

## Air Quality 2 - GC/FID Determination of Toluene in Air

### Introduction:

In the first part of this experiment we found that there are measureable amounts of benzene and toluene (and higher molecular weight aromatics) in gasoline. And we noted that a significant fraction of the aromatics in the fuel ends up in the air we breathe via tailpipe emissions and direct releases associated with the storage and transfer of the fuels. There are other sources of these compounds but the transportation sector represents a major source of aromatic hydrocarbons in the atmosphere. When we do measurements of the volatile organic compounds (a.k.a., VOCs) in Portland's air during our atmospheric chemistry research, toluene is typically at the highest concentration of any hydrocarbon except for methane (which has a host of sources, both *biogenic* or natural and *anthropogenic* or man-made).

In this experiment you will measure the volume fraction concentration (in parts per billion by volume, ppbv) of toluene in air samples. You will collect the samples in special Teflon bags and return them to the laboratory for analysis. The method of analysis is gas chromatography with flame ionization detection (GC/FID) using cryogenic preconcentration. The quantitation method will be based on an internal standard calibration transfer using m-xylene. Several air samples will be analyzed and optimally some replicate analyses will be conducted (if time allows).

### Apparatus:

HP 5890 series II Gas Chromatograph with FID detection and air sample loop injection  
Tedlar (a type of Teflon) gas sampling bags with valve and septum port  
“Bucket brigade” air sampling apparatus  
Dewar and liquid nitrogen  
1.0 mL Pressure-Loc Gas Syringe

### Standards Available:

~100 ppmv m-xylene air standard bag

(TAs will provide the data needed to calculate the exact concentration of this standard.)

### Experimental Overview:

Your group will first go out into the “real world” and draw a few (three to four) air samples, and bring them back to the laboratory for analysis. You should try to collect samples that will show a variation in hydrocarbon pollution content. Take notes on where you took the samples and the relevant atmospheric conditions.

You’ll record one or two gas chromatograms per sample (with the internal standard) except for the first sample, where you will also run an experiment *without* cryogenic preconcentration. The non-preconcentrated experiment can be compared to the same sample with preconcentration to determine the extent of the preconcentration. The time per analysis (each chromatographic analysis will be referred to as a “run”) is over 20 minutes, so you need to be organized and efficient to get three or more air samples collected and analyzed during the lab period.

You will be pulling the air samples through a small (~ 100  $\mu\text{L}$ ) metal sample loop that is immersed in liquid nitrogen (the *cryogen*) for a pre-planned length of time, usually about 5 minutes. The  $\text{LN}_2$  doesn’t affect the majority components of air (nitrogen and oxygen) under our conditions, so they flow on through to the air pump. The hydrocarbons (and water and carbon dioxide) are trapped in the sampling loop during the passage. Theoretically, the longer you run the air through the cryogenically cooled loop, the more hydrocarbon you will end up with in the loop; but in the interest of time, we won’t test that idea.

After the preconcentration (or shortly after the flow is established in the non-preconcentrated sample) a sample valve similar to those used in liquid chromatography is used to inject the volatile contents of the sample loop onto the column for separation and eventual detection and measurement by a flame ionization detector (FID).

The method of quantitation will be calibration transfer using an internal standard. A small amount of gaseous m-xylene will be added as the chemically similar internal standard. This method will require that you measure the volume of the air in the teflar bag so that you can calculate the concentration of the m-xylene and thus the toluene.

## Detailed Procedure:

### Air sampling

Have the TA show you how to use the sampling bucket and tedlar bags.

- Go out into the “field” and take a few air samples – *i.e.*, fill up three or four tedlar bags with air. Air samples taken in this way are referred to as “grab” samples. Try and fill the bags as completely as possible.
- To make things interesting, try taking samples from areas where you expect there to be a lot of hydrocarbons (high traffic) and areas with less pollution (nearly the city-wide background). Keep records of where you took each sample and other observations (*e.g.*, heavy traffic, wind from South, temperature, barometric pressure, raining...)
- Bring all samples back to the laboratory for analysis.

### Internal Standard Procedure

For each air sample, we will run one or two chromatograms after adding the internal standard m-xylene. (We’re making the assumption here that m-xylene isn’t present in ambient air.) To add m-xylene to the air samples:

- Insert the 1.0 mL graduated **gas** syringe into the standard bag through the septum in the tedlar bag (the tiny hole on the side of the valve/inlet for the bag).
- Press the green button to open the syringe valve.
- Rinse the syringe a few times and then pull a 1.0mL sample of the gas standard.
- Press the red button to close the valve.
- Pull the syringe out of the standard bag and insert it through the septum port in the sample gas bag.
- Press the green button.
- Inject the spike and remove the syringe.
- Mix the sample thoroughly by “squishing” the bag for a few minutes at least. *{It’s boring and noisy, but if you don’t work at it, you will not end up with good results because the diffusional mixing of gases at atmospheric pressure is very slow.}*

- Measure the volume of the bag and calculate the concentration of m-xylene. (We are currently measuring volume using a water displacement method. See the Appendix for directions).

