AirUCI Summer Training
Workshop in Environmental
Chemistry for Science Teachers

UCI Course Code: CHEM X416
6 quarter credits (UCI Extension)
Summer Quarter 2014
June 20 – July 2, 2014

Program Coordinators: Mickey Laux, Sergey Nizkorodov, Melissa Sweet
AirUCI director: Barbara Finlayson-Pitts

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Sponsor: National Science Foundation
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AirUCI Summer Teacher Workshop 2014 Schedule

Friday, June 20
9 am to 10:00 am: Room Rowland Hall 390
- Brief welcome by Prof. Barbara Finlayson-Pitts
- Entrance evaluations

10:00 am to 11:30 am: Room RH 390
- Lecture by Prof. J. Mickey Laux
  - Overview of the atmosphere: regions, pressure and temperature (p. 4–5), inversions (p. 4, 17–18) and composition (p. 5, 37–38, 69–70, 179–180, 189–191 and 274–275)
  - Free radicals (p. 21, 73–74, 755–761), sources/sinks (p. 54, 58, 73, 216–219, 758)
  - VOC’s (p. 77–78) and Polycyclic Aromatic Hydrocarbons, PAH (p. 663–672)
  - Overview of common public environmental concerns
  - Overview of Organic Chemistry (online at: www.whfreeman.com/envchem5e)

11:30 am to 12:30 pm: Lunch with AirUCI faculty and researchers (provided)
- Introductions of the AirUCI faculty and associates (starting at noon)

12:30 pm to 1:30 pm: Room RH 390
- Lecture by Prof. J. Mickey Laux - continued
  - Mathematics in chemistry review (p. 71–72, “Box 3–1”)
- Safety by Prof. Sergey Nizkorodov
  - Discussion of laser and lab safety

1:30 pm to 2:15 pm: Room RH 481
- Overview of wet labs by Prof. J. Mickey Laux
  - Determination of PAH in cigarette smoke by HPLC
  - Determination of ethanol and benzene in gasoline by GC/MS
  - MTBE in gasoline and ethanol in vodka / mouthwash measured by FTIR
  - Ability of catalytic converters to reduce air pollution
  - Laser–Induced Breakdown Spectroscopy (LIBS) of common materials

2:30 pm to 4:00 pm: Room RH 390
- Lecture by Prof. J. Mickey Laux - continued
  - Using Microsoft Excel for plotting on laptops
  - Forming lab groups (20 attendees divided into 5 groups of 4 people)
- Common lab techniques: pipetting, measuring volumes, mixing solvents, using syringes

Monday, June 23
9 am to 10 am: Room Rowland Hall 390
- Lecture by Prof. Sergey Nizkorodov
  - The use of light in analytical chemistry
  - Absorption of light and Beer's Law (p. 6–9, 177–179, 184–186, 193 and 197)
  - Emission and fluorescence
  - Lasers; Overview of the LIBS lab.

10 am to 11 am: Room Rowland Hall 390
- Lecture by Prof. J. Mickey Laux
  - Fundamentals of Chromatography; Overview of HPLC and GCMS Labs

11 am to 12 pm: Lunch with AirUCI faculty and researchers (provided)
12 pm to 4 pm: Rooms RH 481
- Each team does their first wet lab experiment (see handout on website or in email)
**Tuesday, June 24**

9 am to 11 am: Room Rowland Hall 390  
- Lecture by **Prof. Barbara Finlayson-Pitts**  
  - Light and Photochemistry (p. 6–7 and 13–16)  
  - The Chapman reactions (p. 16–20), CFC’s (p. 29, 55–63 and 195–196), and Ozone Depletion (p. 3, 8–12, 18–30 and 37–56)  
  - Chemistry of NOx (p. 23 and 83), Photochemical Smog and Tropospheric Ozone (p. 76–87, 149–150 and 764–771)

11 am to 12 pm: Lunch with AirUCI faculty and researchers (provided).

12 pm to 4 pm: Rooms RH 481  
- Continue with the second wet lab experiment

**Wednesday, June 25**

9 am to 11 am: Room Rowland Hall 390  
- Lecture by **Prof. Filipp Furche**  
  - Overview of electronic structures and calculations  
  - Electronically excited states applied to the atmospheric (HONO, O*, etc.) (pp.: 15, 18–19, 73, 156, 187 and 769)

11 am to 12 pm: Lunch with AirUCI faculty and researchers (provided)

12 pm to 4 pm: Rooms RH 481  
- Continue with the third wet lab experiment

**Thursday, June 26**

10 am to 12 pm: Room Rowland Hall 390  
(shifted by 1 hour because of the PC lab availability issues)  
- Lecture by **Prof. Doug Tobias**  
  - Molecular structure and vibrations (p. 175–177)  
  - Fundamentals of molecular dynamics with examples pertaining to atmospheric chemistry research  
  - Overview of computational chemistry

12 pm to 1 pm: Lunch with AirUCI faculty and researchers (provided)  
  Special lunch talk by **Prof. Eric Saltzman** on ice cores analysis. (p. 179–181)

1 pm to 5 pm: Room MSTB 226B  
- Computer Lab: Chemistry on the computer – Spartan lab (Greenhouse Gases)

**Friday, June 27**

9 am to 11 am: Room Rowland Hall 390  
- Lecture by **Prof. John Hemminger**  
  - Fundamentals of surface science and environmental concerns at surface interfaces  
  - Catalysts and catalytic converters (p. 91–98)  
  - Photovoltaic cells (p. 361–367)  
  - Sea salt aerosols (p. 445)
11 am to 12 pm: Lunch with AirUCI faculty and researchers (provided)
   • Lunch presentation by Prof. John Hemminger on the energy science policy and the importance of basic research in dealing with the combined energy/environment issues.

11 am to 12 pm: Lunch with AirUCI faculty and researchers (provided)

12 pm to 4 pm: Rooms RH 481
   • Continue with the fourth wet lab experiment

Monday, June 30

9 am to 10 am: Room Rowland Hall 390
   • Lecture by Prof. Sergey Nizkorodov
      - Particulate matter (PM$_{10}$ and PM$_{2.5}$) (p. 118–122 and 126–130)
      - Light interaction with particulates (p. 136 and 197–200)
      - Aerosols: Composition and Effects on Global Warming (p. 200–202)

10 am to 11 am: Room Rowland Hall 390
   • Lecture by Prof. Mike Kleinman
      - The health effects of particulate matter (p. 145–152)

11 am to 12 pm: Lunch with AirUCI faculty and researchers (provided)

12 pm to 4 pm: Rooms RH 481
   • Continue with the fifth wet lab experiment

Tuesday, July 1

10 am to 12 pm: Room Rowland Hall 390
(shifted by 1 hour because of the PC lab availability issues)
   • Lecture by Prof. Donald Dabdub
      - Basics of computer modeling and simulations
      - Specific applications to LA basin (p. 76–87 on LA Smog)
      - Global Circulation Models and climate prediction viability (p. 206–207)

12 pm to 1 pm: Lunch with AirUCI faculty and researchers (provided)

1 pm to 5 pm: Room MSTB 226B
   • Computer Lab: Simulations of air pollution in the LA basin – PSE lab

Wednesday, July 2

9 am to 11:05 pm: Room Rowland Hall 390 (initially)
   • Guided tours of research labs of AirUCI Professors (split into 3 groups of 6-7 people)

11:15 am to 12:15 pm (Room 390): Exit evaluations and survey

12:15 pm to 12:45 pm (Room 390): Discussion of lab results/Wrap-up

1:00 pm to 3:00 pm: Special lunch with AirUCI faculty and researchers (provided)
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Fourier Transform Infrared Spectroscopy

FTIR DETERMINATION OF MTBE IN GASOLINE AND ETHANOL IN VODKA AND MOUTHWASH

Last updated: June 17, 2014
Fourier Transform Infrared Spectroscopy

FTIR DETERMINATION OF MTBE IN GASOLINE
AND ETHANOL IN VODKA AND MOUTHWASH

INTRODUCTION

As a part of the 1990 Clean Air Act Amendments, certain urban areas were required to add oxygenates to gasoline in order to meet attainment levels of carbon monoxide. In California, since June 1996, virtually all gasoline sold has contained MTBE (methyl tert–butyl ether) as its primary oxygenate. However, there has been controversy over the use of MTBE as an oxygenate for making cleaner burning gasoline. The additive has been found to contaminate ground water supplies by release from leaking gasoline storage tanks. MTBE has been classified as a possible human carcinogen and drinking water standards for this compound are being established. As a result, MTBE has been banned from being used in gasoline in California since 2003, and other additives, primarily ethanol, are used as the oxygenate. However, small quantities of MTBE are typically found in gasoline, even where it is not the major oxygenate. The amount of MTBE in gasoline samples will be determined in Part I of this experiment.

Ethanol is a nervous system depressant with a broad variety of physiological effects based on the blood alcohol level. It is found in various amounts in different alcoholic beverages and other household items. Ethanol content is most commonly described in terms of proof, which is just the ethanol volume percentage multiplied by 2. The potency of an alcoholic beverage used to be tested by putting it on gunpowder and burning it for “proof” it was at least 50% ethanol by volume. The pervasiveness of alcohol consumption in the general populace, and with high school and college students in particular, is widespread. The effects of alcohol abuse on death rates, drug abuse, violence, health issues and economic costs are beyond the scope of this introduction. In Part II of this experiment, the amount of ethanol in vodka and mouthwash will be measured.

BACKGROUND

I: Qualitative Analysis

The technique of Infrared (IR) Spectroscopy takes advantage of the fact that many molecules strongly absorb IR radiation and that the degree of absorption is proportional to the molecular concentration. The wavelength range of the IR region extends from about 780 nm to 1,000 μm, with the relation between energy (E), wavelength (λ) and frequency (ν) shown in Equations I and II below:

\[ E = hν = \frac{hc}{\lambda} \quad \text{Equation I} \]
\[ c = \lambda ν \quad \text{Equation II} \]

In Equations I and II, \( h \) is Planck’s constant (6.626 ×10⁻³⁴ J s), and \( c \) is the speed of light in a vacuum (taken to be 3.00 ×10⁸ m s⁻¹).

In IR techniques, the absorption or transmission of the IR radiation is commonly measured as a function of wavenumber. A wavenumber is the reciprocal of the wavelength and is
most commonly expressed in units of cm\(^{-1}\). Thus the range of wavenumbers corresponding to the IR spectrum would be about 12,800 to 10 cm\(^{-1}\). This is broken down into 3 main IR regions: near-IR (12,800 to 4000 cm\(^{-1}\)), mid-IR (4000 to 200 cm\(^{-1}\)), and far-IR (200 to 10 cm\(^{-1}\)). The most commonly scanned wavenumbers are from 4000 to 670 cm\(^{-1}\), which encompass absorptions by the majority of common organic functional groups.

For a molecule to absorb IR radiation, it must change its dipole moment upon vibration, and the frequency of the radiation must exactly match the natural vibrational frequency of the molecule, resulting in a change in the amplitude of the vibration. Some simple molecules (O\(_2\), N\(_2\), etc.) have no fluctuating dipole moment, and so they do not absorb IR radiation. But many vibrations of MTBE and ethanol change the dipole moment; such vibrations are said to be IR active.

The two fundamental types of molecular vibrations are stretching and bending modes. The stretching mode consists of a change in the distance along the axis of a bond between two atoms. The bending mode results from a change in the angle between two bonds. There are four types of bending vibrations: rocking, twisting, wagging and scissoring. Organic functional groups have particular absorption peaks that can be used in qualitative analysis, varying only by the molecular environment. For example, the "ether band" of MTBE around 1092 cm\(^{-1}\) is easily distinguishable from absorptions by other components of gasoline and will be analyzed in Part I of this lab.

From quantum theory, the vibrational states are quantized and the allowed vibrational transitions are those in which the vibrational quantum number changes by unity. The more atoms there are in the molecule, the more complicated the IR spectrum becomes due to increased vibrational coupling and possible overtone peaks and combination bands. These effects create a unique IR absorption spectrum for each molecule that can be used as a “fingerprint” in qualitative experiments.

**II: Quantitative Analysis**

Although infrared spectroscopy is used extensively for qualitative analysis in organic chemistry, band intensities are related to the concentration and path length of the sample through the Beer–Lambert Law, shown in Equation III, and so this technique can be used for quantitative analysis as well.

\[
A = \varepsilon l C \quad \text{Equation III}
\]

Where \(A\) is the Absorbance, \(\varepsilon\) is the molar absorptivity in L/(mol cm), \(l\) is the path length in cm and \(C\) is the concentration of analyte solution in moles/L.

If the absorbance of a series of known standard solutions are measured, a plot of Absorbance as a function of concentration can be made and least-square analyzed. Following the expected linear dependence format, \(A = \text{slope} \times C + \text{offset}\), the slope of the linear plot would be equal to \(\varepsilon l\), allowing determination of the molar absorptivity if the path length of the cell, \(l\) is known (typically 1 cm). Also, an unknown solution’s concentration can be determined after its Absorbance is measured and applied to the linear least squares fit.

**III: The Fourier Transform Technique (for Advanced Readers)**

Most IR instruments used today are of the Fourier Transform type. There are three major advantages of using Fourier Transform techniques in IR spectroscopy.

FTIR - 3
1) Fourier transform instruments do not need slits to attenuate radiation and have fewer optical elements. The increased power reaching the detector gives a larger signal to noise ratio.

2) The high resolving power and wavelength reproducibility allow for more accurate analysis of collected spectra.

3) The multiplex advantage, or faster scanning. In Fourier techniques, all wavelengths are scanned simultaneously, allowing an entire spectrum to be scanned in 1 second or less. Since the signal to noise ratio \( \left( \frac{S}{N} \right) \) increases as the number of scans, \( k \), increases (as shown in Equation IV), then Fourier techniques allow many more scans in less time and much better signal to noise ratios.

\[
\left( \frac{S}{N} \right)_{\text{k scans}} = \left( \frac{S}{N} \right)_{\text{one scan}} \times \sqrt{k}
\]

As you can see, the quality of the spectrum increases in proportion to the square root of the number of scans.

Fourier techniques basically differ from conventional techniques in that they measure radiant power as a function of time (time domain) whereas conventional spectroscopy measures power as a function of frequency (frequency domain). This time domain spectrum is then mathematically converted into a frequency domain spectrum using a Fourier transform. The process is so complex that it requires a high speed computer and will not be covered here.

Power variations at the very high frequencies of IR sources (\(10^{12}\) to \(10^{14}\) Hz) cannot be measured directly with today's electronics (transducers measure averages instead of variations at these high frequencies). Therefore the high frequencies must be scaled down to much lower values in order to measure time domain signals. This is commonly accomplished using a Michelson Interferometer.

A Michelson Interferometer essentially splits the IR radiation beam from the source (high frequencies) into two beams using a beam splitter. One beam is directed to a fixed mirror and the other to a mirror moving at a constant speed, \( v_m \). The two beams are then recombined and directed to the detector. The moveable mirror causes the radiation power at the detector to fluctuate in a predictable manner based on the constructive and destructive interference patterns of the recombined beams. These interference patterns are based on the difference in path length (or retardation, \( \delta \)) for the two beams. The plot of output power from the detector vs. retardation is called an interferogram.

The resolution of the spectrometer, which is the difference in wavenumber between two peaks that can just be separated by the instrument, is equal to the inverse of the retardation. The relationship between the molecular emitter's frequency, \( \nu \), and the interferogram frequency, \( f \), is based on the moveable mirror speed, \( v_m \), according to Equation V below.

\[
f = \frac{2 \nu}{c}
\]

Assuming a typical mirror velocity of 1.5 cm/sec and with the speed of light being 3.00 x \(10^8\) m/sec, then the interferometer reduces the frequency of the source radiation by a factor of \(10^{-10}\) (i.e.: \( f = 10^{-10} \nu \)). This brings the frequency into the audio range and allows transducers to measure the power variations and thus record a time domain spectrum. The Fourier
In the first part of the experiment, you will quantify the amount of MTBE in gasoline from its absorption of infrared radiation transmitted through the solution. The "ether band" of MTBE around 1092 cm$^{-1}$ is easily distinguished from other absorptions due to the hydrocarbon components of gasoline. A series of MTBE/hexane standards can be used to prepare a linear calibration plot of absorbance at the ether band vs. concentration of MTBE. From this plot, the concentration of MTBE in a sample of gasoline can be derived.

### Experimental Procedure

**Note:** Detailed instructions on the start up, use, and shut down of the Jasco FT/IR–615 instrument are provided in the four page handout near the machine in the lab, please read them carefully before beginning.

1) In the fume hood, prepare a stock solution of 5% (volume/volume) MTBE by carefully adding hexane to 2500 µL of MTBE until you obtain a total volume of 50.0 mL in a volumetric flask. There are pipettes available for adding 250 µL of the MTBE. Be sure to condition the flasks and pipettes first.

2) From this stock solution, make five standard solutions:

<table>
<thead>
<tr>
<th>Volume of 5% Stock Solution</th>
<th>Add Hexane to Total Volume</th>
<th>Final Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 mL</td>
<td>10.0 mL</td>
<td>0.5 % (v/v)</td>
</tr>
<tr>
<td>3.0</td>
<td>10.0</td>
<td>1.5 %</td>
</tr>
<tr>
<td>4.0</td>
<td>10.0</td>
<td>2 %</td>
</tr>
<tr>
<td>6.0</td>
<td>10.0</td>
<td>3 %</td>
</tr>
<tr>
<td>8.0</td>
<td>10.0</td>
<td>4 %</td>
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Be sure to condition each flask and label with tape. Close the flasks after preparation to avoid evaporation.

3) Dilute the “old” gasoline sample with hexane to make a 25% (volume/volume) solution by adding hexane to 2500 µL of the gasoline to a total volume of 10.0 mL of solution. Label the flask and close it. Make a similar solution with “new” gasoline.

4) Set the spectrometer resolution to 1 cm$^{-1}$ and the number of scans to 16 by clicking on “Measure” and then “Parameters”.

5) Using a plastic pipette, flush the transmission IR salt crystal cell with the hexane solvent four times, then fill with hexane. After that, load this cell into the spectrometer compartment.

6) Take a background spectrum of the hexane solvent and save this spectrum for later use. To do a single beam spectrum, click on “Measure” then “Parameters + Background” and under vertical axis choose “single” for the background and “abs” for the sample. Click “OK” to run the background. (or click on the “B” icon with a box in it as a shortcut). The spectral analysis software will then automatically ratio the sample spectra with that of the most recent background spectrum. When the run is complete, the colors of the top tabs will return.
7) Now take the cell out and flush it four times with the standard solution you are going to use next. After that fill it with the standard solution and place it back into the spectrometer. Take a spectrum for your first standard by clicking on the “S” tab with no box in it (for run Sample) and save it.

