Data Analysis IV

CU- Boulder

CHEM-4181

Instrumental Analysis Laboratory

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Lecture will be posted on course web page – based on lab manual, Skoog, web links

Business Items

- Data analysis HW due on Friday
- We'll likely have class on Fri (finish writing)
  - If not, bring HW to my office (Ekeley M329, corridor above)
    - Put under door if I am not there
  - Penalty for being late: same as for labs, see notebook

Hypothesis Testing (HT)

- A hypothesis is put forward and tested statistically
- Examples:
  - Check for absence of systematic differences between 2 sets of measurements
    - E.g. your COD measurements before pooling to estimate σ
  - Check whether the measurement is above or below a cutoff value
    - E.g. Mn content in steel
- Calculations: just use distribution of $\bar{x}$
- Calculate probability for z or t:

$$z = \frac{\bar{x} - \mu}{\sigma / \sqrt{N}} \qquad t = \frac{\bar{x} - \mu}{s / \sqrt{N}}$$

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{N}}$$

$$\mu = \bar{x} \pm \frac{z\sigma}{\sqrt{N}}$$

- http://www.chem.uoa.gr/Applets/AppletTtest/Appl_Ttest2.html

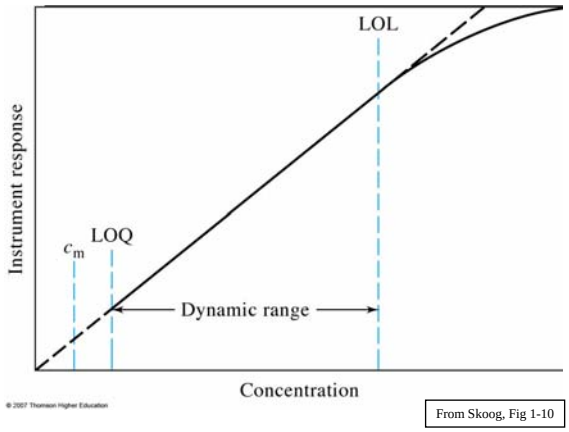
Hypothesis Testing Example

- A new faster method has been developed to determine Mn in steel
- We use the new method 3 times for a sample known to contain 100.0 ppm Mn
  - Results: 102, 104, 103 (s = 1)
- CQ: at 95% confidence level, is the new method biased?

A. Yes
B. No
C. It depends
D. I don't know

Calibration Curves I

- Linear Dynamic Range (LDR)
  - Different for each instrument and *analyte*
  - Interpolation is safe; Extrapolation is very dangerous



From Skoog, Fig 1-10

Calibration Curves II

- Limit of Detection (LOD)
  - Also $\overline{x}_b$+3 s_b
  - Specify how you estimate LOD
- Limit of Quantification (LOQ)
  - Level above which a concentration is considered quantitative
  - LOQ = $\overline{x}_b$+10 s_b
- Method Detection Limit (MDL)
  - LOD converted to concentration in the original matrix
    - E.g. apply percent recovery

$$LOD = \bar{x}_b + ts_b\sqrt{\frac{N_{sample} + N_{blank}}{N_{sample}N_{blank}}}$$

From p.14 of laboratory notebook & Chapter 1 of Skoog

Propagation of Uncertainties I

- Situation
  - The final calculated result may be a function of several experimental measurements
    - $x = f(p, q, r, \ldots)$
  - We need to estimate the error in x from the errors in p, q, r…
- It can be shown (p. 980-981 of Skoog) that:

$$s_x^2 = \left(\frac{\partial x}{\partial p}\right)^2 s_p^2 + \left(\frac{\partial x}{\partial q}\right)^2 s_q^2 + \left(\frac{\partial x}{\partial r}\right)^2 s_r^2 + \ldots$$

- Q: estimate s_x when:

  (1) $x = p + q - r$ (2) $x = p/q + r$

Propagation of Uncertainties II

- Using the rule in the previous slide, the following relationships can be shown:

TABLE a1-6 Error Propagation in Arithmetic Calculations

Type of Calculation	Example[a]	Standard Deviation of y
Addition or subtraction	$x = p + q - r$	$s_x = \sqrt{s_p^2 + s_q^2 + s_r^2}$
Multiplication or division	$x = p \times q/r$	$\frac{s_x}{x} = \sqrt{\left(\frac{s_p}{p}\right)^2 + \left(\frac{s_q}{q}\right)^2 + \left(\frac{s_r}{r}\right)^2}$
Exponentiation	$x = p^y$	$\frac{s_x}{x} = y\left(\frac{s_p}{p}\right)$
Logarithm	$x = \log_{10} p$	$s_x = 0.434\frac{s_p}{p}$
Antilogarithm	$x = \text{antilog}_{10} p$	$\frac{s_x}{x} = 2.303\, s_p$

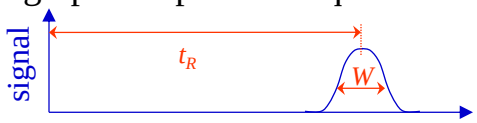
[a] p, q, and r are experimental variables with standard deviations of s_p, s_q, and s_r, respectively.

From Skoog

Propagation of Uncertainties III

- The number of plates, N, in a chromatographic separation equals:

$$N = 16\left(\frac{t_R}{W}\right)^2$$



- CQ: If t_R = 100 ± 1 s (1σ) & W = 1 s What is the 95% CI in N?

A. 160,000 ± 100
B. 160,000 ± 1100
C. 160,000 ± 3200
D. 160,000 ± 4300
E. I don't know

Quality Control Procedures

- Method blank
  - Do analysis with DI water (or purified sand etc.)
  - Measure of interferences, contamination…
  - Convert to concentration, report, subtract if > LOQ
- Duplicate
  - Another sample for which you do all analysis steps
    - (Not only last measurement)
  - Another measure of precision, need to report
    - Concerned if RSD > 15%
- Matrix spike
  - Add a known amount of standard to sample before analysis
  - Used to control for extraction efficiency & matrix effects
  - Obtain % recovery, report, use for your sample

From p.16 of laboratory notebook

Sigfigs vs. Confidence Intervals

- CQ: which of the following is correct?
  A. 95% CI = 300.1253 +/- 0.0234
  B. 95% CI = 300.125 +/- 0.023
  C. 95% CI = 300.12 +/- 0.02
  D. 95% CI = 300.1 +/- 0.0
  E. 95% CI = 300.12536 +/- 0.02347