Week 6

Intro to Long Reports

6.1 Lecture 10: Scientific Visual Communication

2/7:

- Long report submissions delayed until Friday.
  - The content of today may be useful!
- Thursday.
  - Anna Wuttig on the current state of EChem.
  - Tokmakoff will stick around after for us to chat about our reports with him.
- There are many aspects beyond *visual* communication, but this is one that isn't always seen, so Tokmakoff decided to focus on it today.
- Take all the guidelines and extra chapters seriously; they're exactly what is being graded for.
- We should care about communication because it's as important to our career development as anything.
  - Our science must be distributed; otherwise, we're just a hobbyist.
- We need to convey very complicated, quantitative information to other scientists, management, government agencies, policy makers, investors, and the general public.
- Reduce complex quantitative data accurately into clear, concise messages: Data interpretation.
- Often, there are real requirements on content and formatting.
- Excellence in communication.
  - Content is key, but saying it well will really level you up.
  - It develops *trust* in your methods, results, and communications.
  - A well-communicated report and graphic can change the world, e.g., the hockey stick curve.
- **Communication**: The means of exchanging information.
- **Medium**: Any channel of communication.
- Media we will discuss.
  - Print (text, graphics).
    - Graphics are how people digest scientific information.
  - Oral (in person with visual support).
  - Never use double columns if you want transport to online.

- The common starting point for all communication.
  1. Audience.
     - Identify; sets the objective, expectations, language, and aspects of your work to focus on.
     - You need to know if you're talking to fellow bench scientists, or senior management.
  2. Message.
     - What are you trying to say? Just say what you need to, and get rid of the rest.
     - When your TA or Tokmakoff reads your report, what are they going to think of my magenta line.
  3. Media.
     - What tools are at your disposal, and how are they best employed.
- Visual presentation tips for text and graphics.
  - Our goal: Communicate quantitative information clearly and concisely.
  - Make your viewer's life easy (be consistent, define the purpose of each element, etc.).
  - Simplicity is good; clutter is bad.
  - Color should be chosen with a real focus in mind.
- Typefaces and fonts.
  - The visual representation of language. Its style should help, not interfere, with your communication.
- **Typeface**: The design elements for lettering. A collection of glyphs.
- **Glyph**: A single representation of a character.
- **Font**: A variation of a typeface like size, weight, and spacing.
- Classes of typefaces: **Serif** and **sans serif**.
  - Sans-serif is good for titles, headings, and labels.
  - Serifs are good for presenting large amounts of text.
- History of typefaces.
  - Use legacy typefaces; they're still supported.
  - "Microsoft is your friend."
  - Computers revolutionized typography; Microsoft drove the development with proprietary stuff, which eventually caused them to lose the edge, and now there's great open-source fonts.
- Typefaces for equations.
  - Times New Roman and Garamond have full math support.
  - Computer modern (TEX) is probably still the best in terms of being able to distinguish things since it includes so many helpful flourishes.
    - You're probably encountered difficulties with the lab manual (e.g., v vs. ν) because it's not in Computer modern.
- Tokmakoff's recommendations for formatting: Typed 8.5×11 documents should have a...
  - Single column format.
  - $1''$ margins.
  - 11-12 point type.

  - $\sim$ 90 characters per line including spaces (15 characters per linear inch).
  - 4-5 lines per vertical inch.
- Why worry about font size?
  - Legibility vs. readability; too small impacts legibility, and too big impacts readability.
- Why worry about line spacing?
  - 1.5$\times$ is Tokmakoff's recommendation.
  - 2$\times$ is legacy from typewriters, when single and double were the only options.
- Why worry about margins?
  - White space helps with clarity.
  - Don't just insert figures; make figures break text.
- Equations should be numbered.
- Color.
  - Don't let it distract; let it help you make a cleaner presentation.
  - Really bright colors draw the eye too much.
- Scientific figures.
  - Purpose: To convey quantitative information on the relationship between different physical variables with minimal effort.
  - Each figure should convey information on exactly one topic.
  - Again, know your audience, be aware of your medium (typed vs. oral), clarity, etc.
  - Additional consideration for scientific reports: Often the figure is the only documentation of the data.
    - If the reader wanted to analyze your data, can they read data values off the graph using the axis labels?
    - Raw Excel sheets, other records may not be saved, so the literature report may be the only way for future scientists to reanalyze your data.
- Examples of good and bad figures.
  - As you see scientific figures going forward, take note of what you like and what you don't like and learn.
  - Tokmakoff asks for the class's feedback on his examples.
- You should have 4-6 axis labels and 4-10 tick marks.
  - More tick marks than labels is a good idea!
- Make sure colors translate to black and white, so maybe I should vary both shapes and colors in my Birge-Sponer plot.
- Rowan is very picky about what Excel settings you use.
  - Don't cut and paste into word; stuff gets realigned.
- Tokmakoff doesn't look for units for unitless quantities (e.g., absorbance).
- Use a legend when there are two or more series being plotted.
- Caption.

