

CHEM 221
Instrumental Analysis
FINAL EXAM

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Name: Serkey, Anne

INSTRUCTIONS: Read through the entire exam before you begin. For questions involving calculations, show **all** of your work -- **HOW** you arrived at a particular answer is **MORE** important than the answer itself! Similarly, you must *explain* how you arrived at an answer to a question if you are to receive full credit for your answer.

All questions are worth 25 pts each – answer **any 16** of the 20 questions (for a total of 400 points). You can receive extra credit by answering additional questions (up to 5 extra credit points per question) – if you do so, you must **CLEARLY** identify those questions which are to be graded as extra credit by writing “EC” next to the question number. If no questions are marked “EC” and more than 16 questions are answered, then I will grade the first 16 answers at full credit value (25 points each) and any remaining questions at extra credit value (5 points). Attached are a periodic table and a formula sheet jam-packed with useful stuff!

Good Luck!

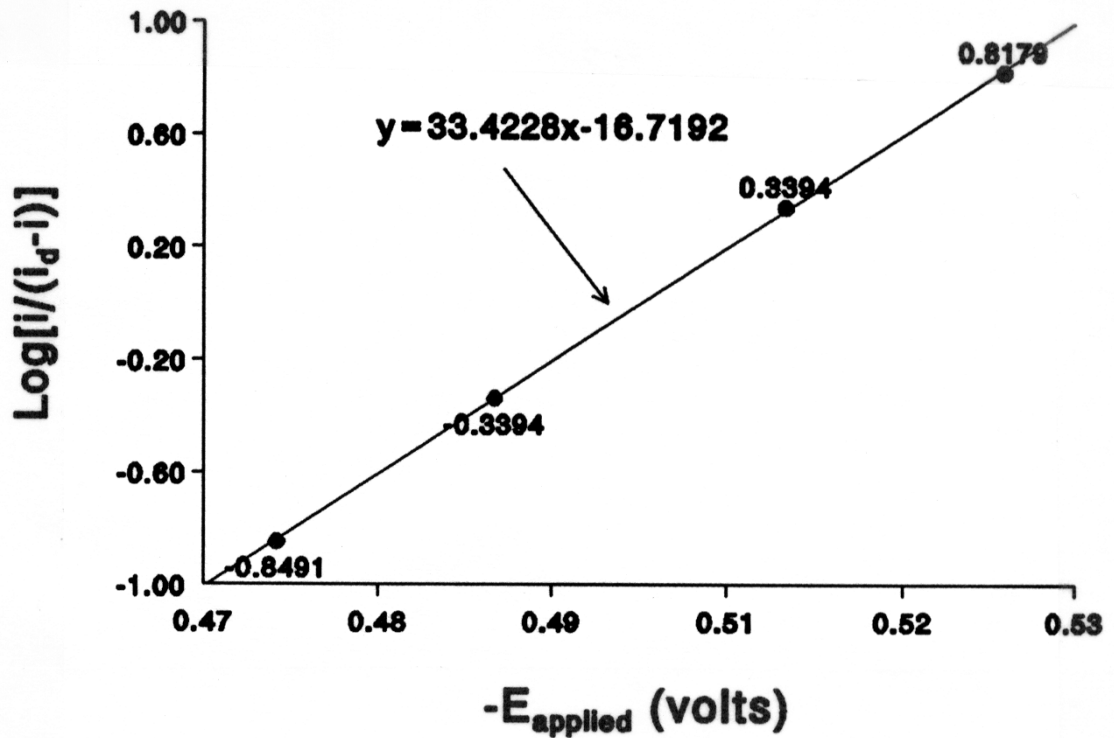


Professor E. F. Gizmo and some of his many inventions

A current-sampled dc polarogram of an unknown solution containing either Cd or Cr was acquired and found to have a limiting current of 5.00 μA . From the rising portion of the polarographic wave, the following data were obtained:

<u>E(applied), volts</u>	<u>Current, μA</u>
-0.475	0.62
-0.490	1.57
-0.510	3.43
-0.525	4.38

Further processing of these data produced the following plot, with the included linear least squares fit to the data:



- From the data and plot provided on the previous page, determine the value of E° for the reduction – you must show how you determined E° and any assumption implicit in that determination in order to receive credit for your answer.

Since the plot of $\text{Log}[i/i_d - i]$ versus $-E_{\text{appl}}$ is linear, the system is *reversible*.