8) Scale the spectra to focus on the ether peak around 1092 cm$^{-1}$. Do this by clicking on “View” then “Scale” and type in the desired x and y axis ranges (~1150 to 1050 cm$^{-1}$ and 0 to 2, respectively). Use “Peak Find” to locate all peaks (click on “Processing ----> “Peak Process” ----> “Peak Find” ----> “Execute”) and choose the appropriate peak from the Table listed.

9) Repeat steps 7-8 for your remaining MTBE standard solutions.

10) Now, record the spectrum of the 25% gasoline samples (old and new). Make sure the absorbance of the ether band falls on the calibration curve. Determine the absorbance of the sample from the same ether peak used in the standards as you did in step 8.

**Data Analysis**

1) Make a Table of MTBE % concentration vs. Peak Absorbance measured at the top of the ether band around 1092 cm$^{-1}$ for the standard solutions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance</th>
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<tbody>
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</table>

2) Develop a Beer-Lambert Law plot for the MTBE in hexane standards and perform a least squares analysis of the linear best fit line on a computer or by hand on graph paper if a computer is not available (Microsoft Excel instructions for graphing are in the Appendix if needed). This will give you a dependence in the form:

\[ \text{Absorbance} = \text{slope} \times C + \text{offset} \quad (y = mx + b) \]

3) Using the slope and offset parameters determined from your fit, calculate the % MTBE in the diluted gasoline sample.

4) Calculate the volume percent of MTBE in the original undiluted gasoline samples. Make sure you take into account the various dilutions.

5) Assign the vibration responsible for the peak at 1092 cm$^{-1}$ in the MTBE absorbance spectrum.
PART II: Determination of Ethanol in Vodka and Mouthwash

This part of the experiment will show that infrared spectroscopy can be carried out in water solutions using appropriate infrared-transmitting, but water-insoluble, crystals (of ZnSe in this case) using the technique of attenuated total reflectance (ATR) FTIR. You will use this technique to determine the ethanol concentration in vodka and mouthwash.

Figure 1. Schematic diagram of single-bounce ATR accessory.

This technique allows you to quantitatively measure the absorbance of ethanol in water, even though water is a very strong absorber of infrared radiation itself. As seen in Figure 1, in the ATR technique the sample is placed on an internal reflection element and the IR beam is directed into the element. It strikes the internal crystal-air interface at an angle greater than the critical angle, and as a result undergoes internal reflection inside the crystal. Most radiation is reflected at the point of internal reflection, but a small fraction is absorbed by molecules present at the surface of the ATR crystal. This absorption of infrared radiation can then be detected and measured.

Increased sensitivity can be obtained by using a multipass ATR accessory. Figure 2 shows a schematic of the light path in such a device; the increased number of internal reflections leads to a proportional increase in the absorbance and hence in the sensitivity.

Figure 2. Schematic diagram of multiple reflections inside a multipass ATR accessory.
Experimental Procedure

1) Prepare a 10 % (by volume) 95% ethanol in water solution by adding nanopure water to 5.0 mL of ethanol to a total volume of 50.0 mL in a volumetric flask.

2) Now place the liquid multi-pass ATR accessory in the sampling compartment. Be sure not to turn any of the screws on the accessory as they have been tuned to make sure the infrared beam passes into the crystal and back out to the detector properly. When properly aligned, you should be able to see red dots where the HeNe laser is reflecting at the crystal surface along the center of the crystal. Try to count the number of reflections you can see in the crystal. You may want to do this in the dark, since it makes the spots easier to see.

3) Carefully fill the top of the crystal with nanopure water using a pipette (DO NOT SPILL WATER IN THE SAMPLE COMPARTMENT). Take a background absorbance spectrum using 16 scans and 1 cm\(^{-1}\) resolution (hit the “B” icon with a box in it). Remove the water carefully with a plastic pipette and then dab the trough with clean, lint-free tissue. Do not exert any pressure on the glass surface during this procedure.

4) Now condition, then fill the ATR accessory with the 10% ethanol sample. Take a spectrum of this sample and then take another scan immediately afterwards for reproducibility. Scale the spectra around the alcohol peak near 1044 cm\(^{-1}\). Find the absorbance at that peak and record it in your lab book.

5) Prepare a set of standard solutions by diluting the 10% Ethanol solution with Nanopure H\(_2\)O.

<table>
<thead>
<tr>
<th>Volume of 10% Stock Solution</th>
<th>Add Nanopure H(_2)O to Total Volume</th>
<th>Final Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0 mL</td>
<td>10.0 mL</td>
<td>1.0% (v:v)</td>
</tr>
<tr>
<td>3.0</td>
<td>10.0</td>
<td>3.0%</td>
</tr>
<tr>
<td>5.0</td>
<td>10.0</td>
<td>5.0%</td>
</tr>
</tbody>
</table>

Label each flask with tape. Close the flasks after preparation to avoid evaporation. Find the absorbance of each solution as you did for the 10 % sample in step 4. Record the values in the Table below.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance</th>
</tr>
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<tbody>
<tr>
<td></td>
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</table>
6) Prepare a diluted vodka solution by adding nanopure H₂O to 1.0 mL of the original vodka solution in a 10.0 mL volumetric flask. Record the spectrum of the diluted vodka sample as before and make any necessary dilutions so the absorbance falls on the calibration curve. Record the value in the previous Table.

7) Prepare a diluted mouthwash solution by adding nanopure H₂O to 2.0 mL of the original mouthwash solution in a 10.0 mL volumetric flask. Record the spectrum of the resulting sample as before and make any necessary dilutions so the absorbance falls on the calibration curve. Record the value in the previous Table.

8) Record the dimensions of the crystal as well as its angle of incidence from the label in the ATR cabinet.

9) If there is extra time there are 2 possible solutions to test. First, if a non-alcoholic mouthwash is available, prepare a diluted solution as in Step 7 and scan it. Second, if a sample of newer (supposedly MTBE free) gasoline is available, make a diluted solution as in Step 3 in Part I and scan it. See if the MTBE peaks disappear and if the ethanol peaks appear.

**Data Analysis**

1) Calculate the theoretical number of reflections, \( N \), along the crystal given the formula

\[
N = \frac{l \cot \theta}{2t}
\]

where \( l \) is the crystal length, \( \theta \) is the angle of incidence (determined by the optical configuration and provided by the manufacturer of the ATR accessory) and \( t \) is the thickness of the crystal.

2) Develop a Beer-Lambert plot for the ethanol in water standards. Use the least squares fit to determine the % ethanol in the diluted vodka sample, as well as for the Listerine. Follow the same instructions as the plot made in Part I.

3) Calculate the volume percent of ethanol in the original undiluted vodka and mouthwash samples. Make sure you take into the account the various dilutions. You can show your work calculations below.

4) Determine the proof of the original vodka sample.

---

**IF THERE IS STILL TIME LEFT, DO THE FOLLOWING EXTRA SECTION:**

**PART III: Instrumental Noise**

A standard method for improving signal-to-noise (S/N) is to increase the number of scans. The S/N should improve by the square root of the number of scans as described in the background section.
**Experimental Procedure**

1. Set the spectrometer to capture an interferogram. Set the number of scans to be 1 and the resolution at 1 cm\(^{-1}\). Make sure there is no accessory inside the sample compartment of the spectrometer.

2. Take a background spectrum with no cell in the sample compartment. Convert the interferogram into a single beam spectrum.

3. Now take another spectrum with no cell in the sample compartment. Convert the interferogram into a single beam spectrum and ratio this spectrum to your background spectrum. The resulting spectrum will be a transmittance spectrum of the noise of the instrument. Convert this transmittance spectrum to absorbance.

4. View the spectrum of noise from 2100 to 2000 cm\(^{-1}\) to find the lowest valley and the highest peak in this region. The difference gives you the peak-to-peak noise. Mark the valley and peak on the spectrum and print out.

5. Now set the number of scans to be 4 (leave the resolution at 1 cm\(^{-1}\)). Repeat step one through four to find the peak-to-peak noise with 4 scans.

6. Now set the number of scans to be 64 (leave the resolution at 1 cm\(^{-1}\)). Repeat step one through four to find the peak-to-peak noise with 64 scans.

**Data Analysis**

1) Make a table showing the number of scans and the peak-to-peak noise for each.

2) Quantitatively compare the change in the noise with the number of scans and compare to theoretical expectations.

**REFERENCES**


**Additional References:**


INTRODUCTION

The United States and most of the world are exceedingly dependent on fossil fuels for their energy needs. For Americans, gasoline is the most common energy source for transportation. Due to the large quantities of pollutant species emitted and formed from regular and diesel fuel combustion (CO, NO, unburned hydrocarbons, particulate matter, and polycyclic aromatic hydrocarbons, to name a few), there is an increasing number of air pollution regulations in the U.S. and worldwide.

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). Due to some gasoline leakage from underground storage tanks into drinking water supplies, MTBE has been, or is in the process of being phased out in many areas.

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 (2, 2, 4 – trimethylpentane), which is assigned an octane number of 100, and heptane, which is assigned a value of 0. So gasoline with an octane rating of 87 would have similar performance characteristics of a standard fuel mixture consisting of 87% isooctane and 13% heptane. The higher the octane rating, the better the fuel performance and the greater the price per gallon (i.e.: 89 and 91 premium fuels).

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 separate the components in a sample of gasoline using Gas Chromatography. Mass Spectrometry will then be used to identify as many components in the gasoline as possible and to determine the concentration of ethanol and benzene in the sample.

BACKGROUND

GC-MS is a “hyphenated” experimental technique that incorporates two widely used methods in tandem. The GC portion is the Gas Chromatography used for separating components in a mixture, and the MS portion is the Mass Spectrometry used in the qualitative and quantitative analysis of each component that was separated by the GC. The combination of these two highly applicable techniques creates possibly the most commonly used instrument for analytical scientists. Each technique will be briefly discussed below. A schematic layout of a GC/MS instrument is shown in Fig. 1.

I: Gas Chromatography

Gas chromatography is the most powerful and applicable separation technique for complex mixtures of volatile chemicals. Gas chromatography uses a gaseous mobile phase, or eluent, to carry the analyte being analyzed through a column packed or coated with a stationary
phase. Some GC columns are up to 100 meters long! The column you will be using in this lab is about 30 meters long.

The stationary phase in Gas Chromatography is commonly a packing of inert, small diameter particles (such as diatomaceous earth) with a nonpolar liquid coating them, or just a liquid coating on the inner surface of the column. This liquid is a very thin layer (0.1 to 5 µm), usually a polydimethyl siloxane (shown below) where some of the –CH₃ groups can be altered so as to match the polarity of the analytes. A parameter common in chromatography used for this is called the Partition Coefficient (or Ratio), K, which is the ratio of the concentration of the analyte in the stationary phase to that in the mobile phase.

\[
\begin{align*}
\text{CH}_3 & - \text{Si} - \text{O} - \text{Si} - \text{O} - \text{Si} - \text{CH}_3 \\
\text{CH}_3 & - \text{Si} - \text{O} - \text{Si} - \text{CH}_3 \\
\text{CH}_3 & - \text{Si} - \text{O} - \text{Si} - \text{CH}_3 \\
\end{align*}
\]

The mobile phase is an inert gas such as Argon, Helium or Nitrogen that only carries the analyte molecules through the column. The carrier gas does not interact with the analyte and column packing material. In this lab, ultrahigh purity Helium is used as carrier gas.

The retention time (time it takes to pass through the column) for an analyte is based on the time spent in the stationary phase vs. the mobile phase, with longer retention times for analytes with polarities closer to that of the stationary phase. In the sample chromatogram shown in Fig. 2, two different molecules have distinct retention times, t₁ and t₂. Dead time, t₀, is the time it takes for the carrier gas to go through the column.

The analyte peaks tend to broaden as they pass along the column, resembling Gaussian peaks. This is due to the random motions of molecules as they migrate down a column, passing in and out of the stationary phase. This peak broadening affects the efficiency of the column as well as its ability to distinctly separate the peaks of two different analytes (the resolution). Another common parameter used in chromatography is the Selectivity Factor, which is the ratio
of the migration rates between two different analytes, A and B, and provides a measure of how well the column separates A from B. In Figure 2, molecules 1 and 2 are well separated in spite of the substantial peak broadening.

In order to optimize the column resolution and efficiency, one can change the column dimensions and/or the stationary phase. However, altering the temperature has the greatest effect on column resolution and efficiency. Gradually increasing the temperature, manually or in a predetermined software program, can greatly increase scan speeds as well as increase resolution between peaks.

![Figure 2: Sample chromatogram.](image)

Samples are commonly injected in very small volumes through a septum or diaphragm into the column head to prevent evaporation of the sample. If the sample is a liquid, then it must be vaporized before being sent into the column. The chromatogram can be used for qualitative and quantitative analysis, but a better method is to direct the output of the chromatographic column into a mass spectrometer (or other identification method) which can then analyze each analyte as it elutes off the column.

**II: Mass Spectrometry**

Mass Spectrometry refers to a group of analytical techniques that precisely measure masses of molecules, atoms and/or ions. Because each species is characterized by a unique mass, mass spectrometry is the most common identification technique used by chemists, biologists, forensic scientists, etc. There are many different types of mass spectrometry based on the various sections of the instrument and the application desired. In most approaches, vaporized samples are ionized (and commonly fragmented), and these ions are separated based on their mass to charge ratios (m/z) and then detected and processed.

1) **Sample Injection:** There are many different methods used to inject a sample into a mass spectrometer depending on the original phase of the sample. The main requirement is that the sample is converted into the gas phase at very low pressures (down to $10^{-10}$ atm) for the instrument to function properly. In this lab, the sample will be injected as a liquid with a syringe. The injected liquid will then be heated to convert it into a vapor.

2) **Ionization:** Of the numerous ways to ionize the sample, electron impact is the most commonly used. There are several methods that combine vaporization and ionization in one step, especially for solid samples. In electron impact ionization, a filament is used to
generate fast moving electrons that strike gas phase sample molecules, knocking off electrons, and thus ionizing them. This must be done in a vacuum environment (otherwise the electrons would strike N₂ and O₂ molecules instead).

Commonly, the molecular ion produced by the collision of the parent molecule with an electron has excess energy and fragments into daughter ions as a result. The fragmentation pattern is used as a qualitative identification method, and many instruments have a library of references for automatic comparison.

Note that ethanol has a molecular weight of approximately 46 g/mol. However, the peak corresponding to m/z = 46 in its electron impact mass spectrum is not the largest peak. This happens because molecules like ethanol often fragment upon electron impact ionization:

\[
\text{Molecule} + e^- \rightarrow \text{Molecular ion}^+ + \text{neutral fragment(s)} + 2 \text{e}^-
\]

In the case of ethanol, the largest peak appears at m/z = 31 instead, which corresponds to the loss of a CH₃ group from the molecule upon ionization. You can view the electron-impact mass spectra of ethanol as well as the other molecules probed in this lab in the appendix.

3) **Mass Analyzer:** This is the heart of a mass spectrometer and there are several types of mass analyzers used, including Quadrupole, Time of Flight, and Magnetic Sector Analyzers. The most common, and the one used in our instrument, is the Quadrupole Mass Analyzer. How this device separates out ions based on their m/z (mass-to-charge) ratios can be a bit technical, but is summarized below and will be explained further in lab. A 2-part video by Professor Laux on YouTube is also available to be viewed on this topic.

The quadrupole, as implied by the name, consists of 2 sets of parallel cylindrical rods (4 total). Opposite rods are electrically connected, two being charged negative and the other two positive by a variable dc source. Each set of rods also has variable radio frequency AC potentials applied to them.

Based on the DC and AC voltages, each set of rods act as a mass filter. The combination of both voltages limits only a particular m/z ratio value through the quadrupole. Ions move through the filter in a spiraling manner (Fig. 3). If the DC and AC voltages are scanned through in an increasing fashion, then the entire range of ion m/z values can be separated and analyzed. This can be done extremely fast, with all m/z values being scanned in a few milliseconds!

4) **Detection and Processing:** The ion signal is converted into an electronic signal using a *transducer*. The most common transducer is the *Electron Multiplier* in which the ions strike the surface of a cathode, emitting a burst of electrons. These electrons are accelerated through a series of dynodes at higher and higher voltages that each emit another burst of electrons when struck. The result is a greatly amplified electron current. The greater the number of ions striking the cathode, the larger the resulting current, and the higher the peak intensity on the mass spectrum.
EXPERIMENTAL

I: General Suggestions for making solutions

A pure gasoline sample is provided in a brown vial. Make sure this vial is capped at all times to prevent evaporation and inhalation. DO NOT remove the cap unless you run out of gasoline. Use this gasoline to make all the solutions in the experiment.

Brown vials are used for storing the other chemicals used in this experiment (benzene, ethanol, toluene, and o-xylene). Use the hood for preparation of all samples. The brown vials will also be used to store solutions in Parts II & III. The vials MUST be capped as soon as possible to prevent evaporation and inhalation as all chemicals in this experiment are volatile. Other techniques to keep in mind when making solutions:

- Rinse (condition) the 1 mL volumetric flasks at least three times with small amounts of solvent.
- Add the first solute component (gasoline in most cases), then (if applicable) the next component. Dilute with the required amount of solvent and mix thoroughly.
- Syringe needles bend easily when pushing through the septum; be careful when going through a septum by using your gloved fingers as a guide.
- WARNING: The possibility of contamination of samples is very high. Please make sure to use the dedicated, labeled syringes for each solution.

II: GC/MS Analysis of Species of Interest

1. On the computer, load the method called “gas2013.m”. Your TA will assist you in setting the parameters for the scans.

2. Teachers should each take a turn making a solution and injecting it into the GC-MS instrument for this lab (4 solutions will be made). Make a mixture of ethanol, benzene, toluene, and o-xylene (the four species of interest) in the solvent (1-octanol). Properly condition a 1 mL volumetric flask with the solvent using a disposable glass pipette provided. Using the designated syringes, add 100 µL of ethanol, 10 µL of benzene, 10 µL of toluene, and 10 µL of o-xylene to the flask. Then add enough
solvent to bring the meniscus bottom just onto the line in the neck of the flask. Cap tightly and invert multiple times to mix thoroughly. Transfer this solution to an amber vial and cap.

3. Click on the **One Sample Icon** on the computer (picture of a bottle). Name the file for the sample about to be injected into the GCMS and then click on **Run Method**. Wait for the red “Not Ready” LED on the GCMS to turn off before injecting the sample.

4. Condition the injection syringe with your solution from your amber vial, and then inject **0.05 \( \mu \text{L} \)** of the solution into the GCMS through the septum on top of the instrument. Keep the syringe vertical and inject in a quick, repeatable manner. Immediately after the injection, press “start” on the front of the GCMS. On the computer, “**Override the solvent delay (1.00 minutes)?**” will be displayed. **Choose NO**… this is very important so as to not damage the electron impact filament from the large amount of solvent passing through the system.

