Analytical Chemistry – what is it?

Analytical Chemistry Definitions

"Analytical chemistry involves separating, identifying and determining the relative amounts of the components in a sample of matter"
Fundamentals of Analytical Chemistry, Skoog, West & Holler, pg. 1

"Analytical chemistry is concerned with the theory and practice of methods used to determine the composition of matter"
Quantitative Analysis, Day & Underwood, pg. 1

"Analytical chemistry is the field of chemistry dealing with the theory, development and practice of methods used to probe the composition of all phases of matter"
Chem 2080 course notes, Robert McLaren, page 1

Qualitative analysis - identifying *what* is present in a sample

Quantitative Analysis - determining how much (the amount of) analyte present in a sample.

Analyte – the chemical material we analyze for.

Subfields of Analytical Chemistry

Classical Analytical Chemistry
usually refers to volumetric and gravimetric methods of analysis. Still used today in small scale analysis. The theory is still absolutely essential for modern instrumental analysis.

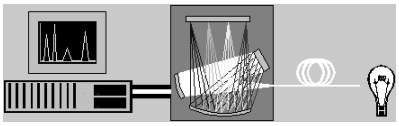
Instrumental Analysis
theory and operation of instruments used in analytical chemistry. Many, many,… types of instruments.

Analytical Separations (chemical equilibrium + detectors)
- gas chromatography
- liquid chromatography
- supercritical fluid chromatography
- electrophoresis

Electroanalytical methods (electrons)
- coulometry
- voltammetry
- amperiometry

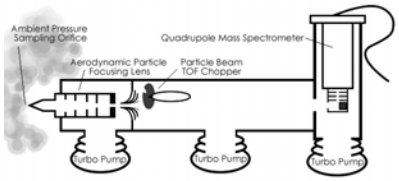
Subfields – cont'd

Analytical Spectroscopy (photons)



- **absorbance**
- **fluorescence, phosphorescence**
- **Raman**
- **infrared**
- **photothermal**
- **atomic absorption/atomic emission**

Other (photons, electrons, magnetic fields)



- **refractive index**
- **mass spectrometry**
- **scattering**
- **optical activity**
- **radiometry**

Interfaces & Hyphenated methods

separation method + detection method
gas chromatography + mass spectrometry (GC/MS)
liquid chromat + nuclear magnetic resonance (HPLC/NMR)
capillary zone electrophoresis + laser induced fluorescence (CZE/LIF)

Analytical chemistry plays an essential role in several other fields of science including physical, organic, inorganic and atmospheric chemistry, biochemistry, medicine, biology, environmental sciences, geology, forensic science, space exploration, etc.

The Analytical Method

Steps to take in an analytical procedure (eg- you are handled a sample and told to analyze it.

1. **D**ecision
2. **S**ampling
3. **S**eparation
4. **M**esurement
5. **E**valuation

DSS ME !

What role do nitrogen oxides play in air pollution episodes in the Strait of Georgia between Vancouver and Vancouver Island?

The Analytical method – cont'd

Steps in a quantitative analysis

1. **Decision - definition of problem and method selection**
   - **what is the question and what steps must we take to answer it**
   - **what analytes are we looking for?**
   - **major, minor or trace constituents in sample?**
   - **how many samples?**
   - **what accuracy?**
   - **most cost effective method?**

2. **Sampling - sampling and preliminary treatment**
   - **sample must represent average composition of material**
   - **how do we sample water in the ocean?, an ore sample in a railcar? air sample representative of a 5 x 5 km region? (day or night), snow composition in the arctic? Caffeine in chocolate?**
   - **dissolution and preconcentration of sample**

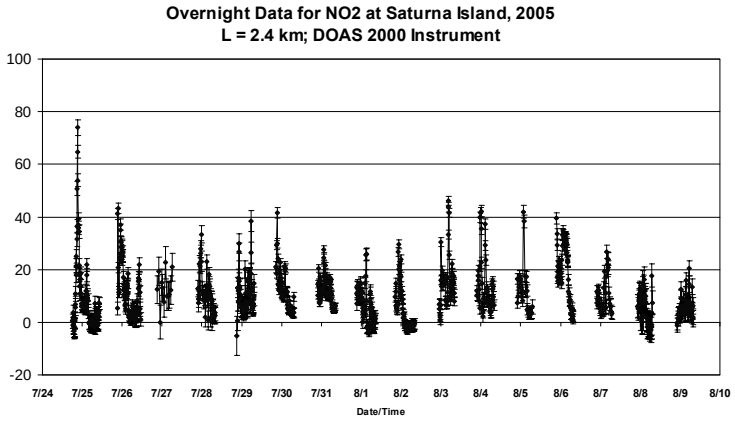
3. **Separation**
   - **elimination of interferences (ie- fat in chocolate)**
   - **separation of multiple components for analysis (ie. Gas chromatographic analysis of a gasoline sample)**

Steps in Analytical method – cont'd

4. **Measurement**
   - **final preparation of sample for analysis**
   - **calibration of instrument**
   - **measurement of replicate samples**

Evaluation

5. **Evaluation - calculation, evaluation and interpretation**
   - **what is the expected accuracy and precision?**
   - **what is the statistical uncertainty in the analysis.**
   - **is the sample representative?**
   - ***what does the analysis tell us with reference to the original question?***



Units of Operation

Mass - gram or kilogram

g	**-**	**gram**
mg	**-**	**milligram (10^{-3}g)**
μg	**-**	**microgram (10^{-6}g)**
ng	**-**	**nanogram (10^{-9}g)**
pg	**-**	**picogram (10^{-12}g)**
fg	**-**	**femtogram (10^{-15})**
ag	**-**	**attogram (10^{-18})**
zg	**-**	**zeptogram (10^{-21})**

Amount - mole
(1 mole = 6.022 x 10^{23} units)

Volume - liter or m^3 (SI unit) are standard

1 dm x 1 dm x 1 dm = 1dm3 = 1000 cm^3 = 1 L
1 cm x 1 cm x 1 cm = 1cm^3 = 1 x 10^{-3}L = 1 mL
1 mm x 1 mm x 1 mm = 1mm^3 = 1 x 10^{-6}L = 1 μL
.1 mm x .1 mm x .1 mm = .001mm^3= 1 x 10^{-9}L = 1 nL

Concentration - Molarity (M) - moles/L
- most frequently used. Convenient unit since we frequently do manipulations of liquid material in the lab using known volumes

Units – cont'd

Molality (m) - moles/kg
- used infrequently *but* advantage is that it is temperature independent. (ie-volume changes with temperature, mass doesn't). disadvantage is that all materials must be weighed.

ppm & ppb - parts per million (billion)

- grams of substance per 10^6 grams of solute
- can be mass based or volume based
- assume mass based if ppm
- otherwise ppmV specifies volume
-in gaseous samples, ppm and ppb usually refer to ppmV since ideal gas law states that n = PV/RT = K * V. ppm and ppb in this respect are *mole ratios*

ie - Canadian Air Quality objective for O_3 is <u>82 ppb (V).</u>
this means 82 x 10^{-6} mole of ozone per mole of air molecules.

Amount = concentration x volume *<u>or</u>* concentration x mass

eg. How many moles in 230 pL of a solution that is 7x10^{-9}M of analyte dye

Amount = CV = 7x10^{-9} mol/L x 230x10^{-12} L = 1.6 x 10^{-18} moles = 1.6 attomoles

The Laboratory Notebook

A hardbound record of your activities in the laboratory, including procedures, measurements & special observations. The notebook should (and could!!) be considered to be a legal record of your activities in the lab. The requirements of a good notebook are:

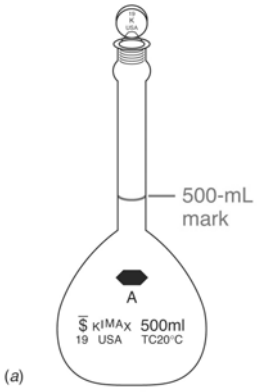
- **hardcover**
- **consecutively numbered pages**
- **index of experiments in first few pages referencing pages**
- **pages dated**

Use of the Notebook

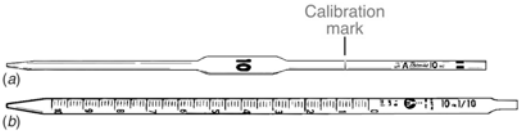
- ☺ **always use pen**
- ☺ **record data and observations directly in your notebook**
- ☺ **date each page as it is used**
- ☺ **record title of new experiment**
- ☺ **use descriptive subheadings (ie. <u>Titration volumes (ml)</u>)**
- ☺ **cross out mistakes with a single line 1.2374 ~~1.2347~~**
- ☺ **SHOULD BE UNDERSTANDABLE TO A STRANGER**

- ***X*** **never use pencil**
- ***X*** **never use scraps**
- ***X*** **don't assume you will remember all details. Record it!**
- ***X*** **do not obliterate results or rip out pages**

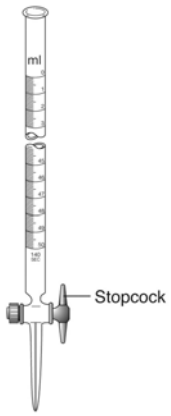
Glassware



Volumetric Flask



Transfer pipets – TD (to deliver)

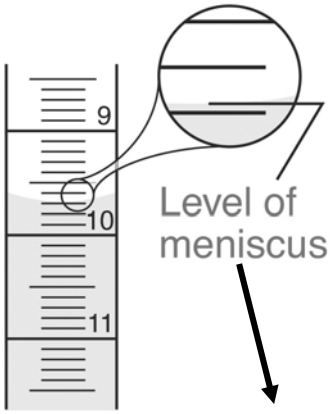


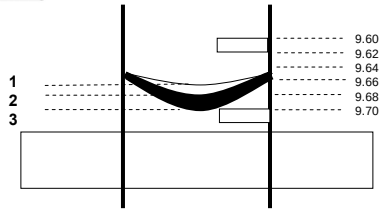
Buret

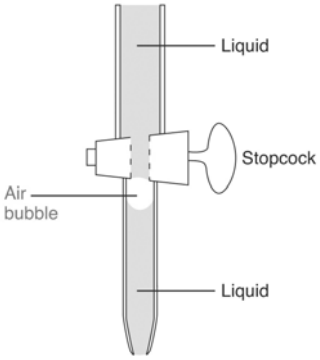
Table 2-3 Tolerances of Class A volumetric flasks

Flask capacity (mL)	Tolerance (mL)
1	±0.02
2	±0.02
5	±0.02
10	±0.02
25	±0.03
50	±0.05
100	±0.08
200	±0.10
250	±0.12
500	±0.20
1 000	±0.30
2 000	±0.50

Reading Burets







- **Ensure there are no air bubbles**
- **read buret to 0.01 mL digit**
- **use reading card just below meniscus for high precision**
- **try to read using "position 2" on meniscus, but otherwise BE CONSISTENT; 9.67 or 9.68 mL**
-- **watch out for parallax error**

Calibration of Glassware

Purpose:

i. **to obtain higher accuracy than could be obtained based upon the tolerance alone**
ii. **to allow one to practice proper technique and show the limits of very precise work.**

Method:

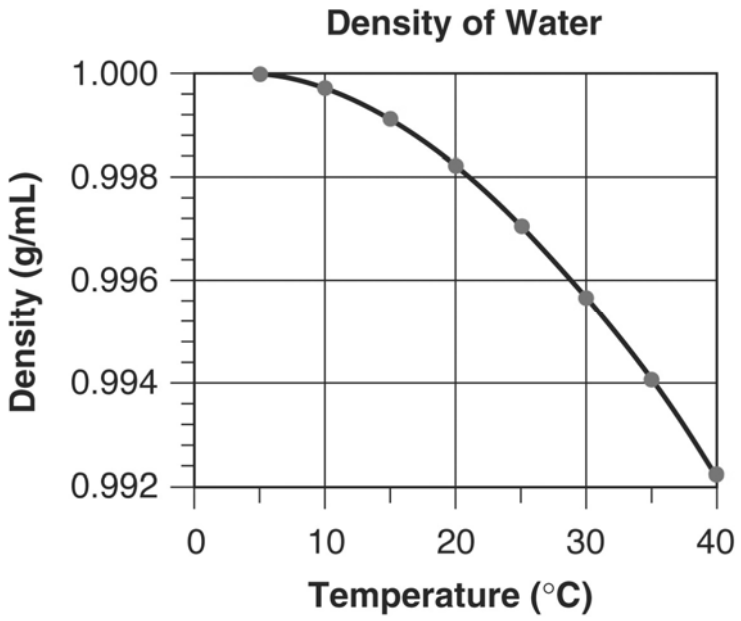
accurately weigh volumes of distilled water that have been delivered (pipet or buret) using volumetric glassware. Since the density of water is known very accurately, we can calculate the *exact* volume using:

$$V_{H2O} = \frac{m_{H2O}}{\rho_{H2O}}$$

where V_{H2O} = volume of H_2O, m_{H2O} = mass of H_2O, ρ_{H2O} = density of H_2O

Minor modifications are made to the above calculation to take into account the bouyancy correction and the variation in volume of glassware wrt temperature. These are given in tabular format. See lab manual for a more complete discussion.

Variation of Density of Water with Temperature



Variation of $1/\rho_{H2O}$ with Temperature

Table 2-7 Density of water

Temperature (°C)	Density (g/mL)	Volume of 1 g of water (mL) At temperature shown[a]	Volume of 1 g of water (mL) Corrected to 20°C[b]
10	0.999 702 6	1.001 4	1.001 5
11	0.999 608 4	1.001 5	1.001 6
12	0.999 500 4	1.001 6	1.001 7
13	0.999 380 1	1.001 7	1.001 8
14	0.999 247 4	1.001 8	1.001 9
15	0.999 102 6	1.002 0	1.002 0
16	0.998 946 0	1.002 1	1.002 1
17	0.998 777 9	1.002 3	1.002 3
18	0.998 598 6	1.002 5	1.002 5
19	0.998 408 2	1.002 7	1.002 7
20	0.998 207 1	1.002 9	1.002 9
21	0.997 995 5	1.003 1	1.003 1
22	0.997 773 5	1.003 3	1.003 3
23	0.997 541 5	1.003 5	1.003 5
24	0.997 299 5	1.003 8	1.003 8
25	0.997 047 9	1.004 0	1.004 0
26	0.996 786 7	1.004 3	1.004 2
27	0.996 516 2	1.004 6	1.004 5
28	0.996 236 5	1.004 8	1.004 7
29	0.995 947 8	1.005 1	1.005 0
30	0.995 650 2	1.005 4	1.005 3

a. Corrected for buoyancy with Equation 2-1.

b. Corrected for buoyancy and expansion of borosilicate glass (0.001 0% K^{-1}).

For very very careful work, it is necessary to know the T at which solution is prepared, T° AND used, T. The Concentration of solution can then be corrected for changes in the density of H_2O, ρ° and ρ respectively.

$$C(T) = C(T^{\circ}) \times \frac{\rho(T)}{\rho(T^{\circ})}$$

Buoyancy

Buoyancy refers to the upward force exerted on an object of density ρ_{int} by it's surroundings of density ρ_{ext}.