For a reversible system, $E^\circ = E_{1/2}$ which occurs when $i = i_d/2$

If we set $i = i_d/2$, then $\text{Log}[i/i_d - i] = 0$, so we can solve the linear least squares equation for x when $y=0$ to get the value of E° :

$$\begin{aligned}
 y &= 33.4228x - 16.7192 = 0 \\
 33.4228x &= 16.7192 \\
 x &= \frac{16.7192}{33.4228} = 0.5002333 = -E_{\text{appl}}
 \end{aligned}$$

So: $E^\circ = -0.500 \text{ volts}$

- Both the reduction of Cr^{3+} to Cr^{2+} as well as the reduction of Cd^{2+} to Cd have the same E° (and it is equal to the E° value determined in question #1, above). Based on the data provided on the previous page, is the polarographic reduction wave due to Cr^{3+} or Cd^{2+} ?

We need to determine the number of electrons transferred per mole (n) which we can get from the *slope* of the plot:

$$\text{slope} = n/0.0592$$

$$n = \text{slope} \times 0.0592 = 33.4228(0.0592) = 1.98 \approx 2$$

Since $n=1$ for Cr^{3+} to Cr^{2+} and $n=2$ for Cd^{2+} to Cd , the reduction must be due to: Cd

3. Explain why differential pulsed polarography (DPP) gives superior detection limits to sampled-dc polarography.

-Pulsing E_{appl} enhances the Faradaic current (i_f) more than it enhances the charging current (i_{cc}), giving improved S/B.

-Differential measurement reduces i_{cc} further by subtracting out background nearly simultaneously with signal measurement (giving even better S/B).

4. Give two reasons why the dropping mercury electrode (DME) is the electrode of choice for routine voltammetry.

-Fresh electrode surface provided with each drop (minimizes build-up of reduced species on the electrode surface)

-Increasing drop surface area (with time) helps counteract the naturally decreasing current (with time).

5. Describe the two main steps involved in an analysis using anodic stripping voltammetry (ASV) and indicate why it has detection limits superior to the other Echem methods we discussed.

• **Electrolysis: apply potential about 200 mV more negative than the E° of the analyte, stir to ensure high rate of reduction; reduced analyte forms an amalgam with Hg, preconcentrating the analyte within the HMDE - this is what is responsible for the superior detection limits with ASV.**

• **Anodic Linear Sweep Voltammetry. Slow anodic sweep to oxidize analyte in HMDE; measure anodic current (proportional to concentration of analyte)**

6. How would the chemical ionization mass spectrum for a compound differ from its corresponding electron impact ionization mass spectrum?

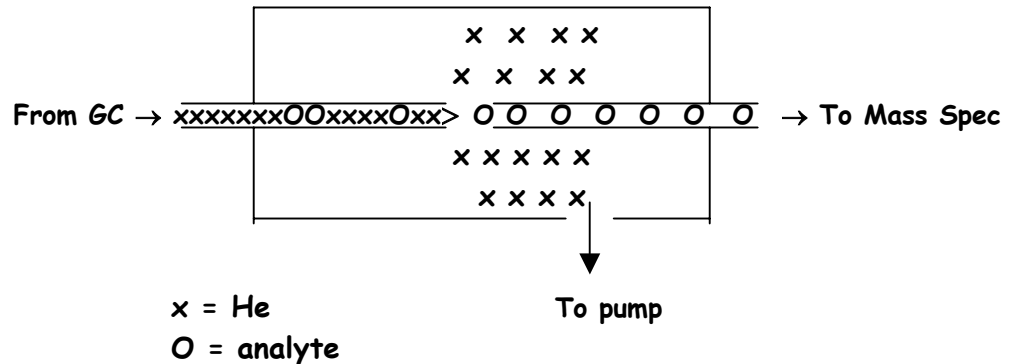
-Decreased fragmentation due to lower energy ionization

-Molecular ion peak will occur at either $M+1$ or $M-1$ due to addition or abstraction of proton during ionization process.

7. The jet separator serves what function in a GC-Mass Spectrometer? Briefly describe how it works (a simple diagram would help!).

The jet separator serves as the interface between the GC and the inlet system of the mass spectrometer. This is a critical component that serves both to remove the massive amounts of helium carrier gas from the GC effluent stream and to transfer the eluting analyte from the atmospheric pressure environment of the GC to the low pressure environment of the mass spec.