4. When the run is completed, open the appropriate file and load the TIC (total ion chromatogram). Print the TIC and quickly try to predict which peak corresponds to which analyte based on the retention times and the nonpolar stationary phase. View and print the mass spectrum for each peak by double right clicking on the desired peak. Use the fragmentation patterns to piece together and identify each peak. Confirm your designations by double right clicking on each mass spectrum to perform a library search for the correct analyte.

5. Use these retention times and mass spectra to locate the appropriate peaks in the gasoline samples in the next section.

### III: Analysis of Gasoline using the Method of Standard Additions

1. You will measure the ethanol and benzene concentrations in gasoline using the method of standard additions. That is, you will add measured quantities of ethanol and benzene to gasoline and use these as your calibration standards to measure how much ethanol and benzene exist in the original gasoline sample.

2. Table 1 lists the solutions you will be making. Have a new person properly prepare solution A in the hood with the designated syringes (with conditioning!) in a 1 mL volumetric flask. Following the same steps as in Part II, inject **0.05 \( \mu \text{L} \)** of the new sample into the GCMS and take its chromatogram. Prepare solution B while you wait for the chromatogram of solution A to finish. In a like fashion, prepare Solution C while Solution B is running. This will save you a lot of time.

**Table 1:** Composition of mixtures of ethanol, benzene, gasoline and 1-octanol solvent for the Method of Standard Additions.

<table>
<thead>
<tr>
<th>Solution Number</th>
<th>Volume of Gasoline (( \mu \text{L} ))</th>
<th>Volume of Ethanol (( \mu \text{L} ))</th>
<th>Volume of Benzene (( \mu \text{L} ))</th>
<th>Add 1-octanol to a total volume (mL) of:</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>750</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>750</td>
<td>50</td>
<td>7</td>
<td>1</td>
</tr>
<tr>
<td>C</td>
<td>750</td>
<td>150</td>
<td>15</td>
<td>1</td>
</tr>
</tbody>
</table>
3. For the three samples, plot the single ion chromatograms for the ions at m/z = 31, 78, 91 and 106, corresponding to major ions characteristic of ethanol, benzene, toluene and o-xylene respectively. This technique is called “single ion monitoring”, or SIM. This can be done by bringing up each file name in turn and clicking “Chromatogram” → “Extract Ion Chromatogram”. Type in the ion m/z values of interest listed above and click OK. Click on “Chromatogram” → “Percent Area Report” → “Signal to Screen” to get the peak areas displayed on the computer screen, then locate the specific retention times and peak areas for ethanol, benzene, toluene and o-xylene. Record these peak areas.

4. Calculate the ratios of the peak areas corresponding to ethanol/toluene, benzene/toluene, ethanol/o-xylene and benzene/o-xylene. Using the ratios to toluene and o-xylene, in effect, uses these as internal standards to correct for any differences in injection volumes.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Ethanol toluene</th>
<th>Benzene toluene</th>
<th>Ethanol o-xylene</th>
<th>Benzene o-xylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

5. Plot the ratio of ethanol to toluene and ethanol to o-xylene (i.e. two separate lines on one graph) against the added volume of ethanol on Microsoft Excel (as taught on Day 1). See the Appendix for plotting instructions on Excel if necessary. For comparison, to illustrate the advantages of using an internal standard, also plot the absolute peak area of ethanol against the added volume of ethanol in a separate graph.

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

7. Carry out a least squares analysis for each of the lines (easily done on Microsoft Excel) to obtain the slope (m) and the y-intercept (b). The relationship between the ratio, R, of the ethanol (or benzene) to the internal standard and the volume of ethanol (or benzene) added to the mixture (V_{ethanol}) is as follows:

\[
R_{\text{ethanol/Std}} = m V_{\text{ethanol}} + b \quad (y = mx + b) \tag{I}
\]

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

\[
b/m = f V_{\text{gas}} \tag{II}
\]

Use the slope and intercept of these plots to calculate the volume fraction of ethanol 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 ethanol and benzene respectively in gasoline.
High Performance Liquid Chromatography

HPLC MEASUREMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN CIGARETTE SMOKE

Last updated: June 17, 2014
**High Performance Liquid Chromatography**

**HPLC MEASUREMENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN CIGARETTE SMOKE**

**INTRODUCTION**

Even though cigarette smoking is stated as a known health hazard by the Surgeon General, it still remains a problem in America, and is actually on the rise in many foreign countries. The addictive nature of nicotine in tobacco is well known, as is its link to respiratory disorders, such as emphysema, due to tar and other compounds. The increased risk of cardiovascular problems from smoking has helped make heart disease the number one killer in the United States. There are even radioactive species within tobacco smoke. But the major health concern due to smoking for most people is the increased risk of cancer from the carcinogenic compounds present, and these are what will be monitored and discussed in this experiment.

Polycyclic aromatic hydrocarbons (PAH) are ubiquitous components of diesel exhaust, wood smoke and cigarette smoke. Many of them are mutagenic and/or carcinogenic. This experiment is designed to qualitatively identify as many PAH as possible in cigarette smoke using high performance liquid chromatography (HPLC). A particular focus is placed on quantifying benzo[a]anthracene because it is well-resolved in HPLC analysis.

The HPLC is equipped with a diode array detector (DAD). Absorption spectra for the PAH to be measured will be compared to standard spectra for identification and are also on reserve in the library under this experiment. Quantitatively, the amount of benzo[a]anthracene in a cigarette will be determined, using a set of standards for comparison. Solutions containing known concentrations of PAHs of interest will be used as standards.
BACKGROUND

I: General Description of Chromatography

Chromatography is the most powerful and widely-used separation technique for complex mixtures. All chromatographic methods use a Stationary Phase (solid or liquid) and a Mobile Phase or Eluent (gas or liquid) that carries the analyte through the column. The nature of the mobile phase determines the category of chromatography:

1) Liquid Chromatography (LC) uses a liquid mobile phase
2) Gas Chromatography (GC) uses a gaseous mobile phase

Traditionally, in Column Chromatography, the stationary phase is attached to small silica beads that are held in a column, which is essentially a long narrow tube. The mobile phase is forced through the column using pressure. This particular lab uses High Performance Liquid Chromatography (HPLC), sometimes called High Pressure Liquid Chromatography. In HPLC, pressures up to several hundred atmospheres can be used to force the mobile phase through the column in order to achieve chromatographic runs in reasonable times.

The HPLC instrument in our lab uses reversed-phase partition chromatography, in which the stationary phase liquid is nonpolar and the mobile phase liquid is polar. The stationary phase is usually a packing made of porous silica particles with a nonpolar liquid coating chemically bonded to them (commonly siloxanes). The mobile phase is commonly a mixture of solvents that can be combined in certain ratios to give an eluent with the desired effective polarity.

II: Chromatograms

Chromatograms show the peaks of each component vs. elapsed time traveling along the column (Figure 1). The migration rates of analytes down a column differ based on the time spent in the stationary phase vs. the mobile phase, allowing separation of the components in a mixture. If the mobile phase is polar, then the more polar the analyte, the faster it is eluted due to it having greater attraction to the mobile phase than the nonpolar stationary phase.

The retention time (time for an analyte to pass through the column) allows for qualitative identification and peak areas allow for quantitative analysis. Each molecule will have a unique retention time in a given column and for a given solvent. In the sample chromatogram shown in
Figure 1, two different molecules A and B have distinct retention times, $t_A$ and $t_B$. Dead time, $t_{\text{dead}}$, is the time it takes for an unretained (solvent) molecule to go through the column.

**Figure 1:** Schematic representation of separation of two compounds in an HPLC column and the resulting chromatogram.

![Chromatograms](image)

A key factor in chromatography that determines the rate of migration of a solute down a column is the *Partition Ratio* (or Partition Coefficient, K), which is the ratio of the concentration of the analyte in the stationary phase to the mobile phase ($K = c_s/c_m$). The larger the value of $K$, the longer the solute resides in the stationary phase, and thus the longer it takes to go through the column.

The peaks tend to broaden as they pass along the column, decreasing the column efficiency and resolution. The resulting peaks have approximately Gaussian shapes, which arise from random motions of molecules as they migrate down a column, passing in and out of the stationary phase, leading to a range of elution times for each analyte.
III: Column Efficiency and Resolution

The ability of a particular column to give distinct, separate peaks for each analyte in a reasonable period of time is based on column efficiency and resolution. Two main factors affect the efficiency and resolution of a column: The Partition Coefficient, \( K \), (covered in Part II) and the Selectivity Factor, \( \alpha \), which relates to the relative migration rates between two solutes, A and B, providing a measure of how well the column separates A from B:

\[
\alpha = \frac{K_B}{K_A} = \frac{(t_B-t_{\text{dead}})}{(t_A-t_{\text{dead}})}
\]

There are several experimental factors that can be altered to increase column resolution and/or efficiency, as summarized below:

1) Decrease the flow rate of the mobile phase.
2) Alter the composition of the mobile phase
3) Increase the surface area of the stationary phase.
4) Use a smaller column diameter.
5) Increasing column length

To increase the resolution between peaks, the easiest way is to increase the length of the column. Unfortunately, this may lead to elution times that are too long and the peaks become too broad (this is called the General Elution Problem).

The solution for this is to experimentally alter the mobile phase composition as elution takes place via gradient elution or solvent programming. Once the faster moving components are eluted, the mixing ratio of solvents used in the mobile phase is altered to maximize the resolution and elution rate of the next components, and so on.

IV: Qualitative and Quantitative Analysis

Chromatography by itself is great if the components of the mixture are already known, and it is used to test for the presence or absence of these species, but for identification of unknowns in a mixture, the exit of the chromatographic unit must be linked to a suitable detection technique. In HPLC, the most common detectors are UV absorption and fluorescence.

The premise for the quantitative analysis in HPLC is that the area under the peak of the eluting compound is directly proportional to the concentration of this compound:

\[
\text{peak area} = \text{slope} \times \text{concentration} + \text{intercept} \quad (y = mx + b)
\]
The peak areas can be measured using automatic peak integration software. The calibration slope for the compound of interest is usually determined by graphing the HPLC response to standard solutions against the known concentrations of those solutions. For increased precision, not just one but several standard solutions are injected in the HPLC, and the slope and intercept values are determined from a least squares analysis as shown in Figure 2. Unknown sample concentrations can then be determined from this calibration curve.

\[
\text{concentration} = \frac{\text{peak area} - \text{intercept}}{\text{slope}}
\]

**Figure 2:** Sample calibration plot for an HPLC quantitative experiment. In your calibration, you will be using three standard solutions with different concentrations. Therefore, your calibration plot will have three points instead of the six shown here. In the sample calibration, the intercept value is zero.

**EXPERIMENTAL**

Note: An overview of the instrument (Figure 3) and safety instructions will be provided by your T.A.. More specific instructions for operation of the HPLC instrument and data analysis are provided in the CHEM 152 HPLC Operational Guide, which is always near the instrument.
Part I: Instrument Set Up

1. Unless they are already on, turn on the four lowest HPLC modules (Degasser, Pump, ColComp and Diode Array Detector). Then turn on the computer and printer (if not already on). Refer to the Chem 152 HPLC Operational Guide for schematics and instructions.

2. Check to be sure the degasser is on (first module from top of stack, button on bottom left). Visually inspect the solvent lines from the solvent bottles to the degasser to be sure there aren't any air bubbles in any of the lines. If there are, call your TA and ask them to purge the lines.

   NOTE: The solvent bottles should be at least ¼ full and there should be no leakage of solvent anywhere in the system. Make sure the switch lever of the Injector is in the LOAD position.

3. If already in the ChemStation program, load the appropriate software by double clicking on the "HPLC 1 Online" icon.

   NOTE: Software and file loading on this instrument takes a while, indicated by a blue “Busy” in the lower right corner of the screen. Do NOT perform any software options while this
busy signal is on! The program expects to interface with a fluorescence detector, which we are not going to use, so click “OK” when the software says it cannot find the FLD detector.

4. Go to Instrument and then System ON.

5. Set up the conditions for your run, which are shown below and are most likely already loaded. Do this under Method and then Load Method to scroll down to the desired method. Load the method called "PAH-288.M". Check to be sure the following conditions are shown in this method by clicking on the Method menu and then under that, on Edit Entire Method:

   **NOTE:** The software will store each run under sequential numbers in this directory, e.g. as "SIG10001, SIG10002" etc., for the first and second runs. This means you need to be sure to keep a good lab book record of your runs. Even if you end up not using one, make sure you record it so you know what run number corresponds to what sample injection.

**Pump Set-up:**

Starting conditions:
- Flow rate: 1.00 mL/min
- Stop time: 21 minutes
- Post time: off

Solvents and Gradient Timetable:
- A: 40.0 % Acetonitrile
- B: 50 % Water
- C: 0 % Methanol
- D: 10 % THF

<table>
<thead>
<tr>
<th>Time</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>50</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

This starts the solvent mixture with the 50:40:10 mixture which stays constant until 4 minutes into the run. Then it changes the solvent mixture using a linear gradient until it reaches a 90:10 mixture at 18 minutes.

The pressure limits should be set to 350 bar maximum and 10 bar minimum.
Column Thermostat:

The thermostat is set to 19°C.

DAD Signal:

This is the absorption signal using the diode array detector (DAD). Check to be sure that DAD is set to monitor at 241, 252, 269, 289 and 297 nm with bandwidths of 10 (reference off). Both the UV and visible lamps should be checked.

Signal Detail:

Check to make sure everything is OK: Start time at 0, end time at 20, delay at 0.

Remaining Sub-menus:

For the remaining sub-menus, just say "OK" for each one. After you close the window, be sure to use "File...Save…Method."

Naming andInjecting the Sample

Now click on the "RunControl" menu at the top, click on “Sample Info”. In the “subdirectory” box, type the date in the DDMONYY format 25JUN10. Set to sample name to “prefix/counter”, name PAH and start at 0001. Then click “Run Method” and click “OK” when prompted to create a new directory. When you load the injector and then turn the valve to the Inject position, the run is started automatically using the method you loaded and saved.

Part II: Preparation and Initial Chromatography of Standards

1. Make up 20 mL of a 1:1 methylene chloride (CH₂Cl₂)-methanol (CH₃OH) mixture (solvent), by measuring 10 mL of each chemical using a graduated cylinder (chemicals are in the hood) into a 100 mL beaker. Condition a 100 µL HPLC syringe three times with the CH₂Cl₂-CH₃OH mixture.

2. Make sure the injector is in the LOAD position. Use the 100 µL HPLC syringe to repeatedly inject 1:1 CH₂Cl₂-CH₃OH solvent (about 4–5 times; there is a lot of solvent and the sample loop is only 20 µL). Watch the outlet of the stainless steel overflow tubes projecting out
of the rear of the injector and keep injecting solvent until you see drops forming on the end of the overflow tube. This sweeps out the injector loop.

3. Inject the solvent by rotating the injector handle clockwise as far as it will go to the **INJECT** position. Do this in a smooth, rapid motion so you get injection of the sample as a plug onto the column.

Use "View...Online Signals" to monitor a representative DAD signal (currently set to 252 nm). When the baseline on the DAD signals is stable, use “Balance” signal to “zero” the DAD. Once this is done, stop the run using “**Run Control**”....“**Stop Run/Inject**” sequence. **DO NOT USE THE “ABORT” COMMAND**... THIS WIPES OUT ALL OF THE DATA TAKEN DURING THE RUN! Do not return the lever to the LOAD position until the run has finished.

**WARNING:** Make sure the injector handle is moved fully over as far as it will go and the same when you move it back to the **LOAD** position. **DO NOT LEAVE IT HALF WAY BETWEEN THE TWO POSITIONS!!**

**Part III: Calibration Using the Standard PAH Mixture**

1. You are provided a mixture of 16 PAH to use for identification and calibration purposes. However, it must be diluted first. To do so, measure 200 µL of the standard mixture, using the 200 µL pipette, into a clean 1 mL volumetric vial. Fill the rest of the vial to the 1.0 mL line with the 1:1 CH$_2$Cl$_2$-CH$_3$OH solvent. Put the vial cap on and swirl well to mix. Be sure to record the original concentration of the PAH compounds in the undiluted mixture (this will be needed later) here: __________________________

2. Measure 50 µL of the diluted standard into a small, clear vial with a screw cap. Prepare three different vials this way. To the first add 50 µL of the 1:1 solvent mixture (CH$_2$Cl$_2$:CH$_3$OH). To the second, add 150 µL and to the third add 250 µL. Put the lids on the vials and swirl to mix. It is a good idea to label these vials with tape.

3. Set up the software for each run as before at the end of Part I and inject each standard (be careful to use smaller amounts to flush the loop since there is limited solution in the vials). When the run is finished, open up an Offline version of the software to view the chromatogram and integrate peaks in the “Data Analysis” screen. Do not use the Online version to view data because if the run is active, you cannot get out of the Data Analysis window to view the run progress. Take note of the file number of your run.
It may be more time efficient to jump ahead to Part IV and start preparing the cigarette sample while running the chromatograms for last few standard solutions.

4. In order to identify the benzo[a]anthracene peak, compare your chromatogram to the reference chromatogram (given on the last page) in each of the three standard solutions. You will need to know the initial concentration in the undiluted solution of the standard and account for all dilutions made.

5. Examine the instrument data in the “Data Analysis” screen. Take note of the integrated peak areas for the compounds of interest for each DAD signal and record them in your lab book. Your TA will assist you with navigating through the “Data Analysis” screen.

Create a calibration table as follows to record the integrated peak area for the peak you identified as the benzo[a]anthracene.

<table>
<thead>
<tr>
<th>Sample (conc. in $\mu$g/mL)</th>
<th>241 nm</th>
<th>252 nm</th>
<th>269 nm</th>
<th>289 nm</th>
<th>297 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>STD 1 ($______\mu$g/mL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STD 2 ($______\mu$g/mL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>STD 3 ($______\mu$g/mL)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cigarette (unknown conc.)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Part IV: Preparation and Analysis of the Cigarette Smoke Sample**

**SAFETY CONSIDERATIONS:** Do not burn the cigarette anywhere near the flammable solvents!!!! The TA should set up a separate area with adequate air suction for the cigarette burning, which is away from all the organic solvents.

1. Place the funnel with the fritted disc upside down in the hood (it will go over the cigarette). Using the Tygon tubing, connect the funnel to the yellow vacuum line in the hood and turn the vacuum on. Place the small filter on the fritted disc (the vacuum should make it stay in place). Measure the length of the cigarette, then light it with a match near the hood. Suck on the cigarette with a rubber pipette bulb to keep it burning under the funnel and filter.