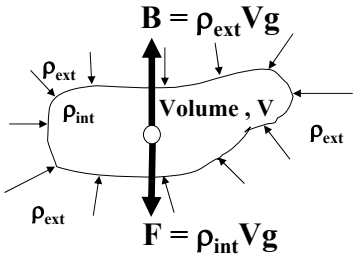
Archimedes established the magnitude of this buoyant force over 2000 years ago. The buoyant force which acts upwards on the object is independent of the density of the object : $B = \rho_{ext}Vg$

The force of gravity also acts on the object,

$F = ma = mg = p_{int}Vg$

The net upward force acting on the object is:

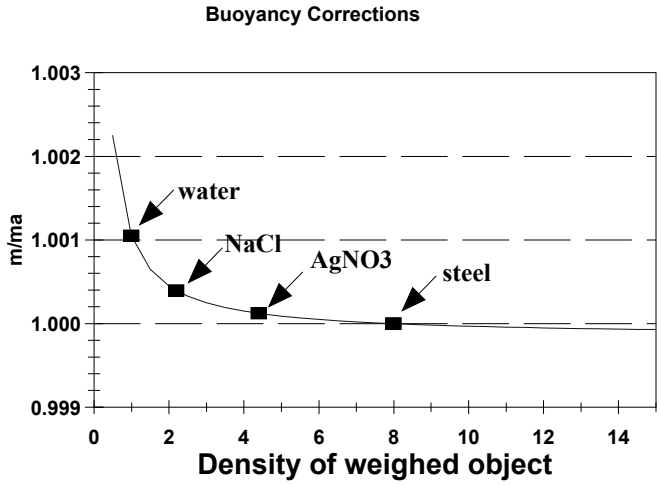
$$F = B - mg = \rho_{ext}Vg - \rho_{int}Vg$$
$$= (\rho_{ext} - \rho_{int})\, Vg$$



For our purposes in this course, the mass of an object weighed on the CALIBRATED analytical balance needs to be corrected for the change in a buoyant force operating on steel weights (r ~ 8.0 g/mL) compared to the buoyant force operating on the material being weighed with different density, ie water with r ~ 1.0 g/mL.

$$m = \frac{m'(1 - \frac{\rho_{air}}{\rho_{weights}})}{(1 - \frac{\rho_{air}}{\rho_{material}})}$$

Buoyancy Corrections



m = true mass m_a = apparent mass

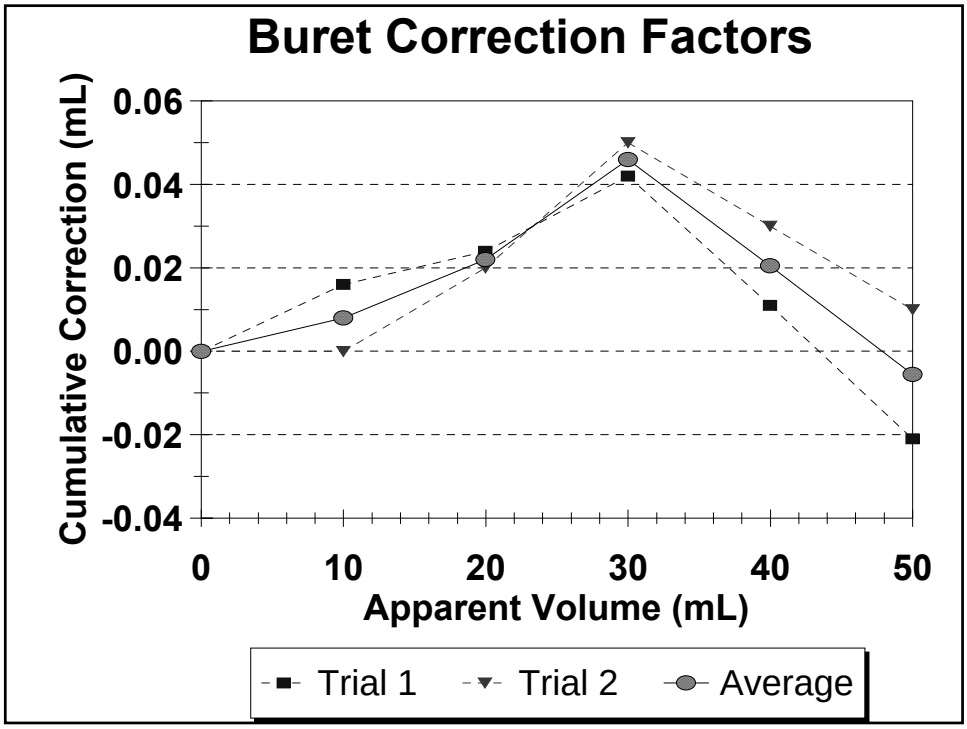
Example Calibration for Buret

Table 1: Example Calculations for Buret Calibration at 25°C

Interval	Buret Reading (mL)	Apparent Volume (mL)	Weight (g)	Weight of Water (g)	True Volume (mL)*	Correction (mL)**	Cumulative Correction (mL)
Initial	0.03		36.4505				0.00
0-10	10.02	9.99	46.4202	9.9697	10.00659	+ 0.016	+ 0.016
10-20	20.01	9.99	56.3818	9.9616	9.99846	+ 0.008	+ 0.024
20-30	30.01	10.00	66.3624	9.9806	10.01753	+ 0.018	+ 0.042
30-40	39.98	9.97	76.2643	9.9019	9.93854	- 0.031	+ 0.011
40-50	49.99	10.01	86.2053	9.9410	9.97778	- 0.032	- 0.021

* at 20°C
** Correction = True Volume - Apparent Volume

we then draw a graph of cumulative volume correction vs. *apparent* buret reading (ie- ~0, 10, 20, 30, 40, 50 mL). This graph can be used to correct ALL measurements made in the term with your own calibrated buret.



How to use a Buret Correction factor

Example 1:

	final volume:	**35.24 mL**		
	initial volume :	**<u>0.16 mL</u>**		
	apparent volume:	**35.08 mL**		
True volume	**= apparent volume**	**+**	**cumulative correction**	
	= **35.08**	**+**	**0.03 mL**	**= 35.11 mL**

Example 2:

	final volume:	**35.24 mL**		
	initial volume :	**<u>10.16 mL</u>**		
	apparent volume:	**25.08 mL**		
True volume	**= apparent volume**	**+**	**cumulative correction**	
	= **25.08**	**+**	**(0.03 - 0.01)**	**= 25.10 mL**

The Analytical Balance

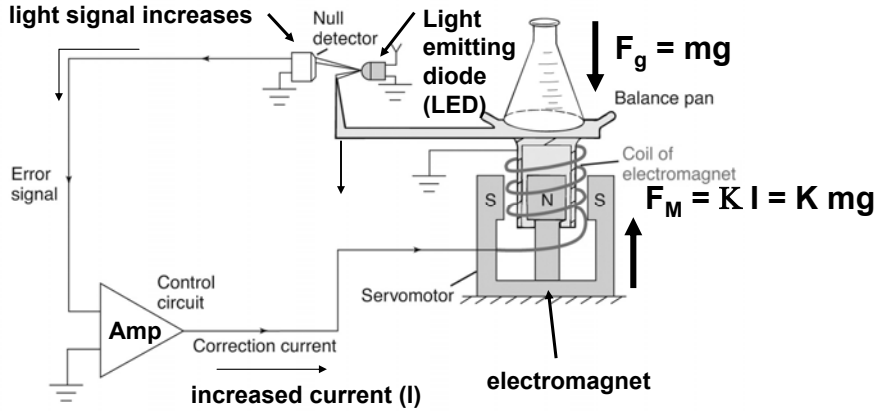
Capable of weighing masses accurately with uncertainties down to +/- 0.0001 g (some models down to 0.00001g.)

PROCEDURES

- **Use a brush to clean the balance pan before every weighing.**
- **Use finger cots or kimwipe to pick up objects being weighed. Never use fingers directly on the object.** *(Fingerprint residue can add significant error.)*
- **Keep doors closed when weighing**
- **If signal "drifts", this could indicate a static electricity problem…wipe anti-static solution on balance**
- **Allow signal to stabilize for a consistent amount of time before recording mass.**
- **Never weigh material directly on the pan**

Analytical Balance - Principle of Operation

An increased downward displacement of the pan from an increased gravitational force results in increased light signal, increased correction current, increased magnetic field. The increased magnetic field is repelled by a permanent magnet, giving increased magnetic force upward on the pan; returning the balance pan to original position; $F_g = F_M$. The "analytical" signal is the magnitude of the correction current, which is read by an electronic circuit and is proportional to F_g.



Schematic of an analytical balance

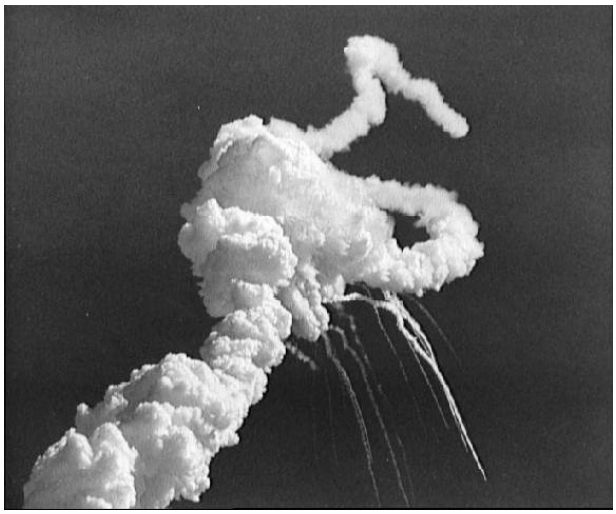
Weighing with the Analytical Balance

The analytical balance is used for weighing the mass of material to a high accuracy and precision (ie. 0.0001 or .000001g). Precision is assumed to be ± 1 of the last digit. If instrument drifts, precision will be poorer and may indicate a problem (ie- static or a hot object).

- **balance may be "tared" or "not tared".**
- **use weighing by difference (or addition) for a balance that is not tared or when weighing dry but hygroscopic materials**

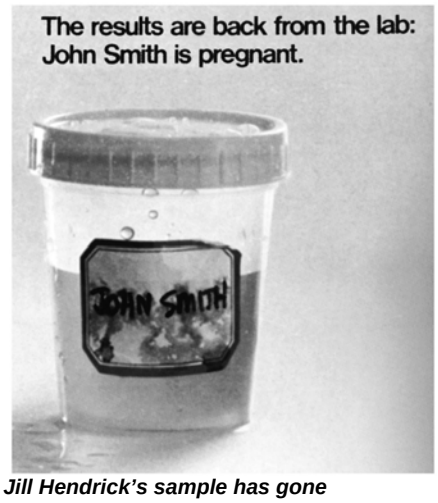
Example: weighing by difference			**Order**
initial mass bottle + material	**.....**	**4.3567**	**1.**
final mass of bottle	**.....**	**4.1274**	**2.**
mass of material		**0.2293**	**calculate**
Example: weighing by addition			
bottle + material	**.....**	**3.1899**	**2.**
empty bottle	**.....**	**2.7765**	**1.**
mass of material		**0.4134 g**	**calculate**

Errors and Statistics



Errors, Uncertainty, Statistics and Data Analysis

the derailment on October 22, 1895 of the Granville-Paris Express that overran the buffer stop.



Jill Hendrick's sample has gone missing. She wonders why she can't stand the smell of sea food anymore…

An error is a difference between a computed, estimated, or measured value and the true, specified, or theoretically correct value.

Errors and Uncertainties – Concepts

- every measurement has errors and uncertainties associated with it. The true value of a measurement is never known.
- we must be able to estimate the errors and uncertainties in our measurements so that we know how reliable our data and conclusions are.
- data of unknown quality are worthless!

Replicates
- repeat measurements on different samples
- usually 3 - 5 are standard, more if you are getting information from analysis of variance.

Why do we replicate?
- our central value will have a higher probability of being more accurate (reliable).
- variation in the data tells us something about the reliability of our result.

Accuracy and Precision

What can we say about the reliability of our results?

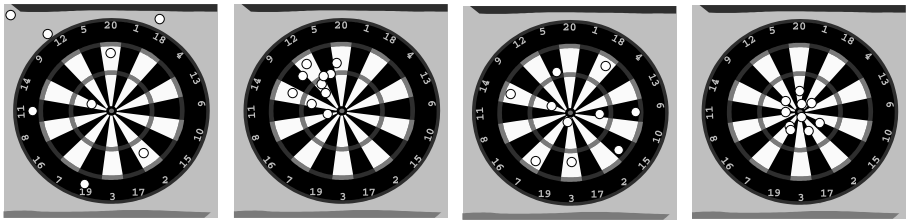
1. Accuracy

the closeness of our result to the "true value". True value is abstract since we can never know a measured quantity exactly. But we can compare our value to an "accepted value" (ie- a prepared standard, or a NRC or NIST certified reference material).

2. Precision

the reproducibility of our measurements; how close the data are to each other. We will learn various measures of this.

Accuracy and Precision are not the same! In chemistry, they have vastly different meanings . . . Picture the dartboard analogy



low precision
low accuracy

high precision
low accuracy

low precision
high accuracy

high precision
high accuracy

Central Estimates from Multiple Replicates

Mean (average)

$$\bar{x} = \frac{\sum_{i=1}^{N} x_i}{N}$$

N = number of measurements
x_i = individual measurements

Median
central value when replicate measurements are arranged in order (central value for odd number and average of middle two when even number). The median is sometimes used when you have a non standard (guassian) distribution, or to minimize the impact of outliers

Example
6 replicate measurements on an air sample by GC give the following concentrations of benzene (ppb):
9.72, 10.24, 9.91, 10.08, 9.99, 13.32

mean = (9.72+10.24+9.91+10.08+9.99+13.32)/6 = 10.54 ppb
Is this representative??
Median = average of 3rd and 4th data points in increasing order.
Median = (9.99 +10.08)/2 = 10.04 ppb
it appears much more representative!
Normally we use the mean, but will look at data and test for outliers.

Measures of Error

Absolute Error

Error = $x_i - x_o$ **or** **Error = $x - x_o$**

(error in a measurement) **(error in the mean)**

x_o=our best estimate of the "true value"
example:
in previous example with 6 measurements of benzene, it was found by exhaustive measures that the "true" level of benzene at our sampling location was 9.95 ppb; then the errors would be:

error in mean = 10.54 - 9.95 = + *0.59 ppb*
error in median = 10.04 - 9.95 = + *0.09 ppb*

Relative Error

$$\text{error}_{\text{relative}} = \left(\frac{x - x_o}{x_o} \right) \times 100(\%) \text{ OR } \times 1000 \text{ (pp thousand)}$$

Relative error
The relative error in our mean value was + 5.9 %. The relative error in our median value was 0.9 % or 9 parts per thousand.

Types of Error

We can classify errors as *determinate* (aka. systematic) and *indeterminate* (aka. random, non-systematic, or statistical).

Determinate (systematic) error

Determinate error causes the mean of a set of data to be different than the true value in a statistically significant manner. The source of the error can usually be determined and corrected with varying degrees of work. This error usually creates a *bias* in the results, high or low.

Dartboard analogy - A world champion darts champion has just had surgery on his elbow. While he still retains his ability to group the darts, the stretching of his tendon causes him to consistently shoot high and to the left. He will need time to adjust (calibrate) to the stretched tendon.

Analytical example - RM brought his electronic analytical balance from Ottawa which he had meticulously calibrated before leaving. He works in the lab for a month before he realizes that all his balance readings appear to be too low by 4 parts per thousand. *Why?*

Answer: The "g" force (W=mg) in Toronto is slightly different than in Ottawa and he forgot to recalibrate the balance after it was set up here.

Determinate Error – sources

Instrument Errors
Systematic errors in our measurement apparatus such as incorrect calibration values, instrument deterioration that goes undetected (ie- decreased light transmittance of a fibre optic cable with time) or operating an instrument outside of it's optimum temperature range. Can usually be corrected by recalibration.

Method Error
there is a systematic error in the analytical methodology. This could be a reaction that does not go to completion, the small excess of indicator that is needed beyond the equivalence point in a volumetric titration or an incorrect assumption in a sampling methodology of 100% capture. These errors go undetected at first but can be corrected after they are discovered.

Personal Errors
Errors in personal judgement. Examples include prejudice (recording results in a direction that favours increased precision), parallax error when reading a calibrated pointer, and the colour of solution at an end point. Also biasing results by recording 0.00 mL as default initial reading on a buret. These personal errors can be eliminated with good laboratory practices.

How does systematic error manifest itself in our results and how would we detect them??

Determinate Error – cont'd

Constant Errors
The absolute error in our measurements remains the same despite the variation in the amount of analyte.

Example - titration error caused by excess indicator. The amount of reagent needed to react with the indicator beyond the equivalence point is constant and independent of the amount of analyte. It can be eliminated with a *blank*. measurements
Blank measurement – measurement of a sample containing no analyte, all steps in the measurement process are *IDENTICAL* as other samples

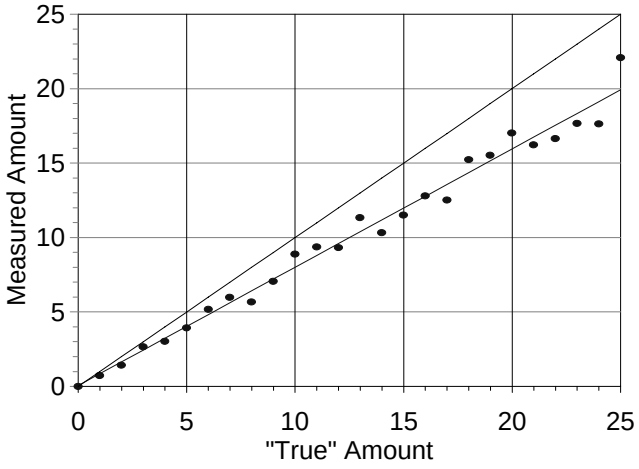
Constant errors are more problematic for small analyte amounts than large.

ie- what is % error in titrations of 5.00 and 50.00 mL that both have endpoint errors of +0.20 mL?

ANSWER
a) % error = (5.20-5.00)/5.00*100 = + *4.0%* (40 parts per thousand)
b) % error = (50.20-50.00)/50.00*100 = + *0.4%* (4 parts per thousand)

Determinate Error – cont'd 2

Proportional Errors
The relative error in our measurements remains the same despite the variation in the amount of analyte. This of course means that the absolute error increases with analyte concentration. Below is shown a typical calibration error.



