CHEM 155 Instrumental Analysis  Terrill  DH-007 924-4970 terrill@upstate.scsu.edu  Page 1 of 10

Name: Key

Exam 1 – 100 points

Thursday, March 25, 2004

1. The following measurements of absorbance were made:
   0.120, 0.118, 0.119, 0.119.
   \[ \text{Sum} = 0.476 \]
   \[ \sigma_a = 0.119 \]
   Calculate the mean, standard deviation, and 95% confidence interval for this population.
   \[ \text{mean} = \bar{x} = 0.119 \]
   \[ \text{std dev} = \sigma = \sqrt{\frac{(0.119 - 0.120)^2 + (0.118 - 0.119)^2 + (0.119 - 0.119)^2}{N}} \]
   \[ \text{df} = N - 1 = 3 \]
   \[ \frac{0.1192 + 0.0013}{0.00082} = 0.119 = 0.0012 \]
   \[ 0.120 \pm 0.0012 = 95\% \text{ confidence interval} \]

2. The absorbance for a particular set of measurements was 0.0502±0.003.
   The extinction coefficient for the absorbing species was known to be
   \[ \varepsilon = 1015 \pm 15 \text{ M}^{-1} \text{cm}^{-1} \] and the pathlength, \( b = 1.00 \pm 0.05 \text{ cm} \). What is the concentration of the absorber and the standard deviation of the concentration?
   \[ A = \varepsilon b c \]
   \[ c = \frac{A}{\varepsilon b} = \frac{0.0502}{1015 \text{ M}^{-1} \text{cm}^{-1}} = 4.95 \times 10^{-5} \text{ M} \]
   \[ \sigma_c = \sqrt{\frac{(1015 - 1005)^2 + (0.0502 - 100)^2}{1015 \text{ M}^{-1} \text{cm}^{-1}}} = 0.079 \]
   \[ \sigma_c = 4.95 \times 10^{-5} \text{ M} \]
   \[ c = (4.95 \pm 0.079) \times 10^{-5} \text{ M} \]

3. a. Draw an energy level diagram for a 4-level laser. b. Label this diagram assuming that it is a KrF excimer laser, note what molecules and atoms are involved in each level.
4. Explain why adding KCl to samples and standards improves the sensitivity of FAAS measurements of Ba.

K atoms in the flame tend to ionize, generating significant levels of free electrons. These free electrons suppress the ionization of Ba.

\[ \text{Ba} = \text{Ba}^+ + e^- \text{. Ba is the atomic absorber responsible for the FAAS signal.} \]

5. How does EDTA reduce sulfate interference in FAAS determination of Ba?

EDTA forms a stable (in solution) complex with Ba\(^{2+}\) that subsequently volatilizes in the flame, yielding Ba atoms.

\[ \text{EDTA} + \text{SO}_4^{2-} \rightarrow \text{Ba} \]

6. Indicate true answer(s) below. A matrix effect is:

- A chemically induced change in measurement sensitivity.
- An electrically induced change in measurement sensitivity.
- A thermally induced change in measurement sensitivity.
- Due to changes in detector sensitivity.
- Due to differences between samples and standards.

7. Elaborate the acronym for PMT and CCD detector:

\[ \text{Photo} \quad \text{Multiplier} \quad \text{Tube} \quad \text{Charge} \quad \text{Coupled} \quad \text{Device} \]
8. The photodiode is partly depicted below. Fill in the blanks to indicate the important parts and properties of the photodiode.

a. The photodiode is made of what material: Si
b. The charge carriers on the left hand side are: \( h^+ \) "holes"
c. The charge carriers on the right hand side are: \( e^- \) "electrons"
d. The voltage applied to the photodiode is called reverse bias

16. Explain how the photodiode functions as a transducer. (5 pts)

Reverse bias creates a depletion of \( h^+ \) (on the p-side) and \( e^- \) (on the n-side) of the photodiode P-N junction. No current normally flows. When light strikes the junction, it can create \( h^+/e^- \) pairs that are then detected as a current in the external circuit.
9. Why are hollow cathode lamps used in atomic spectroscopy? The HCL produces atomic emission that exactly matches the absorption wavelength of the analyte atoms. Hence selectivity the monochromator need not have ultra-high resolution.