2. Let the smoke be drawn through the filter until the entire cigarette has burned if it is a filtered cigarette (have a beaker ready to catch any falling ashes). If it is an unfiltered cigarette, burn as much as possible, and measure the lengths of a new cigarette and the leftover amount. The percent burned can be calculated. Then extinguish the cigarette using a beaker filled with water. Turn off the vacuum before removing the filter funnel.
3. Using the filter flask connected to the vacuum, wash the cigarette residue collected with 2 mL of the 1:1 solvent. Turn off the vacuum.

4. Filter the extract with the 0.2 µL syringe filter (this may be easiest by pulling out the plunger and pouring the sample into the syringe, then push the plunger so that the solution goes through the filter) and dispense the filtered brownish liquid into a small sample vial.

5. Evaporate the sample to dryness using a gentle stream of N₂ or dry air directed into the vial (a dry air nozzle should be just below the vacuum line in the hood). Connecting a glass pipet to a rubber hose from the N₂ (or air) line would give more control.

6. Using the 200 µL pipette, add 50 µL of the 1:1 solvent along the walls of the vial to wash the sample into the bottom and swirl to mix well.

7. When ready to run the sample in the HPLC, load the software, check the method and name the file as before.

8. Inject around 10 µL of the cigarette sample into the HPLC (usually twice) with the Injector in the LOAD position to flush the sample loop (be careful…you only have 50 µL of solution!). Add another 20 µL and rotate the sample loop into the Inject position.

9. Record the chromatogram.

10. Record the Peak Areas of benzo[a]anthracene, but use the DAD wavelength you used to make the Standard Curve when calculating the amount of benzo[a]anthracene present in the cigarette.

11. Clean out the loop by injecting the 1:1 solvent mixture repeatedly until the overflow is clear, not yellow. Do this with the injector in Load position.

12. Shut down the software and instrument according to directions from the 152L instrument manual.
**Data Analysis:**

*Benzo[a]anthracene Quantification*

1. From your recorded DAD integrated peak areas, you only need data at one representative DAD wavelength to perform calibration in order to quantify the amount of benzo[a]anthracene in cigarette smoke.

   Plot the measured absorption peak area vs. concentration for the standard solutions at the representative wavelength. Carry out a least squares analysis as shown in Figure 2. Instructions for using Microsoft Excel to do this are in the Appendix.

2. Now use your linear fit to calculate the concentration of benzo[a]anthracene in the unknown sample obtained by dissolving the cigarette smoke.

3. Finally, calculate how many ng of benzo[a]anthracene there was in the cigarette. Correct for any unburned lengths of the cigarette if it was not completely burned.

**References:**

Appendix: Reference Chromatogram of an PAH mixture

1. Naphthalene
2. Acenaphthylene
3. Acenaphthene
4. Fluorene
5. Phenanthrane
6. Anthracene
7. Fluoranthene
8. Pyrene
9. Benzo[a]anthracene
10. Chrysene
11. Benzo[b]fluoranthene
12. Benzo[k]fluoranthene
13. Benzo[a]pyrene
14. Dibenzo[a,h]anthracene
15. Benzo[g,h,i]perylene
16. Indeno[1,2,3-cd]pyrene

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Laser-Induced Breakdown Spectroscopy

LIBS ANALYSIS OF METAL SURFACES

Last updated: June 17, 2014
Laser–Induced Breakdown Spectroscopy (LIBS)

LIBS ANALYSIS OF METAL SURFACES

INTRODUCTION

Two increasingly popular areas of research in environmental science are the chemistry at surfaces (surface composition, reactivity and contamination) as well as remote sensing to determine concentrations of species at a distance or in hard-to-reach or hazardous environments. Laser–Induced Breakdown Spectroscopy (LIBS) is a rapidly growing technique used in both of these areas.

LIBS uses a powerful, pulsed laser to both prepare the sample by ablation of the surface and create the plasma where analysis of the species formed occurs. The laser pulse delivers enough energy to not only vaporize a small fraction of the surface of the sample but also to induce electronic excitation of the atoms and ions in the resulting plume of rapidly expanding vaporized material. Upon relaxation of the excited electrons, energy is released in the form of electromagnetic radiation that is detected by a spectrophotometer. Each element has a unique line spectrum of electron energies that act as a “fingerprint”, allowing qualitative and quantitative determination of the elemental surface composition.

This technique has been successfully applied in studies of soil composition, aerosol detection and analysis in the atmosphere, steel and coal analysis, corrosion in nuclear reactors, surface contamination, and recently has branched into analysis of biological materials (the popular laser eye surgery procedure being an example).¹

This experiment acts as a first-hand experience with laser operation and introduces the LIBS technique in the surface analysis of several common metals. The main goals of this lab are:

- Learn about pulse lasers, plasmas, and emission spectroscopy
- Identify elements in metal samples by their emission spectra from the laser induced plasma
- Measure spectra emitted by various light sources such as lamps, light emitting diodes, TV remotes, lasers, etc.

BACKGROUND

To better appreciate the LIBS technique, there are several key concepts in which a basic understanding should be developed. The laser is the main component of any LIBS instrument. Plasma is a unique state of matter that is the key to LIBS analysis. Finally, spectroscopy is a scientific art of interpreting colors in terms of atoms and molecules that emit them.

I: Lasers

The development of lasers began in the 1960’s, and has since completely revolutionized science and technology. Lasers are used in most areas of our life, from basic CD player operation to major surgical procedures. Laser is an acronym for “Light Amplification by Stimulated Emission of Radiation”.

Typically, a laser operates by exciting atoms in a lasing medium using a bright flash of light from a flash lamp (see Figure 1 on the next page). A population inversion is created in which there are more atoms in an excited higher energy state than the lower energy ground state. This
lasing medium is placed in a cavity that is capped by two aligned mirrors. The mirror on one side is 100% reflective, and the other allows some radiation to escape. When an atom loses its excess energy and falls back to the ground state, a photon of electromagnetic radiation (“light”) is emitted. This photon can stimulate emission of another photon from a neighboring excited atom, and so on, causing a “cascade” of photon emission. The light is then reflected back and forth by the mirrors through the lasing medium, forming an amplified, highly coherent (all photons are in phase) and monochromatic (all photons have the same wavelength) beam of radiation that exits the cavity as either a continuous beam or in pulses.

**Figure 1:** Basic diagram of a typical solid state Nd:YAG laser and timing sequence involved into firing of a laser pulse.

(a) Nd:YAG schematic diagram

(b) Nd:YAG timing

There have been different lasing mediums used, ranging from the original Ruby crystal to gases, dye solutions, and semiconductors. The particular laser medium used in this experiment (Figure 1) is Nd:YAG crystal, which is shorthand notation for yttrium aluminum garnet doped
with neodymium. The flash lamps that deliver energy to the Nd:YAG rod are quartz tubes filled with pressurized Xenon. This laser is classified as a nanosecond (ns) pulsed laser, because it emits repetitive pulses of light, with each pulse lasting about 5 ns (1 ns = 1 \times 10^{-9} \text{ s}). The laser repetition rate, the number of laser pulses emitted every second, is 10 Hz.

The energy of a pulsed laser is commonly measured in Joules (J) per pulse. The power is measured in Watts (W = Joule per second), and the irradiance, or the power density distributed over the laser beam area, in W/cm². There are two ways to report power. The most common way is to specify the average power, which is total energy divided by the period of time over which the energy is delivered. Average power is calculated by averaging energy from multiple laser pulses. Sometimes it is more convenient to use peak power, which is the effective power of a single pulse equal to the pulse energy divided by the pulse duration.

The following example illustrates these concepts. The laser used in this experiment is capable of delivering 0.2 J per laser pulse, with a pulse duration of 5 ns. The laser emits 10 such pulses per second, thus delivering 10 \times 0.2 = 2 \text{ J} of energy every second. This is equivalent to average power of $2 \text{ J} / 1 \text{ s} = 2 \text{ W}$. The peak power is considerably higher because the pulse duration is so small. It is equal to pulse energy / pulse duration = $0.2 \text{ J} / 5 \times 10^{-9} \text{ s} = 4 \times 10^7 \text{ W}$ ( = 40 megawatt) during the laser pulse! The laser beam is typically focused on an area that is about 0.01 cm², therefore, the irradiance used in this LIBS experiments can be as high as $4 \times 10^9 \text{ W/cm}^2$, or 4 gigawatts per square centimeter! It is the large peak powers that make it possible to efficiently vaporize the sample in LIBS. Therefore, it is advantageous to use very short laser pulses to achieve high peak powers.

II: Plasmas

Plasma can be defined as a local assembly of atoms, positive ions, negative ions, and free electrons. Although there are charged particles present in plasma, it is normally neutral on the whole. Particles in the plasma are typically characterized by high temperature, which make the plasma glow in a color that depends on the plasma composition. Figure 2 shows typical plasmas generated in a LIBS experiment.

**Figure 2:** Sample plasmas induced by LIBS

![Sample plasmas induced by LIBS](image)

The leading edge of the laser pulse rapidly heats, melts and vaporizes the surface of the solid sample into a layer just above the surface. For the irradiance values used in LIBS, the
temperatures of most plasmas created may approach 10,000 K. The vaporization and initial ionization of atoms generated can be represented by the following highly simplified equations:

Vaporization: \[ M_{(s)} + h\nu \rightarrow M_{(g)} \]
Vaporization & Ionization: \[ M_{(s)} + h\nu \rightarrow M_{(g)}^+ + e^- \]

where “s” stands for solid, “g” stands for gas, “M” stands for metal atom, plus denotes a positively charged atom, and e− stands for a free electron. Further ionization can occur as the free electrons collide with other atoms in a self-accelerating process that causes gas ionization and breakdown:

Ionization by electrons: \[ e^- + M_{(g)} \rightarrow M_{(g)}^+ + 2 e^- \]

The spatial and temporal characteristics of the plasma after a laser pulse can be quite complicated, especially in a vacuum environment as in our experiment. We will only qualitatively look at plasma shapes and colors.

III: Spectroscopy

As stated previously, the atoms and ions of each element have unique electronic energy levels (per quantum mechanics). When atoms absorb energy that is equal to the difference between two energy levels, they become “excited” and promoted to a higher energy level. In the case of LIBS, this excitation is done by electrons, photons, and excited atoms present in the plasma.

Excitation by photons: \[ M_{(g)} + h\nu \rightarrow M_{(g)}^* \]
Excitation by electrons: \[ M_{(g)} + e^- \rightarrow M_{(g)}^* + e^- \]
Excitation by atoms: \[ M_{(g)} + A^* \rightarrow M_{(g)}^* + A \]

Similar equations can be written for ions. These excited atoms or ions rapidly relax back to their lower energy states in a process called spontaneous emission, releasing energy as electromagnetic radiation of specific wavelengths (Figure 3).

**Figure 3**: Schematic representation of spontaneous emission: Before emission the particle is in the excited state. After relaxation of the electron, a photon is emitted and the electron returns to the ground state energy level.
A spectrophotometer measures the intensities of the photons emitted, and displays the output as an emission spectrum as a function of wavelength. The wavelength is related to the energy of electronic energy levels involved in the transition as follows ($E_i$ and $E_k$ are the upper and lower state energies, respectively):

$$E_i - E_k = h \nu_{ik}$$

$$\lambda_{ik} = \frac{hc}{E_i - E_k}$$

With increasing energy the wavelengths get smaller and are higher in frequency. Radio waves have the largest wavelengths and are about the size of buildings. Gamma rays are the smallest and are on the order of atomic nuclei. Visible wavelengths are right in the middle and are the size of bacteria. The spectrometer will provide measurements of plasma and various light sources within the electromagnetic spectrum (Figure 4).

This spectrum can be compared to reference spectra to qualitatively identify what atoms and ions are present in the plasma. The peak intensities can also be used to quantitatively determine the amounts of each species (not done in this experiment).

With the advent of fiber optics, the spectrophotometer could be separated from the plasma via a fiber optics cable, allowing remote analysis of samples in hazardous, distant, or difficult to reach areas. A fiber optics cable will be used in this experiment to transmit light from the vacuum chamber, where plasma will be located, to a USB-powered spectrophotometer.

**Figure 4:** The electromagnetic spectrum. The spectrometer used in this lab is capable of resolving the colors ranging from UV (200 nm) to near-infrared (1000 nm).
SAFETY

The Nd:YAG laser used in this experiment is a Class IV laser that can cause permanent vision and skin damage. It is NOT a toy. The infrared beam produced by the laser is INVISIBLE, so avoid standing in any location where you can accidentally look into the laser beam or catch the reflection of the beam off of a smooth surface. Likewise, make sure that the laser beam path is clear, and remove any reflective accessories (e.g., jewelry, watches, etc.) from your hands and arms. Laser safety goggles should be worn when the laser is in use. Appropriate laser goggles for this project should absorb 1064 nm and UV, but not the visible radiation. The green or red laser goggles next to the LIBS setup are suitable for this purpose. When you are not collecting data, reduce the laser power output by increasing the delay time between pulses or close the internal cavity shutter on the laser. Become familiar with the lab protocol and review UCI’s Laser Safety Guidelines prior to starting the experiment.

EXPERIMENTAL

The experimental apparatus has three main components: the laser, the sample chamber, and the spectrometer, as shown in Figure 5. The laser generates a pulsed beam that travels through a focusing lens, strikes the sample disc in the vacuum chamber, and induces the formation of plasma. Radiation emitted by the plasma is focused onto a fiber optics cable that carries the signal to a spectrometer. The computer analyzes and displays the data collected by the spectrometer.

Note that the Nd:YAG laser used in this experiment fires in repetitive pulses. The time between pulses is fixed and equal to 0.1 seconds (inverse of the laser repetition rate). The energy of each pulse can be adjusted by changing the time delay between the flash lamps (the Q–switch), which charges the lasing medium (the longer the time delay, the lower the pulse energy). The laser cavity then electronically opens and forces the laser to emit a pulse. This delay time can be controlled by setting the Q-Switch delay on the laser control panel.

Figure 5: Diagram of the LIBS apparatus

![Diagram of the LIBS apparatus](image)

Also note that this laser has the ability to create three different wavelengths by using a special attachment with a doubling and tripling crystal in it. The laser itself produces an infrared beam at 1064 nm which can be doubled with a doubling crystal to make a weaker green beam at
532 nm, or tripled with a tripling crystal to generate a UV beam around 355 nm. The rotating sample disc is centered in a vacuum chamber that is pumped by a mechanical pump ($\sim 10^{-3}$ torr pressure). Be sure that the pump is on before powering up the laser. The sample disc can be removed without turning off the pump by closing the pump valve.

The default setting for the spectrometer is to continuously record data. The spectrometer can also be configured to only collect data for a brief period of time after the laser pulse if necessary. The amount of time the spectrometer waits after the laser fires is controlled by the delay controller. The longer the delay, the longer the spectrometer waits before collecting and displaying data.

**PROCEDURE**

**I: Laser Warm–Up and Orientation**

1. Refer to the laser diagram in Figure 1. Have your TA carefully pull off the laser cover of the unused laser on the counter top and locate the lasing medium (plasma chamber) and flash lamp (together inside a water-cooled cylindrical container), internal laser cavity shutter, mirrors and optics. Do not touch anything inside. Carefully replace the laser cover. The laser being operated will not be opened.

2. Warm up the laser. This takes about 20 minutes, and during this time the orientation of the LIBS apparatus can be completed in step 3. Refer to Appendix A and complete up through step 4 to begin warming up the laser.

3. While the laser is warming up, familiarize yourself with the experimental setup by locating the following parts of the LIBS apparatus (Refer back to Figure 5):
   a) the rotatable shutter on the top left of the laser (should be shut)
   b) the external knob on the left side of the vacuum chamber that rotates the sample disc inside the chamber
   c) the valve of the vacuum pump line
   d) the on/off switch on the vacuum pump (make sure the pump is on)
   e) the spectrometer and fiber optic cable

**II: Spectra of Different Radiation Sources**

The goal of this part of the lab is to observe the spectrum of various light sources and to become familiar with the spectrometer.

1. You will be using a compact Ocean Optics spectrometer, which is controlled by a computer. Locate the OOIBase32 icon on the computer and double-click it to start up the Ocean Optics spectrometer program.

2. If the spectrometer does not start measuring right away, do the following: select SPECTROMETER > CONFIGURE from the menu at the top to open the Spectrometer Configuration dialog box. Click on the A/D INTERFACE tab and check that S2000/PC2000/USB2000/HR2000 is selected in the Spectrometer. If it is,
you do not have to do anything (press Cancel). If there is no spectrometer selected ask your TA for help.

3. Before you start the LIBS project, use the spectrometer to record emission spectra of more common radiation sources (see step #6). For each light source, mount the fiber and your light source appropriately so that you can view the emission spectrum. Please DO NOT bend the fiber too much as it will damage it. DO NOT touch the end of the fiber-optics cable with your hands.

4. On the main screen of the program, locate the Integration Time box (labeled “Data Acquisition Box” when hovered over by the mouse) and select an appropriate integration time (500 milliseconds is a good starting value). This is the time the detector spends collecting photons, so the longer the integration time, the more intense the peaks should be. Locate the Average box and set the average to 1 so that spectrometer responds faster.

5. If the signal is too large, the spectrum can be “saturated” at the peak wavelengths. If this is the case, reduce the integration time, move the fiber further away from the source, or rotate the fiber away from the source slightly. Conversely, if the signal is too small do the opposite. Once you are happy with the integration time you may want to increase the averaging to 5-10 in order to improve the quality of your recorded spectra.

6. The following are specific suggestions for different sources. For each, attempt to predict the region (IR, Visible, UV, etc.) and, if possible, an estimated wavelength that should be seen (if in the Visible region). You can use the provided electromagnetic spectrum (Fig. 4) to help with your predictions. Record your observations in the spaces provided.

   a. Incandescent lamp: Point the lamp (old nightlight) provided towards the fiber and adjust the lamp position to give an acceptable signal intensity. Avoid saturating the detector.

   b. Fluorescent lights: Point the fiber towards the lights on the ceiling and find a position giving acceptable intensity level. Record the spectrum; you may be surprised at what you see.

   c. Green laser pointer: This light source should be monochromatic (only one wavelength emitted). Predict this wavelength. Do NOT shoot the laser into the fiber – it may destroy the detector. Instead, scatter the laser off a white piece of paper and record the scattered light.¹ There may be more than one color available.

