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CEE 772: Instrumental Methods in Environmental Analysis

Lecture #2

Introduction: Error and Statistics

(Skoog, Chapt. 1D)

(pp.11-18)

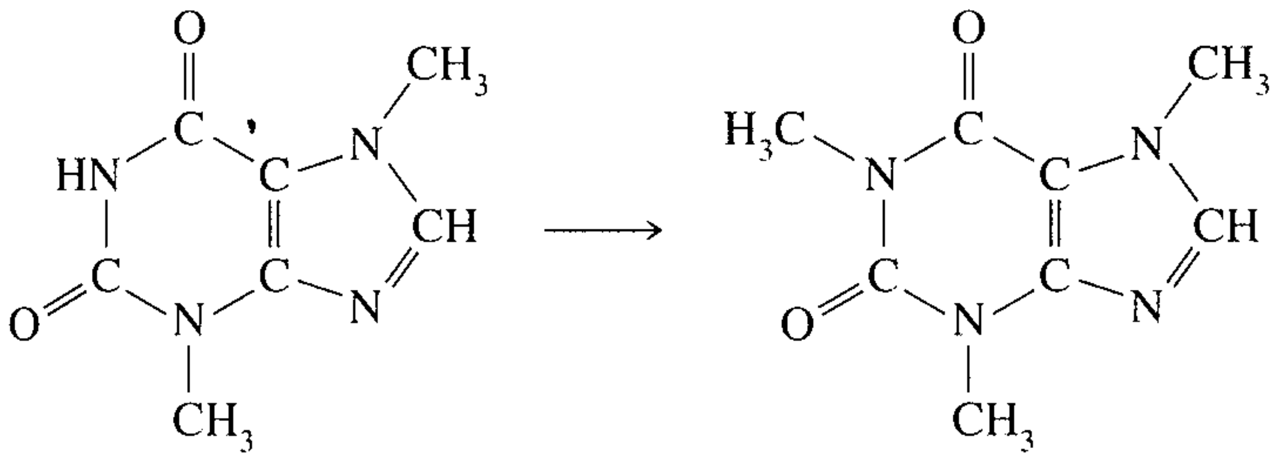
(Harris, Chapt. 1-4)

(pp.13-86)