Indeterminate Error (Random)

Random error causes the measurement values to be scattered about the mean value. If enough measurements are made, despite our random error, we expect that the calculated mean will be the same as the true value.

Dartboard analogy - A junior darts player is playing with the world champion. His grouping (precision) is not as good as our champion but he has not required surgery lately and tends to group around the "eye" when he tries. His grouping is not as good since he has not learned to control his breathing. Therefore, there is a random chance that he is inhaling or exhaling when he releases the dart, causing a random error in his shot.

Analytical Example - Rob has recalibrated his balance in Toronto now. He makes 100's of measurements of a 10.0 g standard weight, and despite his meticulous work, discovers that his results are not always the same, ie- the balance does not always report 10.0000 g, despite the fact that his mean mass of a standard is equal to the true source within a few hundred parts per million. *Why?*

***Answer:* The analytical balance has internal electronics which are subject to various types of electrical "noise" that give rise to voltage and current fluctuations at various points in the circuitry. This gives rise to fluctuations in the reported mass on the display.**

Indeterminate Error – sources

Indeterminate error is usually the accumulation of many type of random error. The sources cannot be always be determined individually but many types have been well characterized.

Examples of sources:

- **temperature fluctuations, voltage fluctuations, shot noise (statistical uncertainty in counts of photons or electrons), Johnson noise (applies to resistors in circuits), 1/f noise (f is the frequency at which the analytical signal is measured), other environmental noise (ie- E fields penetrating circuits , external light fluctuations, vibrations), individual human judgements in taking readings - randomness of physical excercises (this applies very much so to titrations).**

The random errors combine to give a distribution of measurement results that are not always the same. In the absence of determinate error, this distribution will be centered about the "true value".

What is the nature of this distribution?

..Look at some experimental data

Example Data – Pipet Calibrations

Trial	Volume	Trial	Volume	Trial	Volume	Trial	Volume	Trial	Volume
1	9.988	11	9.980	21	9.992	31	9.985	41	9.986
2	9.973	12	9.989	22	9.984	32	9.977	42	9.982
3	9.986	13	9.978	23	9.981	33	9.976	43	9.977
4	9.980	14	9.971	24	9.987	34	9.983	44	9.977
5	9.975	15	9.982	25	9.978	35	9.976	45	9.986
6	9.982	16	9.983	26	9.983	36	9.990	46	9.978
7	9.986	17	9.988	27	9.982	37	9.988	47	9.983
8	9.982	18	9.975	28	9.991	38	9.971	48	9.980
9	9.981	19	9.980	29	9.981	39	9.986	49	9.983
10	9.990	20	9.994	30	9.969	40	9.978	50	9.979

We know how to characterize the central value of the data set…
Mean = 9.982 mL Median = 9.980 mL

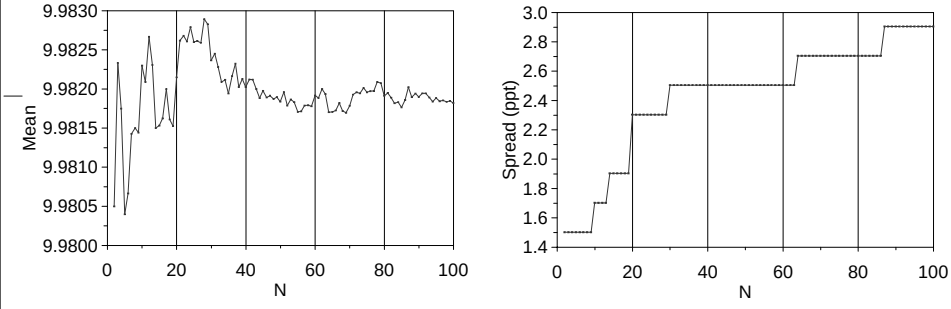
How do we characterize the "width" of the dataset.

Highest – Lowest?? : 9.994 – 9.969 = 0.025 mL

Or relative Spread = (Hi – Low)/mean = 0.025 / 9.982*1000pt = 2.5 pp thousand

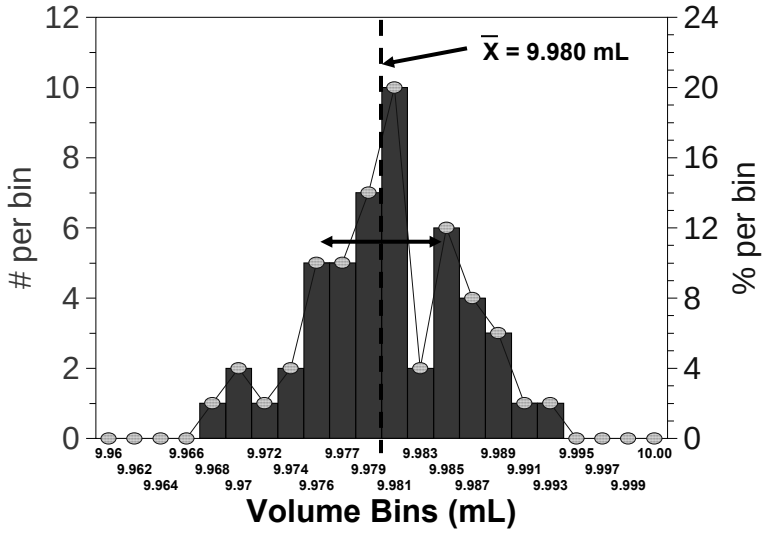
Problem with spread or relative spread…they depend on the number of measurements.

Buret Calibration Dataset



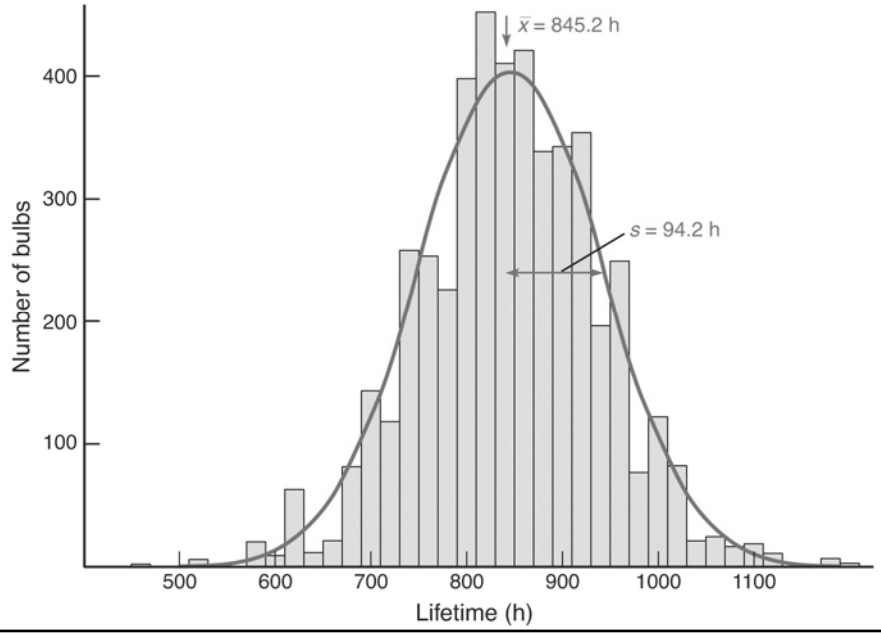
Pipet Results - Histogram

Pipet Calibration Results



What is the true nature of this "distribution" if we were to make infinite # of measurements? How do we characterize the width of the distribution?

Light Bulb Lifetimes (Harris, pg 62)



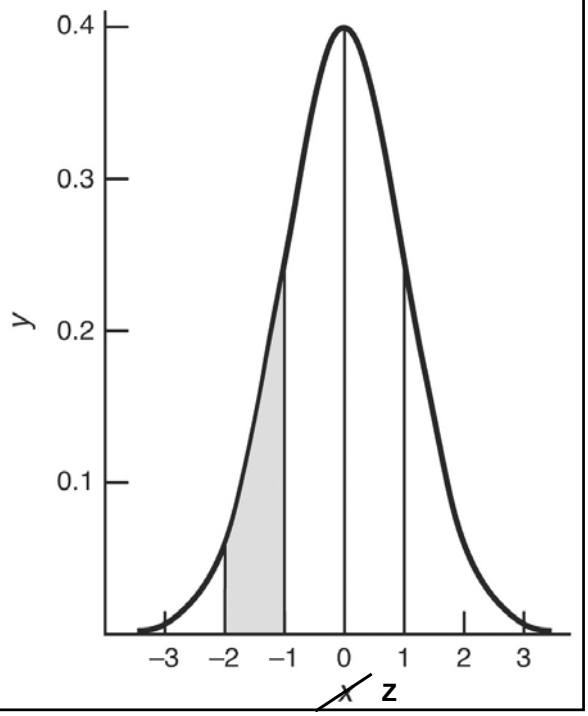
Gaussian Curve

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)^2}{2\sigma^2}}$$

IF

$$z = \frac{(x-\mu)}{\sigma}$$

$$y = \frac{1}{\sqrt{2\pi}} e^{\frac{-z^2}{2}}$$



How do we calculate σ ?

Any Guassian distribution is characterized by 2 values:

i) True mean, μ

ii) standard deviation, σ

We can estimate μ; $\bar{x} \rightarrow \mu$ AS N → infinity

How do we find σ??

If we have a large number (infinite) of data points, we can determine the "population standard deviation", σ.

$$\sigma = \sqrt{\frac{\sum_i (x_i - \mu)^2}{N}}$$

where x_i = measured value
μ = population mean (true value)
N = # of observations

With a limited number of observations, we determine the "sample standard deviation", s.

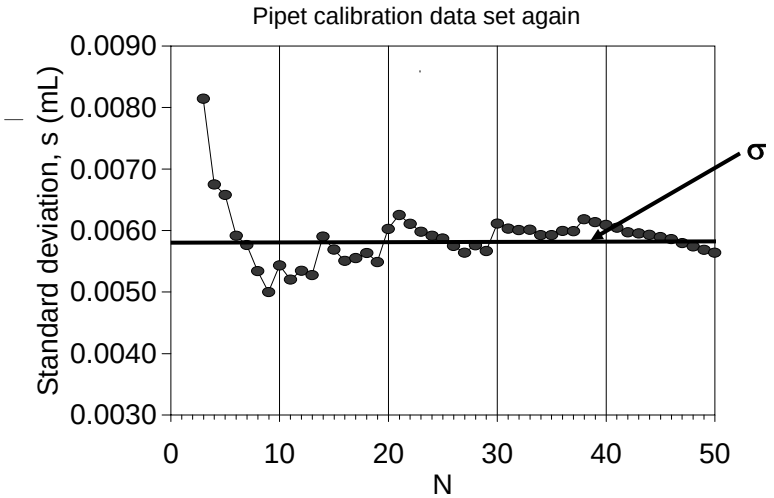
$$s = \sqrt{\frac{\sum_i (x_i - \bar{X})^2}{N-1}}$$

Note that s → σ as N → infinity. Also note that s and σ are independent of N!!!

Problems to work on

Chapter 0 - do all problems 0.1 .. 0.6
Chapter 1 - Problems 1.1, 1.3, 1.18, 1.19, 1.20, 1-25, 1-30, 1-33
Chapter 2 - Problems 2.6, 2.8, 2.9, 2.22.
Chapter 3 - Problems 3.4, 3.5, 3.7, 3.9, 3.10, 3.11.

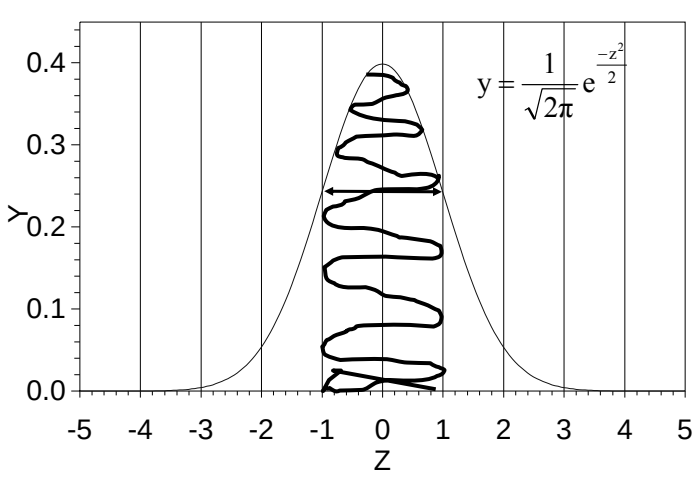
Calculating s or σ



For N < 100, you should be using the formula given previously for s (not σ!!)
Learn how to calculate s: i) manually with calculator, ii) using the statistics functions on your calculator, iii) using a spreadsheet (ie Excel or Quattro Pro). This will be necessary for future tests and exams.

Properties of Normal error Curve

Area under the curve gives probability that measurements fall within a certain range.



$$\int_{-\infty}^{+\infty} y(z)dz = 1.0$$

$$\int_{-1}^{+1} y(z)dz = 0.683$$

$$\int_{-2}^{+2} y(z)dz = 0.955$$

$$\int_{-2}^{+2} y(z)dz = 0.997$$

Other Statistical terms

Variance

σ^2 = variance (***Note we can use s instead of σ in these equations***)

variances are additive

For different random error processes (1,2,3…n) that contribute to a measurement error, we can say:

$$\sigma^2 = \sigma_1^{\,2} + \sigma_2^{\,2} + \sigma_3^{\,2} + \ldots \sigma_n^{\,2}$$

$$\sigma = \sqrt{\sigma_1^{\,2} + \sigma_2^{\,2} + \sigma_3^{\,2} + \ldots \sigma_n^{\,2}}$$

where σ is the total standard deviation.

Coefficient of Variation (CV)
This is a relative measurement of the variation in the measured value compared to the size of that value expressed in % terms.

$$CV = \frac{\sigma}{\mu} \qquad (\times 100\% \text{ OR } \times 1000\text{ppth})$$

$$CV \approx \frac{s}{\bar{x}}$$

Standard Error of the Mean

- remember the guassian (error) curve.
- The probability that any single measurement will lie within :
± 1 σ is 68.3%
± 2 σ is 95.5%
± 3 σ is 99.7%
The standard error of the mean of a single measurement is 1 σ

What is the error in the mean if we make multiple measurements?

Intuitively we know that if we make more measurements, the error in our calculated mean will be less . . .

$$\bar{x} \pm \sigma_n = \frac{(x_1 \pm \sigma) + (x_2 \pm \sigma) + (x_3 \pm \sigma) + \ldots + (x_n \pm \sigma)}{n}$$

$$= \frac{x_1 + x_2 + x_3 + \ldots + x_n}{n} \pm \frac{\sqrt{n\sigma^2}}{n}$$

$$= \bar{x} \pm \frac{\sigma}{\sqrt{n}}$$

$$\sigma_n = \frac{\sigma}{\sqrt{n}} \qquad \text{OR} \qquad s_n = \frac{s}{\sqrt{n}}$$

Lowering Uncertainty with Multiple Measurements

# of measurements n	s_n
1	1.0 s
2	0.71 s
3	0.58 s
4	0.50 s
9	0.33 s
25	0.20 s
100	0.10 s

- with 100 measurements, the standard error in our mean value is 10% of what it is with a single measurement!

Ultimately, we need to decide if it is worth the time. Other factors may also degrade the expected results shown here.

Pooled Standard Deviation

The use of multiple data sets to calculate an overall standard deviation that is more representative of the true σ than we could get with an individual dataset.
Q: Why would we do this???
A: *Because "noise is noisy".*

$$\sigma \approx s_{pooled} = \sqrt{\frac{\sum_{j=1}^{J}\sum_{i=1}^{Nj}\left(x_{i,j} - \overline{x_j}\right)^2}{\left(\sum_{j=1}^{J} N_j\right) - J}}$$

j = incremental pools of data, J pools in total
i = incremental data in pool J, Nj in total.

Example: *we are making routine daily measurements in the lab and we need to calculate the error (or confidence) in our mean, but we don't want to have to calculate "s" for every set of measurements. In this case, we will want to estimate s to a higher degree of accuracy.* Remember that s → s as N → ∞

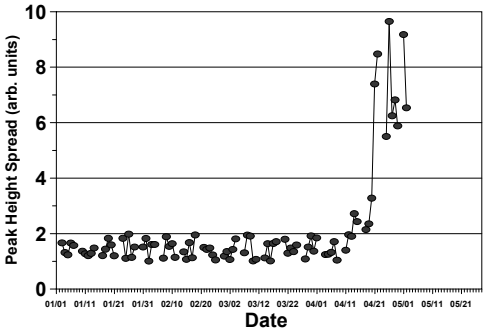
Options
1) make 20 or more measurements (up to 100) and calculate s. This s is a good representation of σ
2) Make use of data that has already been taken for different samples or make a plan to use the data from your daily calibration over a period of a couple of weeks. You would use this data to calculate a pooled standard deviation.