¹ This is a battery operated device. If the signal is too weak, take the batteries out and check their voltage with a multimeter. If the battery voltage dropped below 1.3 V, replace the batteries.
d. Mercury vapor lamp: *Warning: wear protective eye wear.* This lamp is commonly used for wavelength calibration. The lamp should run for 30-60 seconds to warm up before you take its spectrum. The light emitted by this lamp is caused by a transition between different quantum levels in electronically excited mercury atoms. Would you expect broad peaks (polychromatic) or emission lines? Take two spectra: the first one with the strongest line not in saturation, and the second one with this line saturated so that the weaker lines are also visible.

e. Small battery-operated UV-A lamp: *Warning: wear protective eye wear.* Do not forget to turn off the lamp when finished.¹

f. White-light LED: Use the same lamp from part e, which has the LED built into it. Record the spectrum of this seemingly white light source.¹

g. TV remote: Keep pressing one of the buttons of the remote and shoot directly into the fiber. What type of emission would you expect?¹

h. RGB color matrix: Bring up a color wheel and image the colors directly off the laptop screen. By moving the spectrometer around your screen you should be able to record spectra corresponding to distinct colors (R-red; G – green; B – blue). Also record the spectrum of a WHITE portion of the computer screen. The signal is going to be *quite weak* – you may want to adjust the screen brightness to the maximum and make the fiber touch the computer screen. You may need to set averaging to a reasonably large number, 20-30.
III: Vacuum

The goal of this part of the lab is to understand the importance of vacuum to the experiment.

1. Close the shutter on top of the laser if it is open.

2. If the chamber is under vacuum, close the valve on the vacuum line and vent the chamber by unscrewing the vacuum line. You will hear a hissing sound as the chamber vents to atmospheric pressure. Reattach the vacuum line to the chamber.

3. Remove the sample disc from the vacuum chamber. First, locate the bolts holding the left side of the vacuum chamber in place (see Figure 6 below). Remove the bolts and carefully pull the entire left side of the chamber out (it may be heavier than expected). Since the sample disc is attached to the left wall of the chamber, keep the entire piece level to remove it.

   **Figure 6:** LIBS vacuum chamber

   ![LIBS vacuum chamber](image)

   - sample disc bolts
   - fiber optic cable
   - vacuum line valve

4. Place a laser screen to block the backside of the now open chamber.

5. Make sure you are wearing laser goggles and then open the shutter.

6. Lower the Q-Delay switch value until sparking from the laser beam is clear (do not go below 280 units).

7. What do you observe? Why is the vacuum important for this experiment?

8. Once you are done, increase the Q-Delay switch value to 365 units.

9. Make sure that the shutter is closed.

10. The sample disc should still be outside of the chamber and ready to load sample on.
IV: LIBS Setup

1. Your TA will provide you with various samples without telling you what they are. Affix the samples onto the sample disc using bits of double-sided tape. The samples should be small enough to fit comfortably onto the sample disc. If needed, cut the samples down to approximately 1-2 cm² in size. Be sure to record the order of your samples and describe each carefully so they can be located in the chamber. The disc can rotate, so the angular position of each sample is irrelevant. However, the center of each sample should be aligned with the circle created by the previous laser pulses (easily visible on the sample holder). Make sure the double sided tape is not sticking out from under the samples.

2. Write down the order or draw a picture of the approximate location of your samples with respect to each other in the space below. Example: beer cap: 3 o’clock; penny: 5 o’clock; white soft metal sample; 7 o’clock; etc. This will help you know which sample you are hitting with laser. For reference, the laser is aligned to hit the sample wheel below the middle.

3. Slide the sample disc back into the vacuum chamber and bolt it closed (this will require 2 people). When bolting the chamber closed, make sure the O-ring is sitting in its groove (this is the trickiest part!). If the O-ring is not properly seated, you will not get a good seal when you pump the chamber to vacuum. If you do it correctly there should be a barely visible gap between the flanges. If the gap is bigger or if you hear hissing sound when the chamber is under vacuum, the O-ring must have slipped out of place. Repeat the installation.

4. Open the vacuum line valve (two to three turns) to pump the chamber to vacuum.

V: Plasma of Unknown Metals

The goals of this part of the lab are to observe the characteristics of plasmas induced on several different surfaces and to determine the identity of the unknown metals by using the emission spectra and comparing to the known spectra provided in Appendix B. You will be recording the descriptions, plasma colors and plasma shapes of each unknown sample provided by the TA directly onto your Postlab Worksheet.

1. The laser should be warmed up by now.

2. Make sure there are no objects obstructing the path of the laser beam. Put on your laser safety goggles (the green or brown ones).

3. Open the shutter on the laser cavity by rotating it.
4. Press start on the Q-Switch control section of the laser control panel

5. Optional: To test for the presence of the invisible infrared beam, take a piece of photographic paper wrapped in plastic and lower it carefully into the path of the beam. The laser should leave burn marks on the photographic paper.

6. On the laser control panel, press the **Center (symbolized by enter key) key** button to scroll through the settings using the up/down arrows and find the **Q-Switch** menu. Push **Enter** again, Scroll down to **FL-QS Dly.** Use the arrow buttons to reduce the delay time between laser pulses to 340 (or any value > 330). Make the laser hit one of your samples. What will lowering the Q-Switch delay do to the power? This will increase the laser power as shown in Figure 7.

**Figure 7:** Laser power calibration (as of June 2014)

![Laser Power (W) vs. Q-Switch Delay Setting](image)

7. On the computer set the spectrometer integration time to 350 milliseconds (the spectrometer will now record in 350 ms windows, which covers 3 laser pulses). Set the average to 1.

8. Adjust the position of the fiber optics cable mount to maximize the intensity of the peaks generated by the plasma. Place a piece of paper just in front of the mount holding the fiber optics cable to locate where the lens is focusing the radiation. Then, move the mount so that the opening of the fiber optics cable is where the imaged radiation is the most intense. Monitor the intensities of the peaks on the screen to determine which position is best (the higher the peaks are the better). If the signal is too strong and is saturated, reduce the integration time or reduce the laser power.

9. Now that the fiber optics cable is properly aligned, set the Average box to 10 to average 10 spectra together before displaying the data. Although there will be lag in the display of the spectra, this will considerably improve the signal-to-noise ratio.
10. Rotate the sample disc a miniscule amount (~1 mm) so that the beam is striking a fresh spot on the first sample. You can also “freeze” a spectrum by clicking on the Camera Icon on the upper left of the screen.

11. Look into the sample chamber through the large viewing window (not through the small window where the laser enters!) to observe the plasma. If the laser is striking the middle of a flat sample it may be safe to briefly lift up your goggles for a better view. Warning: DO NOT lift up your goggles when the laser is striking an edge or when you are rotating the sample disc. Record the color and characteristics of the plasma generated by the laser striking your target. Your notes may look something like this: “Pale-yellow spherical puff about 1 cm in size from the soft white metal sample.”

12. Rotate the disc so that the laser strikes the next sample, and record the shape and color of the generated plasma in your lab book. You may increase the laser power (by reducing the Q-switch delay) if the plasma is too weak. However, do not reduce the delay below 260 units, the setting that corresponds to about 2 Watts of laser power according to Figure 7.

13. If a digital camera is available, take photographs of the different types of plasma. You will have to secure your camera and play with the exposure to get good results.

14. Rotate about 1 mm to a fresh portion of the sample and collect the emission spectra of the plasma as before in Step 9.

15. Collect the spectra and plasma descriptions for the rest of the samples.

16. After you are done, set the delay on the laser control box to 365 and close the shutter button on the laser to disable the laser beam.

**VI: Depth Profiling**

You may need to vent the chamber as done in Part III to load new samples for Parts VI and VII. Try to have different people get the practice each time.

One of the unique features of LIBS is its ability to drill into the sample and probe different depths during the analysis. When the laser beam starts to hit the sample it vaporizes elements from its surface. As the laser keeps heating the same spot, it slowly penetrates deeper into the sample, and probes the composition of the interior. The easiest way to observe this effect is to look at the spectrum of a penny or a zinc-plated or chrome-plated steel sample. To observe this effect, set averaging to 1 (to make the spectrometer respond faster), move the laser onto such a sample, and look at what happens to the spectrum as a function of time. For the first few seconds, you should see a spectrum corresponding to the outer coating. A few seconds later, the spectrum should change drastically as the laser bores into the inner material. Try to capture and save the spectra in the early and late stages of the depth profiling through zinc- or chrome-plated steel. A “capture” icon (that looks like a camera) is a convenient tool in the Ocean Optics software for freezing the spectrum at a particular time. Next, try to do the depth profiling for a pure material such as copper. Does the spectrum change as you drill through?
VII: Spectra vs. Laser Power

The goal of this section is to observe the effect of different laser powers on the plasma induced. To change the laser power you will be changing the Q-switch delay as shown in Figure 7. Spectra of plasma induced at different laser powers will be recorded and then compared to one another. Your TA will supply you with samples to try. The default set of materials is: W (tungsten), Mo (molybdenum), and Si (silicon).

1. Install the samples provided by the TA in the vacuum chamber as instructed in Parts III and IV, unless the samples are already in the chamber.
2. Set the spectrometer integration time to 350 milliseconds (the spectrometer will record in 350 ms windows, which covers 3 laser pulses). Set the average to 1.
3. Set the Q-switch delay to 340 units (or any value > 260 at which the plasma starts to be visible) and direct the laser beam onto one of your samples.
4. Adjust the position of the fiber optics cable mount to maximize the intensity of the peaks generated by the plasma. Monitor the intensities of the peaks on the screen to determine which position is best (the higher the peaks are the better). If the signal too strong and is saturated reduce the integration time or reduce the laser power.
5. Now that the fiber optics cable is properly aligned, set the Average box to 10 to average 10 spectra together before displaying the data. Although there will be lag in the display of the spectra, this will considerably improve the signal-to-noise ratio.
6. Rotate the sample disc a miniscule amount (~1 mm) so that the beam is striking a fresh spot on your sample.
7. Similarly, record spectra for Q-Switch delays of 320, 300, and 280. Make sure that the beam is hitting a fresh spot on the disc just prior to recording the spectrum.
8. Set the delay on the laser control box to 360 after you are done collecting spectra.

VIII: Clean Up

1. Close the shutter and power down the laser according to the instructions in Appendix A.
2. You may leave the pump running and chamber under vacuum.
3. Exit the computer software.
Appendix A

Standard Operating Procedures (SOP) for the Quantel Laser

Turning on the laser:

1) Turn the key switch to the “on” position (clockwise). Wait a few seconds for the laser to finish its diagnostics. The box is situated behind the optical table towards the back right corner.

2) Slide the shutter wheel on the laser head.

3) Press the Center (symbolized by enter key) key button to scroll through the settings using the up/down arrows and find the Q-Switch menu. Push Enter again, Scroll down to FL-QS Dly. The delay should read ~340µs, if it does not, use the +/- or Left/Right arrows to adjust it.

4) Press the Start button on the Flashlamp controls. The yellow LED will come on (If the laser has not been warming up then the Flashlamp may shut off until the laser is at 29°C) The laser head is now flashing at 10 Hz frequency. Let it warm up for approximately 20 minutes for thermal stabilization. You should familiarize yourself with the rest of the LIBS apparatus and experimental procedures while waiting for the laser to warm up.

5) Put on your laser safety goggles, which block out the specific radiation being emitted by the laser (specifically 1064 nm in the Infrared region which is not visible to the naked eye!).

6) Press the Start button on the Q-Switch controls. The LED will come on as laser radiation is now leaving the laser. You should hear a click sound as the laser radiation hits the bare carousel surface in the chamber (this sound will diminish as the vacuum is turned on).

7) Change the Q-Switch delay settings to alter the laser power as instructed in the lab procedure:

<table>
<thead>
<tr>
<th>Delay Settings</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>360-375</td>
<td>Low power; Good for laser alignment.</td>
</tr>
<tr>
<td>330-340</td>
<td>Enough power to generate a weak LIBS signal.</td>
</tr>
<tr>
<td>300-330</td>
<td>Enough power for a sufficiently bright LIBS plasma.</td>
</tr>
<tr>
<td>280</td>
<td>Maximum power allowed without instructor approval!!</td>
</tr>
<tr>
<td>180</td>
<td>Maximum power....very dangerous!</td>
</tr>
</tbody>
</table>

Turning off the laser:

1) Press the Stop button on the Q-Switch and then the Flashlamp. The LED will go off as well as the LED on the Flashlamp button should also go off. The flash lamps should stop flashing.

2) Slide the shutter wheel on the front of the laser to Closed.

3) On the Laser Power Supply, turn the key counter clockwise to the O position.
Appendix B: Spectra of different materials you may use in this lab

LIBS spectra of Copper (Cu) samples

![LIBS spectra of Copper (Cu) samples](image)
LIBS spectra of Aluminium (Al) samples
LIBS spectra of Steel samples
Pure HOPG (highly-oriented pyrolytic graphite, C)

These bands correspond to emissions from C2 molecule

Lower-quality pyrolytic graphite

Sharp lines likely correspond to impurities in graphite
Molybdenum (Mo)

Zinc (Zn) from the inner layers of a new penny
LIBS spectra of Silicon (Si) samples
LIBS spectra of Tungsten (W) samples
Ability of Catalytic Converters to Reduce Air Pollution

MEASUREMENT OF SELECTED AIR POLLUTANTS IN CAR EXHAUST

Last updated: June 17, 2014
ABILITY OF CATALYTIC CONVERTERS TO REDUCE AIR POLLUTION

MEASUREMENT OF SELECTED AIR POLLUTANTS IN CAR EXHAUST

INTRODUCTION

Automobile engines convert the energy stored in chemical bonds into mechanical energy through the controlled combustion of gasoline (hydrocarbons, C\textsubscript{x}H\textsubscript{y}) in air:

\[ C_xH_y + O_2 \rightarrow CO_2 + H_2O + \text{heat} \]  

(1)

When there is the correct balance of O\textsubscript{2} and hydrocarbons in the combustion chamber (i.e., under “lean” conditions), complete combustion occurs and CO\textsubscript{2} and H\textsubscript{2}O are emitted in the exhaust. When the mixture is not in balance, such as the case when there is too much fuel and not enough oxygen (i.e., under “rich” conditions), combustion is incomplete and the exhaust can contain CO and excess hydrocarbons. Since both nitrogen and oxygen are present in air used for combustion, the following reactions may also take place within the engine, especially when the combustion temperature is high:

\[ O_2 + \text{heat} \rightarrow 2 O\cdot \]  

(2)

\[ O\cdot + N_2 \rightarrow NO\cdot + N\cdot \]  

(3)

\[ N\cdot + O_2 \rightarrow NO\cdot + O\cdot \]  

(4)

\[ 2 NO\cdot + O_2 \rightarrow 2 NO_2 \]  

(5)

As a result, nitrogen oxides (NO\textsubscript{x} = NO + NO\textsubscript{2}) are also present at high concentrations in car exhaust. Typical untreated car exhaust may contain CO concentrations of 1–2% by volume, unburned hydrocarbons levels between 500-1000 ppm and NO\textsubscript{x} levels between 100-3000 ppm. The unit of ppm, or parts-per-million, is called a mixing ratio. In fact, scientists prefer to measure the amount of trace pollutants such as NO\textsubscript{x} or ozone in the air in terms of ppm or even parts per billion (ppb), which are defined as follows:

1 ppm = 1 molecule reported per 1,000,000 molecules of other gases in air
1 ppb = 1 molecule reported per 1,000,000,000 molecules of other gases in air

With 10 million cars in the South Coast Air Basin alone, the health of humans, agriculture, and natural places depends on our ability to reduce or eliminate emissions of toxic gases such as NO\textsubscript{x}, CO and hydrocarbons from automobiles. One of the consequences of all these pollutants is the occurrence of smog in urban areas such as Los Angeles. Photochemical smog is the brown, noxious haze surrounding downtown Los Angeles on a summer day that obscures the view of the San Bernardino Mountains. The typical conditions for smog to develop are:

1. A lot of sunshine
2. Warm air (T > 290 K or 63 °F)
3. Sources of NO\textsubscript{x}, CO and hydrocarbons (i.e., combustion exhaust of automobiles and industry)
4. A stable air mass (i.e., a city surrounded by mountains) with the possibility of having an inversion layer that traps gases close to the ground

Los Angeles satisfies all these requirements. One of the most toxic components of smog, and the one that makes breathing difficult for children playing outside on smoggy days, is ozone (O$_3$). It is formed from a series of chain reactions that are initiated by sunshine and involves free radicals, hydrocarbons and NO$_x$ from automobiles. The concentration of ozone in clean air is around 0.02-0.04 ppm (or 20-40 ppb). Smoggy air can contain considerably more ozone, and 0.1 ppm is quite typical for the Los Angeles area today. In the past, ozone concentrations in L.A. were known to reach values as high as 0.7 ppm. For reference, the air quality standard for ozone today is 0.07 ppm, set by the California Air Resources Board (ARB). The standards are defined as the highest average concentration of ozone that should not be exceeded during a given interval of time.

Automobile emissions have a huge impact on human health and the well-being of our planet. Not only do they lead to elevated ozone levels, but the CO emitted by engines is toxic. Also, both CO$_2$ and ozone are greenhouse gases. After the link was made between automobiles and air pollution, and after overcoming strong opposition from the automobile industry, regulations to control automobile emissions were finally enacted in the U.S. when Congress passed the Clean Air Act in 1970. Since then, the Environmental Protection Agency (EPA) has established emission standards that automobile manufacturers must abide by when producing cars, and these regulations have become more stringent over time as pollution abatement technology has improved. California and its air pollution regulation body, the Air Resources Board (ARB) has set yet more stringent emission standards for passenger cars; they are listed in Table 1. The most effective way to meet the emission requirements of the Clean Air Act and those of the ARB has been through the implementation of catalytic converters. These days, ULEV and ZEV vehicles are also possible through recent advances in hybrid, fuel-cell and battery technology. In addition, cars in California and many other States make car registration contingent upon a car’s ability to pass a “Smog Check” that ensures CO, hydrocarbon, and in some cases, NO$_x$ levels in car exhaust are below the regulated levels.

<table>
<thead>
<tr>
<th>Category</th>
<th>NMOG</th>
<th>CO</th>
<th>NO$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>TLEV</td>
<td>0.125</td>
<td>3.4</td>
<td>0.4</td>
</tr>
<tr>
<td>LEV</td>
<td>0.075</td>
<td>3.4</td>
<td>0.2</td>
</tr>
<tr>
<td>ULEV</td>
<td>0.040</td>
<td>1.7</td>
<td>0.2</td>
</tr>
<tr>
<td>ZEV</td>
<td>zero</td>
<td>zero</td>
<td>zero</td>
</tr>
</tbody>
</table>

_Abbrev.:_ LEV = low emission vehicle; T = transitional; U = Ultra; Z = zero; NMOG = non-methane organics. *Units are in grams per mile

The catalytic converter is located under the automobile between the engine and the muffler (Figure 1). When the car is first started (i.e. “cold start”), the catalytic converter is cold and the catalyst does not efficiently remove NO$_x$ and CO from the exhaust. As the engine warms up, the exhaust warms the catalytic converter to a high enough temperature to initiate the catalytic reactions that remove pollutants. The catalytic reactions occur heterogeneously (i.e. when
gaseous combustion products adsorb onto the surface of a ceramic monolith and react with the various metal atoms present there) and convert toxic gases into less harmful chemicals.

