

## **Air Quality 1 - GC/MS Analysis of Benzene in Gasoline**

### **Introduction:**

Benzene is listed as a class 3 transportation hazard with the following OSHA HAZARD COMMUNICATION STANDARD: Flammable liquid. Carcinogen. Irritant. CNS Effects. Target organ effects. As with most organic substances, benzene was not always recognized as a health risk. One of the early uses of benzene was as a lamp fuel in large cities like London, and a few decades ago it was used in dry-cleaning and as a common solvent in organic chemistry labs. Today it is more tightly regulated and is not commonly used as a solvent.

Probably none of the above comes as a surprise to you, since the carcinogenicity of benzene is known by most scientifically literate people. But given the potential health impacts, it is a little surprising to consider that you can readily purchase a solution that is ~ 1% benzene (by volume) in various other hydrocarbons for a little over \$3.00 a gallon (as of this writing). Of course the source I'm referring to is gasoline, which is cheap, readily available, and can be purchased without any kind of license or certification. Moreover, a significant fraction of the benzene and toluene (also a few volume percent in gasoline) escapes during storage or remains uncombusted in the automobile exhaust and ends up in the atmosphere. In this lab class, we will be doing a two-part sequence of experiments to explore the possible impact on human health of two known urban air quality problems. In part one of the sequence, we will use gas chromatographic separation of the components of gasoline with mass spectrometric detection of specific compounds (a.k.a. GC/MS) to determine the benzene content in a gasoline sample from a local station. In the second part we will measure the concentrations of lead and cadmium (both toxic metals, where cadmium is also carcinogenic) in ambient aerosol collected from in Portland, OR.

### **Apparatus:**

- Small Glass Vials with septum lids (2) containing 4 mL gasoline sample and neat benzene
- 100  $\mu$ L graduated syringe (for spikes)
- 1  $\mu$ L graduated syringe (for GC injections)

### **Instrumentation (See Appendix for Operating Instructions):**

HP 5890/5970 GC/MS with associated Data System

### **Solutions available:**

Gasoline (in hood, in sealed septum vial)

Neat AR grade benzene (in hood, in sealed septum vial)

### **Experimental Overview:**

The method of quantitation will be a standard addition method using integrated peak areas from Selected Ion Chromatograms (SIC). To improve the precision of the individual chromatographic measurements, we will use the toluene that is also present in the gasoline as an internal standard (chemically similar compound). Review the methods of standard addition and internal standards if you feel unfamiliar with their use. The advantages to using standard addition here are that it would be difficult to simulate the complex matrix of gasoline in constructing standards for an external calibration curve and because calibration transfer for GC-MS is problematic under the best of conditions. The use of peak areas (as opposed to peak heights) in chromatography is standard, and you will find that the data systems for modern computer-controlled chromatographs will integrate the peaks for you. The utility of using selected ion chromatograms will become apparent as soon as you see the complex mass spectra and unresolved chromatograms that you will obtain from the gasoline samples. You may also wish to quickly review the basics of mass spectrometry, although for the purposes of this experiment, the level of understanding obtained during sophomore-level organic chemistry will be sufficient.

### **Experimental Procedure:**

1. Carry out all transfers of gasoline and benzene in the hood. Obtain a gasoline sample in a sealed vial with a septum cap. Follow the directions provided in the appendix for preparing the GC/MS acquisition up to the point where you would click "start". When you are ready (and the GC is at the right temperature) inject 0.3  $\mu\text{L}$  from the 1  $\mu\text{L}$  syringe (be sure that you are consistent in the size of your injections!) and push the "start" button on the GC (or click the "start" button on the mass spec computer). After the chromatogram has finished, open the ChemStation software according to the directions and access your data file.

When you open your data file, you will see the total ion chromatogram (TIC) which is similar to the information you would get from one of the other general GC detectors like the FID or TCD. Clearly there is not a complete separation of the many similar compounds in gasoline. Double right click on any point in the chromatogram and in the bottom display you will see the mass spectrum of all of the components that eluted at this time. Notice the extensive fragmentation of the C<sub>8</sub> alkane compounds that elute at early times. Under the menu item Chromatogram find the command Extract Ion Chromatogram and select it. In the first two empty boxes for the selected ions, enter **78** and **92** (the molecular weights of benzene and toluene) to see the chromatograms that are due to benzene and toluene. Note how much more ideal the selected ion chromatogram (SIC) for benzene looks vs. the TIC. The first peak in the mass 92 SIC is toluene, but there are usually other, later peaks due to high MW aromatic hydrocarbons that also produce the m/z 92 fragment ion. Verify that toluene separates from benzene. You can track other interesting compounds (check the NIST chemistry webbook for major fragment ions) if you wish. With the selected ion chromatograms for mass 78 and 92 on the display, integrate the peaks as

described in the appendix and record the peak areas. Choose one set of TIC and SIC results to use as a figure in your report (the procedure for this is described in the appendix).

2. Because of memory/carryover effects, record at least two chromatograms of each sample that you analyze during the standard addition procedure, including the initial gasoline sample. If the ratio of the peak areas for  $m/z$  78/92 (from the integrations) for the two chromatograms are not similar, another run can be useful (if there is time – this experiment tends to consume the whole five hour lab period). As always we will be using the replicate results to establish the uncertainty of the method.
3. Next you will carry out the standard addition method. You will construct and analyze three to five additional samples containing the initial gasoline sample plus precisely known amounts of added benzene (the *spikes*) that span the expected percentage or concentration range. Typically spikes of 20  $\mu\text{L}$  (x1, 2, 3, etc). will span the concentration range of the benzene. By injecting the benzene into the capped septum vial in the hood, and then mixing and transporting to the other room, you can minimize your exposure to both benzene and gasoline vapors. Keeping the gasoline sample on ice seems to give better results, presumably preventing benzene from escaping from the sample.
4. As always, you will find that you obtain better results if you analyze them while you are conducting the experiment. After the addition of the first spike, you will know the approximate concentration of the benzene in the gasoline and can tailor the rest of the additions accordingly. You should have prepared a suitable spreadsheet for the analysis ahead of time. Keep in mind that you can't "unspike" a sample, and you don't have time to start over with a new sample, so be careful to not use too large of a spike at the beginning. Try to at least double the initial value of the peak area ratio (78/92) by the end of the last spike. But be forewarned that the signal begins to saturate at a concentration that is only a few times the initial value.

**Report:** In preparing the partial report for this two-week experiment set, you should consider/complete/discuss the following:

1. Provide the results for the replicate determinations of the integrated peak areas and the peak ratios (78/92) for all of the neat and spiked gasoline samples in tabular format.
2. Include a figure of the results of the standard addition procedure and the linear regression analysis of this data. The slope, intercept, and correlation coefficient should be shown on the graph.
3. The standard deviation in the calibration (or the intercept, depending on how you analyze the results) should be used to estimate the error limits on the final value of the benzene concentration in gasoline. Keep in mind

(during your calculations) that the spikes are increasing the benzene concentration, but also increasing the total volume and hence *decreasing* the toluene concentration. Should this be a measurable effect?

4. You can either express the answer as weight percent or volume percent (if you assume negligible volume change of mixing). You may find it interesting to comment on how much benzene is riding around in the gas tank of your car at the current time. Is it within the legally mandated (EPA) limits?

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