Analysis and Comparison of Diesel Fuel for Organic and Metal Content via MP-AES and GC-MS

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Introduction

According to the US Energy Information Administration, little more than 10% of the nation's households still use heating oil as a source of heat. Of this small portion, 80% are located in the Northeast.[1] ProGreen Labs LLC. recently developed a fuel efficient pre-combustion apparatus specifically for heating oil furnaces. By focusing on improving atomization—the breaking up of fuel into smaller droplets— through the use of Bernoulli's equation, they were able to improve on the efficiency of their previous product.[2] Experiments reveal that a furnace modified with this apparatus saves 60-70% more fuel compared to the conventional furnace. The cause of this efficiency can either be attributed to the manipulation of pressure on the fuel to initiate atomization, or by some chemical alteration of the ignitable liquid as it travels through the apparatus. This summer, diesel fuel samples collected during product development were analyzed to determine if the apparatus had altered the fuel chemically.

While testing the pre-combustion apparatus, a total of 6 mechanical adjustments were made following each trial run. These trials involved collecting a sample of the diesel fuel that had flowed through the apparatus before reaching the furnace's electrode, which is where the fuel combusts. A total of seven samples were collected: samples A1-A6 and the control sample. Samples A1-A6 are diesel samples that have each passed through a specific adjusted model of the apparatus, while the control sample was diesel fuel that had not gone through the invention.

Since the apparatus was composed predominantly of copper and steel, each sample except for A4 was chemically analyzed with the microwave plasma-atomic emission spectrometer (MP-AES) for concentrations of copper, zinc, iron, cobalt, and manganese. A4 was not analyzed at all during the experiment because the apparatus it ran through was missing a nozzle and other components. Throughout this paper, samples A1-A6 excludes A4. Copper was chosen to be analyzed because most of the invention was composed of copper rods. The other elements were chosen because they are commonly included in steel, which is a metal alloy.[3] Higher concentrations of these elements in samples A1-A6 than the control may suggest that the apparatus is fuel efficient due to possible chemical alterations of the fuel caused by metal.

Methods and Materials

Before running the MP-AES, a calibration curve must first be set on the instrument according to a Blank and a set of standard solutions. A calibration curve is a function (usually linear) the instrument uses to determine the concentration of samples. The Blank is a solution that determines which intensity and concentration would be considered 0. The standard solutions contain a known concentration of the elements being detected.

The Blank was made by making a 5% mixture of nitric acid. This was done by mixing 25mL of nitric acid in 475mL of deionized water. Normally, trace analysis nitric acid would be used because of its guaranteed purity. However, ACS Standard nitric acid was used for this experiment because of the lack of trace analysis nitric acid in the lab. There was a chance that the purity of ACS Standard nitric acid may not be sufficient for MP-AES standard. Therefore, both the ACS Standard and the trace analysis were run through the MP-AES. The results ensured that the ACS Standard's purity would suffice for the Blank preparation.

Three standards were made based off a premade standard already in the lab that had the following concentrations: [Co]=250.55ppm, [Cu]=247.90ppm, [Fe]=248.55ppm, [Zn]=248.00ppm, and [Mn]=248.55ppm. The premade standard itself was not used because it was deemed too concentrated for the MP-AES based on previous experiences. The first standard was made by diluting 10mL of the premade standard with 240mL of the Blank making the concentration of all the elements approximately 10ppm. The second standard was made by diluting 10mL of the first standard with 90 mL of the Blank, making the element concentrations approximately 1ppm. The third standard, which was 0.1ppm, was made by diluting 10mL of the second standard in 90mL of the Blank. The Blank and three standards were run through the MP-AES to set the calibration curve.

Once the calibration curve was set, the samples were run through the instrument as well. Unfortunately, diesel fuel cannot be run through the MP-AES for reasons discussed in the Conclusion. Therefore, the metal content of each diesel fuel sample was extracted with Ethylenediaminetetraacetic acid solution (EDTA). EDTA is a chelating agent, meaning that the compound binds tightly to metals.[4] 10 mL of the control sample was mixed with 10 mL of 0.05M EDTA in a 20 mL capped vial. Because my EDTA was dissolved in deionized water, the solution is polar. Diesel fuel, however, is non-polar. Therefore, both solutions naturally separated from each other. Left alone, the metal ions will gradually diffuse from the diesel sample into the EDTA solution, but the length of time this process would take is likely very long. As a result, the 20 mL vial was placed in the Enviro-Genie, a machine that shakes solutions for a selected period of time. As the mixture is being shaken, EDTA molecules would be able to extract the metal ions much quicker. The capped vial was left in the machine for approximately 16 hours shaking at 28 rocks/min. This procedure was repeated for samples A1-A3 and A5-A6.

