

Chem 201 Lecture 2a

Brief discussion of Experiments:
Ni, pH, Cu-ASV, Cu-AA
Propagation of Errors
Statistics

Last time, we discussed...

- 2 lab experiments: Mn and Fe
- Dilutions
- Concentration units
- Significant figures
- Rules for sig figs

Today we discuss

- 4 lab experiments: Ni, Cu-AA, pH, F
- Uncertainty, precision, accuracy
- Basic statistical concepts: standard deviation

Nickel Experiment (Ni)

- Gravimetric: involves selective precipitation of Ni
- Ppt'n rxn: $\text{Ni}^{2+} + 2 \text{DMG} \rightarrow \text{Ni}(\text{DMG})_2$ (red ppt) (pH9)
- Ni ore: dry to const wt ($\Delta m = \pm 0.0004\text{g}$); use weighing bottle
- Red precipitate filtered on glass crucible and dried.
- $\Delta \text{mass} = (g_{\text{crucible}} + \text{ppt}) - (g_{\text{crucible}}) = g_{\text{Ni}(\text{DMG})_2}$
- $\% \text{Ni} = \frac{g_{\text{Ni}(\text{DMG})_2} \times (58.69 \text{ g Ni})}{g_{\text{Ni ore}} (288.94 \text{ g Ni}(\text{DMG})_2)} \times 100\%$

Ni ...procedures and reagents

- Understand roles of various reagents and 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 not enough time to finish digestion... (Where's a good place to stop?) (answer: On day 1, at point right after DMG is added)

Soda Ash Expt. (pH)

- Acid-base titration involving diprotic base, Na_2CO_3 .
- Start drying ASAP:
 - a) 1 g std Na_2CO_3 (good to 4 dec. places) and
 - b) Soda ash unknown.
- Standardize 0.1 M HCl standard using std Na_2CO_3 .
- Unknown ore contains Na_2CO_3 + inert soluble material
- Goal: Determine $\% \text{Na}_2\text{CO}_3$ (or as $\% \text{Na}_2\text{O}$) in unknown, 2 titration methods used:
 - a) indicator method;
 - b) pH-meter/**Gran Plot method**.
- Use 2nd eq. pt. for $\% \text{Na}_2\text{CO}_3$ determination of unk. ore.

Soda Ash Expt. (pH)

- Theory: 2 equiv. pts (2 diff. pH's, thus 2 diff indicators):
 - (1) $\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^-$ here, $V_{\text{HCl}} = V_{\text{ep}}$ ("ep"=equiv. point)
 - (2) $\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3$ here, $V_{\text{HCl}} = V_{2\text{ep}}$ (total added)
- Net: $\text{CO}_3^{2-} + 2\text{H}^+ \rightarrow \text{H}_2\text{CO}_3$
- Standardization: $M_{\text{HCl}} = \frac{2(g \text{ Na}_2\text{CO}_3 / 105.99)}{V_{2\text{ep}}}$
- Unk: $\% \text{Na}_2\text{CO}_3 = M_{\text{HCl}} V_{\text{HCl}} (105.99) (100\%) / 2g_{\text{ore}}$
- Note relation: $\text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{O} + \text{CO}_2(\text{g})$
- Sometimes $\% \text{Na}_2\text{O}$ is calculated instead of $\% \text{Na}_2\text{CO}_3$ (use gravimetric factor, $g \text{ Na}_2\text{O} / g \text{ Na}_2\text{CO}_3$)

To determine $V_{2\text{ep}}$

Problems often encountered in indicator titrations:

- Unclear 1st equiv. pt. (phenolphthalein used)
 - Unclear 2nd e.p. (methyl orange used)
- 3rd titration: meas. pH vs mLs of HCl every 1 mL.

- Use Gran Plot (**read it in book!**)
- Gran plot: $V_{\text{HCl}} \times 10^{\text{pH}}$ (y-axis) vs mL HCl (x-axis)

Cu-AA (Copper atomic absorption)

- Dry unknown Cu ore for 1 hour (once is enough)
 - Prep standard Cu^{2+} solutions. As per instructions.
 - Plot Signal (A) vs ppm Cu. Important for Cu unk absorption to be within linear range of A vs ppm curve.
 - Theory: Cu atoms vaporized in flame absorb at very specific wavelengths.
- In the linear range, absorption is proportional to ppm Cu:
- $$A = k[\text{Cu}] \text{ where } k = \text{a constant.}$$

Cu-AA Equipment

Fluoride (F) experiment

- Uses ion-selective electrode (ISE) specific for F
- Requires acidic buffered solution (read up)
- Plot of log ppm vs mV gives straight line

Uncertainty, Accuracy, Precision

- Uncertainty= "error" : systematic vs random
- Systematic=determinate, can be corrected
- Random ="indeterminate", can't be corrected
- Absolute uncertainty, $\pm ex$, associated with measurement, x
- Relative unc. = $\pm ex / x$; $\%ex = 100\% (ex/x)$
- Precision = measure of reproducibility of measurement
- Accuracy = measure of closeness to true value
- Know Table 3.1

Know Table 3.1

Statistics: many measurements

- Mean = “average” = $\bar{x} = \sum x_i / n$
- Standard deviation, $s = \{(\sum(x_i - \bar{x})^2) / (n-1)\}^{1/2}$
- Learn to use the std deviation function in your scientific calculator

Gaussian curve:

Confidence intervals

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

$$\mu = \bar{x} \pm (ts) / \sqrt{n} \quad \text{where } s = \text{measured std deviation;}$$

$t = \text{student's } t \text{ value (from a table) and } n = \# \text{ measurements}$

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

Case I Comparing measured result with a “known” value

- Example: We measure O_3 in the air 5 times, and obtain an average \pm sd
- Use: $\mu = \bar{x}_{\text{ave}} \pm \frac{ts}{\sqrt{n}}$
- Compare t_{table} with t_{calc} : if $t_{\text{calc}} > t_{\text{table}}$ then it's different.

$$t_{\text{calc}} = \frac{|\bar{x} - x_{\text{ave}}| \sqrt{n}}{s}$$

Case 2: 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.

Case 2...

- $t_{\text{calc}} = \frac{|x_1 - x_2|}{s_{\text{pooled}}} \sqrt{\frac{n_1 n_2}{n_1 + n_2}}$
- Where $s_{\text{pooled}} = \sqrt{\frac{(s_1^2 (n_1 - 1) + s_2^2 (n_2 - 1))}{n_1 + n_2 - 2}}$

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.

Case III: Paired t test for comparing indiv. differences

$$t_{\text{calc}} = \frac{d_{\text{ave}}}{s_d} \sqrt{n}$$

$$d_{\text{ave}} = \sqrt{\frac{\sum (d_i - d_{\text{ave}})^2}{n - 1}}$$

Q-test : for outliers

- Outliers= data numerically distant from rest of the data
 - Example: 2.79, 2.33, 2.31, 2.34, 2.35
 - Rearrange: 2.31, 2.33, 2.34, 2.35, 2.79
 - $Q_{\text{calc}} = \frac{\text{gap}}{\text{range}} = \frac{2.79 - 2.35}{2.79 - 2.31} = 0.92$
- If $Q_{\text{calc}} > Q_{\text{table}}$, discard