### **Analysis:**

- Make sure that the computer and the GC are on and that the FID is lit and has stabilized.
- Get a transfer dewar full of liquid nitrogen from the big stainless steel storage dewar. (If you haven't done this before, ask the TA for help.)

### **For the one non-preconcentrated run**

- Choose the tedlar bag that you think will have the highest toluene concentration and insert the valve stem into the flexible tubing coming out of the center of the sampling valve on the front of the GC. (It's a tight fit, but you don't have to have more than a few mm on to make a seal.)
- Make sure the GC sampling valve is in the LOAD position, turn on the air pump, open the valve on the bag, and allow the sample to flow through the loop for a few seconds.
- Switch the GC sampling valve to the INJECT position and press the START button on the GC. Within a few seconds, a red vertical line should appear on the continuous output screen on the computer, signifying the beginning of a chromatogram.
- Close the valve on the Tedlar bag and remove it from the flexible tubing.
- After ~ 1 minute, return the GC sampling valve to the LOAD position to get ready for the next run. {You can leave the air pump on all the time, to help flush the last sample from the sampling loop before the next chromatogram.}
- The run takes 18.75 minutes and the toluene and m-xylene elute well before the end, but you should always let the chromatograph run for the full time to drive higher molecular weight compounds from the column.
- When the chromatogram finishes, the status bar on the computer will change from BLUE (running) to RED (not ready) and the temperature of the oven will start to go down. The chromatogram will briefly appear on the computer screen (then the screen will go back the running signal display) and the Report Screen will refresh.

**For ALL preconcentrated runs (i.e., all the rest of the analyses)**

- Attach the tedlar bag's valve to the flexible tubing on the sampling valve.
- Make sure the GC sampling valve is in the LOAD position and turn on the air pump, open the valve on the bag, and allow the sample to flow through the loop for a few seconds.
- Next you will simultaneously place a Styrofoam cup full of liquid nitrogen around the sample loop, immersing the bottom half of the coils in the cryogen, and start a timer. {The length of time that the cryogen is on the loop determines the extent of preconcentration, and thus should be as consistent as possible. You could change the trapping time between samples if more preconcentration was desired for some samples, but this is usually not necessary and can cause confusion.}

***Read through the next three steps as they are all time critical***

- At the end of the predetermined trapping time (usually 5 minutes) remove the cup with the liquid nitrogen cryogen and wait for ~3 seconds to allow liquid oxygen to escape from the sampling loop
- then switch the GC sampling valve to the INJECT position
- then place a cup full of room temperature (or warmer) water around the loop and press the START button on the GC. {The water heats the loop and rapidly drives the volatile contents out of the loop and onto the GC column.}
- Close the valve on the gas sampling bag, remove it from the flexible tubing, and measure the new air bag volume.
- After ~ 1 minute, return the GC sampling valve to the LOAD position to get ready for the next run.
- Again, when the chromatogram finishes, it will briefly appear on the computer screen (then the screen will go back the running signal display) and the Report Screen will refresh. {At this point, the chromatogram and peak integrations should print automatically. If not, you can print this information by selecting Tabulate → Print on the top of the Report Screen. Don't forget to print before the next chromatogram finishes, or you will lose your data.}

On the report printout, locate the toluene and m-xylene peaks and obtain the peak areas. Calculate the toluene concentration in the air sample using: the presumed relative response for toluene and m-xylene in the FID detector, the concentration of the standard and the volume transferred and in the sample bag after the transfer (and the ideal gas law).

**Report:** In preparing the full air quality report, you should add the following to the items already presented during the partial report for the GC/MS:

1. Present the relevant peak areas, concentrations, and quantitative results (in ppbv toluene) in tabular form.
2. Be sure to explain in the Introduction how toluene concentration was calculated.
3. Comment on the extent of preconcentration, based on your sample run without the cryogen – quantitatively if possible (*i.e.*, you have to have seen something to figure out how much it increases – otherwise the answer might just be “a lot”.)
4. Provide a map of your sampling locations and say whether your results were consistent with your expectations during sampling.
5. In addition to quoting the volume fraction concentration for the “unknown” air samples, also give the ppbvC (volume fraction carbon.) This is the relevant parameter in calculating the ozone producing potential of VOCs.
6. Comment on the possibility (box model?) that the toluene present in the air could have come from the fuel source examined in the first part of the lab. If benzene behaves similarly, how large of a public health problem would this be?

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