CHEM 213
Chemical Analysis
Exam 1

1  __20___ (of 20)
2  __10___ (of 10)
3  __4____ (of 4)
4  __10___ (of 10)
5  __6____ (of 6)

Σ__50__ (of 50)

110%

KEY

Name: ___________________________________________
(please print)
1. Quinine may be determined by measuring the fluorescence intensity in 1 M H₂SO₄ solution. Standard solutions of quinine gave the following fluorescence values.

<table>
<thead>
<tr>
<th>Concentration of quinine x (µg mL⁻¹)</th>
<th>0.00</th>
<th>0.10</th>
<th>0.20</th>
<th>0.30</th>
<th>0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescence intensity y (arb. units)</td>
<td>0.00</td>
<td>5.20</td>
<td>9.90</td>
<td>15.30</td>
<td>19.10</td>
</tr>
</tbody>
</table>

a. Calculate by the least squares method the equation of the best straight line for the calibration curve. Report your result in the form \( y = [m(\pm s_m)]x + [b(\pm s_b)] \).

\[
\begin{array}{c|c|c|c|c|c|c|}
 x_i & y_i & x_i^2 & y_i^2 & x_i y_i \\
 0.00 & 0.00 & 0.00 & 0.00 & 0.00 \\
 0.10 & 5.20 & 0.01 & 27.04 & 0.52 \\
 0.20 & 9.90 & 0.04 & 98.01 & 1.98 \\
 0.30 & 15.30 & 0.09 & 234.09 & 4.59 \\
 0.40 & 19.10 & 0.16 & 364.81 & 7.64 \\
 \end{array}
\]

\[
\begin{align*}
\Sigma x_i &= 1.00 & \Sigma y_i &= 49.5 \\
\Sigma x_i^2 &= 0.30 & \Sigma y_i^2 &= 723.95 & \Sigma x_i y_i &= 14.73 \\
\end{align*}
\]

\[
\bar{x} = 0.20, \quad \bar{y} = 9.9
\]

\[
S_{xx} = \Sigma x_i^2 - (\Sigma x_i)^2/N = 0.30 - 1/5 = 0.1
\]

\[
S_{yy} = \Sigma y_i^2 - (\Sigma y_i)^2/N = 723.95 - 2450.25/5 = 233.9
\]

\[
S_{xy} = \Sigma x_i y_i - (\Sigma x_i)(\Sigma y_i)/N = 14.73 - (1)(49.5)/5 = 4.83
\]

\[
m = \frac{S_{xy}}{S_{xx}} = \frac{4.83}{0.1} = 48.3
\]

\[
b = \bar{y} - mx = 9.9 - (48.3)(0.20) = 0.24
\]

\[
s_r = \sqrt{\frac{S_{yy} - m^2S_{xx}}{N-2}} = \sqrt{\frac{233.9 - (48.3)^2(0.1)}{5-2}} = 0.4512944
\]

\[
s_m = \frac{s_r}{S_{xx}} = \frac{0.4512944}{0.1} = 4.512944
\]

\[
s_b = \frac{s_r}{\sqrt{\frac{\Sigma x_i^2}{N\Sigma x_i^2 - (\Sigma x_i)^2}}} = \frac{0.4512994}{\sqrt{\frac{0.30}{(5)(0.30)}}} = 0.3495677309
\]

Equation of best line:

\[
y = [48.3(\pm 1.4)]x + 0.24(\pm 0.35)
\]

b. An unknown quinine sample gave a fluorescence intensity of 10.20. Calculate the number of quinine in µg/mL in the unknown and estimate its uncertainty.

\[
x = (y - b)/m = (10.20 - 0.24)/48.3 = 0.2062112 = 0.21
\]

Uncertainty in x:

\[
s_c = \frac{s_r}{m} \left(\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_c - \bar{y})^2}{m^2S_{xx}}\right) = 0.4512994 \left(\frac{1}{1} + \frac{1}{5} + \frac{(10.20 - 9.9)^2}{(48.3)^2(0.1)}\right)
\]

\[
= 0.01 \text{ µg/mL}
\]