The samples were taken out the next day and given time to settle until there was a distinct separation of fuel and EDTA. Because diesel fuel is less dense than EDTA, the top 10 mL of each 20 mL vial was composed of the fuel, while the rest of the container had EDTA. Since the metal content was already within the EDTA solution, the diesel fuel was no longer necessary. Therefore, the fuel was extracted and deposited from each sample leaving only the EDTA to analyze. To prevent EDTA from being over saturated, an additional 10 mL of deionized water was first added to each sample. 1 mL of each EDTA solution was then mixed in another 20mL vial containing 9mL of Blank, hence causing the end concentration of EDTA to be $2.5x10^{-4}$M. A sample of 0.05M EDTA was also prepared by diluting 1mL of the solution with 9mL of deionized water. The samples analyzed through the MP-AES were: 0.005M EDTA, A1-A3, A5-A6, and the control.

The control, A1-A3, and A5-A6 were further analyzed through the gas chromatograph-mass spectrometer (GC-MS). A sample of the control was prepared by mixing 0.15mL of control diesel fuel with 10mL of pentane, which functions as the solvent for this experiment. Because pentane is also a non-polar hydrocarbon, diesel fuel can dissolve in the substance.[5,6] The rest of the fuel samples were prepared in the same manner.

1µL of each sample was then individually injected by the GC-MS auto sampler. The scan of each sample lasted 20 minutes and ranged from M/Z= 50-600. 1µL of pentane was injected into the instrument between each sample injection to clean out the GC column ultimately preventing sample contamination from previous scans.

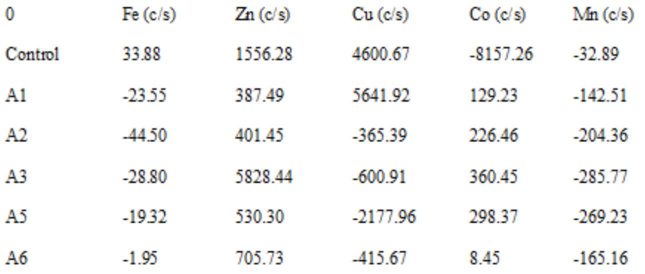
After scanning the diesel fuel, a sample of hexadecane ($C_{16}H_{34}$) was run through the instrument. $C_{16}H_{34}$, also known as cetane, is one of many hydrocarbons that contribute to the complex mixture of diesel fuel.[7,8] Therefore, $C_{16}H_{34}$ will definitely be within the diesel fuel samples. The mass spectrum and chromatograph of this hydrocarbon will provide a standard to compare with those of the diesel fuel samples. The $C_{16}H_{34}$ sample was prepared in the same manner as the diesel fuel samples. Because the auto-sampler eventually stopped working, however, the $C_{16}H_{34}$ sample was injected manually with a syringe.

To determine which region of a diesel fuel chromatograph represents hexadecane, 1µL of the control diesel fuel spiked with a diluted sample of $C_{16}H_{34}$ was also scanned by the instrument. 1mL of $C_{16}H_{34}$ was diluted in 9mL of pentane. The control diesel fuel was diluted in the same manner. 1mL of the $C_{16}H_{34}$ mixture was then added to 10mL of the control mixture. This sample was run through the instrument.

Results and Conclusion

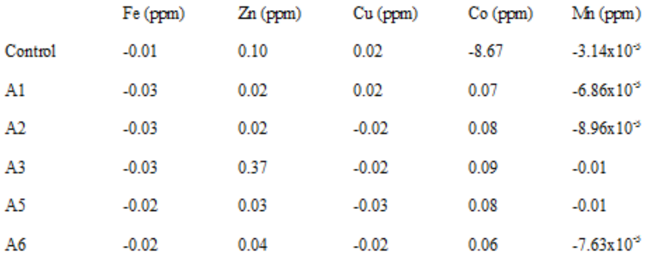
The MP-AES quantized the presence of Cu, Co, Fe, Mn, and Zn in counts per second (c/s), which are units of intensity. These values were then converted to concentration (ppm) through the calibration curve. According to **Table 1**, there are several samples that have a negative intensity. Such negative values simply mean that certain samples have even less concentrated or intense elements than the Blank, which sets 0c/s and ppm for the instrument. Therefore, these negative values should be treated as 0c/s or ppm.