  - Use for report figures.
  - It should describe what is plotted and is needed to interpret the data beyond what is in the figure.
  - For data, typically quote specific experimental conditions.
- Titles are only for oral presentation graphics.
- Don't mislead! Rescaling your axes can mislead about growth.
- Make everything 300 dpi.
- Publishers use JPG in CMYK color profile.
  - Online: Use RGB color profile.
  - Everything else is up to us.
- Takeaways.
  - Clarity and conciseness.
  - White space is good!
  - Microsoft is (mostly) your friend.
    - Their templates, colors, and fonts have been professionally designed... with everyone in mind.
    - Use recommended formatting, but be aware it isn't for scientists.
  - There are no firm rules — just guidelines. It is an art.

6.2 Lecture 11: Electrochemistry

2/9:

- Guest lecture by Anna Wuttig.
- Ben Masters (our TA) is one of her grad students.
- Electrochem can solve important problems, and we know the mechanisms in principle because we can measure the flow of electrons in it as current.
  - Thus, we can modify whatever we want and have an *in situ* handle on reaction rate.
  - This is why it's important for physical chemistry, which seeks to understand, predict, and rationally design future reactions.
- We will focus on CO_2-reduction today.
  - Wuttig hopes to **upconvert** it to other things.
- We currently do this with the water-gas shift reaction and Fischer-Tropsch chemistry.
  - But this is both energy-intensive and has poor selectivity.
- Alternative: Electrochemistry.
- Example.

$$2\,CO_2 + 2\,H_2O \rightleftharpoons C_2H_4 + 3\,O_2$$

  - Produces ethylene (used in a lot of things in industry) and O_2 (benign).
  - Allows you to store $\Delta G = 1343\,\mathrm{kJ\,mol^{-1}}$ of energy, corresponding to $\Delta E = -1.16\,\mathrm{V}$.
  - This involves two electrochemical half-reactions (recall from gen-chem).

$$2\,CO_2 + 12\,e^- + 12\,H^+ \rightleftharpoons C_2H_4 + 4\,H_2O \qquad E^0 = 0.07\,\mathrm{V} \text{ vs. RHE, pH} = 7$$
$$2\,H_2O \rightleftharpoons O_2 + 4\,e^- + 4\,H^+ \qquad E^0 = 1.23\,\mathrm{V} \text{ vs. RHE, pH} = 7$$

    - The first one is kinetically very difficult, though — it requires you to input *twelve* electrons.

- In the EChem module, we'll study RHEs and other kinds of electrodes.
  - Essentially, these allow us to pin EChem reactions on a common axis.
  - The axis does move as a function of pH, though.
- We have no electrolyser or catalyst that can run the example reaction right now.
  - Thus, we so far have to put in more energy to store that energy.
  - A focus of the chemistry world: Find catalysts and conditions such that this is possible.
- CO_2 reduction as an energy storage scheme.

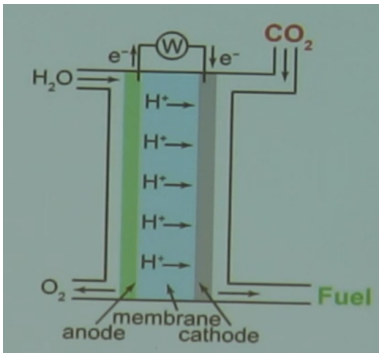

Figure 6.1: CO_2 reduction as an energy storage scheme.

