One of my biggest problem in answering the discussion, statistical analysis, significance and conclusion is I have trouble determining what the results really mean. Would you please help me interpret my results, such as what did the experiment demonstrate and how do I know? Like in the last one I knew to discuss time and peaks. It is just very confusing to me and I only have this one and one more and my grade still needs improving.

Chemistry 3211

Experiment #10

Identification of MTBE, Octane and BTEX in Gasoline by GC/MS

9 July 2013

**ABSTRACT**

 The goal of this experiment was to separate gasoline components using gas chromatography and to identify the separated components by mass spectrometry. Also, to determine the concentration of specific target analytes in gasoline using total ion chromatogram and specific m/z ratios.

**INTRODUCTION**

 The objective of the experiment was to separate gasoline components using gas chromatography and to identify the separated components by mass spectrometry. In addition, to determine the concentration of specific target analytes in gasoline using total ion chromatogram and specific m/z ratios.

 Gas chromatography/mass spectrometry (GC/MS) is a tool to separate, quantify and identify unknown organic compounds and permanent gases. The principle of GC/MS requires a sample solution to be injected into the gas chromatography (GC) inlet where it is vaporized. The carrier gas then moves the vapor onto a chromatographic column. The sample flows through the column and the compounds are separated by their interaction with the stationary phase (column coating) and the mobile phase (carrier gas). Finally, the last part of the column passes through a heated transfer line and ends at the entrance to ion source. From there compounds eluting from the column are converted to ions and detected according to their mass to charge m/z ratio. The gas chromatograph uses a capillary column in which the stationary phase consists of silica. The CG consists of a carrier gas, gas controls, column, injector, detector and oven. An interface is used between GC and mass spectrometry (MS) to solve the pressure incompatibility. The mass spectrometry is a technique used for measuring molecular weight and structure of both organic and inorganic compounds and the identification of analytes in mixtures. MS consists of an ion source, vacuum system, a mass-selective analyzer and an ion collector. The combination of gas chromatography and mass spectrometry allow for a much finer degree of substance identification. Gas chromatography/mass spectrometry was employed in determining if Bisphenol A (BPA) which has been determined to be an endocrine disruptor resulting in reproductive defects, diabetes, cancer and obesity was present in bottled water in Riyadh, Saudi Arabia. A calibration standard curve was compared with internal standard. The results were inconclusive as to where the detected BPA was from the bottle or the water and further research will need to be conducted (1). GC/MS was used to determine the level of pesticides on food commodities to determine the level of toxicity and potential human health hazards. The study examined the effectiveness of five different mass spectrometers interfaced to gas chromatography or liquid chromatography on screening targeted and non-targeted of pesticides on spinach and ginseng. GC/MS or LG/MS is an effective process for identifying compounds and produced the lowest false-negatives (2). Increasing abuse of methamphetamine

(MA), amphetamine (AM), and methylenedioxy-phenylalkylamine derivatives have been linked to severe and even fatal intoxications. GC/MS has been employed to identify these drug derivatives in the clinic and forensic laboratories because of their low molecular and high polarity, GC/MS has been effective in separating the components and identifying the drug from biological samples (3).

**EXPERIMENTAL SECTION**

**METHODS**

 The procedures established in the “Identification of MTBE, Octane and BTEX in Gasoline by GC/MS” protocol posted on T-square were used to conduct the experiment (4) with some deviations/modifications. In Part 1 step 7 the density of gasoline’s tared vial equaled 21.1485g. In Part 1 step 8 the concentration of flurobenzene was 1mg/mL. The standards provided were:

0.020mg/mL working solution; 0.10mg/mL working solution; 1.0mg/mL working solution

2.0mg/mL working solution; 5.0mg/mL working solution; and 25mg/mL internal standard

 **MATERIALS**

 The Hewlett Packard 5890 Series II Gas Chromatograph and the Hewlett Packard 5971A Mass Selective Detector manufactured by Hewlett Packard of Palo Alto, California was used to conduct the experiment. A 10 microliter syringe manufactured by Hamilton of Reno, Nevada was used to perform the experiment. The software employed was CSS Analytical Mass Spectrometer made by CSS Analytical Company, Inc. of Shawnee, Kansas.