Standard Procedures #1

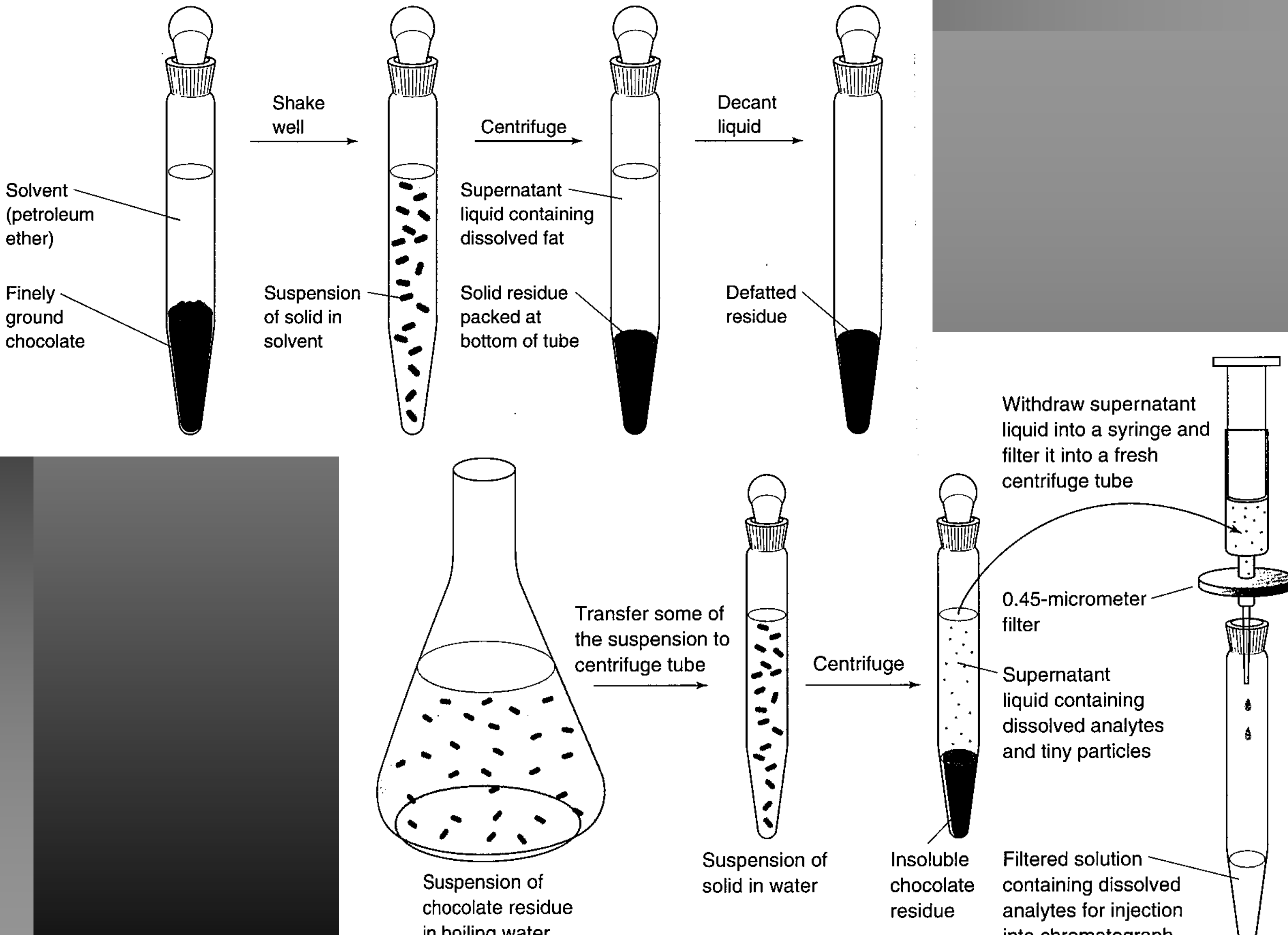
- Quantitative Transfer
  - Question of quantity
    - How low can you go?
  - Exchanges with atmosphere
    - Volatilization
    - absorption
- Preparation of standard solutions
  - Measure analyte & solvent precisely