Table 1



0	Fe (c/s)	Zn (c/s)	Cu (c/s)	Co (c/s)	Mn (c/s)
Control	33.88	1556.28	4600.67	-8157.26	-32.89
A1	-23.55	387.49	5641.92	129.23	-142.51
A2	-44.50	401.45	-365.39	226.46	-204.36
A3	-28.80	5828.44	-600.91	360.45	-285.77
A5	-19.32	530.30	-2177.96	298.37	-269.23
A6	-1.95	705.73	-415.67	8.45	-165.16

Table 2



	Fe (ppm)	Zn (ppm)	Cu (ppm)	Co (ppm)	Mn (ppm)
Control	-0.01	0.10	0.02	-8.67	$-3.14x10^{-5}$
A1	-0.03	0.02	0.02	0.07	$-6.86x10^{-5}$
A2	-0.03	0.02	-0.02	0.08	$-8.96x10^{-5}$
A3	-0.03	0.37	-0.02	0.09	-0.01
A5	-0.02	0.03	-0.03	0.08	-0.01
A6	-0.02	0.04	-0.02	0.06	$-7.63x10^{-5}$

The conversion of the intensity values to concentration values reveals that almost all samples have approximately 0ppm for Fe, Zn, Co, Cu, and Mn. The control and A1 sample in **Table 2** clearly have more Cu concentration than other samples. However, these concentrations are extremely small and essentially 0ppm in reference to the calibration curve. This small difference in concentration could have been affected by multiple small factors during sample preparation, such as where in the EDTA solution the pipette was placed to extract and dilute 1mL of the solution. The small differences in concentration for all the elements can be justified by small factors of this nature. However, the concentration of Zn in sample A3 was significantly above 0ppm. Sample A3 came from an apparatus that was composed mostly of Cu. Zn that was not initially in the diesel fuel could have only accumulated in the sample from steel components, suggesting a possible error was made in the process of preparing and analyzing Cu for sample A3. This particular concentration failed Dixon's Q-test, deeming the data point insignificant. Therefore, the concentrations of all five metals are essentially 0ppm.

Because diesel fuel is a mixture of fuel additives and hydrocarbons, there is no consistent chemical composition for the fuel. The composition of this ignitable liquid can depend on numerous factors of its origins including the petroleum source and the oil refining company.[10] As a result, analyzing diesel fuel is extremely difficult and can take months to identify just a few separated compounds of its mixture with absolute certainty.

After comparing the chromatographs and mass spectra of samples A1-A6 to those of the control, it is concluded that there are no chemical differences between any of the samples.

According to the MP-AES data, virtually 0ppm of Fe, Zn, Cu, Co, and Mn were found in the diesel samples suggesting the apparatus did not chemically alter the diesel fuel through means of mixing small amounts of metal compounds with fuel. The negative values shown in **Table 2** and **3** reveal that the samples have lower concentrations of the tested metals than the Blank. These values should be considered 0c/s and ppm.

MP-AES data quality can be improved if the instrument's capillary tube were cleaned out with a Blank between each sample trial run. During this experiment, each sample was run through the MP-AES consecutively. As a result, each sample may have become contaminated by the small amounts of residue left by previous samples in the capillary tube.

An External Gas Control Module (EGCM) is an MP-AES accessory that could have also been used to improve data quality. Because diesel fuel is an organic compound, each sample run will result in large amounts of dark carbon residue being left on the instrument's flame torch. [10,11] This residue will reduce light intensities emitted by excited electrons, which ultimately hampers the instrument's sensitivity. To prevent carbon residue from developing, EDTA was mixed with each sample to extract possible metals. These solutions were then run through the MP-AES instead of the diesel samples for this experiment. However, the EDTA solution may not have extracted all of the metal within each sample. If the MP-AES used for this experiment had an EGCM, the diesel samples could have been run through the instrument, and EDTA extractions would no longer be necessary. The EGCM prevents carbon build-up by injecting air into the plasma torch.[10]

Data from the GC-MS also confirms that the pre-combustion apparatus could not have altered the chemical composition of diesel fuel. The chromatogram of the control sample is nearly identical to those of the other samples. Using $C_{16}H_{34}$ as a standard, analyses of the chemical composition of each peak's mass spectrum were able to be made. A comparison of the control's thirteen mass spectra to those of A1-A6 further confirms that the samples are identical to each other.

Aspects of the experiment that could have been improved include the type of ionization and column used. The instrument's default ionization method was electron impact. Although electron impact is the most common form of ionization, it is not always effective. Often times a mass spectrum produced with electron impact lacks the parent ion peak, which occurs because electron collisions with sample molecules are too rough. As a result, the ionized molecules become too fragmented to the point where an ionized form of the complete molecule does not exist.[12,13]

To prevent fragmentation, the instrument's ionization method can be changed from electron impact to chemical ionization. Chemical ionization is "softer" than electron impact, which means much less fragments are produced during ionization making mass spectrum peaks much more distinct.[12,13] Chemical ionization still utilizes electron impact, but also involves mixing the sample with a reagent gas.[14] The purpose of the reagent gas is to become ionized through electron impact. The reagent gas ions in turn react with the sample to produce sample ions. The reagent gas used must be inert to itself when ionized, but highly reactive to the sample. Methane, isobutane, and ammonia are commonly used. Both the reagent gas and the sample enter the ionization chamber at the same time. The concentration of the reagent molecules is much greater than the sample molecules, which increases the chances that the reagent surrounds the sample to absorb electron bombardment.[15] **Figure 1** displays a diagram of chemical ionization.