Example: using Spread in Quality Control

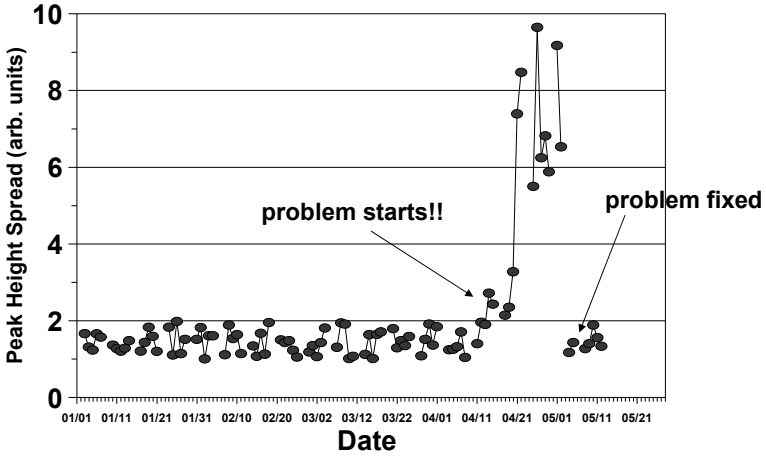
Spread can be used for quality control tracking.

***Example*: Environment Canada monitors hydrocarbons in the atmosphere by GC-FID (gas chromatography with flame ionization detection). The chemist at a certain site calibrates his GC daily with bottled propane. He makes five calibration measurements daily, calculates the spread in the peak height every day and plots it on a control chart in the back of the instrument book.**

Observation
One day he notices that the spread has increased by a factor of 500% over the highest spread he has seen in the last 4 months. At the same time, the average peak height decreased by 5% compared to what it usually is. Thus decreased sensitivity is starting to give systematic error in results.



QC Indicates a Problem



Result

There is some dirt trapped in the acetylene (flame) nozzle. This was causing the flame to flicker, giving him an unstable current signal. Note that the spead was a much more sensitive indicator of the problem than the peak height (mean value) in this case.

Propogation of Errors

Addition & Subtraction

square root of the sum of the squares of the absolute errors!

$$Y \pm s_y = (a \pm s_a) + (b \pm s_b) + (c \pm s_c) + \ldots + (n \pm s_n)$$

$$s_y = \sqrt{{s_a}^2 + {s_b}^2 + {s_c}^2 + \ldots {s_n}^2} = \sqrt{\sum_{i=1}^{n} {s_i}^2}$$

Multiplication & Division

square root of the sum of the squares of the relative errors!

You must know the above.

$$Z \pm s_z = \frac{(A \pm s_A) \times (B \pm s_B) \times \ldots \times (N \pm s_N)}{(C \pm s_C) \times \ldots}$$

$$\frac{s_Z}{Z} = \sqrt{\left(\frac{s_A}{A}\right)^2 + \left(\frac{s_B}{B}\right)^2 + \left(\frac{s_C}{C}\right)^2 + \ldots + \left(\frac{s_N}{N}\right)^2} = \sqrt{\sum_{i=1}^{N} \left(\frac{s_i}{I}\right)^2}$$

Significant Figures

The number of digits required to express a quantity in scientific notation without the loss of accuracy.

ie. $0.0312 = 3.12 \times 10^{-2}$ has 3 significant figures, not 5.

Errors with significant errors
i) too many significant figures
eg. ***The concentration of Pb in the lake water sample is $1.55438976 \times 10^{-8}$M***
not scientifically pleasing but will not result in tragic errors.
ii) not enough significant figures.
eg. ***The concentration of Pb in the lake water sample is 2×10^{-8}M***
This report results in loss of accuracy AND hard work!. Precise work may be thrown out the window. It is better to err on the side of keeping MORE significant figures than less.
error in report value = ($2x10^{-8}$-$1.554x10^{-8}$)/$1.554x10^{-8}$*100% = +28.7%!

How should you report it? It depends on the uncertainty. Generally, expressed in scientific notation, report to same number of decimals as 1st or 2nd digit of the uncertainty.
$(1.55438976 \pm 0.37) \times 10^{-8}$ M ≡ ???

$(1.6 \pm 0.4) \times 10^{-8}$ M OR better still ...$(1.55 \pm 0.37) \times 10^{-8}$ M

Sig Figs- cont'd

Addition and Subtraction
The final answer is limited by the number with the least number of digits beyond the decimal place.

ie. 2.345
\+ 10.1
\+ 19.070
31.515 ≡ 31.5 (round off)

For scientific notation, convert all numbers to the same power and then round the final answer to the number with the least digits beyond the decimal.

$1.1056x10^{3} + 1.1056x10^{-3} = ?$
$= 1.1056x10^{3} + 0.0000011056x10^{3}$
$= 1.1056000011056x10^{3}$
$= 1.1056x10^{3}$

Sig Figs- cont'd 2

Multiplication and Division

The final answer is limited by the number with the least relative precision. A rule of thumb is that the final answer should contain the same number of significant figures as the number with the least, but not always...sometimes we should keep 1 more figure !!

$0.000012 * 17.1 = 1.2\times10^{-5} * 1.71\times10^{1}$

$= 2.052\times10^{-4} \equiv 2.1\times10^{-4}$

Q. When do we have exceptions to this rule?
A. When our *limiting number* (ie- that with least number of significant digits) has a higher numerical first digit than the answer. In this case, keep one extra digit. This is to ensure that we keep at least the limiting amount of precision present in any number in our final answer. Why, because precision costs hard work, therefore we don't want to throw it away!

Example: $8.02\times10^{-6} * (12.011+4.00000000*1.0079)$
$= \underline{8.02}\times10^{-6} * 16.043$
$= 1.28665\times10^{-4} \equiv 1.287\times10^{-4}$ (instead of 1.29×10^{-4})

Sig Figs – logs and antilogs

Refresher
log x = ? ≡ $10^{?} = x$
log 1234 = $\underline{3.0913}$

digit mantissa

Rule of thumb for logs
The number of digits in the mantissa should be equal to to the number of significant figures in the number you are taking the log of.

ie: A = -log T A = absorbance T = transmittance (0<T<1)

if T = 0.624 (62.4% light transmitted)

A = - log 0.624 = 0.2048154 . 0.205

Rule of thumb for antilogs
Reverse! The number of significant figures in the antilog is equal to the number of digits in the mantissa (exponent)

$10^{2.\underline{51}} = 323.59 \approx \underline{3.2} \times 10^{2}$
$10^{2.\underline{52}} = 331.13 \approx \underline{3.3} \times 10^{2}$

Q: TestDetection and Rejection of Outliers

Q-test

Use this test if you suspect you have a wild data point. Normally you would use it only if you have greater than 3 measurements. If you reject a measurement with only 3 values, then you should repeat the measurement in the lab.

$$Q = \frac{|x_q - x_n|}{x_{high} - x_{low}} = \frac{|x_q - x_n|}{\text{spread}} = \frac{\text{"gap"}}{\text{"spread"}}$$

x_q = suspect point;
x_n = closest numerical value

Compare Q to Q_{crit} in statistical tables for number of observations and the required confidence. If $Q > Q_{crit}$, then you can reject the outlier. Normally you would use a 95% confidence interval.

Example **: 4 measurements.**
25.06%, 24.95%, 25.72%, 25.02%

$$Q = \frac{|x_q - x_n|}{x_{high} - x_{low}} = \frac{|25.72 - 25.06|}{(25.72 - 24.95)} = 0.857$$

Q_{crit} = 0.829 Since Q > Qcrit, there is greater than 95% probability that the suspect point does not belong to the same distribution as the other points. Therefore we have a statistical reason for rejecting the data point. Do not use the Q-test blindly when you have a small number of observations. You should have another reason for rejection!

Q-Test Tables

Table: Critical Values for the Rejection Quotient Q*

Number of Observations	90% Confidence	95% Confidence	99% Confidence
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

Table 4-6 Values of Q for rejection of data

Q (90% confidence)[a]	Number of observations
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10

a. Q = gap/range. If $Q_{calculated} > Q_{table}$, the value in question can be rejected with 90% confidence.

SOURCE: R. B. Dean and W. J. Dixon, *Anal. Chem.* **1951**, *23*, 636; see also D. R. Rorabacher, *Anal. Chem.* **1991**, *63*, 139.

Q-test:0.56 GC Data

Remember Previously this Example:
6 replicate measurements on an air sample by GC give the following concentrations of benzene (ppb):

9.72, 10.24, 9.91, 10.08, 9.99, 13.32

mean = (9.72+10.24+9.91+10.08+9.99+13.32)/6 = 10.54 ppb

Median = (9.99 +10.08)/2 = 10.04 ppb

Normally we use the mean, but will look at data and test for outliers.

$$Q = \frac{\text{"gap"}}{\text{"spread"}} = \frac{|x_q - x_n|}{x_{high} - x_{low}} = \frac{|13.32 - 10.24|}{13.32 - 9.72} = 0.856$$

From Q* table, for N=6, $Q_{critical}$ = 0.560 (90% Conf), 0.625 (95%), 0.625 (99%),

Q is greater than Q* at 90%, 95%, AND 99%. Yes we can realistically reject the data point.

What if the 6 measurements were made on different ambient measurements of air samples at York U, and we wanted to calculate median levels people are exposed to at York. Would you reject the point?

Confidence Intervals

The confidence interval is the interval within which we are x% confident that the true mean lies, assuming the absence of determinate error. We choose x to be what we like. 95% is frequently used. There are two situations . . .

When we have a good estimate of σ:

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

with a certain confidence.

The value of z is dependent on the confidence required. Values of z are obtained from integration of the area under the normal error curve and can be found in tables.

ie - for 95% confidence, z = 1.96 (95% of area under the error curve is contained within " 1.96σ).

Confidence Intervals – cont'd

When σ is not known.
Since σ is not known, our confidence interval will be larger for a given confidence level and for a similar data set. As`we have learned, the error in a mean is inversely proportional to the square root of N, and as such our condidence interval should become smaller as N increases.

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

Unlike z, t is a function of not only the confidence we require but also the # of measurements we have made. This is because we get a better estimate of σ as N → ∞. *Approach:* with a given data set, calculate s. Determine the degrees of freedom, DOF (N-1 for N data points). Look up t in the "t" table for the required confidence level. Calculate the CI using the equation above.

T-table (from Harris)

Table 4-2 Values of Student's *t*

	Confidence level (%)						
Degrees of freedom	**50**	**90**	95	**98**	**99**	**99.5**	**99.9**
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

NOTE: In calculating confidence intervals, σ may be substituted for *s* in Equation 4-6 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of *s*, the value of *t* to use in Equation 4-6 comes from the bottom row of Table 4-2.

Example

Example
Buret volumes (mL) : 24.95, 25.02, 25.06, 25.49

Q1. What is 95% confidence interval with just these measurements?

mean = 25.13 s = 0.244 t = 3.182 (DOF = N-1=3, 95% CI)

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{N}} = 25.13 \pm \frac{3.182 \times 0.244}{\sqrt{4}} = 25.13 \pm 0.39$$

What does the Confidence interval mean?? It means that in the absence of determinate error, we are 95% confident that the true volume lies between 24.74 and 25.52 mL.

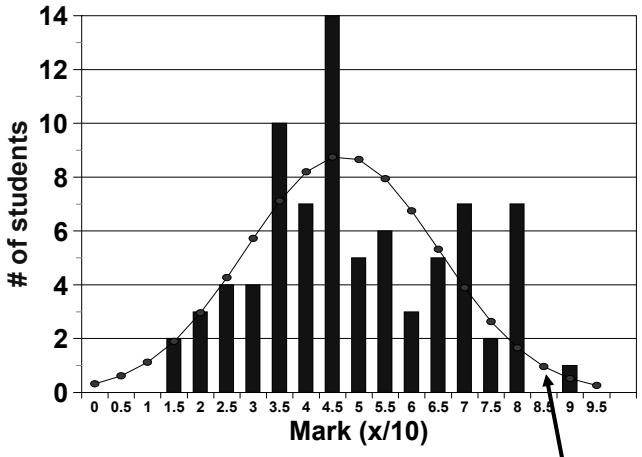
Q2. If we Q tested out the measurement at 25.49, we would end up with a dataset with 3 points. What would be our new confidence interval??
mean = 25.00 s = 0.06 t = 4.303 (DOF = N-1=2, 95% CI)

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{N}} = 25.00 \pm \frac{4.303 \times 0.06}{\sqrt{3}} = 25.00 \pm 0.14$$

Note that our new confidence interval lies within the old interval but it is much narrower, more precise!

Quiz Results

Quiz 1: Results



Statistics:
N=80 (2 unidentified)
mean = 4.931
median = 4.5
s = 1.815

CONFIDENCE IN MEAN

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

$$CI = 4.93 \pm \frac{1.99 \times 1.815}{\sqrt{80}}$$

$$CI = 4.93 \pm 0.40$$

$$y = K \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-(x-\mu)^2}{2\sigma^2}} = 80 \times 0.5 \frac{1}{1.815\sqrt{2\pi}} e^{\frac{-(x-4.931)^2}{2\times 1.815^2}}$$

Comparison of Means (with Student's t)

Two cases:
i) comparison of a measured value to a known value.
ii) comparing two sets of measured values (replicates for each).

Null Hypothesis
As a start, we always assume the null hypothesis: the two means are the same. We then test the hypothesis to see if the means are different. (innocent until proven guilty). We cannot proove the two means are the same. We can only determine if there is statistical doubt in this assumption to a reasonable degree. We set the confidence limit by our willingness to live with a "false positive" (ie- a positive being our determination that the null hypothesis is invalid).

1. Comparison of *measured* value to a *known* value.

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

We determine if the known value is within the confidence interval (ie @ 95%) of our measured value. If not, then we say that this happens less than 5% of the time and reject the null hypothesis, the two means are different.

Example:

Example
The following determinations of Hg levels in a certified reference material are made by ICP-MS (9.0, 8.5, 8.8, 9.1, 8.6 ppb). The CRM value is 9.43 (± 0.01) ppb. Is there a determinate error in our analytical procedure at the 99% confidence level?

Assume μ = 9.43!
N = 5, t = 4.60 (4 DOF), s = 0.255, mean = 8.80
CI = 8.80 ± .52 (8.28→9.32). 9.43 does not lie in the CI.

We would obtain a value of 9.43 ppb <1% of the time with our procedure. We have a determinate error in our determination.
The mean is different from the "true value"!

Comparing two sets of measured values (x_1, x_2)

For two determinations with the same procedure ($\sigma_1 = \sigma_2$) with N_1 and N_2 observations, a statistical difference in 2 calculated means is expected. The maximum statistical difference in the means at a given confidence level is:

$$\left|\overline{x_1} - \overline{x_2}\right| = ts_{pooled}\sqrt{\frac{N_1 + N_2}{N_1 N_2}}$$

Calculate the right side of the equation at the desired confidence level and compare this *"statistical difference"* of two means to the observed difference (left side). If the left side (observed) is greater than the right side (acceptable maximum statistical difference), then we can conclude that the means are statistically different with our chosen confidence level (ie ~ 95% example). Use $N_1 + N_2 - 2$ D.O.F. for t.

If $\sigma \approx s = s_1 = s_2$, AND for the simple case where $N_1 = N_2 = N$, then the equation becomes...

$$\left|\overline{x_1} - \overline{x_2}\right| = \frac{ts}{\sqrt{N}}\sqrt{2}$$

Example- *Raleigh's discovery of argon*

Masses of gas samples of N_2, one after removing O_2 from air, the other by chemical generation of pure N_2.
N_2 from Air (g) : 2.31017, 2.30986, 2.31010, 2.31001, 2.31024, 2.31010, 2.31028.

Generated N_2 (g): 2.30143, 2.29890, 2.29816, 2.30182, 2.29869, 2.29940, 2.29849, 2.29889

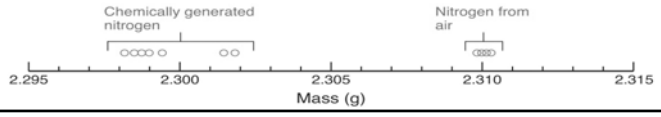
Are the previous masses different at 95% CL? If not, then air with O_2 removed is the same as N_2 (null hypothesis). If so, then something is fishy....air is NOT only $O_2 + N_2$.

