Updated: 31 August 2014

Print version

CEE 772: Instrumental Methods in Environmental Analysis

Lecture #2

Introduction: Error and Statistics

(Skoog, Chapt. 1D)

(pp.11-18)

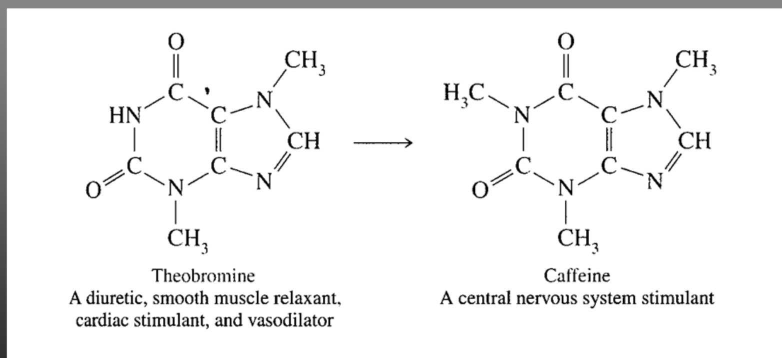
(Harris, Chapt. 1-4)

(pp.13-86)

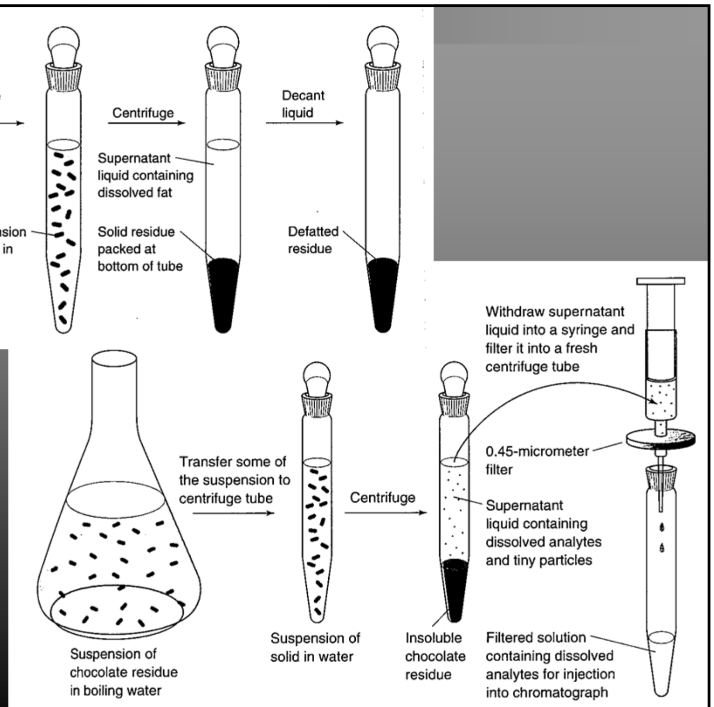
Standard Procedures #1

- Quantitative Transfer
  - Question of quantity
    - How low can you go?
  - Exchanges with atmosphere
    - Volatilization
    - absorption
- Preparation of standard solutions
  - Measure analyte & solvent precisely