  - Use renewable energy sources like wind and solar to drive electrochemical reactions. Specifically, driving the transfer of electrons may facilitate oxication of water to O_2 at the anode reduction of CO_2 to fuels (such as ethylene) at the cathode. Note that the water's protons will theoretically diffuse through a proton exchange membrane.
  - Big idea: Store renewable intermittent electricity in energy-dense chemical bonds.
- Selectivity challenges in CO_2 reduction.
  - One reason we don't know how to do this yet: CO_2 can be reduced to myriad products.
  - A competitive side reaction: Hydrogen evolution.
  - Other carbonatious products include methanol, ethanol, etc. Some of these may be good, but we don't want to produce all of them at once!
  - Though it might be theoretically possible to pin the ΔE thermodynamically, it's practially virtually impossible.
  - Consequently, selective CO_2RR requires control over the relative rates (kinetics) of competing reactions.
- Understanding of interfacial proton coupling is poor.
  - $CO_2 + 2\,e^- + 2\,H^+ \longrightarrow CO + H_2O$ is possible.
  - Things like molecular electrocatalysts allow us to access this at a high rate and selectivity.
    - We can boost the rate even further with *intra*molecular proton donors (esp. phenolic groups).
    - *Inter*molecular proton donors can help, too, but make sure not to make it too acidic, or you'll favor hydrogen evolution!
    - Thus, what you really need is precise proton delivery.
  - These homogeneous catalysts are nice and pretty, but in a functional device, we'll need heterogeneous catalysis.

    - Possible example: Au catalyst.
    - Mathematical models suggest that the concentration profiles at the interface of the solid are higher. Essentially, the pH near the surface becomes much more alkaline very quickly.
    - We don't have control over the proton coordinate here, and we don't actually know what the proton donor is (could be water, hydronium, carbonic acid, etc.).
    - Thus, we need to understand the role of PCET in dictating CO_2RR vs. HER selectivity.
    - This is what Wuttig did her PhD on!

- Electrochemistry is nice because you always know the rate.
  - The velocity v of the reaction is related to the current i, the number of electrons n, and Faraday's constant $F = 96\,485\,\mathrm{C/mol\ e^-}$ via
$$i = nFv$$
  - You can also measure how many product you're forming either by assuming that all current is going to your reaction, or by using in-line gas chromatography.
    - In the EChem module, we'll assume that everything is going to hydrogen evolution.
  - Knowing how much current is going to hydrogen and CO, we can construct a **Tafel plot**.

- **Tafel plot**: The relationship that describes the log-linear dependence of the reaction rate as a function of the applied potential.
  - We will take the partial current going to CO and plot it vs. the applied potential.
  - This yields direct mechanistic insight: Increasing the overpotential decreases the $\Delta G^\ddagger$.

- Example of using a Tafel plot.
  - Assume CO_2 is reduced in a rate limiting step by combining with an electron.
  - Using kinetics, we would have
$$R_{\mathrm{CO}} = k_1(\theta^*)(a_{\mathrm{CO_2}}) \exp\left(\frac{\beta n F}{RT}\right)$$
    - θ^* is the concentration of the active sites on the gold surface; not every atom on the surface is active, as can be shown via fancy microscopy techniques.
    - $a_{\mathrm{CO_2}}$ is the **activity** of CO_2 dissolved in solution.
    - β is the symmetry factor: For reactions in which there is a high reorganizational potential energy, we can take $\beta \approx 1/2$.
  - This yields info on the Tafel slope:
$$\frac{\partial \eta}{\partial \log(j)} = \frac{60\,\mathrm{mV}}{\beta} = 120 - 150\,\mathrm{mV}$$
  - Thus, we check the data: At all potentials in the linear range, check for linear dependence.
  - Tafel data implies ET RLS with slope about 1.

- What if instead, we couple adsorption with proton transfer from?
  - Look at the rate of CO formation vs. the bicarbonate concentration.
    - Nothing here, so it's not this.
    - Moreover, because it's not this charged species, it's not any acidic species (because changes in one would change the pH of all).
  - Nothing for water, too.
  - Thus, the data suggests that there's no proton transfer in the initial step, so it must happen afterwards.

  - Note that changing the partial pressure of CO also doesn't change anything, suggesting that as soon as CO is created, it is released and future adsorption is not inhibited.

- Other data complete the mechanism.

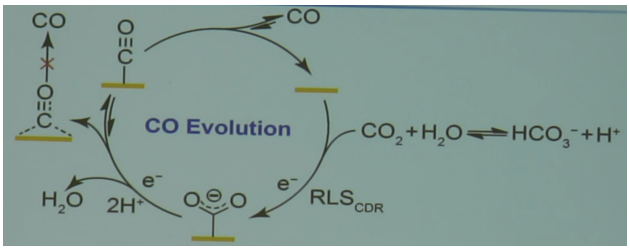

Figure 6.2: CO evolution mechanism.

