Chem 201 Lecture 2a

Brief discussion of Experiments:

Ni, pH, Cu-ASV, Cu-AA

Propagation of Errors

Statistics

Reminder

All the lab protocols are posted in the website:
www.calstatela.edu/dept/chem/09summer/201
Download these protocols
Download the policies on laboratory practice
Determine YOUR sequence of lab experiments. (it depends
on your locker #.)
Pay careful attention to the instructions!

Nickel Experiment (Ni)

Gravimetric: involves selective precipitation of Ni

Ppt’n rxn: Ni^{2+} + 2 DMG ---> Ni(DMG)_{2} (red ppt) (pH9)

Ni ore: dry to const wt (Δm =±0.0004g); use weighing bottle
Red precipitate filtered on glass crucible and dried.

\[ \Delta \text{mass} = m_{\text{ppt}} - m_{\text{crucible}} = g \text{Ni(DMG)}_{2} \]

\[ g \text{Ni(DMG)}_{2} = \frac{58.69g\text{Ni}}{288.94g\text{Ni(DMG)}_{2}} \times 100\% \]

% Ni = 

Nickel …procedures and reagents

Understand the roles of the various reagents and the steps
involved in the process…for example,
nitric acid, tartaric acid, 6M NH_{3},
pH 8-9, alcoholic DMG, heating not boiling,

Digestion what to do if you don’t have enough time to
finish the digestion process…
Where’s a good place to stop?

On day 1, at point in which you added DMG before digestion.

Soda Ash Expt. (pH)

Acid-base titration involving diprotic base, Na_{2}CO_{3}.

Dry ASAP: a) 1g Na_{2}CO_{3} and b) Soda ash unknown.

Standardize HCl standard using Na_{2}CO_{3}.

Unknown ore contains Na_{2}CO_{3} + inert soluble material
Determine %Na_{2}CO_{3} (or as %Na_{2}O) in unknown, 2 methods:
a) indicator method; b) pH-meter/Gran Plot method.

Use 2nd eq. pt. for %Na_{2}CO_{3} determination of unk. ore.

Soda Ash Expt. (pH)

Theory: 2 equiv. pts (at 2 diff. pH’s, thus 2 diff indicators):

(1) CO_{3}^{2-} + H^{+} --> HCO_{3}^{-}
(2) HCO_{3}^{-} + H^{+} --> H_{2}CO_{3}

Net: CO_{3}^{2-} + 2 H^{+} --> H_{2}CO_{3}

You derive: Standardization: M_{HCl} = 2 \left( \frac{g_{Na_{2}CO_{3}}}{105.99} \right) / V_{2eq}

Unk: %Na_{2}CO_{3} = M_{HCl}V_{2eq}(105.99)(100%) / 2_{2eq}

Note relation: Na_{2}CO_{3} --> Na_{2}O + CO_{2}(g)

Sometimes %Na_{2}O is calculated instead of %Na_{2}CO_{3}
To determine \( V_{2e} \)

Problems often encountered in the 2 titrations using indic.

a) Unclear 1st equiv. pt. (phenolphthalein is used)

b) Unclear 2nd e.p. (methyl orange used-color change slight?)

3rd titration needed: pH vs mLs of HCl every 1 mL.

Use Gran Plot (read it in book!)

Gran plot: \( V_{iCl} \times 10^{pH} \) (y-axis) vs mL HCl (x-axis)

Copper-ASV (Cu-ASV)

Technique is ASV = Anodic Stripping Voltammetry

Dry entire unknown for 1 hour. No need for second heating. (save remaining unknown for Cu AA)

Prepare standard Cu\(^{2+}\) solutions by serial dilution.

Solvent used is 0.1N HNO\(_3\).

Plot peak current, \( I_p \) vs ppm Cu\(^{2+}\).

Copper-ASV (Cu-ASV)

alternate calculation

In linear region it’s possible to use standard addition method.

- signal (I) i.e. the current peak, \( I_p \), is directly proportional to the total [Cu\(^{2+}\)] in solution.

Therefore: \( \frac{I_{\text{std+unk}}}{I_{\text{unk}}} = \frac{[\text{Cu}\^{2+}]_{\text{std+unk}}}{[\text{Cu}\^{2+}]_{\text{unk}}} \)

So if you have \( x = [\text{Cu}]_{\text{unk}} \) and \( s = [\text{Cu}]_{\text{std}} \) then

\( \frac{I_x + s}{I_x} = \frac{x + s}{x} \)

You measure the signal for 2 samples: one with unk and one with the unk “spiked” with known std. And solve for \( x \).

Copper-AA

Dry unknown Cu ore for 1 hour (1 time)

Prep standard Cu\(^{2+}\) solutions. As per instructions.

Plot Signal (A) vs ppm Cu. It’s important for Cu unk absorption to be within the linear range of A vs ppm curve.

Theory: Cu atoms sprayed into the flame absorb at very specific wavelengths. In the linear range, absorption is proportional to ppm Cu.