The jet separator consists of a chamber which is pumped to a low pressure - at one end, the GC effluent enters through a tube that is tapered at the end. This releases a jet of the gas stream from the GC which expands rapidly into the low pressure chamber. The light helium carrier gas species expand more rapidly than the heavier analyte which are collected by a tube located close to the end of the jet. Analyte molecules in the tube then flow into the ionization chamber of the mass spectrometer.



8. Elemental analysis at ppb levels can be performed using ICP atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry (GFAAS), and anodic stripping voltammetry (ASV). Which one of these methods would be best for the daily determination of carcinogenic Cr(VI) in water discharged from a manufacturing facility? Briefly justify your choice.

In this analysis, we are interested in a particular oxidation state of Cr, so we need a method that provides some selectivity based on the oxidation state of the metal. ICP-AES and GFAAS measure TOTAL Cr levels but, since ASV is based on measuring electron transfer reactions, it is able to distinguish between Cr in different oxidation states. Although ASV is a *slower* method of analysis than either ICP-AES or GFAAS, it is plenty fast enough for the 1 analysis/day required here. ASV is the best method for this analysis.

9. Elemental analysis at ppb levels can be performed using ICP atomic emission spectrometry (ICP-AES), graphite furnace atomic absorption spectrometry (GFAAS), and anodic stripping voltammetry (ASV). Which one of these methods would be best for daily screening 10 toxic elements in cooling water effluent from a local manufacturing facility? Briefly justify your choice.

Here we need a method that will let us rapidly screen for 10 elements, so we are looking for a method can do rapid *qualitative* analysis. AAS is really a single-element technique and, although multielement analyses can be done via ASV, only about a dozen or so elements will be accessible via ASV. ICP-AES, however, can easily provide a spectrum enabling rapid qualitative analysis of a water sample. ICP-AES is the best choice as it is applicable to a broader range of elements (>40) and results obtained in a matter of minutes. ICP-AES is the best method for this analysis.

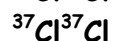
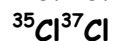
10. Quantitative analysis of environmental samples for trace levels of halogenated pesticides is often accomplished using GC-Mass Spec. If you were to replace the mass spec detector with one of the three common detectors used with GC (i.e., TCD, FID, ECD), which one would best be able to satisfactorily accomplish the analysis task? Briefly justify your choice.

There are two issues here: detectability and selectivity. The TCD is not sensitive enough for trace analysis, but the FID and the ECD are. The ECD is the better choice as it is selective specifically for halogen-containing compounds, while the FID will respond to ALL hydrocarbons (not just halogenated). Thus, the ECD will provide both the sensitivity and selectivity needed for this analysis; ECD is the best detector for this analysis.

11. In the electron impact mass spectrum for Cl₂, there are *three* peaks observed for the molecular ion – Explain.

There are two major isotopes of Cl: ³⁵Cl and ³⁷Cl

Thus, we can combine two Cl's in three different ways:



So, three peaks will be observed at: 70 amu, 72 amu and 74 amu.

12. Calculate the frequency of electromagnetic radiation (EMR) in the IR spectral region at a wavelength (in a vacuum) of 8.136 μm . Compare this with the frequency of EMR commonly encountered in NMR spectroscopy and explain why an interferometer is only needed for FT-IR but not FT-NMR.

$$\nu = c/\lambda = \frac{2.9979 \times 10^8 \text{ m/sec}}{8.136 \times 10^{-6} \text{ m}} = 3.684735 \times 10^{13} \text{ sec}^{-1}$$

$$\nu = \boxed{3.685 \times 10^{13} \text{ sec}^{-1}}$$

In NMR, the frequencies are in the 10^8 MHz range, which is 100,000 times lower frequency than EMR in the IR. At these lower frequencies (MHz), the oscillations of the EMR can be measured *directly*, which is not possible at the frequencies encountered in the IR (which then requires an interferometer to modulate the intensity of the EMR at frequencies proportional to the frequencies of the IR EMR).

13. Thanks to the rapid scanning capabilities of FT-IR, you've been busy watching the FT-IR signal-average a noisy spectrum for an hour. You are interested in determining whether or not a feature appearing at 1620 cm^{-1} is due to noise or a real absorption band. Suppose that the S/N for this feature after 100 scans is equal to 1.2 – assuming you can average 100 scans each hour, how much longer (hours) must you scan before this feature can be positively differentiated from noise (i.e., has a S/N equal to 3.0)?