- Simultaneous hydrogen evolution is dependent on the proton donor environment.

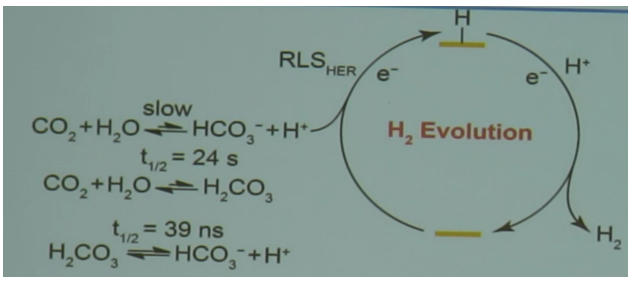

Figure 6.3: H_2 evolution mechanism.

  - Mechanism is deceptively simple, but profound all the same.
  - We first get adsorption of a proton to a hydride.
    - But Tafel slope is super high, so you may be being limited by the ability of the protons to get to the surface in the first place.
    - Suppose that the protons are special, i.e., donated by the relatively slow dissociation of H_2CO_3.
      - ➢ Note that H_2CO_3 dissociates with $t_{1/2} = 24\,\text{s}$ in real life; it is only super fast in our body because of an enzyme we have that takes it to $t_{1/2} = 39\,\text{ns}$.
    - Changing the concentration of H_2CO_3 and rerunning the experiment confirms this.
  - We do observe an explicit change in the rate of hydrogen evolution based on the concentration of H_2CO_3, but the relationship is complex and potential dependent.
  - This is an independently occurring catalytic reaction on *some* catalytic site (maybe one that was occupied by CO, maybe not, we don't know).

- Utilizing this mechanism to design a better, more selective reaction.

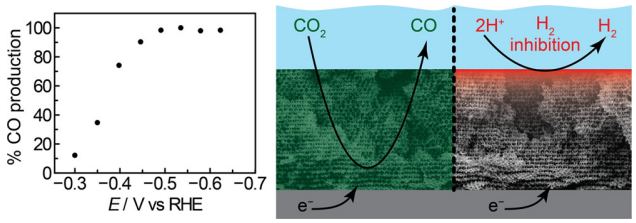

Figure 6.4: Enhancing heterogeneous CO_2RR with mesoporous membranes.

  - If we couple the two reactions, because they both depend on $CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+$, we can increase selectivity by slowing down this equilibration even further.
  - We make the environment at the gold catalysis further out of equilibrium with the bulk.
  - Wuttig teamed up with other scientists to develop a mesoporous gold structure, forcing everything that wants to touch the gold to go through the structure.
  - The CO_2 reaction does not care how thick the structure is, but H_2 does! This leads to near-selective CO formation.

- In our module, however, we need to *increase* H_2 evolution, though!
  - We'll use all the same principles Wuttig just discussed, but it'll be simpler.
  - H_2 evolution is also an important reaction.

6.3 Lab 4: GCMS

Lab Manual

2/9:

- Goal.
  - Use GCMS to quantify how much benzene there is in 87 gasoline.
  - We will use a **standard addition method** with respect to an internal standard reference.
- Why we are interested.
  - Gasoline is a complex mixture of hydrocarbons, and refineries are known to include aromatics such as benzene, toluene, and xylenes to increase the octane rating.
  - However, there is increasing concern about the hazards associated with these compounds.
- **Standard addition method**: The quantitation of a substance of interest in a complex mixture performed by spiking in increasing known amounts of that substance and plotting the resulting signal from this series of samples to determine the original amount.
- Description of how gas chromatography works.
- **Electron ionization** (mass spectrometry): A "hard ionization" source that results in a charged ion likely to fragment into a characteristic fragmentation pattern. *Also known as* **EI**.
  - As discussed in Labalme [1], electrons are generated via thermionic emission from a hot tungsten filament and then accelerated by applying a large potential between the filament and anode.
- **Chemical ionization** (mass spectrometry): A "soft ionization" soruce through which the major product is the molecular ion and very little fragmentation occurs. *Also known as* **CI**.
- EI is more useful for molecular identification against a library of known fragmentation patterns; CI is more useful for calculating the molecular weight of an unknown or newly synthesized compound.
- Common MS peaks in EI spectra.
  - Molecular ion at $m/z = \text{MW}$.
  - $[C_4H_3]^+$ at $m/z = 51$, which is often a tell-tale sign that the analyte is an aromatic.
  - $[C_7H_7]^+$ at $m/z = 91$, which often arises from the rearrangement of a benzyl fragment and suggests that the analyte contains a benzyl moiety.
- Mass analyzers.
- Methods of mass analysis: Quadrupole, time of flight, ion trap, ion cyclotron, etc.