**RESULTS**

**RAW DATA**

Table I. TIC uncorrected calibration curves data of slope, y-intercept and correlation coefficient.

|  |  |  |  |
| --- | --- | --- | --- |
|   | Slope  | y-intercept | Correlation Coefficient |
| MTBE | 2.00E+07 | -7.00E+06 | 0.9533 |
| benzene | 3.00E+07 | -1.00E+07 | 0.95908 |
| tolulene | 4.00E+07 | -1.00E+07 | 0.97217 |
| ethyl benzene | 4.00E+07 | 1.00E+07 | 0.94951 |
| o-xylene | 4.00E+07 | -8.00E+06 | 0.97601 |
| m+p-oxylene | 1.00E+08 | -3.00E+07 | 0.96592 |
| octane  | 2.00E+07 | -6.00E+06 | 0.95596 |

Table II. TIC corrected calibration curves data of slope, y-intercept and correlation coefficient

|  |  |  |  |
| --- | --- | --- | --- |
|   | Slope  | y-intercept | Correlation Coefficient |
| MTBE | 2.00E+07 | -7.00E+06 | 0.96876 |
| benzene | 4.00E+07 | -1.00E+07 | 0.97691 |
| tolulene | 3.00E+07 | -9.00E+06 | 0.95186 |
| ethyl benzene | 5.00E+07 | 3.00E+07 | 0.88284 |
| o-xylene | 6.00E+07 | -7.00E+06 | 0.99369 |
| m+p-oxylene | 1.00E+08 | -3.00E+07 | 0.98487 |
| octane  | 2.00E+07 | -7.00E+06 | 0.97231 |

Table III. M/Z uncorrected calibration curves data of slope, y-intercept and correlation coefficient

|  |  |  |  |
| --- | --- | --- | --- |
|   | Slope  | y-intercept | Correlation Coefficient |
| MTBE | 1.00E+07 | -4.00E+06 | 0.96219 |
| benzene | 2.00E+07 | -5.00E+06 | 0.96888 |
| tolulene | 1.00E+07 | -3.00E+06 | 0.97358 |
| ethyl benzene | 7.00E+06 | 4.00E+06 | 0.85444 |
| o-xylene | 9.00E+06 | -1.00E+06 | 0.97992 |
| m+p-oxylene | 2.00E+07 | -5.00E+06 | 0.96888 |
| octane  | 4.00E+06 | -833296 | 0.98187 |

Table IV. M/Z corrected calibration curves data of slope, y-intercept and correlation coefficient

|  |  |  |  |
| --- | --- | --- | --- |
|   | Slope  | y-intercept | Correlation Coefficient |
| MTBE | 2.00E+07 | -5.00E+06 | 0.97308 |
| benzene | 2.00E+07 | -5.00E+06 | 0.98092 |
| tolulene | 1.00E+07 | -3.00E+06 | 0.98493 |
| ethyl benzene | 9.00E+06 | 6.00E+06 | 0.77726 |
| o-xylene | 1.00E+07 | -1.00E+06 | 0.99355 |
| m+p-oxylene | 3.00E+07 | -6.00E+06 | 0.9803 |
| octane  | 5.00E+06 | -861580 | 0.9923 |

Table V. TIC uncorrected data concentration for each as determined by the TIC and by using the m/z ratios