Harris's Chocolate example

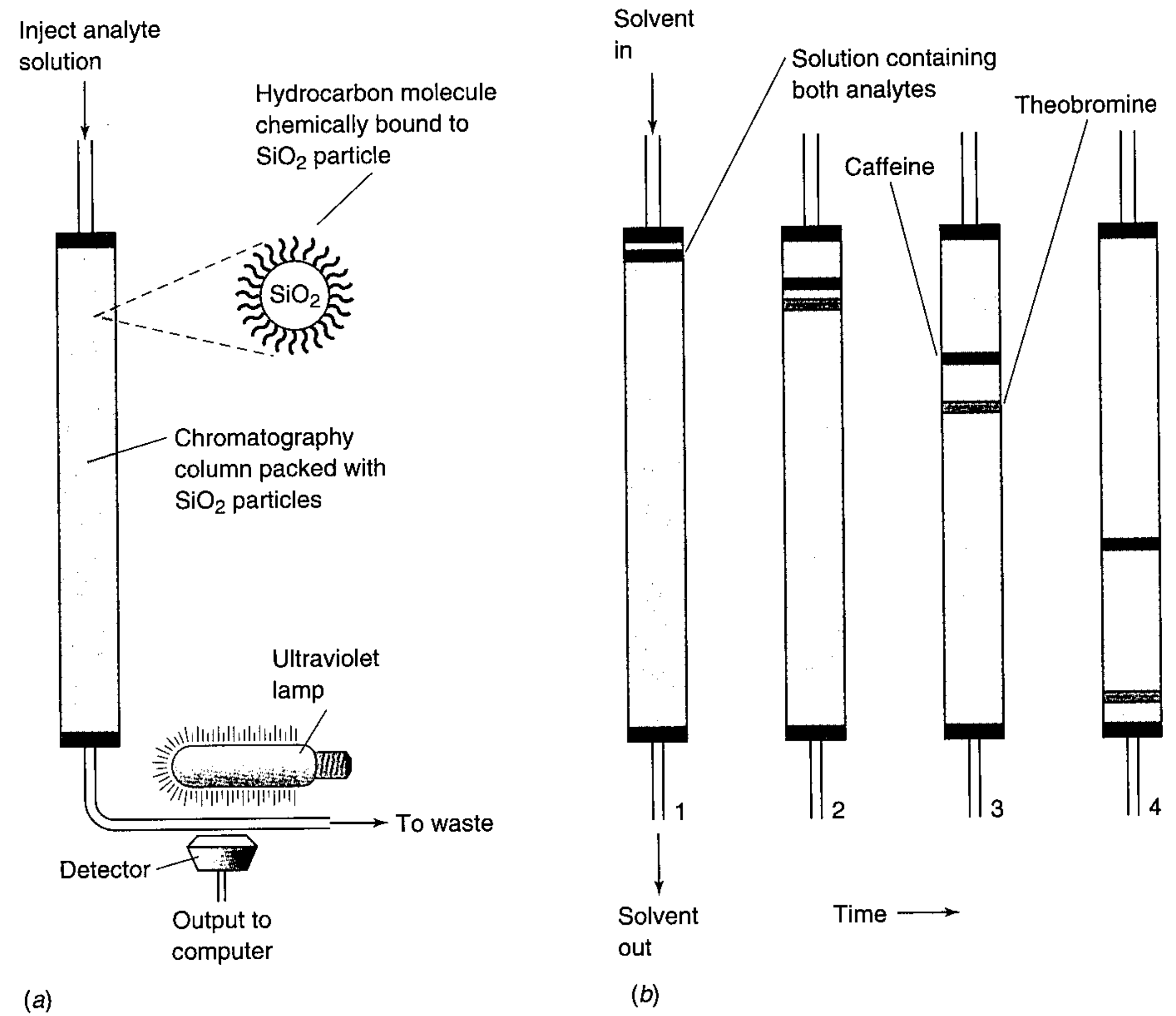


Theobromine
A diuretic, smooth muscle relaxant, cardiac stimulant, and vasodilator

