samples, we suggest that further treatment should be done for the removal of sulfur and nitrogen before material is suitable for fuel blending.

Table 76: Nitrogen and sulfur concentrations in gasoline, diesel and pygas samples (PPM)

Sample	Nitrogen		Sulfur	
	Concentration (PPM)	RSD %	Concentration (PPM)	RSD %
Distillation Standard	1.24	1.92	0.29	7.33
Gasoline Super	2.47	0.70	4.365	0.53
Gasoline Regular	4.93	0.77	16.67	0.52
Marathon diesel	12.13	0.22	8.40	0.41
Diesel Pilot	8.87	1.15	6.59	1.52
130417 Post Scrub	722.38	1.03	60.59	0.96
130313 Post Scrub	467.42	0.48	43.66	0.86
130313 Pyrogas	836.32	0.12	98.11	0.35
130719 11:00 AM	1476.20	0.38	83.42	0.45
130719 12:30 PM	540.23	0.28	25.48	1.05
130719 1:45 PM	844.65	0.36	51.48	1.79
130712- 1 3:00 PM	2469. 17	0.18	46.02	1.54
130712- 2 4:30 PM	1163.5	0.50	16.78	2.64
130712 Treated	1997.05	0.26	38.46	0.86

4.4 Conclusion:

The characterization and quantitative determination of aromatic compounds, nitrogen, sulfur and trace metals in fuel and hydrocarbon samples were performed. The one dimensional and two dimensional gas chromatography measurements of majority of the quantified aromatic compounds in the fuel and hydrocarbon were comparable and reproducible. The gas chromatography method used for analysis was evaluated by running the samples in triplicate. One of the main reasons of running the samples by two dimensional gas chromatography is to completely separate the compounds from each other, to obtain a good peak shape and width over wide volatility range, and to provide up to a ten fold increase in analyte detectability. The LECO Pegasus 4D GC x GC TOFMS provided a significant increase in chromatographic resolution for the most complex samples across a wide volatility range. Complete characterization of the gasoline, regular and pygas samples, including identification of several classes of compounds like aromatics, alkanes, alkenes and heterocyclic compounds is also easily achieved using the ascending temperature program with GC x GC TOFMS. The automated peak find algorithm in the ChromaTOF software locates all the peaks in the chromatogram, including those that coelute with other analytes in the chromatogram. The reproducibility of the results of the most complex samples like gasoline, diesel and pygas samples is high.

The lithium metaborate fusion method was used for the determination of trace amount of elements in gasoline, diesel and pygas samples by ICP- MS. Trace amount of chromium, lead, vanadium and cobalt are present in gasoline, diesel and pygas samples, but the concentration of the element varies. Due to the complex nature of the gasoline,

diesel, pygas samples, a high temperature furnace with a nitrogen/ sulfur chemiluminescence detector had been used for measurement of nitrogen and sulfur. From the results, the pygas samples contain large amount of nitrogen and sulfur when compared to that of gasoline and diesel samples. The presence of large amount of nitrogen and sulfur in pygas samples, suggest that the pygas should be treated to remove sulfur and nitrogen hetero- atoms.

In future study, it would be good to try changing different parameters on the GC like split ratios, temperature programming, modulation period and to try running the samples using an agitator on GC x GC TOFMS and look for any change in the results. Also using a microwave digestion for the sample preparation on ICP- MS should be studied. Finally running the sample by combustion ion chromatography (CIC) for the halide and sulfur should be performed to compare the sulfur results with that of sulfur analyzer.

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