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Type of Gasoline  | Component | Retention Time (min) | TIC Uncorrected | Concentration (mg/mL) |
| Regular Gasoline | MTBE | 1.61 | 3395064 | 5.20E-01 |
| benzene | 2.43 | 10703603 | 6.90E-01 |
| toluene | 4.05 | 81983078 | 2.30E+00 |
| ethyl benzene | 6.18 | 118041493 | 2.70E+00 |
| o-xylene | 6.72 | 2640743 | 2.66E-01 |
| m+p-oxylene | 6.18 | 118123371 | 1.48E+00 |
| octane  | 4.79 | 775743 | 3.39E-01 |
| fluorobenzene | 2.6 | 22802352 |   |

Table VI. TIC corrected data concentration for each as determined by the TIC and by using the m/z ratios

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Type of Gasoline  | Component | Correction Factor | TIC Corrected | Concentration (mg/mL) |
| Regular Gasoline | MTBE | 1.256153795 | 4264722.528 | 5.63E-01 |
| benzene | 1.256153795 | 13445371.53 | 5.86E-01 |
| toluene | 1.256153795 | 102983354.6 | 3.73E+00 |
| ethyl benzene | 1.256153795 | 148278269.4 | 2.37E+00 |
| o-xylene | 1.256153795 | 3317179.341 | 1.72E-01 |
| m+p-oxylene | 1.256153795 | 148381120.8 | 1.78E+00 |
| octane  | 1.256153795 | 974452.5134 | 3.99E-01 |
| fluorobenzene | 1.256153795 | 28643261 |   |

Table VII. M/Z uncorrected data concentration for each as determined by the TIC and by using the m/z ratios

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Type of Gasoline  | Component | Retention Time (min) | M/Z Uncorrected | Concentration (mg/mL) |
| Regular Gasoline | MTBE | 0 | 0 | 4.00E-01 |
| benzene | 2.44 | 2055151 | 6.06E-01 |
| toluene | 4.05 | 23914092 | 2.79E+00 |
| ethyl benzene | 6.18 | 24478888 | 2.85E+00 |
| o-xylene | 6.65 | 9895074 | 1.39E+00 |
| m+p-oxylene | 6.18 | 24485354 | 2.85E+00 |
| octane  | 4.65 | 1281843 | 5.28E-01 |
| fluorobenzene | 2.56 | 37640037 |   |

Table VIII. M/Z corrected data concentration for each as determined by the TIC and by using the m/z ratios

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Type of Gasoline  | Component | Correction Factor | M/Z Corrected | Concentration (mg/mL) |
| Regular Gasoline | MTBE | 0.500792903 | 0 | 2.50E-01 |
| benzene | 0.500792903 | 1029205.035 | 3.01E-01 |
| toluene | 0.500792903 | 11976007.56 | 8.49E-01 |
| ethyl benzene | 0.500792903 | 12258853.38 | 8.63E-01 |
| o-xylene | 0.500792903 | 4955382.834 | 4.98E-01 |
| m+p-oxylene | 0.500792903 | 12262091.51 | 8.63E-01 |
| octane  | 0.500792903 | 641937.8772 | 2.82E-01 |
| fluorobenzene | 0.500792903 | 18849863.4 |   |

Table IX. Regular gasoline listing the identity of each of the 15 most abundant components, their retention times and the area% detected.