Solution:
$N_1 = 7$, $\overline{x}_1 = 2.31011$ $N_2 = 8$, $\overline{x}_2 = 2.29947$
t = 2.16 (13 degrees of freedom (8+7-2))

$$\left|\overline{x_1} - \overline{x_2}\right| = ts_{pooled}\sqrt{\frac{N_1 + N_2}{N_1 N_2}}$$

$$s_{pooled} = \sqrt{\frac{\sum\left(x_{i,1} - \overline{x_1}\right)^2 + \sum\left(x_{i,2} - \overline{x_2}\right)^2}{N_1 + N_2 - 2}} = \sqrt{\frac{(N_1 - 1)s_1^2 + (N_2 - 1)s_2^2}{N_1 + N_2 - 2}} = 0.00102$$

LS = 0.01064 RS = 0.00114 The observed difference between means (left side) is higher than the right side. Therefore, the means are statistically different at the 95% CL (and 99.9% CL in fact!). This led Raleigh to conclude that there is a heavier component in air.... Ar and a Nobel Prize (1904)!!!



Comparison of Precision

F-test

Why?

*** precision can tell us a lot about our system such as fundamental noise limits, reproducibility of the procedure and the system, identifying the existence of unknown errors in our procedure, etc.**

*** precision can be diagnostic (remember example of GC/FID)**

*** precision in measuring any blank in a method determines what our *detection limit* is.**

Therefore there arises from time to time the need to compare precision.

Null Hypothesis: the precision of two sets of measurements are the same.

TEST : calculate the quotient of the two sample standard deviations. *Always put the larger standard deviation in the numerator!*

$$F_{calculated} = \frac{S_1^2}{S_2^2}$$

Compare "calculated value" to $F_{critical}$ in Table. If $F_{calculated} > F_{critical,}$ we can reject the null hypothesis at the 95% confidence level. The precisions are different. If Fcalculated < Fcritical, we cannot conclude that the variances are different. As far as we know, we are just dealing with noisy noise.

Table 4-5 Critical values of $F = s_1^2/s_2^2$ at 95% confidence level

Degrees of freedom for s_2	Degrees of freedom for s_1													
	2	3	4	5	6	7	8	9	10	12	15	20	30	∞
2	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5
3	9.55	9.28	9.12	9.01	8.94	8.89	8.84	8.81	8.79	8.74	8.70	8.66	8.62	8.53
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.75	5.63
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.50	4.36
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.81	3.67
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.58	3.51	3.44	3.38	3.23
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.08	2.93
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.86	2.71
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.84	2.77	2.70	2.54
11	3.98	3.59	3.36	3.20	3.10	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.57	2.40
12	3.88	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.47	2.30
13	3.81	3.41	3.18	3.02	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.38	2.21
14	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.31	2.13
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.25	2.07
16	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.19	2.01
17	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.15	1.96
18	3.56	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.11	1.92
19	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.07	1.88
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.04	1.84
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.84	1.62
∞	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.46	1.00

Example – F-test

A single alloy specimen was used to compare the results of two analytical testing laboratories, that use the same standard method of analysis. The standard deviation, s and degrees of freedom in pooled data sets are shown below. Use the F-test to whether the results from one laboratory works are more precision than the other at the 95% Confidence level. Compare the results separately for Ni and Mn

	Laboratory A		Laboratory B	
Element	s	N	s	N
Ni	0.07	13	0.04	21
Mn	0.020	5	0.035	6

Calibration and Least Squares Analysis

as covered in class...the notes will appear here later. see Chapter 5.

Detection of Outliers

Q-test

Use this test if you suspect you have a wild value. Normally you would use it only if you have greater than 3 measurements. If you reject a measurement with only 3 values, then you should repeat the measurement in the lab.

$$Q = \frac{|x_q - x_n|}{spread}$$ x_q = suspect point; x_n = closest numerical value

Compare Q to Q_{crit} in statistical tables for number of observations and the required confidence.

If $Q > Q_{crit}$, then you can reject the outlier.

Normally you would use 95% confidence.

Example : 4 measurements. You suspect something was wrong with the highest point

25.06%, 24.95%, **25.72%**, 25.02 $x_q = 25.72$, $x_n = 25.06$

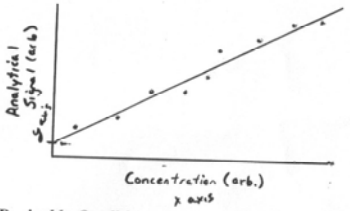
$$Q = \frac{25.72 - 25.06}{25.72 - 24.95} = 0.85$$ $Q > Q_{crit} = 0.829$

Therefore we reject the point.

Do not use the Q-test blindly when you have a smalll number of observations. You should have another reason for rejection!

Calibration

Normally, the determination of the relationship between the chemical concentration and our analytical signal. This allows determination of any concentration in the calibrated range.



Desirable Qualities of a Calibration

- linear
- high level of correlation
- stability
- large dynamic range
- "0" intercept

Least Squares Regression

We assume that the data have some theoretical basis which allows it to be represented by an equation of the following type:

$$y = mx + b$$

y = dependent variable (analytical signal)
x = independent variable (concentration)
m = slope ($\Delta y/\Delta x$)
b = intercept background.

We will also assume that the errors in x are minimal compared to the errors in y. If this is true, then our mathematical problem becomes one in which we find the values of m and b which minimize the sums of squares of the deviations of y_i for individual points from the line.

ie - we minimize $\Sigma [y_i - (mx_i + b)]^2$

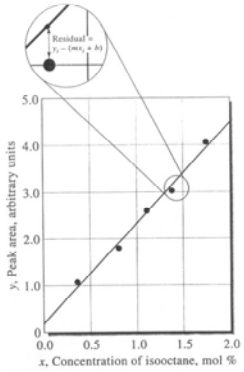


TABLE 4.5 Calibration Data for a Chromatographic Method for the Determination of Isooctane in a Hydrocarbon Mixture

Mole Percent Isooctane, x_i	Peak Area y_i	x_i^2	y_i^2	$x_i y_i$
0.352	1.09	0.12390	1.1881	0.38368
0.803	1.78	0.64481	3.1684	1.42934
1.08	2.60	1.16640	6.7600	2.80800
1.38	3.03	1.90440	9.1809	4.18140
1.75	4.01	3.06250	16.0801	7.01750
5.365	12.51	6.90201	36.3775	15.81992

Skoog/West/Holler, *Fundamentals of Analytical Chemistry, 7/e* overhead transparency 7, text figure 4.4 and text table 4.5, pages 61, 63 Saunders College Publishing

Least Squares Solution

calculate five quantities :

$$S_{xx}=\sum_i (x_i-\bar{x})^2=(N-1)*s_x^2$$

quick method

$$S_{yy}=\sum_i (y_i-\bar{y})^2=(N-1)*s_y^2$$

$$S_{xy}=\sum_i (x_i-\bar{x})(y_i-\bar{y})=\sum x_i y_i-\frac{\sum x_i \sum y_i}{N}$$

$$\bar{x}=\frac{\sum x_i}{N}$$

$$\bar{y}=\frac{\sum y_i}{N}$$

Then we can find the solution as follows:

slope: $m = S_{xy}/S_{xx}$

intercept: $b = \bar{y} - m\bar{x}$

standard deviation about the regression

$$s_r=\sqrt{\frac{S_{yy}-m^2 S_{xx}}{N-2}}$$

standard deviation in the slope

$$s_m=\sqrt{\frac{s_r^2}{S_{xx}}}$$

standard deviation in the intercept

$$s_b=s_r\sqrt{\frac{1}{N-\frac{(\Sigma x_i)^2}{\Sigma x_i^2}}}$$

Calibration results:

If we measure $\bar{y}_c$ for an unknown sample, then we can solve for the unknown concentration by rearranging the equation for the least squares line:

$$\bar{x}_c=\frac{\bar{y}_c-b}{m}$$

If $\bar{y}_c$ was obtained using M replicates and a calibration curve derived from N points, then the standard deviation in $\bar{x}_c$ is given by:

$$s_c=\frac{s_r}{m}\sqrt{\frac{1}{M}+\frac{1}{N}+\frac{(\bar{y}_c-\bar{y})^2}{m^2 S_{xx}}}$$

CALIBRAT.WB1

CALIBRATION

Mole% (x)	Peak Area (y)
0.365	1.000
1.200	1.700
3.000	2.900
7.000	6.000
12.500	13.000

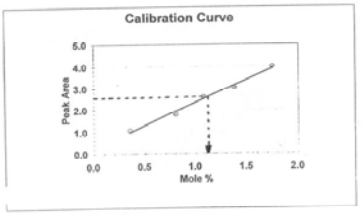
xy
0.38368
1.42934
2.80800
4.18140
7.01750

15.81992

N	5
avg x	1.073
avg y	2.502
Sum (xi2)	6.902
Sum (yi2)	36.378
Sxx	1.1454
Syy	5.0775
Sxy	2.3967
sr	0.1442
m	2.0928 +/- 0.1347
b	0.2567 +/- 0.1583

UNKNOWN ANALYSIS
Replicates
Peak Area
Mole% 1.1437 +/- 0.0767

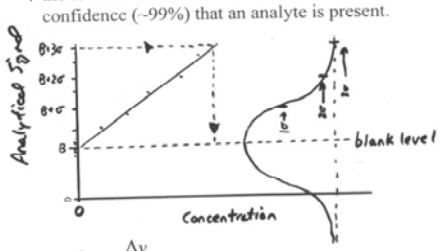
5.365 12.51



01/24/96

Detection Limits

- the lowest limit at which we can say with confidence (~99%) that an analyte is present.



$$slope = \frac{\Delta y}{\Delta x}$$

1 point detection limit (3σ)

σ_B = standard deviation in blank

$$\Delta x = \frac{\Delta y}{slope} = \frac{3\sigma_B}{slope}$$

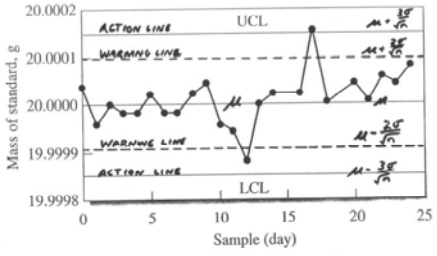
Quality Control, Assurance & Assessment

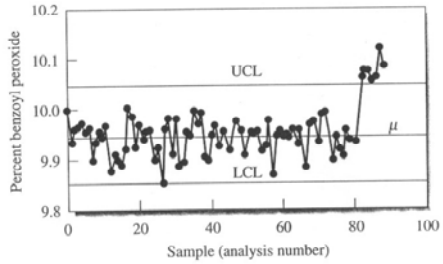
- **maintenance of certain standards in order to ensure that :**
  1. **an analytical method is working**
  2. **a product or chemical stream maintains concentrations at a certain level ~~for various reasons~~.**

Examples of QC

- **intercomparison excercises to allow a lab to determine how their method compares to those of other labs**
- **continual monitoring of a product in a batch or chain manufacturing process. (paint & enamel)**

Control Chart.





Skoog/West/Holler, *Fundamentals of Analytical Chemistry*, 7/e
overhead transparency 8, text figure 4.6 and 4.7, pages 67, 68

Saunders College Publishing

Gravimetric

Any of a variety of method
determination of mass as a

1) ***Precipitation*** - analyt
insolu

eg. $Ag^+_{(aq)} + Cl^-_{(aq)}$

How do we calibrate?

We don't. The molecu
calibration standard. T
analytical signal.

$Mass_{analyte}$ = amount

How do we increase ou

Choose precipitating a
MW.

Limits

Detection Limits:

IUPAC definition

"the limit of detection, expressed as a concentration c_L (or amount q_L), is derived from the smallest measure, y_L, that can be detected with reasonable certainty for a given analytical procedure."

ACS definition

"the limit of detection is the lowest concentration of an analyte that an analytical process can reliably detect".

In order to distinguish the blank signal and the signal arising from a small quantity of material, we need to rely on statistics.

$$y_{analytical} = mC + y_{blank}$$

A detectable signal, y_{DL}, is one that is different (greater) than the blank signal by a statistically significant amount.

$$y_{analytical} - y_{blank} = mC = k\sigma_{blank}$$

Detection Limit, contd

$$mC_{DL} = k\,\sigma_{blank}$$

$$C_{DL} = \frac{k\sigma_{blank}}{m}$$

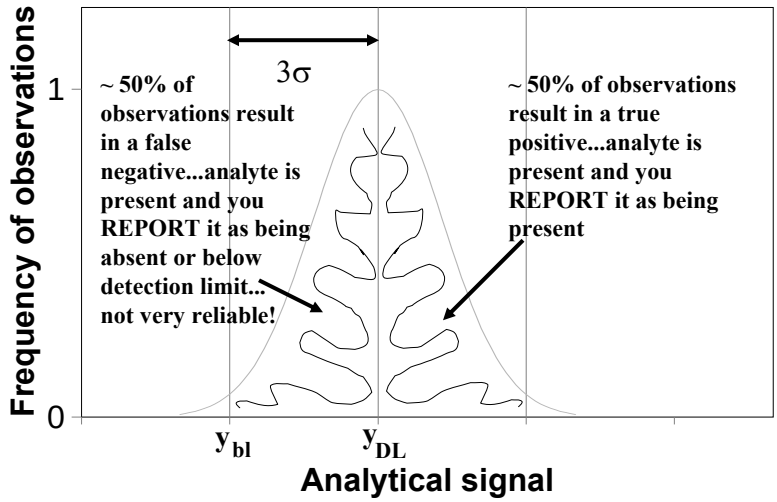
What value of k ??

If we could average significant values of the blank such that it were a well defined value with a low standard uncertainty, AND if the distribution of errors in the analytical signal are normally distributed, then a difference in signal of 2 s_{blank} is statistically significant at the 95% confidence level. BUT not all distributions are normal AND there can be uncertainty in the blank level if we do not have an infinite number of measurements. For this reason, IUPAC recommends that the detection limit be defined with a value of k=3.

$$C_{DL} = \frac{3\sigma_{blank}}{m}$$

This equation defines the concentration detection limit.
- it also defines why we continually strive to lower the instrumental noise, σ. The lower the noise, the lower is our limit of detection.
We also attempt to lower blank levels....Why? because noise increases with signal level usually...if we lower background level, we lower noise.

Working with a sample at the detection limit?



Detection Limit, contd

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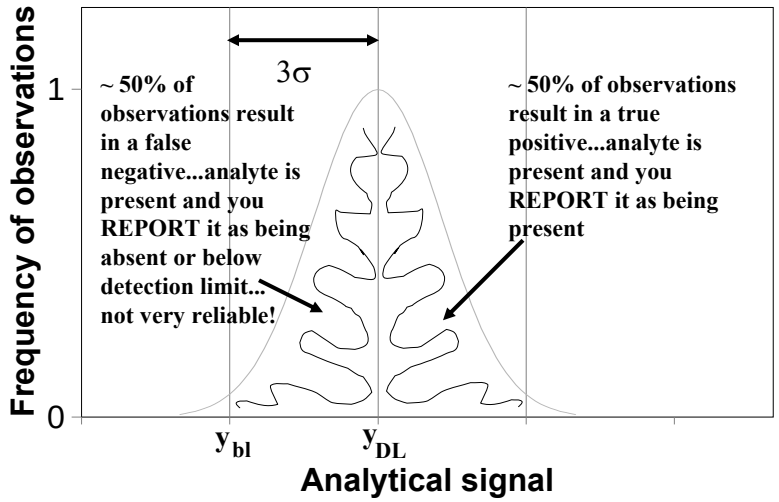


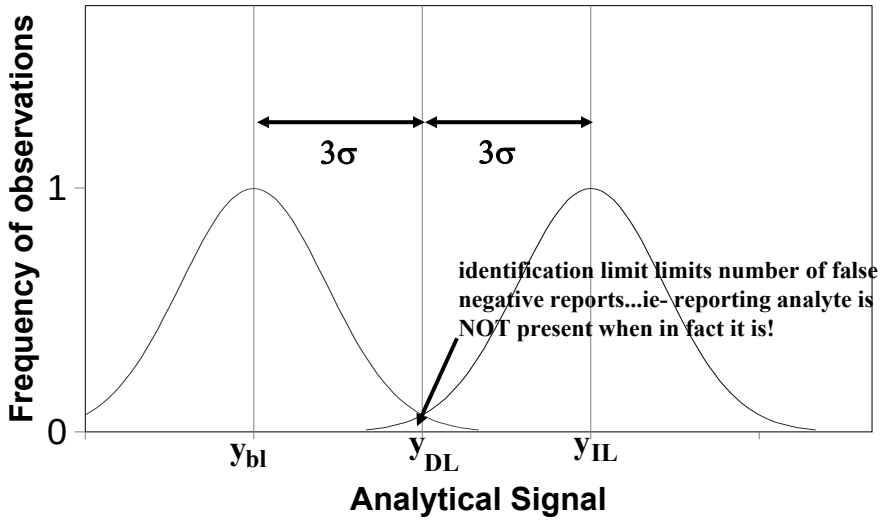
Identification Limit

the amount of material that can be *reliably* detected with a reasonable degree of confidence.