The active components of catalytic converters are precious metals such as Pt, Pd, and Rh dispersed on the high surface area ceramic monolith that is shaped like a honeycomb (see Figure 2). The honeycomb support can be 10 inches in diameter, 7 inches long, have between 10-500 cells per square inch, and is held inside a metal housing (you will have an opportunity in class to take a catalytic converter apart). The honeycomb structure means that exhaust gases travel through the converter at the fastest possible rate while at the same time hitting a lot of catalyst-covered surface on their way out. This design aims at maintaining fuel efficiency and preventing a loss of power that would happen if the exhaust gases build up pressure going through the converter.

Figure 1. Example of the exhaust pathway in the underbody of an automobile.

Figure 2. Left: Drawing of a (MgO)$_5$·(Al$_2$O$_3$)$_2$·(SiO$_2$)$_5$ ceramic monolith used as a support for the catalysts. Right: A close up of a layer of high surface area Al$_2$O$_3$ (the “wash coat”) impregnated with Rh, Pt and Pd catalysts (dotted regions).

What is actually happening in a catalytic converter? In what is known as a three-way catalyst (TWC), hydrocarbons and CO are oxidized to CO$_2$ and H$_2$O:

\[
C_xH_y + (1 + y/4) O_2 \rightarrow x CO_2 + y/2 H_2O \quad (6)
\]

\[
CO + (1/2) O_2 \rightarrow CO_2 + y/2 H_2O \quad (7)
\]
and NO\textsubscript{x} is reduced to harmless N\textsubscript{2} (note these reactions are intentionally unbalanced because the mechanism of catalysis is very complex)

\[
\text{NO (or NO}_2\text{)} + \text{CO} \rightarrow \text{N}_2 + \text{CO}_2
\]

(8)

\[
\text{NO (or NO}_2\text{)} + \text{C}_x\text{H}_y \rightarrow \text{N}_2 + \text{CO}_2 + \text{H}_2\text{O}
\]

(9)

The metals and metal oxides present in the ceramic monolith act to adsorb both NO\textsubscript{x} and O\textsubscript{2}, and then break the normally very strong N–O or O–O bonds. On the surface, the resulting oxygen atoms react with CO or hydrocarbons, while N atoms recombine to form N\textsubscript{2}. The whole system is catalytic, i.e., during a single catalytic cycle the metal species do not themselves permanently change their identity, but through their interaction with the reactants, serve to reduce the energy barrier (Activation Energy, E\textsubscript{a}) to the reaction and speed the reaction up to form more benign gases.

Two conditions must be satisfied for the converter to work properly. First, the temperature of the catalyst must be high enough. This stems from the relation between the temperature and the rate of a chemical reaction, as described by the Arrhenius equation:

\[
k = A \exp \left(\frac{-E_a}{RT}\right)
\]

where k is the rate constant of the reaction, A is the pre-exponential factor, and E\textsubscript{a} is the activation energy for the reaction. The second requirement for the catalytic converter to work properly is that the engine combustion chamber must be operated close to the stoichiometric air-to-fuel ratio. This is because there is a narrow range of air-to-fuel ratios in which both NO\textsubscript{x} reduction and CO/hydrocarbon oxidation readily occur on the surface of the catalytic converter simultaneously. If there is too much O\textsubscript{2} present, the NO\textsubscript{x} reduction does not occur. Conversely, if there is not enough O\textsubscript{2} present, the CO/hydrocarbon oxidation doesn’t happen. This fine balance to keep the gas mixtures in the optimum range is continuously adjusted by an oxygen sensor and engine feedback system placed before the catalytic converter in the exhaust manifold.

**BACKGROUND**

The goals of this experiment are to measure quantitatively the concentration of NO\textsubscript{x} in the exhaust of your vehicle using UV/VIS Spectroscopy, and to study the efficiency of your automobile’s catalytic converter to decrease NO\textsubscript{x} emissions to the atmosphere. We will sample exhaust from the tail pipe of the vehicle immediately at startup and then again after the car has had a chance to warm up for 10 minutes. Each team member will collect one or more exhaust samples to determine the amount of nitrogen oxides present in the gas stream using a chemical indicator.

**The Chemical Indicator for NO\textsubscript{x} in Exhaust.** NO\textsubscript{x} at ppm levels can be determined using Ultraviolet-Visible (UV/VIS) Spectroscopy after it is converted into a brightly colored indicator dye in aqueous solution. In solution, NO and NO\textsubscript{2} undergo the following reactions to form nitrous acid (HONO):

\[
\text{HONO}
\]
\[ 4 \text{NO} + \text{O}_2 + 2 \text{H}_2\text{O} \rightarrow 4 \text{HONO} \]  
(10)

\[ 2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3 \]  
(11)

Nitrous acid reacts with sulfanilic acid and N-(1-naphthyl)-ethylenediamine to form an azo dye:

\[
\text{HONO} + \text{NH}_2\text{SO}_3\text{H} + \text{HN} \text{NH}_2 + \text{HN} \text{NH}_2 \text{N} \text{SO}_3\text{H} \rightarrow \text{purple azo dye} + \text{H}_2\text{O}
\]

The concentration of this purple-colored molecule can be easily determined from its absorption band at 550 nm using a UV/VIS spectrophotometer.

**Ultraviolet-visible (UV/VIS) Absorption Spectroscopy.** The absorption spectrum of a molecule is obtained by measuring the decrease in light intensity passing through the sample (compared to a “blank”) as a function of wavelength:

\[
\text{ABSORPTION}
\]

According to the Beer-Lambert law, the intensity of the transmitted light, \( I \), is related to the initial intensity, \( I_0 \), as \( I = I_0 \times 10^{-A} \), where \( A \) is called absorbance. For sufficiently diluted samples, absorbance is directly proportional to concentration \( (C) \) of the analyte and path length \( (l, \text{in cm}) \) of the sample holder, as shown below:

\[
A = \varepsilon l C
\]

The proportionality constant, \( \varepsilon \), is called molar absorptivity or molar extinction coefficient, and it is usually determined from the slope of a plot of absorbance against concentration at a known path length. Each molecule is characterized by a unique dependence of \( \varepsilon \) on the absorption wavelength. This plot can also be used to determine the concentration of an unknown solution.

The spectrophotometer you will be using is called a double beam spectrophotometer. The light beam is split into two separate beams, and each beam passes through a cuvette. The reference cuvette contains the “blank” solution, in this case the indicator solution. The sample cuvette contains one of the nitrite standards or the exhaust sample solution. Because the cuvettes are not exactly alike, the instrument software has the ability to perform a “baseline correction,” which corrects for differences in the amount of light that passes through the two cuvettes at each
wavelength. To do this, make sure both cuvettes contain the blank solution and click the baseline button in the software. The instrument will scan through the wavelength range and measure the amount of light that passes through each cuvette at each wavelength. It will then automatically correct for any differences, so that a blank solution in the sample cuvette will always have an absorbance of 0.

**EXPERIMENTAL PROCEDURE**

**Note:** Detailed instructions on the start-up, use, and shut down of the Jasco V-530 UV/VIS spectrometer are provided in the handout near the machine in the lab; please read them carefully before beginning with the experiment. Your TA will help you operate the computer software.

**CAUTION!!** You will carry out sampling in a potentially busy parking lot. Please be aware of passing vehicles and make sure to stay a safe distance from them as you carry out this experiment. You will be sampling exhaust from a running vehicle. The vehicle should be in park or neutral gear with the parking brake engaged before it is started. Please keep a safe distance from the car as it starts. When sampling exhaust, make sure the tail pipe is not hot before sampling. A hot tail pipe can cause serious burns to the skin. This may be especially important when sampling exhaust after the car has warmed up for 10 minutes. Everyone must wear gloves and protective eyewear during sampling, as well as back in the laboratory.

I: Preparation of the indicator solution

1) Tare a small beaker and measure ~2.50 g of sulfanilic acid in it. Quantitatively transfer the solid to about 350 mL of nanopure water in a 500 mL volumetric flask and swirl until dissolved. This could take up to 30 minutes, so go through the Prelab with the T.A. and then start preparing the calibration standards (part II) during this time.

2) Once the acid is dissolved, add 70 mL of glacial acetic acid and dilute to almost 500 mL. As before, quantitatively transfer ~0.01 g of N-(1-naphthyl)-ethylenediamine dihydrochloride (NEDA) to the flask and swirl. Dilute to the mark with nanopure water, and invert to mix. Cover the flask with aluminum foil to protect the solution from light.

II: Preparation of the calibration standards

1) A sodium nitrite stock solution containing approximately 1000 µg/mL of NO₂⁻ has been prepared for you. Record the exact mass of NaNO₂ contained in the solution and the volume of the solution from you TA: **mass:** __________ **flask V:** __________

   Using a 1000 µL micro-pipette, transfer 125 µL (0.125 mL) of this solution to a 25 mL volumetric flask and dilute to the mark with nanopure water to make a solution containing around 5 µg/mL NO₂⁻.

2) Transfer 250, 500, 1000, and 2000 µL of the diluted NO₂⁻ solution, respectively, to four 25 mL volumetric flasks using micro-pipettes. Dilute to the mark with the *indicator solution*. This should make solutions containing approximately 0.05, 0.1, 0.2, and 0.4 µg/mL NO₂⁻.
III: Collection of exhaust samples

1) Obtain five 30 mL syringes with valves and aluminum foil to cover them later, a 250 mL beaker, a thermometer, a marker pen, a funnel, and two screw cap 250 mL Erlenmeyer flasks with about 200 mL of indicator solution in each. Mark the plunger of each syringe to indicate when 12.5 mL of material has been drawn into the syringe (this will help in step 4).

2) Be sure that all people who are not operating the car are neither standing in front nor in back of the vehicle. For the person who is operating the vehicle, check to make sure the car is in park or neutral and that the parking brake is engaged before starting it. Stand out of the way while one member of your group starts the car.

3) Once the car is running, rev the engine to 2000 rpm, place a funnel on a syringe and place into the tailpipe to pull exhaust into the syringe up to 30 mL and empty the syringe. Do this twice to flush the syringe.

4) Draw up 12.5 mL of indicator solution into the syringe. Insert the syringe with funnel again into the tailpipe of the car and draw in exhaust until the total volume reaches 30 mL. Close the valve on the syringe, cover the syringe with aluminum foil and shake the syringe vigorously for a few seconds. Label the syringe as “cold” or “hot” and the car model.

5) Take the temperature of the air near the exhaust pipe (“cold”): \( T_{\text{cold}} = \) ________ ℃

6) Repeat steps 3-5 with a new syringe after the car has warmed up for 10 minutes. Regard all safety issues mentioned above and take the “warm” temperature. Turn off the car when done.

7) Repeat steps 1-6 with a different car. \( T_{\text{hot}} = \) ________ ℃

8) Be sure to write down the make and year of each car. There will be a competition for the cleanest/dirtiest car at the end!

9) On the way back to lab and once away from the parking lot, use the last syringe to get a “background air” sample as a reference. Flush the syringe twice with air. Draw in 12.5 mL of indicator solution and then draw in air until 30 mL has been reached in the syringe. Cover the syringe with aluminum foil and shake the syringe vigorously for a few seconds. Label the syringe as “background air”. Take the temperature: \( T_{\text{air}} = \) ________ ℃.

IV: Analysis of the standards and exhaust samples

1) With the UV/VIS turned on, open the software program as shown in the instructions near the spectrophotometer or as shown by your TA. Perform a baseline correction with the indicator solution (solvent) in both cuvettes. Be sure to only touch the frosted sides of the cuvettes and always condition them 3-4 times with new solutions. Tap away any air bubbles before placing the cuvettes in the spectrophotometer and make sure the outside of the cuvettes are clean. Place the cuvettes with the frosted side facing you (allowing the beam of light to pass through the clear side of the cuvette).

2) Replace the indicator solution in the sample cuvette (closest to you) with one of the calibration standards, rinsing it our several times to condition it, and then measure the absorbance spectrum. Record the peak absorbance at 550 nm in the Data Table on the next page.
3) Repeat step 2 for the remaining calibration standards, the background air sample, and the exhaust samples in the syringes. Shake each sample before filling the cuvettes and make sure to condition the cuvette 3-4 times for each new sample.

**Data Table:** NO$_2^-$ concentration vs. Peak Absorbance measured at 550 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>

**DATA ANALYSIS**

1) From the mass of NaNO$_2$ provided on the stock solution flask, calculate the actual NO$_2^-$ concentrations in µg/mL for each standard solution. Watch the dilutions!

2) Develop a Beer-Lambert Law plot (on the laptop computer provided) for the nitrite standards and perform a least squares analysis of the linear best fit line (Microsoft Excel instructions for graphing are in the Appendix if needed). This will give you a dependence in the form:

$$ \text{Absorbance} = \text{slope} \times C + \text{offset} \quad (y = mx + b) $$

3) Using the slope and offset parameters determined from your fit, calculate the concentration of nitrite (in µg/mL) in the cold and warm exhaust samples.

4) Use the equation below to convert the concentration of nitrite in the solutions to the concentration of NO$_2$ µg/L = ppm W (part per million by weight) in exhaust.

$$ \mu g \text{ NO}_2 = \mu g \text{ NO}_2 \left( \frac{1.39 \text{ mol NO}_2}{1 \text{ mol NO}_2^-} \right) \left( \frac{V_{\text{in}}}{V_{\text{gas}}} \right) \left( \frac{1000 \text{ mL}}{L} \right) $$

The stoichiometric factor 1.39 is empirical (it should be 2 according to equation 11), $V_{\text{in}}$ is the volume of indicator solution in the syringe, and $V_{\text{gas}}$ is the volume of exhaust gas in the syringe.
5) The concentration of NO₂ calculated in step 4 represents all the NOₓ in the exhaust sample. To calculate the NOₓ mixing ratio in ppmV (part per million by volume), use the following equation:

$$\text{ppm NO}_x = \frac{\mu L \text{ NO}_x/L}{46.01 \text{ g/mol}} \left( \frac{RT}{P} \right)$$

where 46.01 g/mol is the molar mass of NO₂, R is the universal gas constant (0.08206 L atm/mol K), T is the Kelvin temperature at which the sample was collected, and P is the pressure.

REFERENCES

7. California Air Resources Board website: http://www.arb.ca.gov/homepage.htm
Air PSE (Problem Solving Environment)

MODELLING OF AIR POLLUTION IN THE LOS ANGELES BASIN WITH AIR PSE

Developed by Prof. Donald Dabdub
Computational Environmental Sciences Laboratory
Mechanical and Aerospace Engineering
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THE BASICS OF ATMOSPHERIC COMPUTER MODELS

An air pollution model is a computer program that computes how the different chemical species in the atmosphere move and mix, and how they react with one another. The results from these computations produce a simulation to what is happening in the real world. The model creates a virtual world where virtual experiments can be performed. This is important since there are many experiments that cannot be performed in the real world. For example, the model can compute answers to questions like “what if factories put out half as much carbon monoxide”, or “what if car traffic is reduced by one-third”. Using the model results from these experiments, policy makers can determine the effect of reducing industry emissions or decreasing car use. An air pollution model is never exact in its attempt to simulate the atmosphere, but a well-designed air pollution model provides an approximation to the real atmosphere that is accurate enough to be very useful.

There are many components that affect air pollution. Winds, temperature, anthropogenic and biogenic emissions, and amount of sunlight are a few of these components. The model takes these components from measurements and observations as the input parameters and calculates the concentration of the species of interest in the simulated atmosphere. To take all the needed measurements for the Air PSE is a big job, so these measurements are only available for a relatively small number of days.

THE BASICS OF ATMOSPHERIC CHEMISTRY

Formation of ozone involves complex processes and chemical reactions. Ozone precursors are Volatile Organic Compounds (VOC) and Nitrogen Oxides (NO\(_\text{x}\) = NO + NO\(_2\)).
Formation of ozone is driven by solar radiation, and hence, peak ozone concentration occurs during the day. Higher temperatures also favor ozone formation. As a result, the highest ozone concentrations occur typically during the summer.

The chemical mechanisms associated with ozone production are so complex that emission reductions of ozone precursors may not necessarily decrease the ozone production rate, depending on the area where these reductions are applied. We’ll see some examples of it later.

**FACTORS THAT AFFECT POLLUTANT CONCENTRATIONS**

- **Initial conditions**: initial values for concentration of all species are needed to start the calculations.
- **Boundary conditions**: concentrations of species at the boundaries of the modeling domain are needed to account for influx of pollutants from outside the basin.
- **Wind field**: wind velocity profiles are needed to determine the transport of pollutants from one region to another. In the Los Angeles area, prevailing winds transport pollution from Los Angeles to inland locations. The San Bernardino Mountains located in the northern and eastern part of the basin act as a trap for pollutants.
- **Diffusion**: the magnitude of diffusion forces, driven solely by the difference in concentrations, is needed for the transfer of pollutants from areas of high to low concentrations. In the horizontal direction, transportation by wind (advection) is significantly more important than diffusion.
- **Deposition**: deposition is needed to determine the rate of removal of pollutants from the atmosphere through pollutant uptake by surfaces. Deposition velocity depends on the nature of each species.
- **Emissions**: pollutants directly emitted into the atmosphere (primary pollutants, e.g. NO) are needed to calculate the concentration of secondary pollutants formed as products of chemical reactions involving primary pollutants (e.g. O₃, PAN, etc.).
- **Temperature**: temperature is needed because reaction rates are strongly dependent on it. Hence, reactions that produce and destroy ozone are affected by temperature changes. As a result, temperature affects ozone concentration.
- **Humidity**: humidity is needed since there are species that react with or dissolve into water, so water acts as a sink for these species. However, water can also be a source for other species, such as the OH radical, which is the most important atmospheric oxidant during daytime.
- **Ultra Violet (UV) radiation**: UV radiation drives the photochemical reactions that lead to the formation of ozone. Consequently, ozone concentration peaks during the day.
GETTING STARTED

USING THE DEMO

The following description of the DEMO gives an instructive overview geared for new users.

After reading “the basics of atmospheric computer models”, you are ready to start using Air PSE. The best way for a new user to be introduced to the PSE Air is to watch the demo. Access the DEMO by selecting Help on the menu bar, and then clicking on DEMO.

The DEMO describes the three major steps involved in a model run.

1. Create a new command file that contains the information about the changes made to the model from the default values.
2. Run the model with the new command file.
3. View the results of the model run.