|  |  |  |  |
| --- | --- | --- | --- |
| Component  | Retention Time (min) | Area % Detected  | Coeluting Yes/No |
| hydrizine/methylethene/flouroethanol | 1.18 | 3.94 | Yes |
| 2-butyne-1,4-diol cyclopropane/1,1-dimethyl-2-butyne-1,4-diol | 1.57 | 2.78 | Yes |
| 1-hexene/1-propene/2-methyl-4-pentenal | 1.79 | 2.38 | Yes |
| cyclopropane/1-ethyl-2-methyl/1-hexene | 2.45 | 2.54 | Yes |
| cyclopropane/i-ethyl-2-methyl/2-butene/1-butene | 2.48 | 3.18 | Yes |
| furan/2,5-dihydro-2-butene/2-methyl-1pentene | 2.6 | 2.89 | Yes |
| 2-hexene/5-methyl/(E)-1-butene/1-butene | 2.77 | 3.54 | Yes |
| entane/2,3-dimethyl-1-pentene/1-butene | 2.94 | 2.61 | Yes |
| 3-picoline/2-nitro-toluene/cyclopropanecarboxylic acid | 4.14 | 4.06 | Yes |
| toluene/2H-pyran/2-(2,5-hexadiynyloxy)tet-1,7-octadiyne | 6.33 | 8.97 | Yes |
| benzene/1,3-dimethyl/1,2-dimethyl | 6.77 | 3.68 | Yes |
| benzene/1-methylethyl/1-ethyl-3-methyl | 8.07 | 5.3 | Yes |
| benzene/1-ethyl-4-methyl/1-ethyl-2-methyl | 8.1 | 2.3 | Yes |
| 4-pentenal/benzofuran/2,3-dihydro-/benzaldehyde | 8.67 | 7.5 | Yes |

Table X. Mid-grade gasoline listing the identity of each of the 15 most abundant components, their retention times and the area% detected.

|  |  |  |
| --- | --- | --- |
| **Component**  | **Retention Time (min)** | **Area % Detected**  |
| methane/difluoro-ethenone/tetrafluorohydrzine | 1.05 | 4.45 |
| methane/difluoro-ethenone/tetrafluorohydrzine | 1.07 | 1.31 |
| 1,4-Butanediol,2-buene-1 | 1.18 | 7.72 |
| butane/2-methyl-pentane/propanal | 1.26 | 1.91 |
| pentane,2methy-1-pentene | 1.57 | 3.45 |
| pentane/3-methyl-hexane | 1.66 | 1.22 |
| hexane | 1.78 | 1.59 |
| hexane/2-methyl | 2.46 | 3.14 |
| hexane/3-methyl-pentane/3-ethyl-heptane | 2.58 | 1.83 |
| 2heptene/4-pentenal/1-butanamine | 2.79 | 8.14 |
| Heptane | 2.93 | 1.41 |
| Pentane/2,3,4-trimethyl-pentane/2,3,4-trimethyl-hexane | 3.88 | 2.78 |
| Toluene/1,3,5-Cycloheptatriene | 4.19 | 9.65 |
| cyclopentene/benzene | 6.28 | 6.88 |
| benzene/1,2,3-trimethyl | 8.63 | 4.71 |

Table XI. Premium gasoline listing the identity of each of the 15 most abundant components, their retention times and the area% detected.

|  |  |  |
| --- | --- | --- |
| **Component**  | **Retention Time (min)** | **Area % Detected**  |
| 1-Butanol/Hydrazine,methyl-ethene | 1.17 | 5.64 |
| Furan/2,5-dihydro-2-Butene/cycolpropane | 1.25 | 3.31 |
| Cyclopropane | 1.34 | 1.54 |
| Furan/1-Heptene | 1.57 | 3.60 |
| Cyanic acid/propyl ester/1-Pentene/1-Propene | 2.05 | 2.44 |
| 1-Hexene/Pentane | 2.49 | 3.72 |
| 2-Butane/Furan/1-Butene | 2.84 | 5.12 |
| 1-Heptene/Pentane | 3.48 | 3.10 |
| Cyclopentane/1,2-dimethyl/2-Butane | 3.89 | 5.39 |
| Heptane/1-Heptene/4-methyl-hexane | 3.98 | 3.49 |
| 3-Picoline/Acetoacetic acid/1-thio | 4.21 | 5.09 |
| 2H-Pyran/Carbonochloridic acid/2H-Tetrazole-5-carboxylic acid | 4.27 | 2.91 |
| Benzaldehyde | 6.35 | 8.23 |
| Benzene/4-Pentenal | 6.80 | 3.48 |
| Benzene/1,2,3-trimethyl  | 8.66 | 3.77 |