By reliably detected, we may mean for example, if a sample with this concentration were put into our instrument, we are statistically confident that we would report the sample as containing a statistically significant amount of analyte the majority of the time…

$$c_{IL} = \frac{6\sigma_{blank}}{m}$$

Identification limit



Limit of Quantification

the amount of material that can be reliably *quantified*, C_q. The signal given by this amount of material is y_q and the uncertainty in the signal is σ_q

Typically, we would like to quantify the concentration of material with a relative uncertainty less than 10%.

$$RSD = \frac{\sigma_{ql}}{y_{ql}} = 0.10 \qquad y_{ql} = \frac{\sigma_{ql}}{0.10} = 10\sigma_{ql} \approx 10\sigma_{blank}$$

If we make the approximation that $\sigma_{ql} \sim \sigma_{blank}$, and m is well known, then:

$$C_{QL} = \frac{10\sigma_{blank}}{m}$$

Analytical Ranges

Dynamic Range:

- the range over which the signal is linear, usually defined from the detection limit to the the point where the signal is no longer linear with concentration.

Useful Range:

- the range over which there is useful quantification, usually defined from the limit of quantification (or identification limit) to the the point where the signal is no longer linear with concentration. (Note - that the useful range does NOT include the detection limit, working at the detection limit is NOT reliable.)

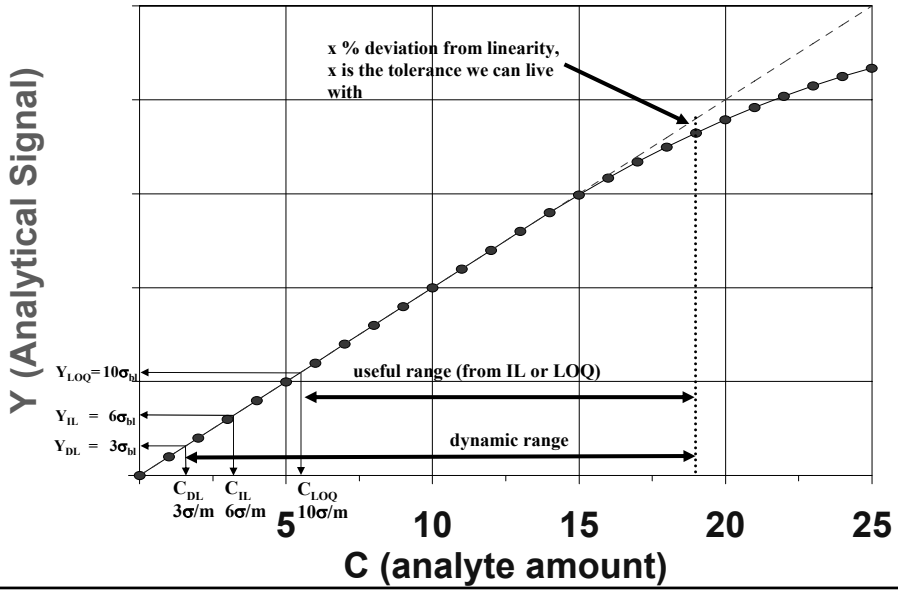
For a general instrumental method, we would like linear dynamic and useful ranges of greater than 2 orders of magnitude...the more the better usually.

-for specific applications we can sometimes get away with less than this:

eg. monitoring CH_4 in natural gas supply where we are measuring a major component that varies by a small amount.

$$85\% < CH_4 < 99\%$$

Summary of limits and ranges in Calibration of Instrumental Analytical methods



Methods of Calibration

1) normal calibration curve (analytical curve)
2) standard additions
3) internal standard

Calibration Curve
- used for simple matrixes
- instrumental signal is measured for a series of calibration solutions of varying analyte concentration.
- a least squares fit of the data to a function establishes a workable mathematical relationship.
- usually the relationship is linear, y=mC + b; if not we must use non-linear least squares analysis (ie- polynomial fit)

How to handle blanks
i) subtract blank signal from all subsequent signals to establish "corrected" or "net" instrumental signal.
ii) include blank signals in regression in which case a non zero intercept establishes the level of the blank.

REVIEW - you are expected to know linear least squares analysis and how to determine unknown concentration (with error!) from the measurement of unknown.
see Skoog Appendix 1 for review of this method.

Standard additions

- used when matrix is complex and will potentially affect the analyte response (ie- sensitivity changes, examples- measuring elemental constituents in blood).
Procedure
- prepare multiple samples of volume V_x and unknown concentration C_x. We spike each sample with a different volume, V_s, of a prepared standard of our analyte of concentration, C_s. Optionally, we further dilute each spiked sample to total volume V_t. Measure the signal for each spiked sample and plot analytical signal, y , vs. spiked sample concentration, C_s'. The original sample concentration is diluted as well as spike. The moles of spiked standard = C_sV_s

$$C_s' = C_s \times \frac{V_s}{V_t} \qquad C_x' = C_x \times \frac{V_x}{V_t}$$

The instrumental signal will be given by:

$$y = m(C_x' + C_s') + y_{blank} \qquad y = mC_s' + (mC_x' + y_{blank})$$

Plot y vs C_s' to get slope, m, and intercept, b. Note intercept, b= $(mC_x' + y_{blank})$
If y_{blank} is negligible, then b = mC_x' OR

$$C_x' = \frac{b}{m} \qquad AND \qquad C_x = \frac{b}{m} \times \frac{V_t}{V_x}$$

Standard additions – cont'd

Note: we frequently use very small spike volumes V_s and no dilution. This simplifies our analysis in that the dilution factors disappear from the above eqn's.
$V_t \sim V_x$ AND $C_x' \sim C_x$ AND $C_x = b/m$

Limitations
- instrument response must be linear over the expected concentration range and we must assume and verify that $mC_x' >> y_{blank}$.

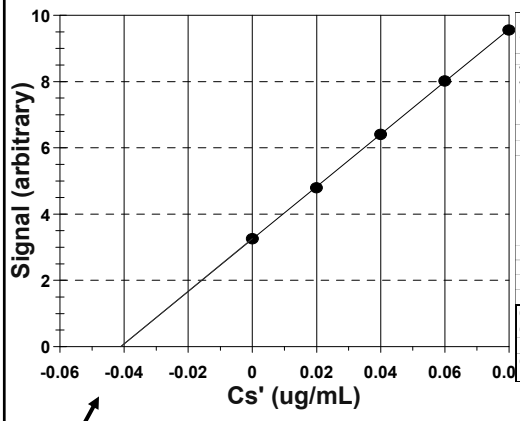
Applications
- wherever matrix effects can be significant,

Example
5.0 mL aliquots of an unkown containing phenoarbital were delivered to 50.0 mL volumetrics. The following volumes of a standard solution of phenoarbital (2.00ug/mL) were then introduced to the volumetrics before diluting to volume:
0.00, 0.50, 1.00, 1.50, 2.00 mL.

The corresponding signals on a fluorometer instrument were:
3.26, 4.80, 6.41, 8.02, 9.56 arbitrary units.

Find the concentration of phenoarbital in the original unknown.

Standard Additions – example



Example 1-11 Skoog, 5 ed.
Standard Additions

Vx (mL)	5
Vt (mL)	50
Cs (ug/ml)	2

Vs (mL)	Cs' (ug/mL)	Y (arb)		Regression Output:	
	-0.041037		0		
0.0	0.00	3.26	3.26	b	3.246
0.5	0.02	4.80		s {b}	0.026
1.0	0.04	6.41		r^2	1
1.5	0.06	8.02		N	5
2.0	0.08	9.56		DOF	3
				m	79.10
				s{m}	0.404

CALCULATIONS			
Cx' (b/m)	0.04104	+/-	0.0004
Cx(b/m*Vt/Vx)	0.4104	+/-	0.0039

negative x-axis intercept gives C_x'

Internal Standard method

- used when sensitive physical variables in analytical measurement are difficult to control. (ie- injection volume in GC, sample flow rate in AA)
- an internal standard is a substance added in a constant amount to all samples, or it may be a major constituent of the sample. I

Procedure
- add equal amount of int. std. to all samples and standards.
- measure analyte and int. std analytical signal for all samples and standards
- the analytical signal, corrected for fluctuations of the physical variable, can be calculated as $y_{analyte}/y_{int.\ std.}$

$$Plot \quad \frac{y_{analyte}}{y_{Int.std.}} \quad vs \quad C_{analyte}$$

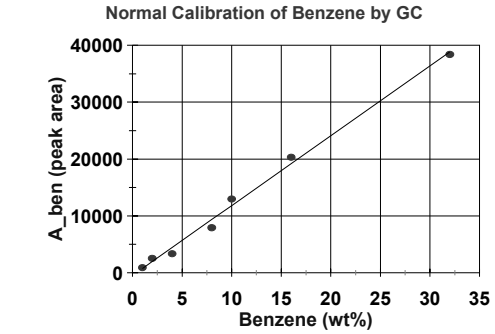
Limitations
- analyte and int. std. must behave similarly.
- analyte and int. std. signals must be proportional to the physical quantity giving rise to instrumental variations.
- method is limited to methods that can resolve the analyte and int. std. signal simultaneously.

Internal Standard-example

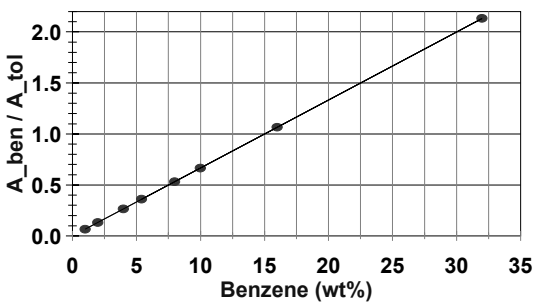
Example: Gas Chromatography

In a separation of benzene and cyclohexane in a hydrocarbon mixture, toluene can be added as an internal standard to EVERY sample and standard. The gas chromatographs will give three peaks. In a normal calibration, our analytical signal is the integrated area of the analyte peak. Using the internal standard, the peak areas for benzene, cyclohexane and toluene A_{ben}, A_{chex} and A_{tol}, are measured for each standard and unknown sample run. The ratio, A_{ben}/A_{tol} is then calculated for each standard and sample (similar for cyclohexane). A least squares analysis of A_{ben}/A_{tol} vs C_{ben} will yield a straight line. The measurement of A_{ben}/A_{tol} for the unkown gives us the concentration of benzene in the unknown sample(s).

Vinj	wt% ben		A_ben	A_tol	A_ben/A_tol
0.93	1		930	13950	0.066667
1.27	2		2540	19050	0.133333
0.842	4		3368	12630	0.266667
0.99	8		7920	14850	0.533333
1.297	10		12970	19455	0.666667
1.27	16		20320	19050	1.066667
1.2	32		38400	18000	2.133333
1.222	5.4		6598.8	18330	0.36
0.178466	<---------	relative std deviation in injection volume			



normal calibration shows large variation, which will contribure uncertainty to our analysis of the unknown.



internal standard method removes ALL variation associated with the physical variable.... reduces the uncertainty in our analysis of the unknown.

Gravimetric Analysis

Any of a variety of methods that depend on the determination of mass of a sample as the analytical signal.

1. Precipitation methods
analyte is converted to a sparingly soluble (a.k.a. insoluble) precipitate.

ie $Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)}$

Method – react unknown solution with excess of Ag^+. Weigh precipitate to determine the amount of Cl^- in sample...excess Ag^+ is washed away.

How do we calibrate?

We don't....directly. The molecular weight of the precipitate is our intrinsic calibration standard. The weight of AgCl precipitate is our analytical signal.

$Mass_{analyte} = amount_{analyte} \times MW_{precipitate}$

We can increase the sensitivity of the method by using precipitating agents that have a large molecular weight.

Gravimetric intro -cont'd

2) Thermogravimetric Analysis
The sample is decompoed at high temperature while monitoring the weight of the sample. The sample will thermally decompose and lose mass.

Example

$$CaCO_{3\,(s)} \xrightarrow{\Delta} CaO_{(s)} + CO_2$$

Analytical signal - the loss of sample mass. This gives us quantitative information.
Qualitative Signal – The temperature at which the mass is lost. This can tell us WHAT species is present.

See example Thermogram

Example Thermogram

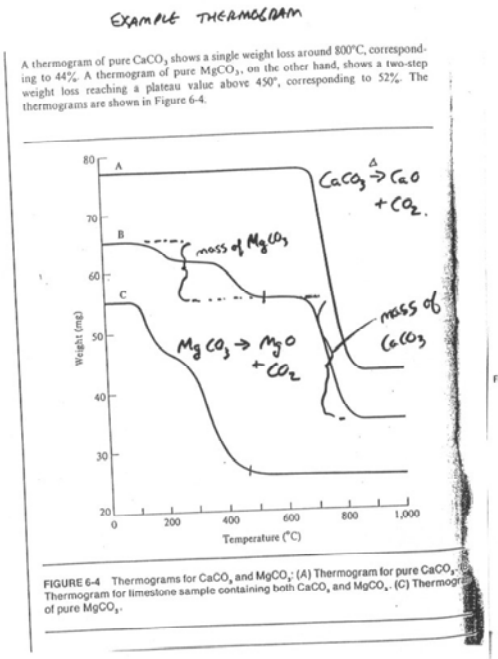


FIGURE 6-4 Thermograms for $CaCO_3$ and $MgCO_3$: (A) Thermogram for pure $CaCO_3$. (C) Thermogram for limestone sample containing both $CaCO_3$ and $MgCO_3$. (C) Thermogram of pure $MgCO_3$.

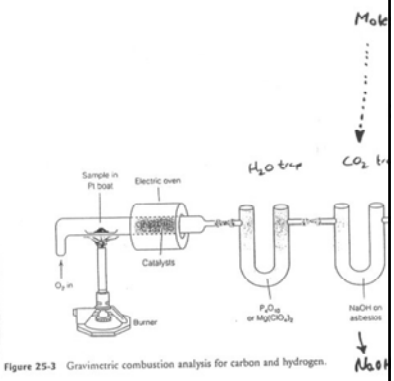
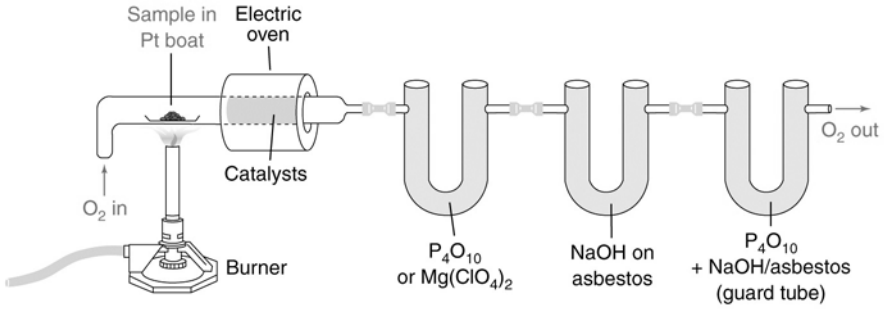


Figure 25-3 Gravimetric combustion analysis for carbon and hydrogen.

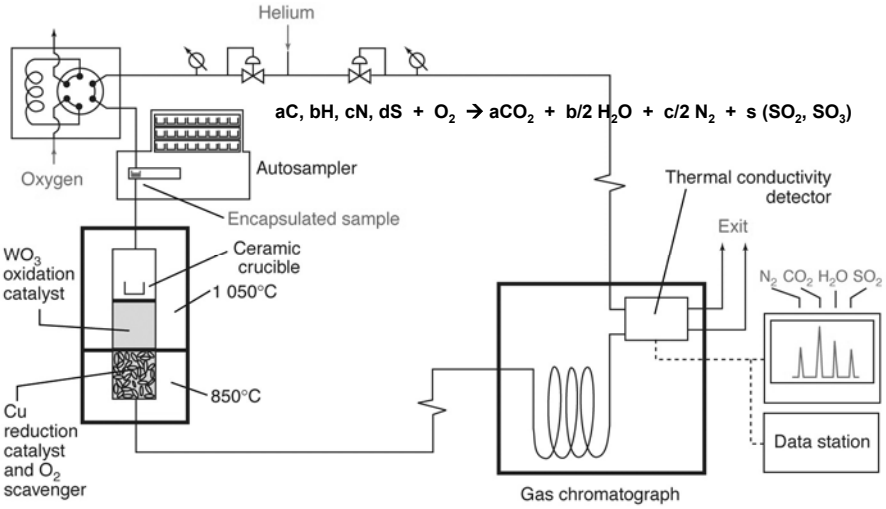
Gravimetric intro -cont'd

3) Volatization (thermal) methods – Combustion Analysis

- similar to thermogravimetric methods except we weigh the mass of the decomposition products.
- we can add change the nature of the gas that the solid is exposed to to change the reaction. We can collect the decomposition products in "traps" for identification purposes.



