Air Quality 2b - PFGC/FID Analysis of Benzene and Toluene in Automobile Emissions

Introduction:

There is a bit of explanation of the health effects of benzene in the Introduction section of the first part of this round of experiments. This experiment is offered as an alternative to the ASV analysis of metals in aerosols for those who want to keep with the general theme of the atmospheric chemistry of volatile organic compounds (aka VOCs).

In this experiment you will use the Pneumatic Focusing Gas Chromatograph, which was invented right here at PSU by one of our (now Emeritus) professors in Chemistry, Dr. Robert O'Brien. Dr. O'Brien formed a company (VocTec, Inc.) that builds and sells these instruments and also does atmospheric measurements on a contract basis. The instrument is designed for continuous field measurements and is thus almost completely automated (which turns out to be a bit of a double-edged sword for this experiment, as you will see when you read the Appendix). Although our instrument (one of the first models produced by VocTec) has trouble measuring ambient levels of the hydrocarbons in Portland, it can easily measure the levels in automobile exhaust and fugitive emissions, so this experiment centers on the determination of benzene and toluene in those samples, as a companion to the GC/MS analysis of gasoline. When I say it "easily" measures these levels, I mean that you have to dilute the samples 1000-fold or more to bring them into the appropriate concentration range!

Because the chromatographic separation is pretty time-consuming (just under one hour per "run" including cool down times) you will only be able to measure and quantitate two samples (two runs and two "spiked" runs ~ 4 hours). I suggest two possible sets of samples, but if you have another idea, just discuss it with your TA before you try it out.

Option 1: Fugitive and exhaust emissions - Obtain a *fugitive emissions* sample (the VOC vapors that escape from the gasoline into the air during storage, either before sale or in your gas tank) by opening the gas cap on your car and using a pen or your finger to hold down the vapor containment plug. Use the 1 mL gas-tight syringe to pull a 1 mL vapor sample and inject it into the Tedlar gas sampling bag through the red septum in the valve. (To avoid puncturing the back side of the bag with the syringe, you should fill the bag approximately 1/4 of the way before leaving the lab to acquire the samples.) Obtain an *exhaust* sample while the car is running from right at the tailpipe. Preliminary experiments indicate that the levels are low in regular idling exhaust, so I recommend either having a partner rev the engine gently (with the transmission in park or neutral!) while you take the sample, or taking more of the exhaust (perhaps five 1 mL gas samples). Inject the samples into the quarter-full bag immediately after pulling them so the vapors do not escape before injection.

Option 2: Comparison of different exhaust emissions - Sample the exhaust as described above into quarter-full Tedlar bags, but either do two different vehicles (one gasoline/one diesel, one old/one new, one hybrid/one standard, etc.) or two different idle conditions (one at normal idle/one at high idle, especially if you have a tachometer). Again, if you suspect one of the exhaust samples is relatively "clean", feel free to use more than one 1.0 mL gas sample in the bag - 5.0 mL into the 5 L gas sampling bags is still a factor of 1000 dilution.

Apparatus:

- Small Glass Vials with septum lids (2) containing 4 mL neat toluene and neat benzene
- 1 mL graduated gas tight syringe (for sampling and spikes)
- 2 x 5-L Tedlar (a special type of Teflon) air sampling bags
- Bucket brigade sampler with Shark vacuum cleaner
- Water displacement chamber (large plexiglas cylinder)

Instrumentation (See Appendix for Operating Instructions):

VocTec PFGC (affectionately known as "the GC in a PC") with integral Data System

Quantitation Overview:

The method of quantitation will be a standard addition method using integrated peak areas based on only a single spike (because of the analysis time). This probably results in less accuracy and precision than we are used to, but cannot easily be avoided. You do have an opportunity to assess the relative uncertainty in the measurement (semi-quantitatively) by comparing the increase in peak area per increase in benzene/toluene concentration for the two spiked samples. This is not enough to obtain a standard deviation, of course, but the difference between the two divided by the average is probably a reasonable estimate of the relative precision of the chromatographic method.

Experimental Procedure:

Important Note: The PFGC was intended to run automatically without user intervention and does not behave as well if we interfere with that. So we will allow it to operate on its own schedule, which is: a sampling, followed by a 40 minute run, followed by a ~ 10 minute cool-down time, and then a repeat of that cycle. Sample bags that you want to analyze are attached to the flexible tubing that comes out of the instrument (open the valve on the bag by pushing it in). <u>Sample bags should be attached to the instrument in the time window between 10 minutes from the end of a run (30 min into a run) and 5 minutes into the cooling period.</u> The sample is pulled continuously through the internal sampling loop, so the latter time is necessary to make sure the sample has fully filled the sampling loop. The former time is to avoid leaving the bag on the instrument so long that it is completely emptied. After the chromatographic injection (about 5 minutes into the run) you can remove the sample bag from the flexible tube and close the valve (and usually do a spike, fill, and re-measurement of the volume, as explained below).