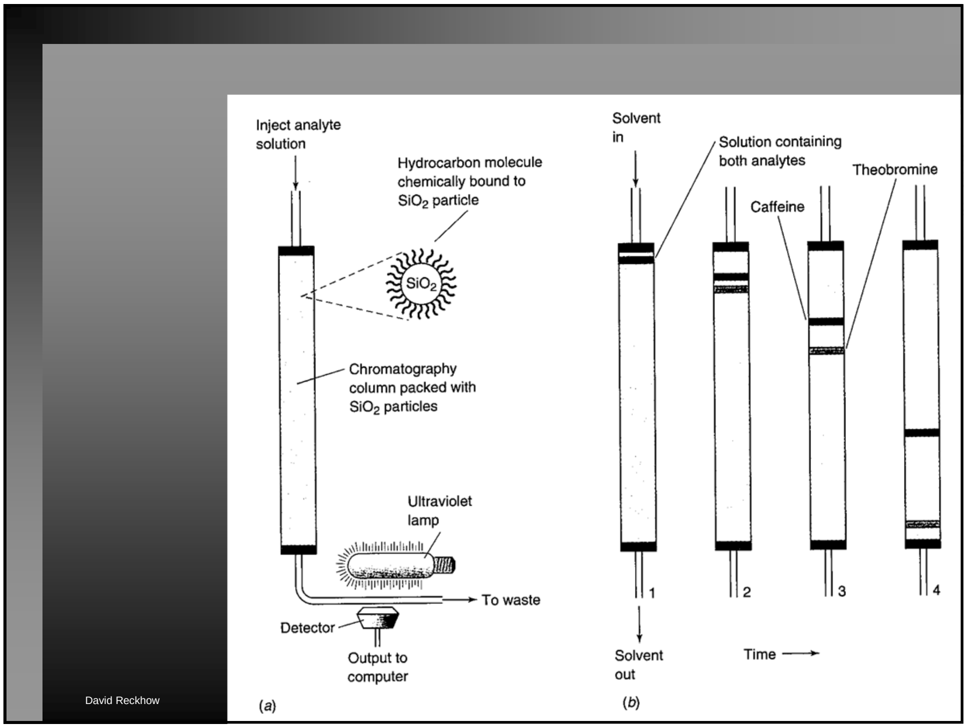
Harris's Chocolate example

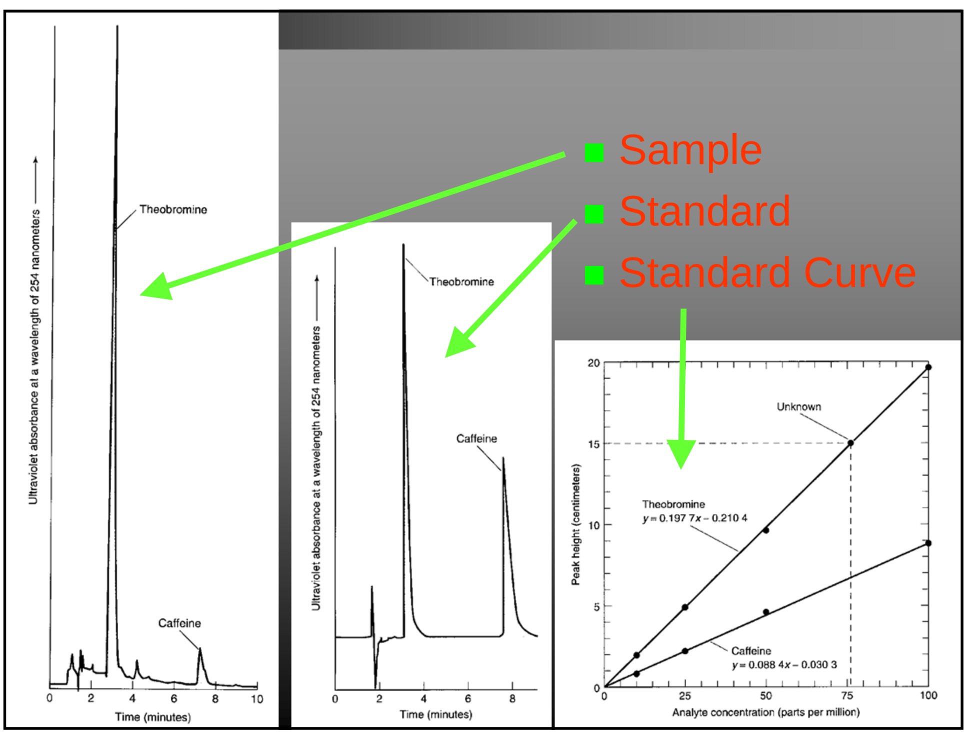


David Reckhow CEE 772 #2 3



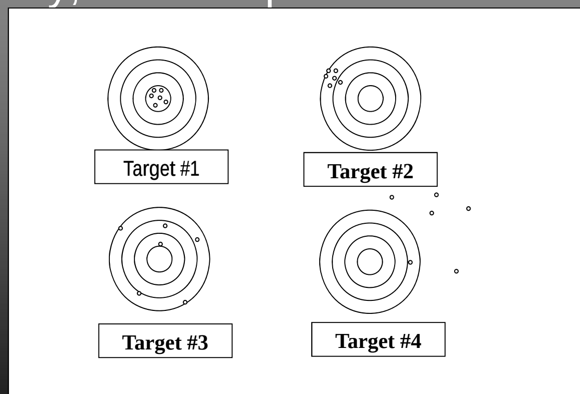
David Reckhow


Inject analyte solution
Hydrocarbon molecule chemically bound to SiO_2 particle
SiO_2
Chromatography column packed with SiO_2 particles
Ultraviolet lamp
To waste
Detector
Output to computer
(a)
Solvent in
Solution containing both analytes
Theobromine
Caffeine
1
2
3
4
Solvent out
Time
(b)
David Reckhow


