1] Calculate the $E^0$ for the $\text{ZnS(s)} + 2e^- = \text{Zn(s)} + S^{2-}$ given the following

$\text{Zn}^{2+}(aq) + 2e^- = \text{Zn(s)}$  \hspace{1cm} $E^0 = -0.746 \text{ V}$

$K_{sp}(\text{ZnS}) = 3\times10^{-23}$

2] Write down the response expected from a Cl$^-$ ion selective electrode:

3] Define the terms, accuracy and precision. How do they differ? Which term is most closely related to standard deviation?

If the true result of sulfur in a steel standard is 0.255% and two new techniques indicate

(A) 0.244% +/- 0.007%

(B) 0.251 +/- 0.021%

Which is more accurate and which more precise?

Confidence Level

<table>
<thead>
<tr>
<th>df</th>
<th>50%</th>
<th>90</th>
<th>95</th>
<th>98</th>
<th>99</th>
<th>99.5</th>
<th>99.9</th>
<th>99.99</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>.765</td>
<td>2.353</td>
<td>3.182</td>
<td>4.541</td>
<td>5.841</td>
<td>7.453</td>
<td>12.92</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>.741</td>
<td>2.132</td>
<td>2.776</td>
<td>3.747</td>
<td>4.604</td>
<td>5.598</td>
<td>8.610</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>.727</td>
<td>2.015</td>
<td>2.571</td>
<td>3.365</td>
<td>4.032</td>
<td>4.773</td>
<td>6.869</td>
<td></td>
</tr>
</tbody>
</table>
4] With the aid of the table above calculate the 95% confidence interval for an experiment of 5 runs with an average of 23.45 ppm +/- 0.09 ppm.

\[ \mu = \bar{x} \pm \frac{t\sigma}{\sqrt{n}} \]

What would the most obvious way of narrowing that interval?

5] With a graph clearly indicate the concepts of
   a. detection limit (what is that value?)
   b. sensitivity
   c. background
   d. linear range

6] Calculate the concentration of analyte in the sample from the following:

The response by a stripping voltammteric analysis of 5 standards of whose concentrations are 0.101, 0.201, 0.302, 0.401, and 0.503 ppm in CuCl\textsubscript{2}(aq) had signals of 16.0, 36.1, 49.3, 63.5, and 79.9 µA respectively. A least squares analysis gave a line of \( y = 155(x) + 2.34 \), \( r^2 = 0.995 \). A sample run yielded a signal of 57.2 µA. What is the concentration of Cu\textsuperscript{2+}(aq) in the sample?

7] Calculate the concentration of analyte in the sample from the following:

A sample was divided into 5 aliquots of 25.00 mL each. To each was added 0.00, 0.010, 0.020, 0.030, 0.040 mL of 1.05e-3 M PbCl\textsubscript{2}. An amperometric analysis was conducted on each. The concentrations of added Pb\textsuperscript{2+} in each aliquot and the respective current responses are below.

<table>
<thead>
<tr>
<th>aliquot</th>
<th>vol Pb\textsuperscript{2+} mL</th>
<th>conc Pb\textsuperscript{2+} (M)</th>
<th>added Pb\textsuperscript{2+} (M)</th>
<th>Signal (µA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0</td>
<td>1.05E-03</td>
<td>0</td>
<td>12.1</td>
</tr>
<tr>
<td>25</td>
<td>0.010</td>
<td>1.05E-03</td>
<td>4.19832E-07</td>
<td>18.9</td>
</tr>
<tr>
<td>25</td>
<td>0.020</td>
<td>1.05E-03</td>
<td>8.39329E-07</td>
<td>24.4</td>
</tr>
<tr>
<td>25</td>
<td>0.030</td>
<td>1.05E-03</td>
<td>1.25849E-06</td>
<td>31.1</td>
</tr>
<tr>
<td>25</td>
<td>0.040</td>
<td>1.05E-03</td>
<td>1.67732E-06</td>
<td>38.7</td>
</tr>
</tbody>
</table>

A least squares line through of the signal (µA) versus added Pb\textsuperscript{2+} (M) yielded a line of

\[ y = 1.56e7(x) + 12.0 \quad r^2 = 0.997 \]
What is the concentration of Pb\textsuperscript{2+} in the sample?