Modern Combustion Analysis



WO_3 catalyst – to complete combustion of C
Cu – heated, helps catalyze reduction of SO_3 to SO_2
dynamic flash combustion- very rapid combustion to ensure a narrow peak of products for GC separation.

Thermal Conductivity Detector (TCD)

Principle of operation: differences in thermal conductivity of analyte gases will give change in temperature of a heated filament, which gives rise to a change in R of filament. The change in R can be detected in a "Wheatstone Bridge" circuit using 4 filaments. One pair (2) is located in column effluent and one pair(2) is located in a split stream (or before the injector). ie- one pair acts as a reference.

- thermal conductivity of carrier gases (H_2 or He) is much higher than organic gases (analytes). When organic analyte enters the detector, the temperature of the filament rises, the resistance increases, the imbalance in resistance between the reference and detector filaments is the analytical signal.

***Wheatstone Bridge* – voltage drop (IR drop) depends on the resistance of the filament. The bridge uses an instrumentation amplifier to amplify small differences in the voltage at the two points shown in the bridge.**

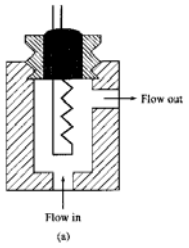
***Advantages* - universal detector, economical, easy replacement**

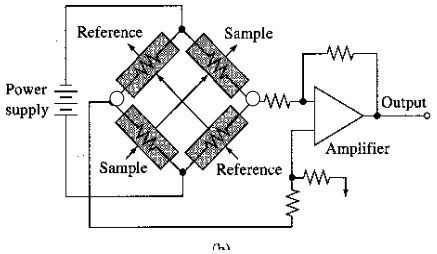
Disadvantages

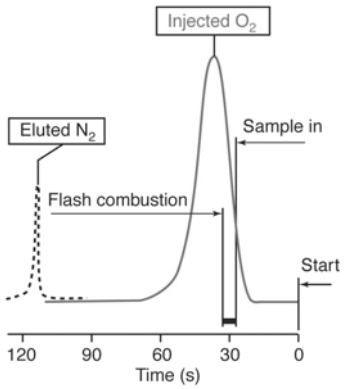
- low sensitivity,

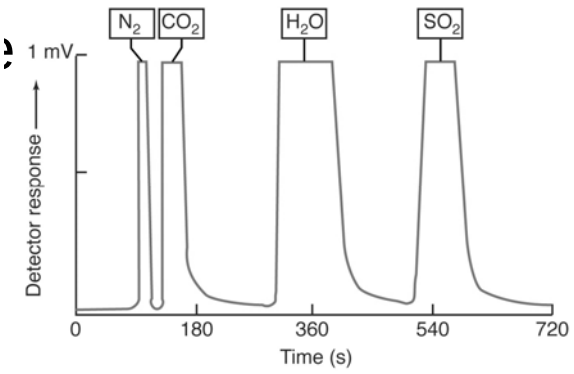
- not selective

(no molecular information)









Dynamic Flash Combustion
-sample in Sn capsule dropped in just after O_2 flow starts.
$Sn + O_2 \rightarrow SnO_2$, uses available O_2, releases heat, heats sample to 1700 C. Sample cracks, N_2 released before O_2 rises to maximum level, preventing formation of NO_x.

Chromatographic Separation of Gases
light gases are separated on chromatographic column and detected with TCD. Analyte is quantified by peak area after calibration of peak area vs injected amount for each analyte. From this, N, C, H, S content of original sample is determined.

Precipitation Methods

Precipitating agent

-should be specific or selective

Properties of a good precipitate

- should be filterable and washable
(determined by particle size and solubility)
- low solubility (*we need quantitative conversion to solid and minimal loss on washing - adjust pH of wash)*
K_{sp} must be very small
- stable and unreactive
- must have known composition
- high molar mass

Particle Size of Crystals

should be as large as possible to ensure:

❶ **precipitate is not lost in filtering**
❷ **larger crystals are purer**

Colloidal Suspension	**Crystalline Suspension**
d_p = 1 nm → 100nm	d_p > 100 μm (0.1 mm)
Not filterable	**will settle and filter**

Harris Table – precipitation examples

Table 27-1 Representative gravimetric analyses

Species analyzed	Precipitated form	Form weighed	Interfering species
K^+	$KB(C_6H_5)_4$	$KB(C_6H_5)_4$	NH_4^+, Ag^+, Hg^{2+}, Tl^+, Rb^+, Cs^+
Mg^{2+}	$Mg(NH_4)PO_4 \cdot 6H_2O$	$Mg_2P_2O_7$	Many metals except Na^+ and K^+
Ca^{2+}	$CaC_2O_4 \cdot H_2O$	$CaCO_3$ or CaO	Many metals except Mg^{2+}, Na^+, K^+
Ba^{2+}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-
Ti^{4+}	$TiO(5,7\text{-dibromo-8-hydroxyquinoline})_2$	Same	Fe^{3+}, Zr^{4+}, Cu^{2+}, $C_2O_4^{2-}$, citrate, HF
VO_4^{3-}	Hg_3VO_4	V_2O_5	Cl^-, Br^-, I^-, SO_4^{2-}, CrO_4^{2-}, AsO_4^{3-}, PO_4^{3-}
Cr^{3+}	$PbCrO_4$	$PbCrO_4$	Ag^+, NH_4^+
Mn^{2+}	$Mn(NH_4)PO_4 \cdot H_2O$	$Mn_2P_2O_7$	Many metals
Fe^{3+}	$Fe(HCO_2)_3$	Fe_2O_3	Many metals
Co^{2+}	$Co(1\text{-nitroso-2-naphtholate})_3$	$CoSO_4$ (by reaction with H_2SO_4)	Fe^{3+}, Pd^{2+}, Zr^{4+}

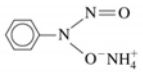
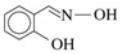
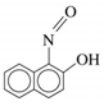
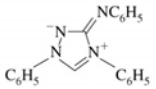
More precipitation examples

Table 27-1 Representative gravimetric analyses

Species analyzed	Precipitated form	Form weighed	Interfering species
Ni^{2+}	$Ni(dimethylglyoximate)_2$	Same	Pd^{2+}, Pt^{2+}, Bi^{3+}, Au^{3+}
Cu^{2+}	CuSCN	CuSCN	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
Zn^{2+}	$Zn(NH_4)PO_4 \cdot H_2O$	$Zn_2P_2O_7$	Many metals
Ce^{4+}	$Ce(IO_3)_4$	CeO_2	Th^{4+}, Ti^{4+}, Zr^{4+}
Al^{3+}	$Al(8\text{-hydroxyquinolate})_3$	Same	Many metals
Sn^{4+}	$Sn(cupferron)_4$	SnO_2	Cu^{2+}, Pb^{2+}, As(III)
Pb^{2+}	$PbSO_4$	$PbSO_4$	Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Ag^+, HCl, HNO_3
NH_4^+	$NH_4B(C_6H_5)_4$	$NH_4B(C_6H_5)_4$	K^+, Rb^+, Cs^+
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
Br^-	AgBr	AgBr	Cl^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
I^-	AgI	AgI	Cl^-, Br^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
SCN^-	CuSCN	CuSCN	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
CN^-	AgCN	AgCN	Cl^-, Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$
F^-	$(C_6H_5)_3SnF$	$(C_6H_5)_3SnF$	Many metals (except alkali metals), SiO_4^{4-}, CO_3^{2-}
ClO_4^-	$KClO_4$	$KClO_4$	
SO_4^{2-}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-
PO_4^{3-}	$Mg(NH_4)PO_4 \cdot 6H_2O$	$Mg_2P_2O_7$	Many metals except Na^+, K^+
NO_3^-	Nitron nitrate	Nitron nitrate	ClO_4^-, I^-, SCN^-, CrO_4^{2-}, ClO_3^-, NO_2^-, Br^-, $C_2O_4^{2-}$
CO_3^{2-}	CO_2 (by acidification)	CO_2	(The liberated CO_2 is trapped with Ascarite and weighed.)

Organic precipitating Agents

Table 27-2 Common organic precipitating agents

Name	Structure	Ions precipitated
Dimethylglyoxime		Ni^{2+}, Pd^{2+}, Pt^{2+}
Cupferron		Fe^{3+}, VO_2^+, Ti^{4+}, Zr^{4+}, Ce^{4+}, Ga^{3+}, Sn^{4+}
8-Hydroxyquinoline (oxine)		Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Bi^{3+}, Ga^{3+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, TiO^{2+}
Salicylaldoxime		Cu^{2+}, Pb^{2+}, Bi^{3+}, Zn^{2+}, Ni^{2+}, Pd^{2+}
1-Nitroso-2-naphthol		Co^{2+}, Fe^{3+}, Pd^{2+}, Zr^{4+}
Nitron		NO_3^-, ClO_4^-, BF_4^-, WO_4^{2-}
Sodium tetraphenylborate	$Na^+B(C_6H_5)_4^-$	K^+, Rb^+, Cs^+, NH_4^+, Ag^+, organic ammonium ions
Tetraphenylarsonium chloride	$(C_6H_5)_4As^+Cl^-$	$Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-

Colloidal Precipitates

Colloidal suspensions form from precipitates that have low solubility.

Precipitate	K_{sp}
$Fe(OH)_3$	2×10^{-39}
$Al(OH)_3$	3×10^{-34}
PbS	3×10^{-28}
HgS	2×10^{-53}
$BaSO_4$	1×10^{-10}
CaC_2O_4	9×10^{-8}

- normally the small colloid particles are too small for gravimetric analysis.

- the colloidal suspension is stabilized through electrostatic forces that prevent small precipitate particles from coming together. The electroststic forces are formed from *strong* adsorption of cations or anions of the precipitate type.

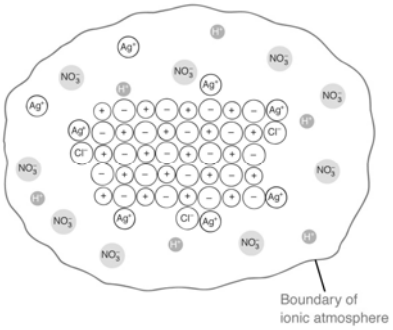
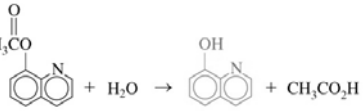


Table 27-3 Common reagents used for homogeneous precipitation

Precipitant	Reagent	Reaction	Some elements precipitated
OH^-	Urea	$(H_2N)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$	Al, Ga, Th, Bi, Fe, Sn
OH^-	Potassium cyanate	$HOCN + 2H_2O \rightarrow NH_4^+ + CO_2 + OH^-$ (Hydrogen cyanate)	Cr, Fe
S^{2-}	Thioacetamide[a]	$CH_3\overset{\overset{S}{\|}}{C}NH_2 + H_2O \rightarrow CH_3\overset{\overset{O}{\|}}{C}NH_2 + H_2S$	Sb, Mo, Cu, Cd
SO_4^{2-}	Sulfamic acid	$H_3\overset{+}{N}SO_3^- + H_2O \rightarrow NH_4^+ + SO_4^{2-} + H^+$	Ba, Ca, Sr, Pb
$C_2O_4^{2-}$	Dimethyl oxalate	$CH_3O\overset{\overset{O}{\|}}{\overset{\overset{O}{\|}}{C}}\overset{\overset{O}{\|}}{\overset{\overset{O}{\|}}{C}}OCH_3 + 2H_2O \rightarrow 2CH_3OH + C_2O_4^{2-} + 2H^+$	Ca, Mg, Zn
PO_4^{3-}	Trimethyl phosphate	$(CH_3O)_3P{=}O + 3H_2O \rightarrow 3CH_3OH + PO_4^{3-} + 3H^+$	Zr, Hf
CrO_4^{2-}	Chromic ion plus bromate	$2Cr^{3+} + BrO_3^- + 5H_2O \rightarrow 2CrO_4^{2-} + Br^- + 10H^+$	Pb
8-Hydroxyquinoline	8-Acetoxyquinoline		Al, U, Mg, Zn

a. Hydrogen sulfide is volatile and toxic; it should be handled only in a well-vented hood. Thioacetamide is a carcinogen that should be handled with gloves. If thioacetamide contacts your skin, wash yourself thoroughly immediately. Leftover reagent is destroyed by heating at 50°C with 5 mol of NaOCl per mole of thioacetamide, and then washing down the drain. [H. Elo, *J. Chem. Ed.* **1987**, *64*, A144.]

Precipitate formation

- is affected by solubility, temperature, reactant concentrations, mixing rates, pH

Relative Supersaturation

$$S_r = \frac{Q - S}{S}$$

where

S_r = relative supersaturation
S = equilibrium solubility
Q = actual concentration

$$ParticleSize \propto \frac{1}{S_r}$$

☹ if S_r is large, particles are small + many.
☺ if S_r is small, particles are large + few

∴ we would like to keep supersaturation ***small*** so that we have fewer larger particles

Nucleation

- dust particles can act as nucleation sites.

Competitive Processes

☹ further nucleation
☺ particle growth on existing particles

Supersaturation enhances nucleation dramatically and particle growth to a lesser extent.

How do we minimize supersaturation?

1. increase temperature, this increases S
2. use dilute solutions, this reduces Q
3. add precipitation reagent slowly
4. stirring
5. control pH

$S_r = \frac{Q - S}{S}$

Example of pH control

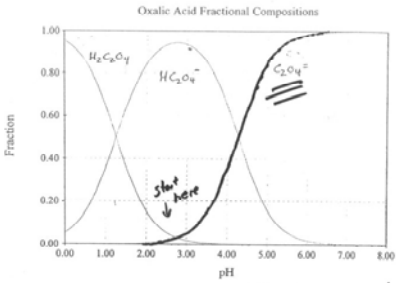
determination of Ca^{+2} by precipitation as calcium oxalate, CaC_2O_4

$H_2C_2O_4 \rightleftharpoons H^+ + HC_2O_4^-$ K_{1a}

$HC_2O_4^- \rightleftharpoons H^+ + C_2O_4^{-2}$ K_{2a}

$Ca^{+2}_{(aq)} + C_2O_4^{-2}_{(aq)} \rightarrow CaC_2O_{4(s)}$

We use pH to control $[C_2O_4^{-2}]$!



- start with acidic solution & use base to titrate off

$Ca^{2+}_{(aq)} + C_2O_4^{2-}_{(aq)} \rightleftharpoons CaC_2O_{4(s)}$

- use acidic solution to wash the precipitate

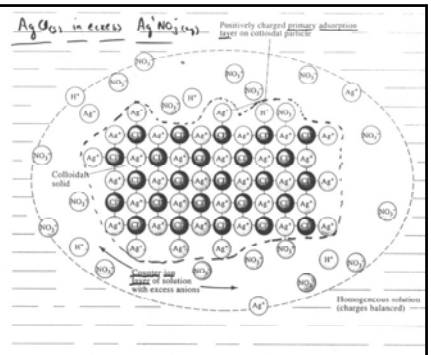
Colloidal Precipitates

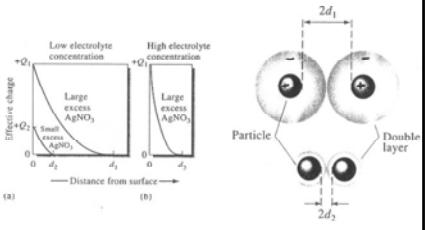
colloidal suspensions form from precipitates that have very low solubility in solution. (S_r is large)

precipitate	K_{sp}
$Fe(OH)_3$	2×10^{-39}
$Al(OH)_3$	3×10^{-34}
PbS	3×10^{-28}
HgS	2×10^{-53}
$BaSO_4$	1×10^{-10}
CaC_2O_4	9×10^{-8}

- normally the small colloid particles are too small for gravimetric analysis.

- the colloidal suspension is stabilized through electrostatic forces that prevent small precipitate particles from coming together. The electrostatic forces are formed from ***strong*** adsorption of cations or anions of the precipitate type.





Skoog/West/Holler, *Fundamentals of Analytical Chemistry*, 7/e
overhead transparency 10, text figure 5.3, 5.4 and 5.5, pages 85, 86, 87

Saunders College Publishing

Coagulation of Colloids

Coagulation is brought about by destabilizing the colloids.

- heat will remove primary adsorption layer (ie- we mimic a precipitate with high solubility), thus decreasing the thickness of the double layer and allowing particles to come together.

- increased electrolyte concentration decreases double layer thickness by allowing penetration of ions into primary and secondary layers.