**GRAPHS**

Graph 1. TIC uncorrected standard calibration curve

Graph 2. TIC corrected standard calibration curve

Graph 3. M/Z uncorrected standard calibration curve

Graph 4. M/Z corrected standard calibration curve

**CALCULATIONS**

Density of Gasoline: tared vial=21.1485g;

0.71344gasoline/1ml = 0.7344g/ml

Determining the appropriate dilution:

(0.08)(Xml of gasoline needed for dilution)(density of toluene 866.90)= m2(10ml)

**DISCUSSION**

*Statistical Analysis*:

*Analysis of Sources of Error*:

 Errors can be a result of contaminations from solvents or glassware. The first contaminant can be addressed by using high quality solvents and the second by thoroughly cleaning the glassware with acid washing or by heating the glassware to excessively high temperatures. Sample decomposition can also occur this can be identified by spike recovery and a new sample created. Another source of error can be with the GC column or the GC/MS interface not properly working. This can be tested by using a mixture of standard compounds of varying polarities. The mass spectrometry may not be working properly; this can be identified by running a performance standard on the equipment. Lastly, human error can be introduced by mishandling parts which may come in contact with sample stream. This can be addressed by wearing nylon gloves.

*Significance*:

*Conclusion*:

**Questions for discussion:**

1. What is the utility of an internal standard? How does it improve the analysis? Is fluorobenzene a good internal standard for all of the analytes in this experiment? The utility of an internal standard is to increase the accuracy and precision of analytical methods and to eliminate variations with the injection volume by adding a known amount of a compound, different from analyte to the unknown. Then a comparison between the analyte signal and the internal signal can be made to determine how much analyte is present in the compound. Fluorobenzene is a good internal standard for the analytes in this experiment because it has similar retention times.
2. Do you detect any MTBE in the regular gasoline sample using the TIC? Do you detect any MTBE in the regular gasoline sample when quantifying your data using *m/z* ratios? Are the results different when you quantify your results using *m/z* ratios, as opposed to the TIC? If so, state which is correct and why.
3. Compare integrated area intensities as determined by the TIC and the use of *m/z* ratios. What is the relative size of each signal? Name an instance when it would be useful to use each type of quantification technique.
4. What is the most useful detection mode for determining your target analytes in gasoline?
5. How much octane is in gasoline? How is octane rating calculated? What is the primary component in each gasoline sample and what is its concentration? What is the total percentage of octane, MTBE, benzene, toluene, ethylbenzene, (*m+p*)-xylene, *o*-xylene and octane in your three samples?

**References**

1. Elobeid, M, Almarhoon, Z, Virk, P, Hassan, Z, Omer, S, ElAmin, M, Daghestani, M, & AlOlayan, E 2012, 'Bisphenol A Detection in Various Brands of Drinking Bottled Water in Riyadh, Saudi Arabia Using Gas Chromatography/Mass Spectrometer', Tropical Journal Of Pharmaceutical Research, 11, 3, pp. 455-459, Academic Search Complete, EBSCOhost, viewed 11 July 2013.

2. Hayward, D, Wong, J, Zhang, K, Chang, J, Shi, F, Banerjee, K, & Yang, P 2011, 'Multiresidue pesticide analysis in ginseng and spinach by nontargeted and targeted screening procedures', Journal Of AOAC International, 94, 6, pp. 1741-1751, MEDLINE with Full Text, EBSCOhost, viewed 11 July 2013.

3. Kumazawa, T, Hara, K, Hasegawa, C, Uchigasaki, S, Xiao-Pen, L, Seno, H, Suzuki, O, & Sato, K 2011, 'Fragmentation Pathways of Trifluoroacetyl Derivatives of Methamphetamine, Amphetamine, and Methylenedioxyphenylalkylamine Designer Drugs by Gas Chromatography/Mass Spectrometry', International Journal Of Spectroscopy, pp. 1-12, Academic Search Complete, EBSCOhost, viewed 11 July 2013.