The final answer is 0.21 ± 0.01 µg/mL.
2. In a Kjeldahl nitrogen analysis, nitrogen in substances such as protein, milk, cereal, and flour is determined.

\[
\text{organic C, H, N} + \text{boiling H}_2\text{SO}_4 \rightarrow \text{NH}_4^+ + \text{CO}_2 + \text{H}_2\text{O}
\]

A typical protein contains 16.2 wt% nitrogen. A 0.500-mL aliquot of protein solution was digested, and the liberated NH$_3$ was distilled into 10.00 mL of 0.021 40 M HCl. The unreacted HCl required 3.26 mL of 0.019 8 M NaOH for complete titration. Find the concentration of protein (mg protein/mL) in the original sample. (10 points)

The initial amount of HCl in the receiver was \((10.00 \text{ mL}) \times (0.02140 \text{ mmol/mL}) = 0.214 \text{ mmol}\). The NaOH required for titration of unreacted HCl in the above reaction was \((3.26 \text{ mL})(0.0198 \text{ mmol/mL}) = 0.0645 \text{ mmol}\). The difference, \(0.214 – 0.0645 = 0.1495 \text{ mmol}\), must be equal to the quantity of NH$_3$ produced in produced and distilled into the HCl.

Because 1 mol of nitrogen in the protein produces 1 mol of NH$_3$, there must have been 0.1495 mmol of nitrogen in the protein, corresponding to:

\[(0.1495 \text{ mmol})(14.00674 \text{ mg N/mmol}) = 2.093 \text{ mg N}\]

If the protein contains 16.2 wt% N, there must be:

\[(2.093 \text{ mg N})/(0.162 \text{ mg N/mg protein}) = 12.9 \text{ mg protein}\]

\rightarrow (12.9 \text{ mg protein/0.500 mL}) = 25.8 \text{ mg protein/mL}\]
3. Analysis of a sample of iron ore gave the following percentage values for the iron content: 7.08, 7.21, 7.12, 7.09, 7.16, 7.14, 7.07, 7.14, 7.18, 7.11. Calculate the a) mean, b) standard deviation and c) coefficient of variation for the values. (4 points)

<table>
<thead>
<tr>
<th>Results (x)</th>
<th>x - (\bar{x})</th>
<th>(x – (\bar{x}))^2</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.08</td>
<td>-0.05</td>
<td>0.0025</td>
</tr>
<tr>
<td>7.21</td>
<td>0.08</td>
<td>0.0064</td>
</tr>
<tr>
<td>7.12</td>
<td>-0.01</td>
<td>0.0001</td>
</tr>
<tr>
<td>7.09</td>
<td>-0.04</td>
<td>0.0016</td>
</tr>
<tr>
<td>7.16</td>
<td>0.03</td>
<td>0.0009</td>
</tr>
<tr>
<td>7.14</td>
<td>0.01</td>
<td>0.0001</td>
</tr>
<tr>
<td>7.07</td>
<td>-0.06</td>
<td>0.0036</td>
</tr>
<tr>
<td>7.14</td>
<td>0.01</td>
<td>0.0001</td>
</tr>
<tr>
<td>7.18</td>
<td>0.05</td>
<td>0.0025</td>
</tr>
<tr>
<td>7.11</td>
<td>-0.02</td>
<td>0.004</td>
</tr>
</tbody>
</table>

\(\Sigma x = 71.30\) \hspace{1cm} \(\Sigma (x - \bar{x})^2 = 0.0182\)

Mean \(\bar{x} = 7.13\%\)

Standard deviation, \(s = \sqrt{\frac{0.0182}{9}} = \sqrt{0.0020} = \pm 0.045\%\)

