Chemistry 152
Experiment #3: Gas Chromatography Mass Spectrometry

GC-MS ANALYSIS OF MTBE AND BENZENE IN GASOLINE

References:


7. See Web site: http://tsrtp.ucdavis.edu/mtberpt/homepage.html

*On reserve in binders in library

Introduction:

Oxygenated compounds are now added to gasoline in many parts of the U.S. They are added to increase the octane number, compensate for the reduction of aromatic and olefinic contents, and to decrease emissions of CO (Calvert et al., 1993; National Academy of Sciences, 1991). Common oxygenates added to gasoline include methanol, ethanol and methyl-t-butyl ether (MTBE).

The octane number is a measure of the burning characteristics of the fuel, such as its ability to resist early ignition. The octane ratings are based on isooctane, which is assigned an octane number of 100, and heptane, which is assigned a value of 0.

In addition to a variety of non-aromatic hydrocarbons in gasoline, there are many aromatic hydrocarbons, some of which are classified as toxic chemicals (this is why you see warnings at gasoline stations). One of the major ones is benzene (Kelly et al., 1994).
The goal of this experiment is to determine the concentration of MTBE and benzene in a sample of gasoline, and to identify as many components in the gasoline using MS as you can.

Experimental:

The brown vials are used for storing your pure gasoline sample. Once you’ve filled the vial fully with gasoline, cap immediately with a septum and cap. DO NOT remove the cap unless you run out of gasoline. Use this gasoline to make all the solutions in the experiment.

The clear vials are used for storing the other chemicals used in this experiment (benzene, o-xylene, toluene, MTBE).

The 1 mL volumetric flasks are used in making the solutions in Part A & B. The volumetric flasks MUST be capped with a septum and cap.

WARNING: The possibility of contamination of samples is very high. Please make sure to rinse the injection syringe at least 5 times when switching between solutions.

A. Analysis of Pure Gasoline:

Note: Read and follow the instructions in the GC-MS operational guide, parts 1-5.

1. Load the method called “gas04.m”. Check to see that the parameters are set as shown in the attached. Especially check that there are two solvent delay times set at 0-1.0 min. and 17.5-21.9 min. To check the second solvent delay click on “More”.

Normally, a solvent is used for analysis of most samples, and the chromatographic column is chosen such that the solvent comes off first, followed by the trace components in a certain order. If this slug of solvent goes into the mass spectrometer when the MS is on, two things happen. First, the filament, the source for the electrons which bombard the sample to form ions, will burn out (disaster!!). Second, the large amount of solvent coming off the column all at once will cause the pressure in the MS to be too high for the high voltages, causing it to shut down or short out.

To avoid these CRITICAL problems, there is a "solvent delay time" set up in the method. During this time, the power is off to both the filament and the quadrupole MS. At the end of the solvent delay time, the power automatically comes on and mass spectra are recorded from this point on.

In your analysis of the gasoline sample, the solvent chosen is 1-chlorohexadecane which elutes at long times, after most of the gasoline components have eluted. Two solvent delay times are used, one for 0-1.0 minute to let any air which was in the syringe come through (which can have the same effect on the filament and MS as a solvent) and one from 17.5-21.0 min., the time when the 1-chlorohexadecane solvent elutes. HOWEVER, you can still wipe out the MS by injecting too large a volume. Be sure NOT to exceed the volume you are instructed to inject.
2. Make a 1:4 (v:v) mixture of gasoline and 1-chlorohexadecane by adding 200 µL of gasoline to a volumetric flask and adding the solvent up to the 1.0 mL mark.

**General Suggestions for making solutions:**
- Make each solution just before you are ready to inject it.
- Rinse volumetric flasks at least three times with small amounts of solvent.
- Use a syringe to fill half of the volumetric flask with solvent (through the septum: DO NOT OPEN CAP! This method will help to prevent evaporation of the components).
- Add the first component, then (where applicable) the next component.
- Use the syringe again to fill the flask with solvent to the mark.
- **Syringe needles bend easily when pushing through the septum; be careful**

3. Inject 0.05 µl of the gasoline/solvent mixture into the GC. Immediately after injection, press “start” on the front of the GC. When asked: “Override the solvent delay (1.00 minutes)?” Choose No… this is very important. Remember to rinse the injection syringe at least 5 times.

4. Print out the TIC (total ion chromatograph) then choose at least 3 distinct peaks in the chromatogram that come out before 12 minutes retention time. Print out their mass spectra and use the library spectra on the computer to identify them (see GC/MS lab manual for instructions).

5. Confirm your identification of peaks due to toluene and o-xylene by spiking your gasoline/solvent solution with toluene and o-xylene. To do this, add 50 µL of toluene and 35 µL of o-xylene to the existing gasoline/solvent mixture and mix well.

6. Inject 0.05 µL of this mixture and observe which peaks have increased. Using a combination of retention time and the mass spectrum, confirm which peak is due to toluene and which is due to o-xylene.

7. For both the gasoline sample from step 2 and the spiked sample in step 4, plot the single ion chromatograms for the ions at \( m/e = 73 \) and 78, and then again for 91 and 106, corresponding to major ions characteristic of MTBE, benzene, toluene and the xylenes respectively. This technique is called “single ion monitoring”, or SIM.

8. For the unspiked gasoline sample in step 2, print an area report (see GC/MS manual) for the single ion chromatograms. Calculate the ratios of the peak areas corresponding to MTBE/toluene, benzene/toluene, MTBE/o-xylene and benzene/o-xylene. Using ratios to toluene and o-xylene, in effect, uses these as internal standards to correct for any differences in injection volumes.

**B. Preparation of Standards:**

You will measure the MTBE and benzene in gasoline using the method of standard additions. That is, you will add measured quantities of MTBE and benzene to gasoline and use these as
your calibration standards to measure how much MTBE and benzene were in the gasoline itself before you added MTBE and benzene.