Sample
Standard
Standard Curve
Theobromine
Caffeine
Ultraviolet absorbance at a wavelength of 254 nanometers
Time (minutes)
0
2
4
6
8
10
Unknown
Theobromine
y = 0.197 7x − 0.210 4
Caffeine
y = 0.088 4x − 0.030 3
Peak height (centimeters)
Analyte concentration (parts per million)
0
5
10
15
20
25
50
75
100

Parametric Statistics

- Accuracy, bias and precision



David Reckhow CEE 772 #2 7

- Central Tendency
  - mean
  - median
  - mode

$$\overline{x} = \frac{\sum x}{n}$$

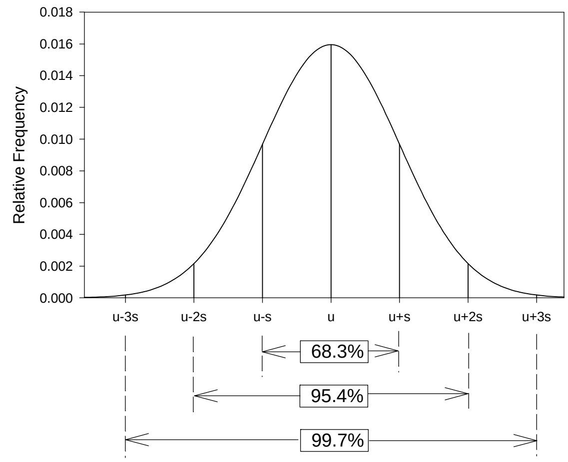
- Variance & standard deviation

$$s = \sqrt{\frac{\sum (x - \overline{x})^2}{n-1}} = \sqrt{\frac{\sum x^2 - \left[(\sum x)^2 / n \right]}{n-1}}$$

$$s_{pooled} = \sum^{k} s_i^2 (n_i - 1) \Big/ \sum (n_i - 1)$$

David Reckhow CEE 772 #2 8

The Normal Distribution



David Reckhow CEE 772 #2 9

Propagation of Errors

- Multiplication or Division by a constant
  - n(x ±s) = nx ±ns
- Addition or subtraction $(x_1 \pm s_1) + (x_2 \pm s_2) = (x_1 + x_2) \pm \sqrt{s_1^2 + s_2^2}$

$$(x_1 \pm s_1) - (x_2 \pm s_2) = (x_1 - x_2) \pm \sqrt{s_1^2 + s_2^2}$$

- Multiplication or Division

$$(x_1 \pm s_1)(x_2 \pm s_2) = (x_1 x_2) \pm x_1 x_2 \sqrt{\left(\frac{s_1}{x_1}\right)^2 + \left(\frac{s_2}{x_2}\right)^2}$$

$$(x_1 \pm s_1) \div (x_2 \pm s_2) = (x_1 / x_2) \pm (x_1 / x_2) \sqrt{\left(\frac{s_1}{x_1}\right)^2 + \left(\frac{s_2}{x_2}\right)^2}$$