10. A monochromator used in a flame atomic absorption spectroscopy experiment has a 0.5 meter focal length, and a 500 line per mm grating. Assuming that your sample had both antimony and nickel in it, what slit width would be required to resolve the atomic absorption lines of Sb ($\lambda = 231.147$ nm) and Ni ($231.095$ nm). Assume that the radiation is incident on the grating at 90$^\circ$. Normal incidence:

a. calculate the grating spacing $d$.
b. calculate the refracted light angle $r$.
c. calculate the reciprocal linear dispersion $D^{-1}$.
d. calculate the slit width $w$.

\[ a) \quad d = \frac{1}{500} \text{ mm} = 2 \times 10^{-3} \text{ mm} = \frac{2 \text{ microns}}{2000 \text{ nm}} \]

\[ b) \quad n \lambda = d (\sin i + \sin r) \]

\[ \sin i = \sin 90^\circ = 1 \]

\[ n \lambda = d + d \sin r \]

\[ r = \frac{\lambda - d}{d} = \frac{\lambda}{d} - 1 = \frac{1(231)}{2000} = 0.1155 \]

\[ r = \arcsin \left( \frac{231}{2000} - 1 \right) = -62.2^\circ \]

\[ c) \quad D^{-1} = \frac{d \cos r}{nF} = \frac{2000 \text{ mm} (0.466)}{1 (0.5 \text{ mm})} = \frac{1866 \text{ mm}^{-1}}{1} \frac{14}{14} = 1.324 \text{ mm}^{-1} \]

\[ d) \quad \Delta \lambda_{eff} = \omega \Delta \lambda \Rightarrow \omega = \frac{\Delta \lambda}{\Delta \lambda_{eff}} = \frac{231(1.07 - 231.095)}{1.324} = 0.028 \text{ mm}^{-1} \]
11. A small hypothetical molecule has the following energy level diagram. Indicate, using arrows, the transitions corresponding to:

- **a.** infrared light absorption,
- **b.** visible light absorption,
- **c.** visible light fluorescence,
- **d.** visible light phosphorescence

![Energy Level Diagram](image)

12. Estimate the approximate energy of the fluorescent emission lines that you expect from this molecule that originate in the S1 state.

- \(2.8 - 0.4 \text{ eV} = 2.4 \text{ eV} = 3.6 \times 10^{-19} \text{ J} \rightarrow 523 \text{ nm} \)
- \(2.8 - 0.2 \text{ eV} = 2.6 \text{ eV} = 4.2 \times 10^{-19} \text{ J} \rightarrow 473 \text{ nm} \)
- \(2.8 - 0.0 \text{ eV} = 2.8 \text{ eV} = 4.5 \times 10^{-19} \text{ J} \rightarrow 440 \text{ nm} \)

13. Draw the corresponding fluorescence spectrum on the axes below. Indicate band / line positions with vertical lines. Use a solid line to indicate the expected band shapes corresponding to the molecule in the gas phase, and then use a dashed line to indicate the condensed phase spectral lineshapes.

\[ E = \frac{hc}{\lambda} \]
\[ \lambda = \frac{hc}{E} = \left(\frac{6.626 \times 10^{-34} \text{ Js}}{5.6 \times 10^5 \text{ Hz}}\right) \times 10^5 \text{ Hz} \]

\[ \frac{E}{\text{E}} = 1.98 \times 10^{-25} \text{ J.m}^2 \]

\[ \text{a.} \]

\[ \text{b.} \]
14. Give the corresponding definition or word:

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<table>
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<tbody>
<tr>
<td>a. An analytical method that employs a rare, non-interfering chemical added to all standards and samples.</td>
<td>sensitivity</td>
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<tr>
<td>b. Measure of difference between measurement and true value</td>
<td>Accuracy</td>
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<tr>
<td>c. Measurement of scatter between repeated measurements</td>
<td>Precision</td>
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<tr>
<td>d. Interval within which one is 95% confident that true mean lies</td>
<td>Confidence Limit</td>
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<td>e. The part of the calibration curve between the detection limit and the limit of linearity</td>
<td>linear dynamic range</td>
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<td>f. Standards are added to analyze in increasing concentration to calibrate with matrix effects</td>
<td>Method of Standard Additions</td>
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15. What is the gain of a PMT that has 8 dynodes, a secondary electron yield of 5 and a quantum efficiency of 0.1?

\[ G = \phi \alpha^n = 0.1 \times 5^8 = 8.9 \times 10^8 \]

16. Is it possible to detect near infrared radiation (wavelength = 1500 nm) with a photomultiplier tube using a Na photocathode? The work function of Na is 2.75 eV. Show work for credit.

\[ \lambda = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 8 \times 10^{-3} \times 2.75 \times 10^{-19}}{4.4 \times 10^{-19}} = 4.5 \times 10^{-7} \text{m} = 45 \text{nm} \]

... no longest detectable \( \lambda = 45 \text{nm} \).