\( A = k[\text{Cu}] \) \( k \) some constant.
Uncertainty, Accuracy, Precision

Uncertainty = “error”: systematic vs random
Systematic = determinate, can be corrected
Random = “indeterminate”, can’t be corrected
Absolute uncertainty, ± e, associated with measurement, x
Relative unc. = ± e / x ; %e = 100% (e / x)
Precision = measure of reproducibility of measurement
Accuracy = measure of closeness to true value

Statistics: many measurements

Mean = “average” = ȳ = Σx / n
Standard deviation, s = (∑(x - ȳ)² / (n-1))¹/²

Learn to use the standard deviation function in your scientific calculator

Gaussian curve:
Gaussian curve: Y vs x

Confidence intervals

Confidence interval = range on either side of the measured mean likely to contain the true mean.

\[ \mu = \bar{x} \pm \frac{t(s)}{\sqrt{n}} \]

- \( \bar{x} \) = measured mean
- \( s \) = measured std deviation
- \( t \) = student’s t value (from a table) and \( n \) = # measurements

Useful for comparing and concluding if “null hypothesis” is disproven, i.e. if there is “significant” difference. (that means 95% confidence usually).

Student’s t

<table>
<thead>
<tr>
<th>( x )</th>
<th>( y )</th>
<th>( t )</th>
<th>( n )</th>
<th>( s )</th>
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<tbody>
<tr>
<td>0.6</td>
<td>0.3989</td>
<td>0.0901</td>
<td>1.4</td>
<td>0.1387</td>
</tr>
<tr>
<td>0.15</td>
<td>0.1325</td>
<td>0.3432</td>
<td></td>
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<tr>
<td>0.91</td>
<td>0.3978</td>
<td>0.0931</td>
<td>1.2</td>
<td>0.1205</td>
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<tr>
<td>0.82</td>
<td>0.3914</td>
<td>0.1179</td>
<td>1.7</td>
<td>0.9041</td>
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<tr>
<td>0.4</td>
<td>0.3643</td>
<td>0.1545</td>
<td>1.8</td>
<td>0.6739</td>
</tr>
<tr>
<td>0.45</td>
<td>0.3553</td>
<td>0.191</td>
<td>1.9</td>
<td>0.6656</td>
</tr>
<tr>
<td>0.6</td>
<td>0.3332</td>
<td>0.2235</td>
<td>2.0</td>
<td>0.8044</td>
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<tr>
<td>0.7</td>
<td>0.3128</td>
<td>0.2569</td>
<td>2.1</td>
<td>0.8648</td>
</tr>
<tr>
<td>0.8</td>
<td>0.2867</td>
<td>0.2891</td>
<td>2.2</td>
<td>0.8303</td>
</tr>
<tr>
<td>0.9</td>
<td>0.2869</td>
<td>0.2139</td>
<td>2.3</td>
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<tr>
<td>1.0</td>
<td>0.2483</td>
<td>0.2413</td>
<td>2.4</td>
<td>0.8024</td>
</tr>
<tr>
<td>1.1</td>
<td>0.1968</td>
<td>0.3639</td>
<td>2.6</td>
<td>0.8136</td>
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<tr>
<td>1.2</td>
<td>0.1771</td>
<td>0.4092</td>
<td>2.7</td>
<td>0.8014</td>
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</tbody>
</table>

Case I Comparing measured result with a “known” value

Example: We measure O₃ in the air 5 times, and obtain an average ± sd of

Use: \( t \) = \( \frac{x_{ave} - \bar{x}}{s} \)

Compare \( t \) with \( t_{calc} \): if \( t_{calc} > t_{table} \) it’s different

\[ t_{calc} = \frac{|x - x_{ave}| \sqrt{n}}{s} \]

Case II Comparing Replicate Measurements

Comparing 2 populations and seeing if they are “significantly different”. E.g. comparing the cholesterol levels of 2 groups of people which differ by diet.

\[ t_{calc} = \frac{|x_1 - x_2|}{s_{pooled} \sqrt{n_1/n_1 + n_2/n_2}} \]

\[ s_{pooled} = \sqrt{s_1^2 (n_1 - 1) + s_2^2 (n_2 - 1) / n_1 + n_2 - 2} \]
Case III. Comparing Individual Differences

For instance, testing whether two different methods of analysis give significantly different results, based on a measurement of various samples.

Use:
\[ t_{calc} = \frac{d_{avg}}{s_d \sqrt{n}} \]

Where:
\[ s_d = \sqrt{\frac{\sum(d_i - d_{avg})^2}{n - 1}} \]

Q-test: for outliers

Outliers = data numerically distant from the rest of the data.

Example:
2.31, 2.34, 2.34, 2.34, 2.79

Q_{calc} = \frac{gap}{range}

If Q_{calc} > Q_{table}, discard

<table>
<thead>
<tr>
<th>Q_{calc}</th>
<th>gap</th>
<th>range</th>
<th>decision</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.94</td>
<td>0.44</td>
<td>2.34-2.31</td>
<td>discard</td>
</tr>
</tbody>
</table>

Table 4.5: Values of Q for rejection of data

\[
<table>
<thead>
<tr>
<th>Q</th>
<th>Number of observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.70</td>
<td>4</td>
</tr>
<tr>
<td>0.76</td>
<td>5</td>
</tr>
<tr>
<td>0.84</td>
<td>6</td>
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<tr>
<td>0.91</td>
<td>7</td>
</tr>
<tr>
<td>0.97</td>
<td>8</td>
</tr>
<tr>
<td>0.94</td>
<td>9</td>
</tr>
<tr>
<td>0.94</td>
<td>10</td>
</tr>
</tbody>
</table>

Note: Q_{table} values are for 10% confidence level.