  - Our setup has both a quadrupole and time-of-flight mass analyzer.

- **Quadrupole**: A device that filters out ions with very low or very high m/z ratios.

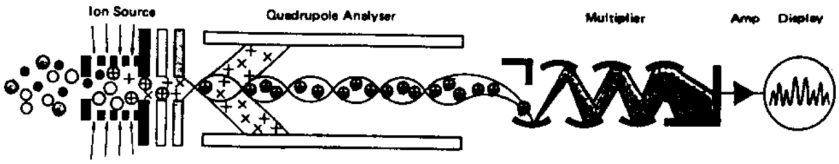

Figure 6.5: Quadrupole mass spectrometer.

  - In our setup, it allows ions of our desired m/z range to pass into the time-of-flight tube where they are ultimately detected.
  - Can be tuned to scan the atomic mass range or pass only a particular mass/charge of interest.
  - Setup: Each parallel plate contains a dc voltage as well as a radiofrequency oscillation with frequency f. How much something moves correlates with its mass. We use one set of plates in the xz-plane, and one in the yz-plane, each meant to filter out an extreme of mass.

- **Time of flight**: A device that accelerates charged particles along a path and measures how long they are in the tube before they crash into a detector. *Also known as* **TOF**.

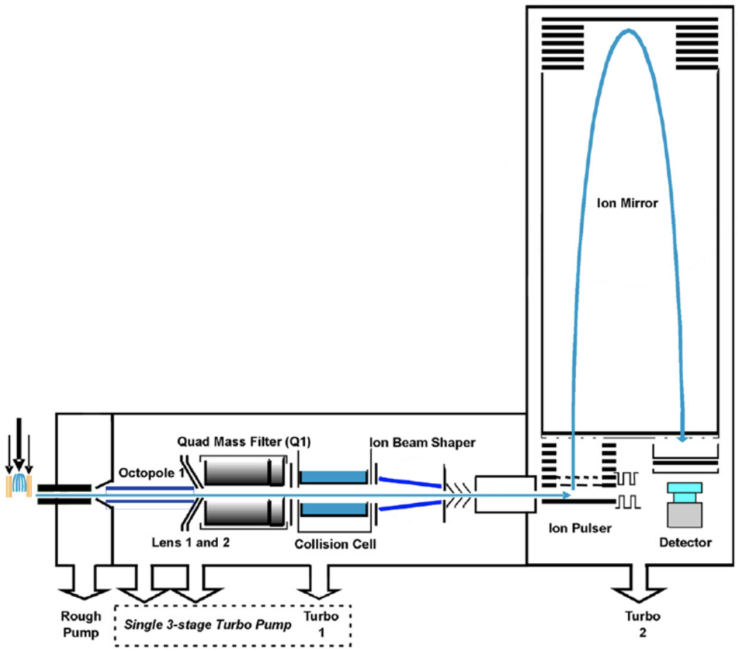

Figure 6.6: Time of flight mass spectrometer.

  - We rearrange $E = (1/2)mv^2$ to
$$m = \left(\frac{2E}{d^2}\right) t^2$$
  - Smaller ions are accelerated to a higher total velocity and arrive at the detector first.

- Standard addition analysis: Largely to be discussed in lab.

- Error analysis discussed.