1. Following the instructions in the Appendix, start the PFGC (if necessary). It will automatically begin collecting an air sample from the lab, which will take an hour.

2. Using the bucket brigade sampler and Shark vacuum cleaner, fill two Tedlar bags 1/4 of the way with lab air. Close the valve after filling by pulling the valve stem out (push it in to open it). This is just to make it easier to do an injection through the septum, so the actual amount isn't very important, but partially full bags are easier to deal with than completely empty or full bags. Decide on which types of samples you will take, referring to the discussion in the Introduction.

3. Go to the car and take the samples, keeping in mind that you probably have a little under an hour to get them, get back to the lab, and finish preparing them for the analysis.

4. When you return to the lab, finish filling the sample bags with laboratory air using the "bucket brigade" sampler and Shark vacuum cleaner (don’t forget to plug it back in after you use it). We fill the bags in this way for two reasons; 1) there is no possibility of "popping" the Tedlar bags in this way by over-filling, and the bags cost $50 each; and 2) the laboratory air is being continuously sampled by the instrument, so the run before your first sample run can be regarded as a very good "blank" measurement.

5. After filling the bag, determine the volume of the resulting air sample using the water displacement method and use this to calculate the dilution ratios for your samples. Connect the sample bag to the instrument using the flexible tube after opening the valve by pushing it in. Pay attention to the note above about when you can connect your sample to the inlet line for the PFGC, since missing this time window costs you a full hour (and thus probably one sample run).

6. After your first sample is injected into the GC (you will hear the valve switch at the beginning of the run and then a loud "whoosh" three minutes later when the GC switches back to the Load position) use the 1 mL gas-tight syringe to sample 0.1 mL of neat benzene vapor from the air space above the liquid in the sealed vial and inject this into the sample bag. Carry out all transfers of neat toluene and benzene in the hood. Repeat this with the toluene vapor. Refill the Tedlar bag with the bucket sampler, and re-measure the volume using the water displacement chamber. Use this volume (and the vapor pressures of benzene and toluene) to determine the added concentration of the benzene and toluene.

7. After running this spiked sample, you can determine which of the peaks in the chromatogram are benzene and toluene (assuming benzene elutes first); and from the peak areas, the original concentration of benzene and toluene. In this last calculation, you can probably assume that the residual benzene and toluene (from

the sample) is negligible with respect to the added concentration, but the right way to do it is to determine the dilution of the original sample from one of the other peaks and subtract the corrected peak areas for the two analytes from that of the standard additions.

8. Repeat the whole procedure for the second sample that you collected.

9. To analyze your data (can be done while the chromatograph is running) open the VOCTec Graph Integrator program (on the toolbar "gr. i."). Choose "import graph" and navigate to the current day's data folder (go up to the desktop, then double-click VOC-5920-PSU, then 5920 C:, then GC.dir, then click the right-most view and sort the folders by date, and finally choose the one that is the current date). Again sort the files by date and choose one or more of them (if you have all of the runs done you can open all of them, but more likely that you will open one at a time to analyze) and click OK to open the chromatograms. If it looks like you selected the correct file, you can use one of the Export options (under the File menu) to make a figure for your report. I suggest just exporting the data and then opening it in Excel, since you know how to make nice graphs in it. You can then integrate the peaks as you did in the LC experiment manually in Excel, or use the GRI program. Assuming you want to do it the easier way (the latter): 1) Use the + magnifying lens tool to zoom in on the peaks that you want to integrate (usually pretty late in the chromatogram); 2) use the tool to the left of that to choose the peaks you want to integrate - note that you click once to start the box and a second time to end it; 3) when you have boxes for all of the peaks you want to integrate, click the "view results" icon on the toolbar (remember, this program is designed to look at days or weeks of data, so this display is kind of weird for one or two samples); 4) under the File menu you will now find an Export results option that will allow you to write the peak positions and integrals for one or all of the runs to a *.csv file that you can open in Word or Excel. You don't have to close one file to open the next and it really helps to have them overlaid in the display when you try to figure out which peaks are benzene and toluene from the spiked samples.

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

1. Provide the results (chromatograms and tabular presentation of peak positions and areas).
2. Be sure to comment on the reproducibility of the retention times for the target compounds and for the analytical sensitivity (peak area per volume concentration from the two different standard additions).
3. (For the "motorheads") - estimate the volume flow rate of the exhaust from the rpm used, engine displacement, and number of cylinders. Use this and the measured concentration in the exhaust to estimate the emission rate of benzene and toluene in mg/minute (or vehicle mile traveled VMT). Comment on whether this is an under or overestimate.
4. If you did the fugitive and exhaust emissions, comment on this as a source of benzene in the environment and on the removal efficiency during the

combustion process (you'll need to make some pretty extreme assumptions).

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