8] Amperometry finds its way into many sensor designs, including chloramines, oxygen, improvised explosives and most famously, glucose. Suppose we design one for the analysis of cadmium based on:

\[
\text{Cd}^{2+}(aq) + 2\text{e}^- = \text{Cd}(s) \quad E^0 = -0.402 \text{ V}
\]

Draw the potential-time program needed to conduct this process. Be sure to carefully label the axes. Are we moving the electrode from negative to positive or positive to negative potentials? Draw the concentration profile of near the electrode surface. This plot would be one of [Cd\textsuperscript{2+}] vs. distance. What varies in this profile as the time grows in value after the potential program is applied?
Selected Answers

1]

\[ E = -0.746 - 0.0592/2 \log (1/[Zn^{2+}]) \]

\[ K_{sp} = [Zn^{2+}][S^{2-}] = 3e-23, \quad [Zn^{2+}] = 3e-23/[S^{2-}] \]

\[ E = -0.746 - 0.0592/2 \log ([S^{2-}]/3e-23) \]

Let \([S^{2-}] = 1 \) for \( E^0 \)

\[ E^0 = -1.41 \text{ V} \]

2]

\[ E = \text{const} - 0.0592 \log [\text{Cl}] \]

3]

Accuracy is related to how close experimental results come to the true one. Precision is one of reproducibility. Standard deviation is most closely related to precision.

Technique B is more accurate while A is more precise.

4]

\[ U = 23.45 +/-(2.776*0.09/5^{1/2}) = 23.45 +/-.011 \]

There is a 95% chance that the true mean lies between the interval 23.56 and 23.34.

A simple way of decreasing that interval would be to simply increase the number of experiments, \( n \).

5]

6]

\[ 57.2 = 155(x) + 2.34; \quad x = 0.353 \text{ ppm Cu}^{2+} \]

7]

\[ 0 = 1.57e7(x) + 12.0 \quad x = 7.64e-7 \text{ M Pb}^{2+} \text{ in the sample} \]
Chem 454 -- Exam 2 -- March 10, 2010- -- 50 total points, each question is worth 10 points each.

1) Plot the signal vs. frequency characteristics of AC line, shot, white, and flicker noise. Which of these is considered environmental noise?

2] a. In the diagram above the three labeled regions represent what types of possible relaxation spectra? Which is emission, phosphorescence or excitation?

b. Explain the difference between emission and excitation spectra. How are they obtained? Are they both forms of fluorescence spectroscopy? Explain.

3] Why is aqueous state analysis by IR difficult? Why does Raman excel here?

4] a. What is Doppler broadening? How does this effect exert an influence on atomic absorption spectra? How and why do atomic spectra in flame AA differ from absorption spectra of aqueous molecular species?

b. A fluorescence analysis of bisphenol-A was conducted on a sample. Emission at 227 nm was measured on that sample with a signal of 194 units. A signal of 344 units was measured when 0.2 µL of 1.5 ppm bisphenol-A was added to 10 mL of the sample. What is the concentration of bisphenol-A in that sample?
Chem 454 – Exam 3 – April 28, 2010

PLEASE READ -- Answer each essay question directly but also to the extent that demonstrates your knowledge of the topic. Use one page of blank paper per question. Write your name and the number of each question and on the top of each answer sheet. You may keep this sheet after you are done with the exam.

50 total points

1] 10 points - Contrast HPLC with CE. Why does CE give narrower peaks when compared to HPLC? Use each of the terms in the van Deemter Equation in your explanation. H = A + B/u + Cu

2] 5 points - What types of analytes are detectable with each of the following GC detectors?
   a) Electron Capture Detector (ECD)
   b) Thermal Conductivity Detector (TCD)
   c) Flame Ionization Detector (FID)

3] 10 points - What is meant by “hard” versus “soft” ionization for mass spectrometry? Characterize each of the following ionization methods as either soft or hard forms of ionization.
   a) Electrospray ionization
   b) Matrix Assisted Laser Desorption Ionization (MALDI)
   c) Electron Impact (EI)
   d) Chemical Ionization (CI)

4] 10 points - Consider 5 analytes with boiling points that range from 110 to 260°C. If all five have about the same polarity, sketch a chromatogram of an isothermal GC separation conducted at 275°C. What would be your guess for the chromatogram if the temperature were ramped from 80 to 275°C for 20 minutes? Explain why.

5] 5 points - Rank the retention times order (short to longest) of the following solutes using reversed phase HPLC. Assume a constant mobile phase composition of 80/20 (v/v) methanol/water. Explain your answer.

\[
\begin{align*}
\text{苯} & \quad \text{乙醇} & \quad \text{苯酚} & \quad \text{间苯二酚}
\end{align*}
\]
6] **10 points** - Results from an HPLC analysis of pentachlorophenol (PCP) are presented below.

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>Peak Height</th>
<th>Retention Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>sample 1</td>
<td>5.661 cm</td>
<td>2.44 minutes</td>
</tr>
<tr>
<td></td>
<td>15.7 ppm phenol</td>
<td>7.223</td>
<td>1.51</td>
</tr>
<tr>
<td>2</td>
<td>24.4 ppm PCP</td>
<td>7.242</td>
<td>2.42</td>
</tr>
<tr>
<td></td>
<td>15.7 ppm phenol</td>
<td>6.991</td>
<td>1.49</td>
</tr>
</tbody>
</table>

What is the concentration of PCP in the sample?