In Lab

- We are not actually solving the linear fit for concentration, but for the added concentration. This will be negative since we're concentrating the amount you would have to remove in order for the peak to disappear, which is the opposite of the initial amount.
- Using an internal standard allows us to divide out volume.
  - Let R denote the substance of interest.
  - We have that
$$A_{\mathrm{R}} \propto [\mathrm{R}] = V \cdot \eta_{\mathrm{R}} \cdot [\mathrm{R}] = V \cdot \eta_{\mathrm{R}} \cdot ([\mathrm{R}]_0 + [\mathrm{R}]_{\mathrm{add}})$$
    where...
    - A_{R} is the GC peak area.
    - V is the sample volume.
    - $[\mathrm{R}]$ is the concentration of R.
    - And η_{R} is the detector efficiency for R.
  - Thus, there will be a linear relationship between $[\mathrm{R}]_{\mathrm{add}}$ and A_{R}, the x-intercept of which occurs when $[\mathrm{R}]_{\mathrm{add}} = -[\mathrm{R}]_0$.
  - When V is nonconstant (there will be slight variations in how much sample we add to the GCMS tube each time), we can use an **internal standard** to correct our work.
  - In particular, if B denotes benzene and T denotes toluene, we have
$$A_{\mathrm{B}} = V \cdot \eta_{\mathrm{B}} \cdot ([\mathrm{B}]_0 + [\mathrm{B}]_{\mathrm{add}}) \qquad A_{\mathrm{T}} = V \cdot \eta_{\mathrm{T}} \cdot [\mathrm{T}]_0$$
  - We can then divide these two equations to obtain
$$\begin{aligned} \frac{A_{\mathrm{B}}}{A_{\mathrm{T}}} &= \frac{\eta_{\mathrm{B}}}{\eta_{\mathrm{T}}} \cdot \frac{[\mathrm{B}]_{\mathrm{add}}}{[\mathrm{T}]_0} + \frac{\eta_{\mathrm{B}}}{\eta_{\mathrm{T}}} \cdot \frac{[\mathrm{B}]_0}{[\mathrm{T}]_0} \\ &= \frac{\eta_{\mathrm{B}}}{\eta_{\mathrm{T}} \cdot [\mathrm{T}]_0} \cdot ([\mathrm{B}]_{\mathrm{add}} + [\mathrm{B}]_0) \end{aligned}$$
    - Notice that V cancels out!
- **Internal standard**: A substance in a solution that is always at the same concentration.
- These last two points are related to Q3-4 of the lab report.
- 0,2.5,5,7.5,10,12.5 are data points.
- **Extract chromatogram** allows you to find all peaks that have a significant concentration of a certain m/z.
  - For example, you can type in $m/z = 78$ and find all peaks corresponding to benzene (there should only be one).
  - $m/z = 91$ will get you all toluene derivatives.
    - Xylenes come in a pair of three (ortho/meta/para).
  - $m/z = 105$ should yield all xylene derivatives.
- Range of masses: 50-600; Solvent pause time: 4 min.
- 0ppm.
  - Rt: 4.696. Benzene. Integration: 321274.63.
  - Rt: 6.858. Toluene. Integration: 329835.47.
  - Rt: 8.540. *para*-Xylene. Integration: 353207.99.

  - Rt: 8.363. Ethyl benzene. Integration: 104551.1.
  - We're now using mesitylene instead of *para*-xylene.

- Notes on how to answer the questions.

  1. Input 0ppm data in to Excel. Plot the regular chromatagram (TIC) vs. retention time.
  2. Plot an EIC for both benzene and toluene. Also plot their extracted mass spectra (peak labels [3-4 per spectrum] should include a name or structure and an m/z value). This can be extracted from the 0ppm data as well.
  3. Using integration data for both benzene and toluene at all concentrations (jotted down) and ppm data (given), normalize the benzene data using the toluene data (toluene is an **internal standard** because it's always at the same concentration, so it makes benzene peaks comparable via normalization), make a scatter plot, find the line of best fit, and calculate the concentration.
  4. Use the Student's t-test, 95% confidence interval, $n - 2 = 3$ DOFs, to get $t = 3.182$. No need to cite a source. For tabulation, make a very simple 2×2 table with headers "Concentration" and "Error" and then place the values below. To get a volume percentage, use HL's Canvas announcement to convert concentration in ppm (not mol/L) to a mass percentage, and then a volume percentage (using density).
     - Hypothetical: Imagine 1 gram of solution (approximate as pentane density). You can convert it to liters pentane using the density and stoichiometry.
     - Now imagine you have 5 µg benzene. You can convert it to liters benzene using the density and stoichiometry.
     - Divide the latter by the former to obtain a volume percentage.
  5. Plot EICs and MSs for both mesitylene and ethyl benzene. The EICs can be the same in both cases. Peak areas are comparable across EICs, so just compare the peak area of benzene which correlates with it's above-derived concentration to estimate the concentrations of mesitylene and ethyl benzene using a simple ratio.