Coefficient of Variation, \(CV = \frac{0.045 \cdot 100}{7.13} = 0.63\%\)
4. To measure the nickel content in steel, the alloy is dissolved in 12 M HCl and neutralized in the presence of citrate ion, which maintains iron in solution. The slightly basic solution is warmed, and dimethylglyoxime (DMG) is added to precipitate the red DMG-nickel complex quantitatively. The product is filtered, washed with cold water, and dried at 110 °C.

\[
\begin{align*}
\text{Ni}^{2+} + 2 \text{DMG} & \rightarrow \text{Bis(dimethylglyoximate)}\text{nickel(II)} + 2\text{H}^+ \\
\text{FM 58.69} & \quad \text{DMG} \\
\text{FM 116.12} & \quad \text{Bis(dimethylglyoximate)}\text{nickel(II)} \\
\text{FM 288.91}
\end{align*}
\]

If the nickel content is known to be near 3 wt % and you wish to analyze 1.0 g of the steel, what volume of 1.0 wt% alcoholic DMG solution should be used to give a 50% excess of DMG for the analysis? Assume that the density of the alcohol solution is 0.79 g/mL. (10 points)

Because the Ni content is around 3%, 1.0 g of steel will contain about 0.03 g of Ni, which corresponds to:

\[
\frac{(0.03 \text{ g Ni})}{(58.69 \text{ g Ni/mol Ni})} = 5.11 \times 10^{-4} \text{ mol Ni}
\]

This amount of metal requires:

\[
2(5.11 \times 10^{-4} \text{ mol Ni})(116.12 \text{ g DMG/mol Ni}) = 0.119 \text{ g DMG}
\]

because 1 mol of Ni\(^{2+}\) requires 2 mol of DMG. A 50% excess of DMG would be

\[
(1.5)(0.119 \text{ g}) = 0.178 \text{ g}
\]

This much DMG is contained in

\[
\frac{(0.178 \text{ g DMG})}{(0.010 \text{ g DMG/g solution})} = 17.8 \text{ g solution}
\]

which occupies a volume of

\[
\frac{(17.8 \text{ g solution})}{(0.79 \text{ g solution/mL})} = 23 \text{ mL}
\]
5. Traces of toxic, man-made hexachlorohexanes in North Sea sediments were extracted by a known process and by two new procedures, and measured by chromatography.

<table>
<thead>
<tr>
<th>Method</th>
<th>Concentration found (pg/g)</th>
<th>Standard deviation (pg/g)</th>
<th>Number of replications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conventional</td>
<td>34.4</td>
<td>3.6</td>
<td>6</td>
</tr>
<tr>
<td>Method A</td>
<td>42.9</td>
<td>1.2</td>
<td>6</td>
</tr>
<tr>
<td>Method B</td>
<td>51.1</td>
<td>4.6</td>
<td>6</td>
</tr>
</tbody>
</table>

a. Is the standard deviation for procedure B significantly different from that of the conventional procedure? \( \left( F_{\text{table}} = 5.05 \right) \) (3 points)

\[
F_{\text{calculated}} = \frac{4.6^2}{3.6^2} = 1.63 < F_{\text{table}} = 5.05. \quad \text{Standard deviations are not significantly different at the 95\% confidence level.}
\]

b. Is the mean concentration found by procedure B significantly different from that of the conventional procedure? \( \left( t_{\text{table}} = 2.365 \right) \) (3 points)

Because \( F_{\text{calculated}} < F_{\text{table}} \), we can use:

\[
s_{\text{pooled}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}
\]

\[
s_{\text{pooled}} = \sqrt{\frac{4.6^2(6 - 1) + 3.6^2(6 - 1)}{6 + 6 - 2}} = 4.13
\]

\[
t_{\text{calculated}} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{\text{pooled}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}}
\]

\[
t_{\text{calculated}} = \frac{|51.1 - 34.4|}{4.13 \sqrt{\frac{(6)(6)}{6 + 6}}} = 7.00
\]

Because \( t_{\text{calculated}} > t_{\text{table}} \) \( (2.228 \text{ for 10 degrees of freedom}) \), the difference is significant at the 95\% confidence level.