Caffeine
A central nervous system stimulant

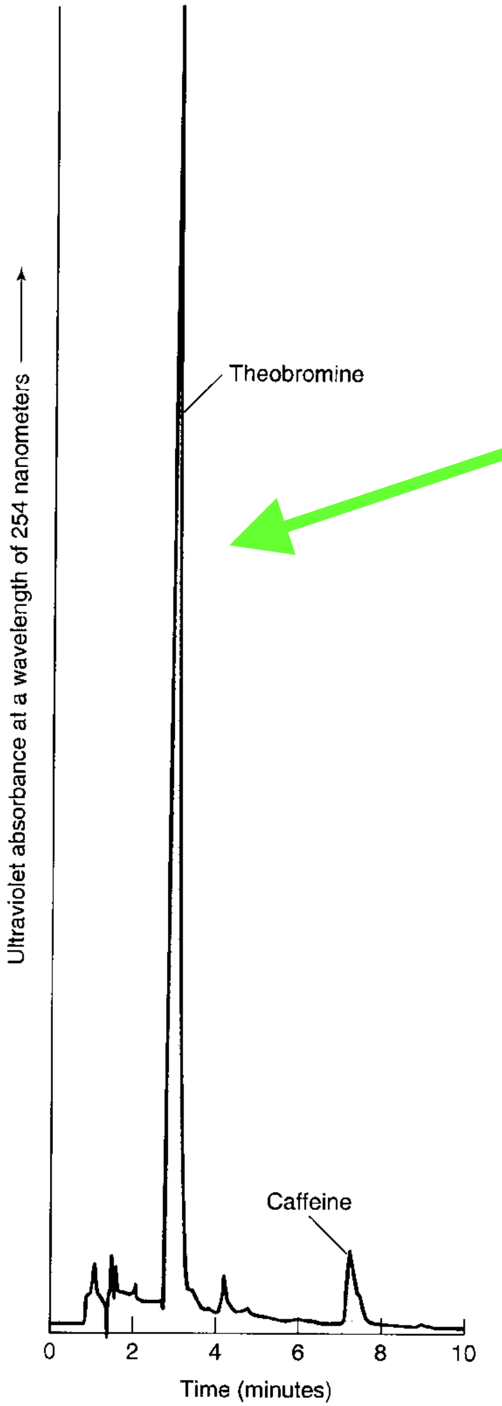


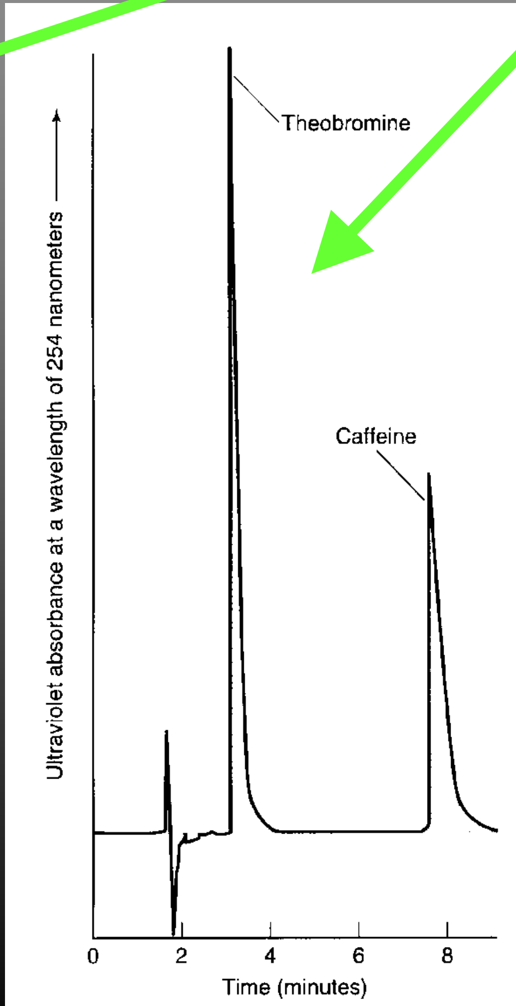
Shake well
Centrifuge
Decant liquid
Solvent (petroleum ether)
Finely ground chocolate
Suspension of solid in solvent
Supernatant liquid containing dissolved fat
Solid residue packed at bottom of tube
Defatted residue
Withdraw supernatant liquid into a syringe and filter it into a fresh centrifuge tube
Transfer some of the suspension to centrifuge tube
Centrifuge
0.45-micrometer filter
Supernatant liquid containing dissolved analytes and tiny particles
Suspension of chocolate residue in boiling water
Suspension of solid in water
Insoluble chocolate residue
Filtered solution containing dissolved analytes for injection into chromatograph