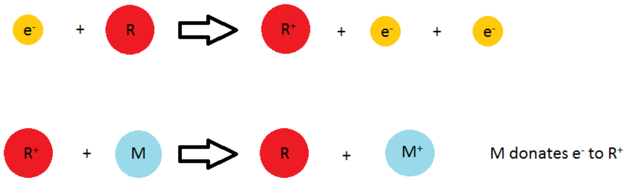


Figure 1: A diagram of chemical ionization, adapted from Skoog et al.[12]

In addition to changing the ionization method, the type of GC column could have also been changed to improve data quality. The particular GC-MS used for this experiment had both a chiral and a non-polar column. Ideally, the non-polar column would be used because diesel fuel is also non-polar. The samples injected would depend solely on van der Waal attractions during the stationary phase since non-polar compounds have no charge. However, the chiral column was used because the non-polar column was not working properly at the time of the experiment. Unlike its non-polar counterpart, the chiral column is usually used for samples containing chiral enantiomer compounds, which are molecules containing carbons attached to four different R groups. These molecules have two forms that are mirror images of each other.[16] Rather than just relying on van der Waal attractions during the stationary phase, chiral columns rely on several other forces including dipole-dipole, hydrogen, and ionic forces.[17] The use of this column may have resulted in less than ideal mass spectra resolutions.

Ideally, the 2D GC-MS and FT-ICR MS could be used to analyze the diesel fuel samples. Both instruments are compatible with each other and are commonly used to analyze crude oil, which is filled with less volatile polar compounds.[18] Although the diesel fuel samples being tested are refined, there is a chance that the samples may still contain polar compounds. The combination of non-polar and polar columns within the 2D GC-MS can be used to separate possible polar compounds from the rest of the sample.[19] The FT-ICR MS is also capable of analyzing less volatile polar compounds. This instrument has a mass resolution within 2ppm and is capable of using APPI, which is a “softer” ionization method than electron impact.[20,21] The sensitivity of the FT-ICR MS paired with APPI will ultimately produce very clear mass spectra. If the samples prove to be completely devoid of polar compounds, both instruments would still function better than the GC-MS used in this experiment. The 2D GC-MS would have a non-polar column to separate the samples, while the FT-ICR MS would have a much higher mass resolution and use a “softer” ionization method than the instrument used in this experiment.[22,19]

Based on MP-AES and GC-MS data, samples A1-A6 are chemically identical to the control fuel. Therefore, fuel efficiency of the pre-combustion apparatus cannot be attributed to chemical alterations of fuel. Although there were flaws in the experiment, many of them were minor. Had they been fixed, there may have been more accurate MP-AES values and cleaner chromatographs and mass spectra. However, these changes would likely not have resulted in different experimental findings.

The implementation of a Blank run between each sample run would likely increase the number of negative MP-AES values because neglecting to clean the capillary between each sample run may have actually helped accumulate the metal content of each fuel run. If a Blank were run between each sample analysis, the lack of previous sample residue in the capillary would cause the instrument to detect even less metal. With the addition of an EGCM, the MP-AES would be able to directly analyze diesel fuel rather than EDTA solutions.[10,11] This may result in more metal being detected, but also not likely change experimental findings. In the experiment conducted, the same amount of EDTA solution was added to each sample. These samples were then shaken for the same time period in the Enviro-Genie, which ensures that the each EDTA solution was given the same conditions to bind to possible metal content. If more metals were found with the EGCM-modified MP-AES, each sample would likely increase the same amount in metal concentration. Therefore, the difference in metal concentration between each sample would be the same regardless if an EGCM were used.

The cleaner chromatographs and mass spectra caused by using chemical ionization and a non-polar column would likely also not alter experimental findings because the results of each sample would change in the same manner. More distinct mass spectra peaks would allow greater accuracy in determining the chemical composition of the thirteen chromatograph peaks, but ultimately the GC-MS results of each sample would be the same.

The implementations stated previously could alter experimental findings but not likely because of the consistencies maintained throughout the experiment. Evidence that samples A1-A6 are chemically equivalent to the control fuel is overwhelming. If this experiment were to be repeated again, the use of a 2D GC-MS and FT-ICR MS would be a better alternative. However, the Hampden-Sydney Chemistry department does not have either of these instruments. Based solely on the results of this project, it can be said that the pre-combustion apparatus developed by ProGreen Labs LLC does not alter fuel composition to improve fuel efficiency. The device’s fuel efficiency can likely be attributed to a manipulation of fluid mechanics, which can be confirmed in a future research assignment.

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