The following is a description of the steps that are performed by the DEMO. (After viewing the DEMO once or twice, it is recommended that the user replicate the steps without the DEMO).
DEMONSTRATIONS

INITIAL STEP

A – Select the Scaling Fields/Numerical Sensitivity box (this allows access to the menu headers needed to do a model run).

CREATE A NEW COMMAND FILE:

B – Under File on the menu bar, select New. Note that nothing visual happens here (the file will be saved later).

C – Under Edit on the menu bar, select Choose Operators. The DEMO will turn off Aerosol Dynamics since it is very time consuming to compute.

D – Under Edit on the menu bar, select Scaling Fields. This is where the majority of changes to the model inputs are made. Each input change requires five steps. The order of these steps is important!

1. Choose the Field Type to be changed. A description of the field types is given in the “Explanation of Terms” section of this manual.

2. Choose a region where the field will be modified. This can be done in two ways. First, a new area can be defined by clicking on PolyLine, Rectangle, or Circle. PolyLine defines an irregular polygon by its vertices, Rectangle defines the region by its diagonal corners, and Circle defines the region by its center and perimeter. After the shape is drawn, click on the area and a red line will outline the area. Alternatively, Copy Field will define a region that has been used in the modification of another field.

3. Enter the factor the field is to be scaled by (e.g. enter 5 to have all values of the field increased by a factor of 5). Then, click on Scale by, followed by a click on the region defined in step 2. Hash marks should appear inside the region.

4. Choose the hours in which the field will be scaled. To have all hours scaled by the scale factor from step 3, click on Uniform. This will change the hourly scale factor to “1” for every hour. If only some hours are to be scaled, enter the scale factor individually for each hour.

5. If desired, choose the species that will be scaled. This works identically to the hour selection in step 4. A description of all the species is given in the “Chemical Species” section of this manual.

NOTE: The final scale by value takes the primary scale by value in step 3, multiplies it by the hour scale by value in step 4 and the species scale by value in step 5.
These 5 steps are repeated for each field that is to be scaled. Again, the order is important. The scale by value for each of the modified fields can be double-check by hovering the mouse over the regions of interest, and the number in the values box should change accordingly.

When all desired fields have been scaled, click on OK.

E – Under File on the menu bar, select Save and save your command file.

RUN THE MODEL USING THE NEW COMMAND FILE

F – Under File on the menu bar, select Execute Gas (this could take a while).

VIEW THE RESULTS

G – Under View on the menu bar, select Contour.

1. Click on Open File and choose the file that has the same prefix as the model run to be investigated.
2. Choose Output Concentrations under Field Type.
3. Choose the Hour (from a 24-hour clock) and Level to be plotted.
   (Note: there is only one option for the Day.)
4. Choose the *Species* to be plotted. (A full list of species is given under “Chemical Species” section of this manual).

5. If you wish to see the locations of cities on the plot, click on *PlotOptions* and select the cities.

6. Click on *Plot*.

Fields from the base case can also be plotted, including emissions, temperature and initial conditions. This can be done by selecting a field other than output concentrations from the fields. Opening a file is not necessary to view these fields.

H – Under *View* on the menu bar, select *Time Series*.

1. Click on *Open File* and choose the file that has the same prefix as the model run to be investigated.

2. Choose *Output Concentrations* under *Field Type*.

3. Choose the *City* and *Level* to be plotted.
   (Note: there is only one option for the *Day*.)

4. Choose the *Species* to be plotted. (A full list of species is given under “Chemical Species” section of this manual).

5. Click on *Plot*. 
The plotting provided in the Air PSE is intended for a quick viewing of results. For more advanced viewing the *Save Matrix* or *Save Vector* buttons will save your results to a file that can be accessed by a plotting program.
1) **The base case.** The base case is doing a model without changing any of the inputs.

**Procedures:**
1. Create a new file.
2. Turn off *Aerosol Dynamics*
3. Save that file as *basecase*.
4. Run the “gas” model.
5. View the output.

**Questions:**
- Look at ozone concentration contours at hours 6-14. What is happening to the ozone level distributions as the day progresses? Why?

- What is the maximum ozone concentration? At what hour does this occur? Where is this peak located (what grid point)? Can you try to explain this phenomenon?
2) **What happens on a really hot day?** Let’s examine the effects of changing the temperature profile of the domain.

**Procedures:**
1. Create a new file.
2. Turn off *Aerosol Dynamics*.
3. Under *Edit* on the menu bar, select *Scaling Fields*. Under *Field Type*, select *Temperature*. Increase the temperature field by a factor of 2 over the entire domain.
4. Save the file as *hightemp*.
5. Run the “gas” model.
6. View the output for ozone on *Level 1 for Hour 16*.

**Questions:**
- What is the maximum ozone concentration? Where?

- How are the ozone concentration contours different from the base case?

3) **A completely clean day.** Suppose a miracle happens and the air is completely clean. Set all the initial concentrations to zero and run the model. Look at the ozone concentration contours for this “clean” day.

- What is the maximum ozone concentration? When does this occur? Where is this peak located?

- How does this compare to the base case? Is it what you would have expected?
4A) **Holiday.** Try to model a busy holiday.
- What input fields would you expect to change on a busy holiday?

- How would you estimate and implement these changes in the named input fields?

Put these changes into the model and run a “holiday” case. Look at ozone concentration through the day
- What is the maximum ozone concentration? At what hour does this occur? Where is this peak located?

- How does the holiday case compare to the base case?
4B) **Cloudy Day.** Try to replicate a cloudy day

- What model input parameters will be affected by a cloudy day?

- How would you estimate and implement the change in these parameters?

- Which parameter would you expect to have the biggest effect on max ozone concentration? Why?

Run a model case with for each parameter you think will vary, changing only that one parameter for that model run. Then run a model case with all the parameters changed included. Examine the ozone concentration contours for all model runs.

- Which individual parameter had the biggest effect on ozone concentration? How does this vary geographically?

- Did the model with all the changes do what you would expect from looking at the models with the individual changes? Explain.
5) **Save the planet!** If you were in charge of making a policy to decrease (max) ozone concentration, but could only vary 1 input field, which one would it be? You may scale any input field by $\frac{1}{2}$ or 2. Look at the chemical mechanism and try to consider all the factors that affect air pollution presented above (Prelab pages 2-3).

- How did the maximum ozone concentration change? Try to explain the change.
LISTING OF OPERATIONS

The following is a listing of all the operations that can be performed within the PSE Air.

File
- **New**
  - Opens a new command file. (You don’t see anything here)
- **Open**
  - Opens an existing command file.
- **Save**
  - Saves a command file under the name given by the user.
- **Execute Air Model**
  - Executes the model with aerosols?
- **Execute Gas Model**
  - Executes the model.
- **Exit**
  - Exit the program.

Edit
- **Scale Fields:**
  - Field Type: Choose the field type to be modified.
  - Values: States the field value at the current location of the curser.
  - Copy Field: Allows the modification area for one field to be copied to another field.
  - Poly Line / Rectangle / Circle: Three types of modification areas that can be drawn.
  - Scale by: This is the primary scale by field.

  **Hours:**
  - Reset: Sets all hours to –1 (no scaling).
  - Uniform: Sets all hours to 1 (scale by primary value).
  - Scale by: Allows individual hours to be scaled.

  **Species:**
  - Reset: Sets all species to –1 (no scaling).
  - Uniform: Sets all species to 1 (scale by primary value).
  - Scale by: Allows individual species to be scaled.

- **Choose Operators**
  - Deselect any operators that are not desired with the model run.

Model Maker
- **This feature is currently not operational.**
View

- **Contours**
  Field Type:
  - Day: Set the day to be plotted.
  - Hour: Set the hour to be plotted.
  - Level: Set the level to be plotted.
  - Species: Choose the species to be plotted

  Bins:
  - Plot: Plot the chosen field
  - Open File: Open the file with output concentrations.
  - Plot Options: Add city dots to the plot.
  - Save Picture: Save graphics
  - Save Matrix: Save data (to be used in another program)

  Close:

- **Time Series**
  Most options are identical to Contours, with the following exception:
  - City: Choose the location to be plotted

Sensitivity

Help

- **Contents**
  Gives a description of the model

- **Demo**
  Runs a demonstration of PSE Air

- **Stop Demo**
  Stops the demonstration run.

- **Demo Config**
  Allows modification to the demonstration run.
EXPLANATION OF TERMS

**Field Type:** There are 11 elements (fields) of the original model that can be changed using PSE Air for experimental purposes.

1) **Initial Conditions** are the concentrations of species at the beginning of the model run.
2) **Boundary Conditions** are the concentrations of species at the edges of the model area.
3) **Wind Fields** are the wind speeds throughout the model run.
4) **Horizontal diffusion**
5) **Vertical Diffusion**
6) **Deposition** is the rate at which species are deposited on the ground.
7) **Area Emissions** are the emissions of species during the model run primarily from cars.
8) **Point Emissions** are the emissions of species during the model run primarily from industry.
9) **Temperature**
10) **Humidity**
11) **Ultra Violet Radiation**
CHEMICAL SPECIES

Gas phase species:

- NO - NITRIC OXIDE
- NO2 - NITROGEN DIOXIDE
- O3 - OZONE
- HONO - NITROUS ACID
- HNO3 - NITRIC ACID
- HNO4 - PERNITRIC ACID
- N2O5 - NITROGEN PENTOXIDE
- NO3 - NITRATE RADICAL
- HO2 - HYDROPEROXY RADICAL
- CO - CARBON MONOXIDE
- HCHO - FORMALDEHYDE
- ALD2 - LUMPED ALDEHYDE
- MEK - METHYL ETHYL KETONE
- MGLY - METHYLGLYOXYL
- PAN - PEROXYL ACYL NITRATE
- RO2 - TOTAL RO2 RADICALS
- MCO3 - CH3CO3 RADICAL
- ALKN - ALKYL NITRATE
- ALKA - >C3 ALKANES
- ETHE - ETHENE
- ALKE - >C2 ALKENES
- TOLU - TOLUENE
- AROM - AROMATICS
- DIAL - UNKNOWN DICARBONYLS
- NPHE - NITROPHENOLS
- NH3 - AMMONIA
- NIT - AEROSOL NITRATE
- ISOP - ISOPRENE
- APIN - a-PINENE
- BPIN - b-PINENE
- MYRC - MYRCENE
- CARN - d3-CARENE
- LIMO - LIMONENE
- MEOH - METHANOL
- ETOH - ETHANOL
- MTBE - METHYL TERT-BUTYL ETHER
- OSD - O SINGLET D
- RO2R - GENERAL RO2 #1
- R2O2 - GENERAL RO2 #2
- RO2N - ALKYL NITRATE RO2
- RO2P - PHENOL RO2
- BZN2 - BENZALDEHYDE N-RO2
- BZO - PHENOXY RADICAL
- H2O2 - HYDROOGEN PEROXIDE
- H2O - WATER VAPOR
- O2 - OXYGEN
- H2 - HYDROGEN
- SO2 - SULFUR DIOXIDE
- SO3 - SULFUR TRIOXIDE (RAPIDLY FORMS H2SO4)
- HCL - Hydrochloric acid
- ATO1 - Condensable vapor 1 from toluene
- ATO2 - Condensable vapor 2 from toluene
- AAR1 - Condensable vapor 1 from higher aromatics
- AAR2 - Condensable vapor 2 from higher aromatics
- AAP1 - Condensable vapor 1 from mono-terpenes
- AAP2 - Condensable vapor 2 from mono-terpenes

Aerosol species:

- Na, sodium
- SO4, sulfate
- NH4, ammonium
- NO3, nitrate
- Cl, chloride
- K, potassium
- Ca, calcium
- Mg, magnesium
- H2CO3, carbonic acid
- H2O, water
- EC, elemental carbon
- TA, toluene product 1
- TB, toluene product 2
- AA, higher aromatic product 1
- AB, higher aromatic product 2
- PA, mono-terpene product 1
- PB, mono-terpene product 2
- OO, other organic species.

Other inorganic species:
This section contains a sample of problems that could be used in the classroom to help students make discoveries about air pollution and air pollution models.

**Problem 1: Tree Pollution**

When he was president, Ronald Reagan stated that trees cause as much air pollution as cars. While not totally correct, there is truth in this statement. Trees are the major producer of isoprene. Should we then cut down trees to reduce pollution? That’s what this problem is about. What would happen if 75% of the trees in the LA basin were cut down? That can be tested in the AirPSE by reducing the isoprene by 75% for both the area emissions and the initial conditions. Students can explore the effects of trees on ozone.

**Problem 2: NOx from Point Emissions**

Power plants and factories all over the U.S. were required to reduce their NOx emissions by 25% between the years 1990-2001. Nine states on the east coast were required to reduce their NOx emissions by 60% over a similar time period (See [www.epa.gov/airmarkets/cmprpt](http://www.epa.gov/airmarkets/cmprpt)). What affect would the additional reduction have for the L.A. basin? This can be tested in the AirPSE by reducing the point emissions of NO and NO2 by .75 and by .6 all over the basin and comparing the differences.

**Problem 3: Emission Reduction from a Single Source**

The web site [www.scorecard.org](http://www.scorecard.org) records emissions from different sources across the US. (They are organized by zip code). The information from this web site makes it possible to approximate the affects of a single source. For example, an Arco in Carson produces large amounts of NOx and CO. On the PSE grid, Carson is located at approximately the point (36,12). By drawing a small circle around (36,12) and reducing NOx and CO by .5, students can get an idea of how much a single source of pollution affects the entire LA Basin.

**Problem 4: NOx/Ozone Relationship**

Study the relationship between NOx and ozone. Does a decrease in NOx always mean a decrease in ozone?
Computational Chemistry Lab Manual

Using Spartan to investigate the molecular properties of atmospherically relevant greenhouse gases
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1 Introduction

The present document will guide you through the set up and actual computation process. Computations will be carried out using the SPARTAN suite of codes in its Microsoft Windows release Spartan ES 1.0.2.

Please note that throughout the present document the word “click” refers to the use of the mouse. Left or right click will mean that you are supposed to press down the left or right button on your mouse, respectively. Additionally, technical terminology that strictly refers to the graphical interface you are using will be reported within quotation marks or in a different font.

The first portion of this document is dedicated to guiding you through the process of building the molecule you have been asked to simulate. The model molecule that will be used in this example is CO$_2$. Carbon dioxide is a linear molecule with a central carbon atom and two oxygen atoms each double bonded to C.

Two sections on the actual computation will follow. The first of these details optimizing the geometry of and calculating vibrational frequencies. A further section guides calculating the distribution of charges and visualizing the electron density. Finally, the last two sections will guide you to connect the results you have obtained with the IR activity of your molecule. A technical appendix closes the document.

We will practice the entire procedure together on CO$_2$, and then you will repeat the whole process individually for H$_2$O, N$_2$O, and O$_3$.

Here are the steps you will have to follow to build your molecule (exemplified with CO$_2$).

2 Building the molecule

1. log on the machine using the username and password that you will be given

2. left double click on the icon Apps on your desktop, a window corresponding to the App(lication)s folder will appear

3. left double click on the 02SpartanES icon
4. the following window will appear:

5. to build your molecule click with the left mouse button on File from the menu bar,
   • click on New from the menu which will appear,

6. the “entry builder screen” depicted below will appear:
7. The “entry builder screen” is divided into two portions (beneath the File, Edit, Model, etc. menu bar):

(a) the “work area” (solid color portion on the left of the window):
   - at the top of the “work area” is the toolbar. You can point your mouse (without clicking) on its different icons to visualize their functions as a small “post-it”-like yellow note appears close to where you are pointing the cursor.

(b) the “model kit” (on the right).
   - at the top of the “model kit” are the Ent. (Entry), Exp. (Expert), etc. bookmarks. By default the Ent. bookmark is selected. The Ent. portion of the “model kit” contains a certain number of atomic fragments and, in some cases, their possible states of hybridizations.
   - Left click on the Exp. bookmark, the “model kit” will change similarly to what shown in the figure below:

8. to build the CO$_2$ molecule left click on the C atom on the periodic table displayed in the “model kit” (with the Exp. bookmark selected).

9. Left click on the appropriate button below the periodic table displayed in the “model kit” representing the kind of valence configuration you desire to have for your atom (in the present case left click on the --- button).
10. Left click on the “work area” (solid color portion on the left of the window) to place the selected atom.

11. Left click on the “model kit” to select the next atomic fragment to add to the unfilled valences of your original atomic choice.

   • NOTE: Any unfilled valences will automatically be converted to hydrogen atoms upon exiting.

In the present case the next atom is oxygen and the valence configuration is given by the $-\cdot$ button.

12. On the “work space” left click (one at a time) on the empty valences of the atomic fragment displayed (C) to add the newly selected fragments (O).

13. Left click on the Minimize icon on the toolbar on top of the “work area” (or on Minimize in the Build pull down menu).

14. You have built your molecule!!! Now left click on File from the upper menu bar and select Save As; choose SaveHere as the destination directory.

15. A window will appear with the cursor blinking in the appropriate location: enter the name with which you desire to call your molecule (CO2, for example). And left click on Save As button.

   **Remember to add your name to the title of your job (i.e., CO2_mynname)**

2.1 About changing representation & rotating/ translating the molecule

Now that we have built the structure let’s familiarize with the different, possible representations of the molecule on your screen:

1. Left click on the Model button on the menu bar and select from the pull down menu, which will appear, the graphical representation of the molecule you prefer, for example: Wire, Ball and Wire, etc. (you can try several to see how do they differ from one another).
2. The model (shown below) of the molecule can be manipulated: rotated, translated and zoomed.

**rotate:** drag the mouse while clicking on the left mouse button;

**translate:** drag the mouse while pressing its right button;

**zoom:** drag the mouse while pressing its right button and holding down the Shift key on the keyboard.

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3 Geometry Optimization & Vibrational analysis

1. To start the actual computation (i.e., the minimization of the conformer you have recently generated) left click on the Setup button of the menu bar. And select (left click) **Calculations** from the pull down menu that has appeared under the Setup button.

2. A pop up window will appear as in the figure below:
The different fields on the Calculations window are explained below:

- **Calculate:** should be set to Equilibrium Geometry meaning that the geometry you have just sketched out is optimized along the energy hypersurface of the molecule until a minimum of such surface is found.  

  suggestion for discussion: would such a minimum necessarily represent the equilibrium structure?

- **with:** You can choose from the following models: Molecular Mechanics, Semi-Empirical, Hartree-Fock

  Each combination of model keywords (such as Semi-empirical and either AM1 or PM3, or Hartree-Fock and 3-21G(*)) refers to a particular model chemistry intended to use for the computation.

  We will be using the Hartree-Fock model.