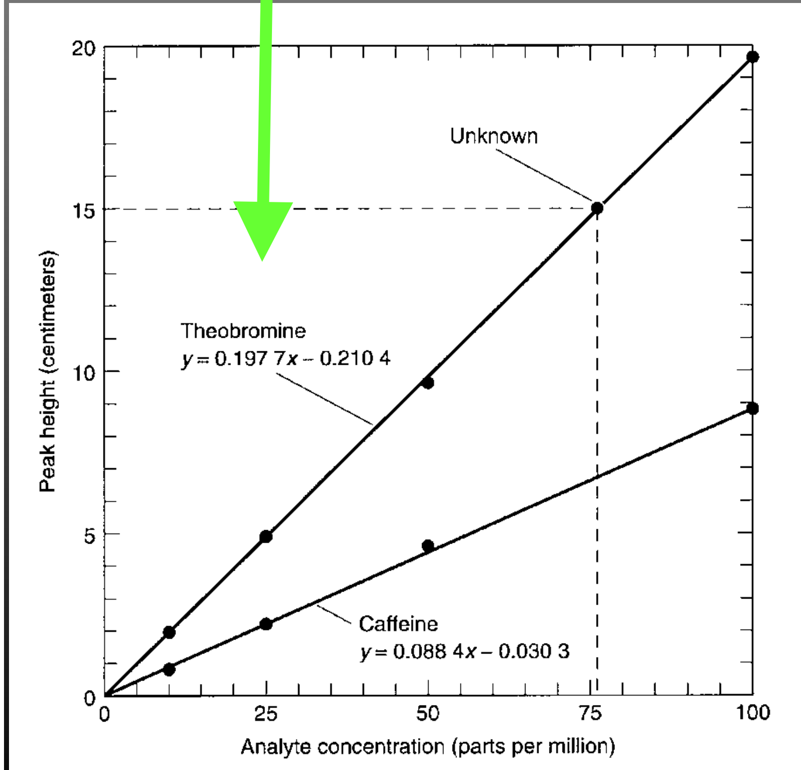


Inject analyte solution
Hydrocarbon molecule chemically bound to SiO_2 particle
SiO_2
Chromatography column packed with SiO_2 particles
Ultraviolet lamp
To waste
Detector
Output to computer
(a)
Solvent in
Solution containing both analytes
Theobromine
Caffeine
1
2
3
4
Solvent out
Time
(b)