David Reckhow CEE 772 #2 10

Confidence Intervals

- Requires an estimate of the standard error of the mean

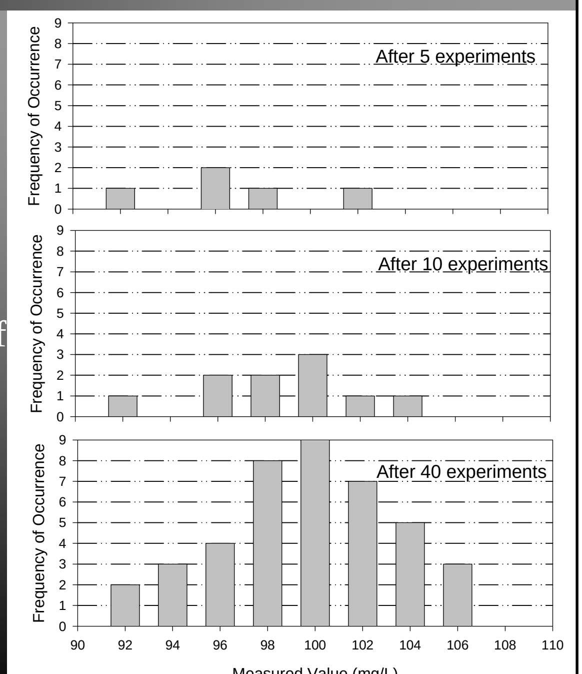
$$s_{\overline{x}} = \frac{s}{\sqrt{n}}$$

- This is then combined with a "t-statistic"

$$\mu = \overline{x} \pm t s_{\overline{x}}$$

David Reckhow CEE 772 #2 11

- Frequency Histogram of Replicate Determinations of an Analyte
  - (the true value is 100 ppm)



David Reckhow

Degrees of Freedom	Alpha Values				
	10%	5%	2.5%	1%	0.5%
1	3.078	6.314	12.706	31.821	63.657
2	1.886	2.920	4.303	6.965	9.925
3	1.638	2.353	3.182	4.541	5.841
4	1.533	2.132	2.776	3.747	4.604
5	1.476	2.015	2.571	3.365	4.032
6	1.440	1.943	2.447	3.143	3.707
7	1.415	1.895	2.365	2.998	3.499
8	1.397	1.860	2.306	2.896	3.355
9	1.383	1.833	2.262	2.821	3.250
10	1.372	1.812	2.228	2.764	3.169
15	1.341	1.753	2.131	2.602	2.947
20	1.325	1.725	2.086	2.528	2.845
inf.	1.282	1.645	1.960	2.326	2.576

Example Problem

- 75 mL sample volume

	TDS	TS
#1	0.0433 g	0.0475 g
#2	0.0401 g	0.0461 g
#3	0.0498 g	0.0495 g
#4	0.0442 g	0.0509 g

Example (cont.)

	TDS	TS	$(TDS)^2$	$(TS)^2$
#1	0.0433 g	0.0475 g	0.0018749	0.0022563
#2	0.0401 g	0.0461 g	0.0016080	0.0021252
#3	0.0498 g	0.0495 g	0.0024800	0.0024503
#4	0.0442 g	0.0509 g	0.0019536	0.0025908
Σ =	0.1774 g	0.1940 g	0.0079166	0.0094225
$\bar{x}$ =	0.0444 g	0.0485 g		
=	591 mg/L	647 mg/L		

TSS = TS-TDS
= 647-591 mg/L = 56 mg/L

David Reckhow CEE 772 #2 15

Example (cont.)

$$s_{TDS} = \frac{1}{0.075L}\sqrt{\frac{0.0079166-(0.1774)^2/4}{3}}g = 53mg / L$$

$$s_{TS} = \frac{1}{0.075L}\sqrt{\frac{0.0094225-(0.1940)^2/4}{3}}g = 28\text{ mg/L}$$

David Reckhow CEE 772 #2 16

Example (cont.)

- What is the standard error of the mean for TSS of the river water from Example 23.1? What is the 95% confidence interval for this number?
- First a standard error of the mean must be calculated for each of the two direct measurements, TDS and TS.

$$s_{\overline{TDS}} = \frac{53}{\sqrt{4}} = 27 mg / L$$

$$s_{\overline{TS}} = \frac{28}{\sqrt{4}} = 14 mg / L$$

- Next, equation 23.7 may be used directly to propagate these standard errors

$$(647 \pm 14) - (591 \pm 27) = (647 - 591) \pm \sqrt{14^2 + 27^2}$$
$$= 56 \pm 30 mg / L$$

Example (cont.)

- Finally, use equation 23.11 to calculate the confidence interval. The number of degrees of freedom will be 6 (i.e, [n_{TDS}-1]+[n_{TS}-1]=6). The alpha value will be 2.5%.

$$\mu = 56 \pm (2.447)(30)$$
$$= 56 \pm 73 mgL$$

- To next lecture