  - **Basis Set:** If you have selected under the Model section the Hartree-Fock theory you will be able to choose from the following basis sets\(^1\): STO-3G, 3-21G(*), 6-31G*, 6-31G**, 6-31+G*, 6-311G*, 6-311+G**.

    Note: In the Basis set pull down menu the basis are generally ordered from smaller to larger. In choosing a basis set the following consideration should be kept in mind. Larger basis sets more accurately approximate the orbitals by imposing fewer restrictions on the location
of the electrons in space. At the same time larger basis sets drastically augment the computation efforts: the larger the basis the better the accuracy, the smaller the basis set the faster the computation. Therefore a practical choice between accuracy and computational feasibility has to be made (this is especially true for molecular systems larger than CO₂). For a very brief explanation of the basis sets nomenclature, see Appendix A.

Choose the 6-31G* basis set for all of your calculations.

- **Start From:** ... geometry Make sure that Initial is selected.
- **Compute:** Check the Frequencies and Electrostatic Charges boxes.
- **Total Charge:** Here you have to enter the total charge of the system. Make sure that Neutral is selected.
- **Multiplicity:** In short, the multiplicity is the number of unpaired spins + 1. Make sure that Singlet is selected if your molecule is a closed shell one.
- **Print:** Select all.
- **Remember to check the Converge box.**

3. Left click on Submit button to start the computation.

### 3.1 Determining the geometrical parameters (bond lengths & bond angles)

You may have noticed that in performing the optimization the bond lengths (and angles where applicable) have changed. To visualize the geometrical information regarding the molecule you have just optimized, use the options in the Geometry pull down menu: To visualize the geometrical info regarding the molecule you have just optimized select from the pull down menu of the Geometry button of the menu bar the following:

**Measure Distance** then left click on the first atom of the couple of which you want to know the relative distance (the selected atom will change color), hence left click on the second atom (this too will change color), a number, corresponding to the distance in Angstrom, will appear on the bottom right of the “work area” (alternatively, if the two atoms are bonded try left clicking on the bond).
Measure Angle works similarly: to measure an angle you will click on three atoms. Annotate the computed values for all bond lengths and angles in the appropriate locations in the chart on your worksheet.

3.1.1 Comparing computed bond distances and angles with experimental values

1. As it was shown above collect the bond distances (and angles).

2. Now open your web browser and go to http://www.hbcponline.com/ which is the on-line version of the CRC Handbook of Chemistry and Physics on the left column of the webpage is the Table of Contents. Click on Section 9: Molecular Structure and Spectroscopy, and then “Structure of Free Molecules in the Gas Phase”. Find the experimentally measured bond lengths and angles of the molecules you are working with (note: CO$_2$ is listed under “carbon dioxide” in part 2 of the table of experimental data), and enter them in the appropriate locations on your worksheet.

3. How do your computed results compare with the experimental values?

3.2 Retrieving the computed vibrational frequencies

On the Spartan main window click on Display on the menu bar and choose Vibrations. A window will pop up with the list of frequencies. Record the frequencies in the appropriate table in your worksheet.

3.2.1 Comparing the frequencies calculated at the different level of theory with experimental data


2. Enter the formula of your molecule and select “Vibrational & electronic energy levels” from Other Data.

Annotate the experimental values of the frequencies for the most abundant isotopomer (e.g., $^{12}$C$^{16}$O$_2$) in the appropriate locations in the chart on your worksheet.
4 CHARGE DISTRIBUTION

4 Charge distribution

To visualize the charge distribution from the Model button on the menu bar select Configure from the pull down menu and check the Electrostatic charge box. The partial charges will appear close to the atoms on your display.

A useful way to depict the charge distribution of your molecule is via electrostatic potential surfaces.

4.1 Computing surface representations of electronic properties

The different types of surfaces include HOMO, LUMO, Electron Density, and Potential. For an explanation of the different kinds of surfaces, please refer to Appendix B.

You will calculate an electrostatic potential surface.

1. Left click on Setup button of the menu bar and select Surfaces. A window will appear. Click on the Add button.

2. To compute the electron density: set the Surface: field to Density, then set the Property: field to Potential, you can leave the Resolution at medium. Left click on OK.

3. Left click on Setup button of the menu bar and select Submit. A window will appear informing you that the computation has been submitted. Left click on OK.

4. A window will appear when the computation is completed (left click on its OK button).

4.2 Retrieving the results of the surface calculation

1. Left click on the Display button on the menu bar.

2. From the pull down menu that will appear select Surfaces.
3. A window will appear: check on the box on the left of the surface you have computed and the electronic density will appear on the main window. You can manipulate the molecule (rotate, translate, zoom).

4. To visualize the molecule (and the labels indicating the partial charges) under the electron density surface you can change the surface texture property from solid to mesh or transparent by clicking on the solid surface displayed and selecting Properties from the menu Display, and choosing the desired Style.

Remove the surface deselecting the box on the window Surfaces.

5 Sketching the dipoles

Using the partial molecular charges computed as explained above (i.e., from the Model button on the menu bar select Configure from the pull down menu and check the Electrostatic charge box), draw a diagram of the molecule along with the bond dipoles you predict from the charges.

Compare your sketched dipole with the dipole computed from Spartan, which can be visualized as follows:

- select Display menu and select Properties.
- the Molecule Properties window will appear.
- check the Dipole box.
- the dipole vector will appear.

Note: to better see the vector representing the dipole of the molecule, it is advisable to switch to the Ball and Wire molecular representation, this can be done by choosing the Model menu and selecting Ball and Wire.

6 Which normal modes are IR active?

1. Now you will animate the vibrational modes whose frequencies you recorded previously on your worksheet. Click on Display on the menu bar and choose
DO THE FREQUENCIES OF THE IR ACTIVE MODES OVERLAP WITH EARTH’S BLACKBODY SPECTRUM?

Vibrations, a window will pop up with the list of frequencies, check, one at a time, the boxes on the left of the frequency value. The picture of the molecule on your screen will undergo the vibration corresponding to the frequency you have checked.

2. Identify which of the normal modes change the electrical dipole of the molecule (i.e., are IR active).

Do the frequencies of the IR active modes overlap with Earth’s blackbody spectrum?

In order for a molecule to be a potent greenhouse gas, it must have IR active vibrational modes, and those modes should have frequencies that overlap with Earth’s blackbody radiation spectrum (reproduced from Baird and Cann’s Environmental Chemistry textbook in Appendix C; note that the spectrum is plotted as a function of wavelength in \( \mu \text{m} \)). In this last part of the exercise, you will determine which modes in each of the molecules considered meet these criteria:

- For each IR active mode in each molecule, convert the \textit{experimentally measured} frequencies you looked up in the NIST database from cm\(^{-1}\) to \( \mu \text{m} \). To do this, take the reciprocal of the frequency in cm\(^{-1}\) to get the wavelength in cm, and then multiply by \(10^4\) (the number of \( \mu \text{m} \) per cm). Record the values on your worksheet.

- Indicate on your worksheet whether or not the wavelengths corresponding to the vibrational frequencies of the IR active modes overlap with Earth’s theoretical blackbody spectrum (Appendix C). You may consider any modes occurring at wavelengths less than 7 \( \mu \text{m} \) as not overlapping significantly with Earth’s blackbody spectrum.

Now repeat this whole procedure for H\(_2\)O, N\(_2\)O, and O\(_3\).
8 Appendix A – Basis Sets

Typically, the quantum calculations for molecules are performed as LCAO MO, i.e. Linear Combination of Atomic Orbitals - Molecular Orbitals. This means that molecular orbitals are formed as a linear combination of atomic orbitals (AO). Early, the Slater Type Orbitals (STOs) were used as basis functions due to their similarity to atomic orbitals of the hydrogen atom. Gaussian-type orbitals (GTO) can be used to describe the radial part of the wave function in order to simplify the computational task. When a linear combination of N GTOs is used to approximate the actual shape of the STO the resulting basis set is known as STO-NG (as STO-3G described above).

The number of basis function used to describe a single STO (also known as zeta) has been a measure for the goodness of the set. So that single zeta means one basis function per STO, double zeta means two basis function per STO, etc. Because valence electrons tend to be more involved in bond making a different number of basis functions are assigned to core and valence orbitals in split valence basis sets, with typically more basis functions per valence orbitals.

The basis sets from 3-21G(*) to 6-311G** are Pople’s basis sets. Symbols like n-ijG or n-ijkG can be encoded as: n - number of GTOs for the inner shells; ij or ijk - number of GTOs for basis functions in the valence shell. The ij notations describes sets of valence double zeta quality and ijk sets of valence triple zeta quality. The + symbol indicates that diffuse gaussian functions (i.e., GTO that decay slowly with distance from the nucleus) have been used for the heavy atoms; whereas the * or ** symbols indicate that polarization functions (i.e., functions having higher values of L, the angular momentum, than those present in occupied atomic orbitals for the corresponding atom) have been added respectively to the heavy atoms and to the hydrogens and the heavy atoms.

Finally the cc-pVTZ basis set consist in a correlation-consistent (cc) polarized (p) valence triple zeta basis set of Dunning (where V denotes split valence kind of basis set and TZ stands for triple zeta, so that VTZ means that one basis function is used for the inner orbitals and three for the valence orbitals).
Appendix B – Molecular Property Surfaces

**(Electron) Density** is a map of the surface that displays the molecules size and shape by displaying the surrounding electron cloud. The electron cloud is determined by selecting a probability that an electron would be found within a given volume (often 90% probability is used) and drawing a surface there. This surface then describes the volume with a 90% probability of finding the molecule’s electrons within that space.

The electron density at isosurface values provides indication of overall molecular size.

**HOMO** is an abbreviation for highest occupied molecular orbital; the HOMO is the molecular orbital of highest energy that is occupied by an electron. This surface will show the spatial area where it is most likely to find the electrons in that orbital.

**LUMO** is short for lowest unoccupied molecular orbital; the LUMO is the molecular orbital of lowest energy that does not contain an electron. This surface will show the spatial area where it would be most likely to find an electron in that orbital if one were there.

- Selection of two of the entries, “HOMO-” and “LUMO+”, results in display of box alongside of the entry. This contains a number providing a decrement value from the HOMO and increment value from the LUMO, and so allows specification of any molecular orbital. This value may be changed.

**Potential (Map)** refers to an electrostatic potential map. The potential is developed by determining the electrostatic force on a positive point-charge at all points at a given distance surrounding the molecule. Points where the point-charge would experience an attraction (negative charge) are displayed in red, and areas where the point-charge would be repelled by a positive charge are displayed in blue.
Appendix C – Earth’s Blackbody Spectra

Theoretical spectrum:
Light emitted from surface

Light leaving the upper atmosphere

Light intensity

Wavelength (μm)
Appendix: Plotting Data on Microsoft Excel 2003

Plotting Data sets on Excel is very easy and occurs in several simple steps. The basics of each step will be explained, but remember that you can always dig in deeper and become more proficient if you wish.

Part I: Enter Data and set up Graph

a) Bring up Microsoft Excel and start a new spreadsheet.
b) Type in your x – axis values (the independent variable concentration) in Column A.
c) Type in your y – axis values (the dependent variable, absorption) in Column B.
d) Place the title of the data set (e.g., absorbance in column B) in the first cell of the column.
e) If you have multiple data sets (series) to be plotted on the same graph, enter the data in Column C, D, etc.
f) Highlight the data sets to be plotted (left click and hold).
g) In the tool bar, click on “Chart Wizard” (looks like a colored bar graph).

Part II: Chart Wizard

This program sets up plots in detail and occurs in 4 basic steps.

Step 1: Choose Chart type

a) Under “Standard Types” (don’t need custom plots yet!) choose: “XY (Scatter)
b) Under chart sub – type, choose the one without lines (we will add lines later).
c) Click Next

Step 2: Set Data Range and Series Labels

a) The data range should already be entered, since we highlighted it on the Excel spreadsheet earlier.
b) Click on the “Series” tab for labeling separate series (data sets), but only if more than one set has been plotted on the same graph.
c) Choose which series to label (series 1 is column B, series 2 is column C, etc.) and type in the appropriate label for it.
d) Click Next

Step 3: Set up and Label the Title, Axes, Gridlines and Series Legend:

a) Under Titles: Type in the name of your Graph (include parameters plotted and the system being studied).
   For example: “Intoxication Level vs. Weight for Males Between age 20 and 35”.
b) Under Axes: Label the x and y – axes (ie: Weight (lbs) or Temperature (K)). Always include the units used on the graph in parentheses after the variable. The axes values are already set and the number range should always be included (computers automatically set the range, whereas by hand you have to figure out the proper data set range yourself).
c) Under Gridlines: Add or remove lines on the graph, like on graphing paper. It is usually best to include the Major X and Y gridlines only to avoid clutter.
d) **Under Legend:** The series legend is the box showing your data sets plotted. Only include this Legend if you are plotting more than one data set (series). You can place this Legend wherever you want, but on the right normally looks best.

e) **Under Data Labels:** Make sure “none” is chosen. On scientific plots, showing the data values next to their points on the graph is redundant and messy.

f) Click Next when finished.

**Step 4: Setting Chart Location**

a) You can set the graph up as a new sheet or have it inserted onto the Excel spreadsheet sowing your Data Table. In reports and labs, it is best to set up the Graph as a new sheet, and include the Data Table on a separate sheet of paper, or in the Data portion of a lab report.

b) Click Finish when done.

**Part III: Adding Best–Fit Lines**

In science, plots are designed to find and show the relationship between two variables. Many times a linear relationship is desired, but non-linear relationships (exponential, curved, etc) can often be expected.

Since the data points are somewhat scattered due to experimental uncertainty, many scientists add “error bars” to their data points to show the spread of uncertainty. We won’t be doing error bars in any of these labs. What is done is finding a “best – fit” line that represents all the data points, but does not necessarily touch all of them. This “Trendline” shows the general relationship between the variables plotted on the Graph.

To add a trendline, follow these steps:

a) Right click on a data point on the Graph from the series you are interested in.

b) Choose “Add Trendline”.

c) Choose a type of trendline: Several are available, but if the relationship looks somewhat liner, choose “Linear Plot”. If the data looks curved, choose “Polynomial at level 2, 3 or 4”. You may need to try several different lines before finding the “best – fit” line.

d) General Rule: Never ever just “connect the dots” on a scientific plot!

e) Under trendline options, select "display equation on chart" so that you can see the mathematical result of the least-square fit.

f) To format the Trendlines, right click on the line. Under **Pattern**, you can choose a color, line thickness or specific style (dashed, dotted, etc.).
Appendix: Plotting Data on Microsoft Excel 2007

Plotting Data sets on Excel is very easy and occurs in several simple steps. The basics of each step will be explained, but remember that you can always dig in deeper and become more proficient if you wish.

There are a lot more “options” with the Excel 2007 version and the set up is quite different from the 2003 version if you are used to that one.

Part I: Enter the Data

h) Click on Microsoft Excel 2007 to start a new spreadsheet.
i) Label each column with the parameters to be plotted. The independent variable goes in Column A (x–axis) and the dependent variable goes in column B (y–axis).
For example, if we are plotting how the absorbance of NO2 depends on its concentration, the concentration is the independent variable and the absorbance is the dependent variable (it depends on the set concentration).
j) Type in your x–axis (column A) values and y–axis (column B) values under the appropriate column labels.
k) If you have multiple data sets (series) to be plotted on the same graph, enter the extra dependent variable data sets in columns C, D, etc. (like multiple species concentrations, O3, NO and NO2 or a known data set and an unknown data set.

Part II: Set Up the Plot

d) Highlight the data sets to be plotted (not the column labels!).
e) Under the “Insert” tab, find the Chart types and click on “Scatter” (without any lines).
f) This should place you under “Chart Tools” and “Design” now.
g) Under “Chart Styles” click on the type preferred (scroll down for options).
h) Under “Chart Layouts” click on the 1st plot that gives Chart and Axis titles.
i) Left click on the Chart Title to name your plot (i.e.: Absorption of NO2 vs. Concentration) as well as on your Axis Labels which need units (i.e.: [NO2] (µg/mL) for the x–axis and ANO2 for the y–axis).
j) Format Labels (optional): Right click on the chart and axis labels to make them bold or to adjust the font type and size. Click on “Format Title” or “Format Axis” to add colors (fun stuff!) or rotate the label.
l) Format Axis: Right click on the x and y axis values and choose “Format Axis”. Use this to add minor and/or major tick marks on the plot (for easier estimation of values). These can be placed inside or outside the axis line. You can also alter the color, font style and size of the values. Adjust the minimum and maximum values on the axis in order to maximize the plot size (you do NOT have to start at zero!).
m) Format Legend: Right click on the legend on the right, commonly to delete it. You can click on “Format Legend” to move it around the plot, change font type, color and size, box it and fill in colors, etc. If there are multiple data series, label these with the legend.
by clicking on “Select Data”. Choose the series you want and click on “Edit”. You can now name the series whatever you wish (i.e.: O₃, NO or NO₂, etc.) and click on “OK”. Do this for each data series.

n) **Format Plot or Chart Area**: You can fill in colors within the plot or outside of it by right clicking and choosing “Format Chart Area” or “Format Plot Area”, respectively.

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**Part III: Adding Best–Fit Lines**

In science, plots are designed to find and show the relationship between two variables. Many times a linear relationship is desired, but non–linear relationships (exponential, curved, etc.) can often be found.

Since the data points are somewhat scattered due to experimental uncertainty, many scientists add “error bars” to their data points to show the spread of uncertainty. We won’t be doing error bars in any of these labs. What is done is finding a “best–fit” line (Least squares analysis) that represents all the data points, but does not necessarily touch all of them. This “trendline” shows the general relationship between the variables plotted on the Graph, in the common “y = mx + b” format if a linear relationship exists.

**To add a trendline, follow these steps:**

g) Right click on any data point on the plot from the series you are interested in.

h) Choose “Add Trendline”.

i) Choose a type of trendline: Several are available, but if the relationship looks somewhat liner, choose the “Linear” Trend/Regression type. If the data looks curved, choose “Polynomial at level 2, 3 or 4”. You may need to try several different lines before finding the “best–fit” line if not linear.

j) General Rule: Never ever just “connect the dots” on a scientific plot!

k) Click on "Display Equation on Chart" near the bottom so that you display the mathematical result of the least-squares fit (“y = mx + b” form for a linear fit).

l) **Format Trendlines**: Right click again on a data point and click on Add Trendline. You can choose a color, line thickness or specific style of line if desired (dashed, dotted, etc.).

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**Part IV: Print Plot**

a) Left click on the “Office” button on the upper left of the page. Scroll down to “Print” and follow the instructions. You can preview the page to be printed, adjust orientation, size, etc.
Part: Example Plot

Absorption of NO₂ vs. Concentration

\[ y = 1.0124x + 0.0032 \]
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