- Sample
- Standard
- Standard Curve

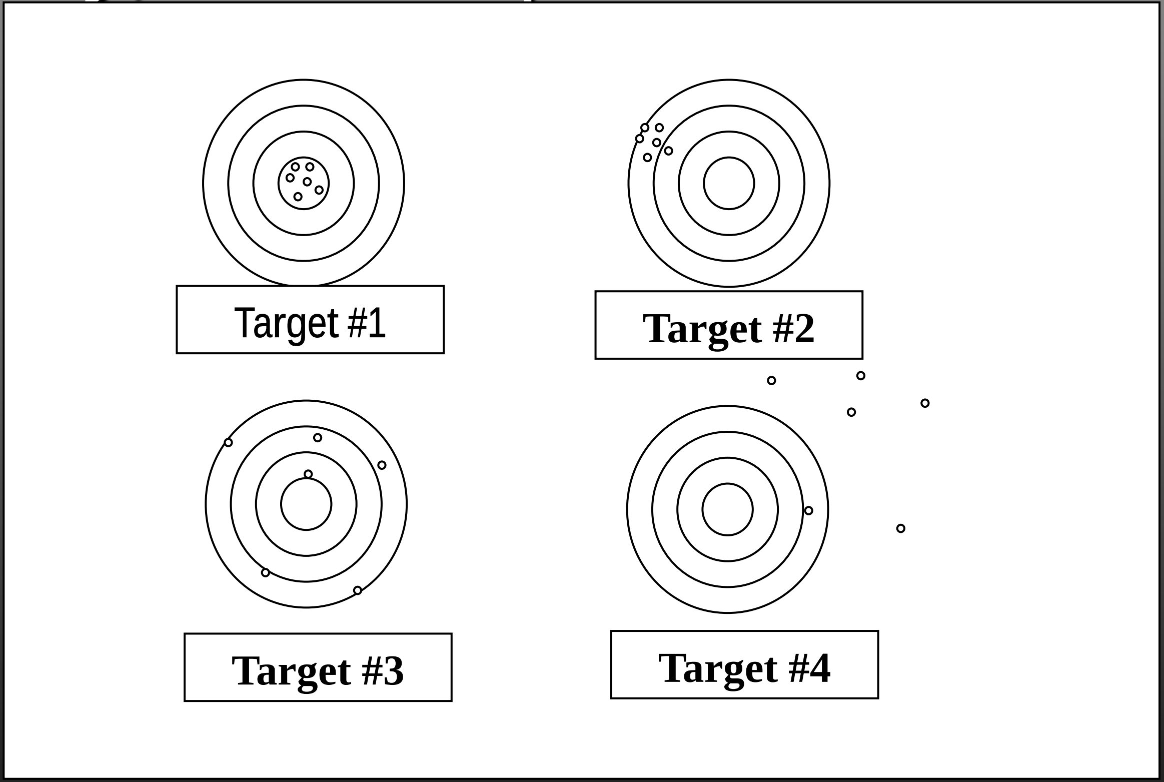






Parametric Statistics

- Accuracy, bias and precision



- Central Tendency
  - mean
  - median
  - mode

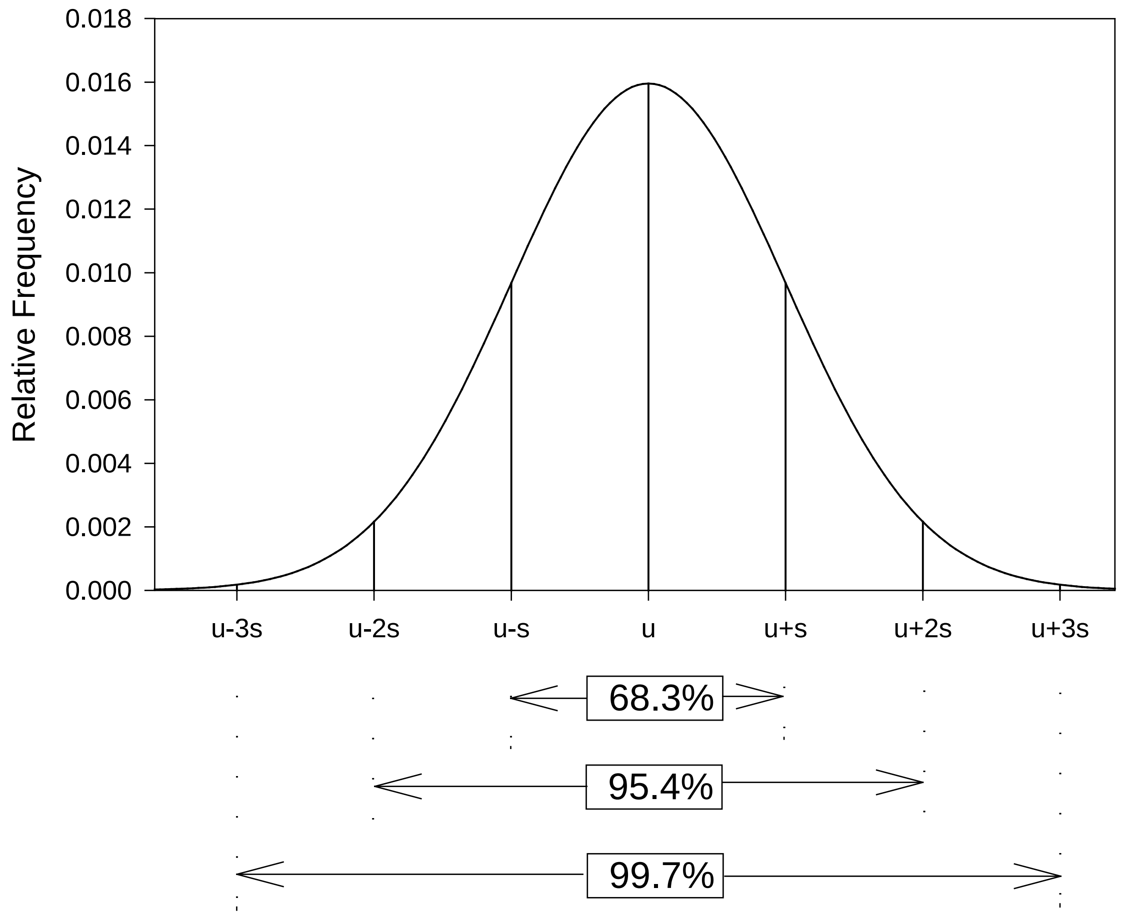
$$\bar{x} = \frac{\sum x}{n}$$

- Variance & standard deviation

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

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

The Normal Distribution



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

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

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

Confidence Intervals

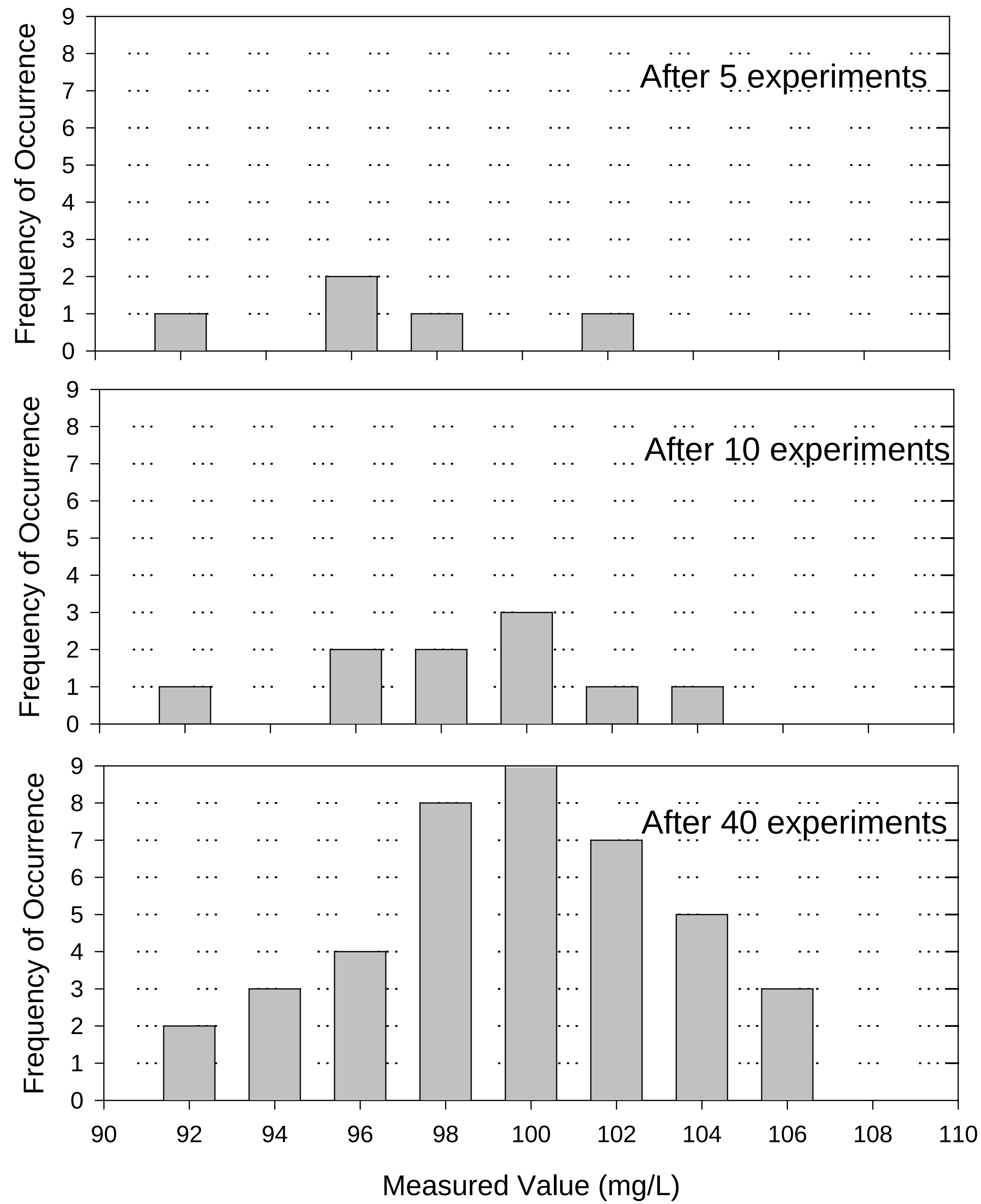
- Requires an estimate of the standard error of the mean

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

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

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

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



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

Example (cont.)

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

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

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.

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

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

- 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