You will make the following mixtures of MTBE, benzene, gasoline and 1-chlorohexadecane solvent:

<table>
<thead>
<tr>
<th>Solution Number</th>
<th>Volume of Gasoline (µL)</th>
<th>Volume of MTBE (µL)</th>
<th>Volume of Benzene (µL)</th>
<th>Add 1-chlorohexadecane to a Volume of:</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>750</td>
<td>0</td>
<td>0</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>2</td>
<td>750</td>
<td>30</td>
<td>3</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>3</td>
<td>750</td>
<td>50</td>
<td>7</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>4</td>
<td>750</td>
<td>100</td>
<td>10</td>
<td>1.0 mL</td>
</tr>
<tr>
<td>5</td>
<td>750</td>
<td>150</td>
<td>15</td>
<td>1.0 mL</td>
</tr>
</tbody>
</table>

C. Analysis of Standards:

1. Inject 0.05 µL of each of these solutions. Do two separate runs with each solution for reproducibility. To avoid evaporation and contamination, it may be helpful to make the solution immediately before injection (i.e. during the previous run).

2. Print the area report for single ion chromatograms of MTBE (m/e = 73), benzene (m/e = 78), toluene (m/e = 91) and o-xylene (m/e = 106) for each injection. Calculate the ratios corresponding to MTBE/toluene, benzene/toluene, MTBE/o-xylene and benzene/o-xylene. Calculate the average and standard deviation for each ratio from your two separate injections. Report your data as the average ± 2σ.

3. Plot the ratio of MTBE to toluene and to o-xylene (i.e. two separate lines on one graph) against the added volume of MTBE.

   For comparison to illustrate the advantages of using an internal standard, also plot the absolute peak area of MTBE against the added volume of MTBE in a separate graph.

4. Plot the ratio of benzene to toluene and to o-xylene (again two lines on one graph) against the added volume of benzene.

5. Carry out a least squares analysis for each of the lines to obtain the slope m and the intercept b. The relationship between the ratio of the MTBE (or benzene) to the internal standard (R) and the volume of MTBE (or benzene) added to the mixture (V_MTBE) is as follows:

\[ R_{MTBE/Std.} = m V_{MTBE} + b \]  

(I)
The ratio of the intercept to the slope of the lines is related to the (constant) volume of the gasoline used in each mixture, $V_{\text{gas}}$, and the volume fraction ($f$) of MTBE (or benzene) in the gasoline, which is the quantity of interest:

$$b/m = f V_{\text{gas}} \quad \text{(II)}$$

Use the slope and intercept of these plots to calculate the volume fraction of MTBE and benzene in the gasoline. Since you are using two different internal standards, toluene and $o$-xylene, you will get two different estimates for each compound. Convert these to the volume percentage of MTBE and benzene respectively in gasoline.

**Points for Discussion:**

1. For at least three compounds you identified using MS, draw the structure of the parent compound and identify the major fragment ions in the mass spectrum.

2. Carry out a complete error analysis and put error bars corresponding to 2 standard deviations on your measurement of MTBE and benzene in gasoline. Compare the answer you get for MTBE using toluene as the internal standard to that using $o$-xylene, and do the same for benzene. Comment on which one you think is more reliable, i.e. accurate, and why.

3. You plotted the absolute area of MTBE against the added volume of MTBE, and carried out a least-squares analysis of the data. Compare the precision of this approach to that using the ratio of MTBE to the toluene and $o$-xylene by comparing the standard deviations of the slopes of the lines. What does this tell you about the advantages of using internal standards?

4. The single ion chromatogram for $m/e = 106$ shows more than one peak. Why?

5. Is it necessary to use single ion monitoring for this analysis? Why or why not? Be specific, using your own data to illustrate.

6. Derive equation (II) from equation (I) using first principles.

7. When the software carries out a “tune” or “verification” initially, what is it adjusting?
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GAS04.M  Method Parameters

Method Name : C:|\BACKUP\CHEMBACK\1\METHODS\GAS04.M
Instrument Name : GCD Plus
Method Last saved : Mon Jan 03 10:36:12 2005

Chromatographic Parameters
Inlet : 210 C
Detector : 230 C
Split injection

Oven Information
Column Max : 250 C
Initial Temperature : 35 C
Initial Time : 1.0 min

Oven Ramp

<table>
<thead>
<tr>
<th>Level</th>
<th>Rate</th>
<th>Final Temperature</th>
<th>Final Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level 1</td>
<td>2.00 C/min</td>
<td>60 C</td>
<td>0.0 min</td>
</tr>
<tr>
<td>Level 2</td>
<td>70.00 C/min</td>
<td>225 C</td>
<td>6.0 min</td>
</tr>
<tr>
<td>Level 3</td>
<td>-----</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

Total Time : 21.9 min

Injection Parameters
Injection Mode : Manual
Sample Volume : 1 Stops
Solvent A Washes : 1
Solvent B Washes : 2
Sample Pumps : 2
Sample Washes : 3

Constant Flow
Column Length : 30.0 m
Column Diameter : 0.25 mm
Gas : Helium
Flow : 1.0 ml/min
Pressure at 50 C : 53 kPa

Detector Parameters
Solvent Delay : 1.0 min
Mass Range : 10:110 m/z

Timed MS Detector Entries

<table>
<thead>
<tr>
<th>time (min)</th>
<th>State (MS on/off)</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.50</td>
<td>Off</td>
</tr>
</tbody>
</table>

Reports
Area Percent : No
Summary Library Search : No
Detailed Library Search : No
Quantitation : No
Graphics : No

Method: GAS04.M
Mon Jan 03 10:37:30 2005