S/N after 100 scans = 1.2

$$\text{So: } (S/N)_{n=100} = (100)^{1/2} (S/N)_{n=1} = 1.2$$

$$(S/N)_{n=1} = 0.12$$

How many measurements (n) to reach S/N = 3?

$$(S/N)_n = n^{1/2} (S/N)_{n=1}$$

$$3 = n^{1/2} (0.12)$$

$$n^{1/2} = 25.0$$

$$n = (25.0)^2 = 625$$

Thus, need to make 525 more measurements

$$\text{At 100 scans/hour: } 525 \text{ scans} \times \frac{\text{hour}}{100 \text{ scans}} = \boxed{5.3 \text{ hours}}$$

14. **TRUE or FALSE (and WHY)?** A common tungsten filament continuum source is ideal for atomic absorption spectrometry.

FALSE! You must use a *line source* (e.g., a hollow cathode lamp) for atomic absorption spectrometry. A continuum source would need a monochromator with extremely high dispersion in order to obtain the spectral bandpass needed for absorption measurements on atoms which would result in low light throughput and would be cost prohibitive.

15. **TRUE or FALSE (and WHY)?** Broad absorption bands are typically observed in UV/Vis molecular spectroscopy due to the limited resolution of the instruments used.

FALSE! Molecular absorption bands of condensed phase materials are typically quite broad (10-50 nm) and require only an instrumental bandpass of 1-5 nm to provide adequate resolution and adherence to Beer's Law.

16. **TRUE or FALSE (and WHY)?** Lasers are intense sources of optical EMR, but are not good sources for absorption spectrophotometry because they are too large and bulky.

FALSE! Lasers can be quite small and even inexpensive - they do not make great sources for absorption spectrophotometry as it is the *noise* in the source that ultimately limits detection in absorption spectrophotometry and lasers are more difficult to stabilize than other sources. Coupled with the fact that tunable lasers capable of replacing a continuum source are expensive and known to be "finicky", lasers have not found routine application in molecular absorption spectrophotometry.

17. Why do open tubular columns produce gas chromatograms with significantly better resolution than do packed GC columns?

OT columns have plate heights that are similar to those found with packed columns, *BUT* because they do not have any packing to restrict the flow of the mobile phase, OT columns can be up to 100x longer than packed columns. This 100-fold increase in theoretical plates greatly improves the resolution obtainable with OT columns.

18. **TRUE or FALSE (and WHY)?** Charge transfer bands arise from $d \rightarrow d$ electronic transitions of the metal ion in metal-ligand complexes.

FALSE! Charge transfer bands result from transitions involving the transfer of an electron within a complex (e.g., electron transfer between a metal ion and ligand in a metal-ligand complex). They are easily distinguishable from bands resulting from $d \rightarrow d$ transitions in that their molar absorptivities are considerably greater (10^4 versus 10^2).

19. Arrange the following stretches in order of *increasing* vibration frequency: C-H, C-C, C=O, C-D. Briefly justify/explain your answer.

Increasing Frequency \rightarrow

C-C < C=O < C-D < C-H

From equation given: $\nu \propto (k)^{\frac{1}{2}}$ - bond strength
 $\nu \propto (1/\mu)^{\frac{1}{2}}$ - mass

Single bond frequencies should increase with decreasing mass, so C-H is at the highest and C-C at the lowest frequencies. How do we place C=O which has the greatest mass BUT has a double bond? Since k is approximately proportional to bond order, C=C should have a frequency about 1.4x that of C-C. Increasing the mass from 12 (C) to 16 (O), will decrease the frequency, but a mass increase to 24 would be needed to decrease it back to the C-C frequency. Thus, the C=O frequency is higher than C-C.

20. **TRUE or FALSE (and WHY)?** With a blank measurement of 0.001 ± 0.0005 (average \pm standard deviation) and a sample measurement of 0.002 ± 0.0005 , it was determined from the calibration curve that Pb was present in the drinking water sample at a level of 500 ppb.

FALSE! Minimum detectable signal ($S/N = 3$) would be:

0.001 - blank
 + 3(0.0005) - 3x noise
 0.0025 - minimum detect. signal > 0.002 (sample)

Thus, sample measurement (0.002) is *below the detection limit* and is indistinguishable from the blank.