Practical treatments

ie. AgCl - to avoid peptization (mass reverts to colloidal solution), we wash the precipitate with electrolyte solution.

digestion - heating of precipitate which allows loss of water from the coagulated mass.
- ↓ gel ↓ ions in counter ion layer.

Experiment 4A - gravimetric determination of Cl^-

Crystalline precipitates

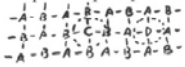
- larger particles and more easily filtered than colloids in general. Again we use digestion to improve filterability and purity.
- slow crystal growth ensures equilibrium, ∴ purity

Errors from Coprecipitation

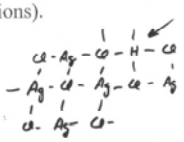
- removal of soluble species from solution through:

i) ***surface adsorption*** - ions that form the solution double layer are removed with the ~~precipitate~~ (more problematic with coagulated colloids because of large surface to mass ratio). Think of coagulated colloid as a sponge.

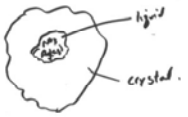
ii) ***mixed crystal formation*** - in a matrix containing "like" ions that form crystals of "like" structure, an interfering ion can be mixed in the crystal. Separation of offending ions prior to precipitation may be required.



iii) ***occlusion*** - ions not of the crystal type become trapped in the crystal lattice because of rapid crystal growth. (non equilibrium conditions).



iv) ***entrapment*** - similar to occlusion except we have regions of solution trapped in the crystal lattice through rapid growth.



Many types of coprecipitation are eliminated though slow crystal growth and digestion. Digestion allows equilibrium conditions to prevail.

- rapid exchange of ions
- low Sr allows slow crystal growth

Precipitation from Homogeneous Solution

- precipitation in which the precipitating agent is formed slowly and homogeneously in situ in the solution. Thus we maintain a small value of Q and relative supersaturation.

ie. OH^- generation through heating of urea in solution

$$(NH_2)_2CO + 3H_2O \rightarrow CO_2 + 2NH_4^+ + 2OH^-$$

$$2OH^- + Al^{3+} \rightarrow Al(OH)_3 \quad \textit{(or other hydroxides)}$$

This method increases filterability and reduces contamination of the hydroxide precipitate. It is similar to the generation of $C_2O_4^{2-}$ by adjustment of pH demonstrated last class.

Drying of Precipitates

- needed to bring precipitate to constant weight (and thus known composition). The heating process can:

* remove loose water
* remove volatile contaminants (ie-HCl for AgCl ppt)
* remove waters of hydration
* decompose sample (loss of CO or CO_2)

∴ the temperature used is dependent on precipitate.

CONSTANT WEIGHT

½ hour dry → cool → weigh → ½ hour dry → cool → weigh → same weight? NO → YES

TABLE 25-2 Common organic precip

Name	Structu
Dimethylglyoxime	
Cupferron	
8-Hydroxyquinoline (oxine)	
Salicylaldoxime	
1-Nitroso-2-naphthol	
Nitron	
Sodium tetraphenylborate	$Na^+B(C_6H_5)_4^-$
Tetraphenylarsonium chloride	$(C_6H_5)_4As^+Cl^-$

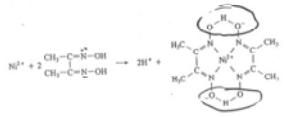
Applications of Gravimetric Analysis

Organic Precipitating Agents

Dimethylglyoxime (DMG)
- for Ni^{++} determination
- highly specific
- [redacted]
- chelating agent!

$$Ni^{2+} + 2\ DMGH \rightarrow 2H^{+} + Ni(DMG)_{2\,(s)}$$

Interferences : $Pd(DMG)_2$ (ph < 5),
$Bi(DMG)_2$ (ph > 11)
- tartaric acid - complexes Fe^{3+}
- NH_3 adjusts pH and complexes metal ions to prevent OH precipitates.



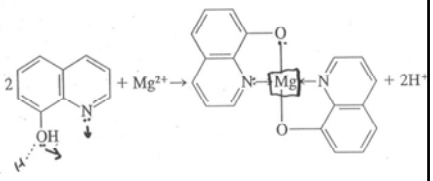
8-Hydroxyquinoline (oxine)

Typical example of another chelating agent. Large hydrophobic molecules such as this are relatively insoluble once they form a complex with the metal ion.

if M^{n+} is metal ion, then

$$M^{n+} + n\ HOx \rightarrow M(Ox)_n + n\ H^{+}$$

$(Al^{3+}, Mg^{2+}, Pd^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+})$



We can control the specificity of the method with pH if we have a matrix with several competing ions.

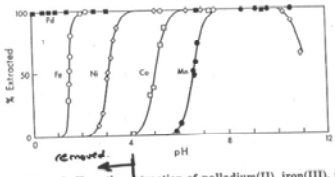


Figure 16-3. Effect of pH on the extraction of palladium(II), iron(III), nickel(II) cobalt(II), and manganese(II) from water into 0.01 *M* 8-hydroxyquinoline in chloroform. From J. Stary, *The Solvent Extraction of Metal Chelates*, Macmillan, N.Y., 1964. By permission.

Gravimetric Factor

In gravimetirc analysis, we try to use precipitates that have large molecular weights so as to increase our sensitivity. In back calculating to determine an analyte of interest, one can use the gravimetric factor:

$$GF = \frac{a}{b} * \frac{MW_{sought}}{MW_{weighed}}$$

a/b - whole number ratio to give us the same number of moles of constituent element of interest in numerator and denominator

MW_{sought} - molecular weight of compound we are interested in determining.

$MW_{weighed}$ - molecular weight of the precipitate we weighed.

Then ...

$$\%X_{sought} = \frac{Mass_{product} * GF}{Mass_{sample}} * 100\%$$

Example Calculation

Determination of Cl^-

A 0.2150 g sample is dissolved and treated with excess $AgNO_3$. The precipitate is filtered, washed, dried and weighed. Product mass ($AgCl$) is 0.4587 g. What is % Cl in original sample?

$$\% Cl = \frac{\text{mass } Cl}{\text{mass sample}} \cdot 100\%$$

$$\text{mass } Cl = \text{moles } Cl \cdot MW_{Cl}$$

$$\text{moles } Cl = \text{moles } AgCl$$

$$\text{moles } AgCl = \frac{\text{mass } AgCl}{MW_{AgCl}}$$

$$\therefore \% Cl = \frac{\frac{\text{mass } AgCl}{MW_{AgCl}} \cdot MW_{Cl}}{\text{mass sample}} \cdot 100\%$$

$$= \frac{\text{mass } AgCl \cdot \frac{MW_{Cl}}{MW_{AgCl}}}{\text{mass sample}} \cdot 100\%$$

cont'd

$$\% Cl = \frac{0.4587\ g \cdot \frac{35.453\ g/mol}{143.321\ g/mol}}{0.2150\ g} \cdot 100\% = 52.78\%$$

IF WE ALSO WRITE THIS AS

$$\% Cl = \frac{\text{mass of product} \cdot \left[\frac{MW_{sought}}{MW_{product}}\right]}{\text{mass of sample}} \cdot 100\%$$

$$= \frac{\text{mass of product} \cdot \text{"GRAVIMETRIC FACTOR"}}{\text{mass of sample}} \cdot 100\%$$

$$\text{GRAVIMETRIC FACTOR} = \left[\frac{MW_{sought}}{MW_{product}}\right]$$

Example 2

A 1.0000 g ore sample is dissolved and treated with excess K_2CrO_4

$$2\ Ag^+ + CrO_4^{2-} \rightarrow \underbrace{Ag_2CrO_4(s)}_{\text{red ppt}}$$

The dried ppt weighed 0.0275 g.
What is % Ag in the ore?

$$\% Ag = \frac{\text{mass } Ag}{\text{mass sample}} \cdot 100\%$$

$$\text{mass } Ag = \text{moles } Ag \cdot MW_{Ag}$$

$$\text{moles } Ag = \text{moles } Ag_2CrO_4 \cdot \frac{2\ \text{moles } Ag}{1\ \text{mol } Ag_2CrO_4}$$

$$\text{moles } Ag_2CrO_4 = \frac{\text{mass product}}{MW_{Ag_2CrO_4}}$$

$$\% Ag = \frac{\text{mass product} \cdot \frac{2}{1} \cdot \frac{MW_{Ag}}{MW_{Ag_2CrO_4}}}{\text{mass of sample}}$$

G.F.

$$= \frac{\text{mass product} \left[\cdot \frac{2}{1} \cdot \frac{MW_{sought}}{MW_{product}}\right] \cdot 100\%}{\text{mass sample}}$$

$$= \ldots 1.79\ \%$$

Equilibrium in Solution

In general, for the following reaction:

$$aA + bB \rightleftharpoons cC + dD$$

we can write the equilibrium expression...

$$K_{eq} = \frac{[a_c]^c * [a_d]^d}{[a_a]^a * [a_b]^b} = \frac{[C]^c * [D]^d}{[A]^a * [B]^b}$$

for dilute solutions

where a_i = activity of species i
$[i]$ = concentration of species i

Chemical equilibrium

A dynamic state in which the rate of forward and reverse reactions is equal. The equilibrium constant tells us about the thermodynamic equilibrium state but does not tell us anything about the rate at which equilibrium is achieved.

Types of Equilibria

i) autoprotolysis (H_2O) K_w
ii) acid-base dissociation K_a & K_b
iii) solubility of solids K_{sp}
iv) complex ion formation K_f
v) redox equilibria K_{redox}
vi) distribution between solvents K_d

Autoprotolysis

self ionization $2HA \rightleftharpoons H_2A^+ + A^-$

Water

$$2\,H_2O \rightleftharpoons H_3O^+ + OH^-$$

$K_{eq} = [H_3O^+]\,[OH^-]/[H_2O]^2$

$K_{eq}\,[H_2O]^2 = [H_3O^+]\,[OH^-]$

$K_{eq}\,[H_2O]^2 = K_w$

$K_w = [H_3O^+]\,[OH^-] \approx 1 \times 10^{-14}$ (25°C)

Example

Calculate $[H_3O^+]$ of pure water at 0, 25, 50, 100°C.

In pure water we have only one source of H_3O^+ and OH^- . $\therefore [H_3O^+] = [OH^-]$

$$K_w = [H_3O^+]\,[OH^-] = [H_3O^+]^2$$

$$[H_3O^+] = \sqrt{K_w(T)}$$

T (°C)	K_w	$[H_3O^+]$
0	0.11×10^{-14}	0.34×10^{-7}
25	1.01×10^{-14}	1.00×10^{-7}
50	5.47×10^{-14}	2.34×10^{-7}
100	$49. \times10^{-14}$	7.0×10^{-7}

Solubility in Solution

For a solid that is sparingly soluble is solution,

$$A_aB_{b\,(s)} \rightleftharpoons aA^{x+}_{(aq)} + bB^{y-}_{(aq)}$$

$$K_{eq} = \frac{[A^{x+}]^a[B^{y-}]^b}{[A_aB_{b(s)}]}$$

$$K_{eq}[A_aB_{b(s)}] = K_{sp} = [A^{x+}]^a[B^{y-}]^b$$

- see values of K_{sp} in Appendix

Examples

Calculate the $[Cl^-]$ in a solution containing only AgCl solid.

$K_{sp} = [Ag^+][Cl^-] = 1.82 \times 10^{-10}$

$[Ag^+] = [Cl^-]$

$$[Cl^-] = \sqrt{K_{sp}} = \sqrt{1.82*10^{-10}} = 1.35*10^{-5}$$

Calculate the solubility of $La(IO_3)_3$ in pure water in grams per mL.

$La(IO_3)_3\,(s) \rightleftharpoons La^{3+} + 3\,IO_3^-$

$K_{sp} = [La^{3+}][IO_3^-]^3 = 1.0 \times 10^{-11}$ from Appendix IV

$[IO_3^-] = 3 * [La^{3+}]$

$K_{sp} = [La^{3+}](3\,[La^{3+}])^3 = 27\,[La^{3+}]^4$

$$[La^{3+}] = \sqrt[4]{\frac{K_{sp}}{27}} = 7.8*10^{-4}$$

$\therefore$ solubility of $La(IO_3)_3 = 7.8 * 10^{-4}$ moles/L

$$S_{La(IO3)3} = 7.8*10^{-4}\frac{moles}{L} * 663.6\frac{g}{mole} * \frac{1L}{1000ml}$$

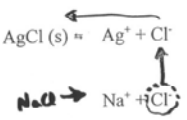
$= 5.18*10^{-4}$ g/mL

Common Ion Effect

Solubility is reduced by the presence of a common ion in solution from another source.

Example

Calculate the solubility of AgCl in a solution containing .01M $NaCl_{(aq)}$



$[Cl^-] = 0.01M + Cl^-_{AgCl} = 0.01M + S_{AgCl}$

$K_{sp} = [Ag^+][Cl^-] = S_{AgCl}\,(0.01M + S_{AgCl})$

From here, we have two methods

Method 1: make an assumption

$S_{AgCl} \ll 0.01M$ (since solubility is know to be small)

then ... $K_{sp} = [Ag^+][Cl^-] = S_{AgCl}\,(0.01M)$

$S_{AgCl} = K_{sp}/0.01M = 1.82\times10^{-10}/0.01M = 1.82\times10^{-8}$

check assumption, OK. For more accuracy, use one more iteration...

$K_{sp} = [Ag^+][Cl^-] = S_{AgCl}\,(0.01M + S_{AgCl})$
$= S_{AgCl}\,(0.01M + 1.82\times10^{-8})$

$S_{AgCl} = K_{sp}/1.00000182\times10^{-2} = 1.8199\times10^{-8}$
$\approx 1.82\times10^{-8}$

Method 2: solve quadratic

$S^2_{AgCl} + 0.01\,S_{AgCl} - K_{sp} = 0$

$ax^2 + bx + c = 0 \Rightarrow x = \dfrac{-b \pm \sqrt{b^2-4ac}}{2a}$

$$S_{AgCl} = \frac{-b \pm \sqrt{b^2-4ac}}{2a}$$

$S_{AgCl} = 1.81995\times10^{-8} \approx 1.82\times10^{-8}$

Note the reduced solubility of AgCl from the common ion effect.

Acid Base Equilibria

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$
(HA: acid; A^-: conjugate base)

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Conjugate Base

$A^- + H_2O \rightleftharpoons OH^- + HA$

$$K_b = \frac{[OH^-][HA]}{[A^-]}$$

$$K_aK_b = \frac{[H_3O^+][A^-]}{[HA]} * \frac{[OH^-][HA]}{[A^-]} = [H_3O^+][OH^-]$$

$\boxed{K_a K_b = K_w}$ $\quad \therefore K_b = \dfrac{K_w}{K_a}$

See Appendix G in Harris for K_a of acids.

Activity

- experimental evidence indicates that *apparent** equilibrium *constants* are affected by the presence of ions in solution, and not necessarily those ions that are involved in the equilibrium process.

  * (*apparent* equilibrium constants are calculated using [concentrations])

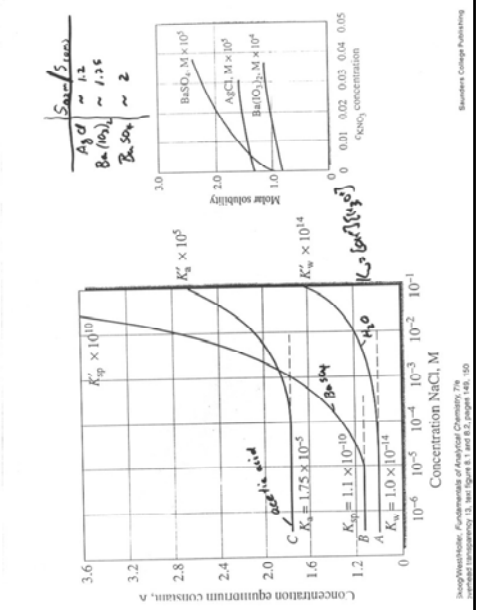
- the effect is dependent on the total concentration of ions and their charge, is largely unaffected by neutral species.

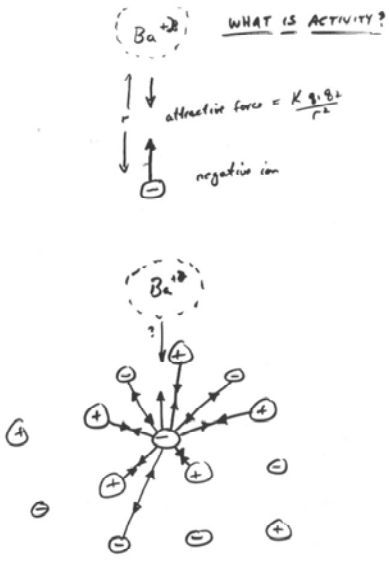
What type of forces are at play??

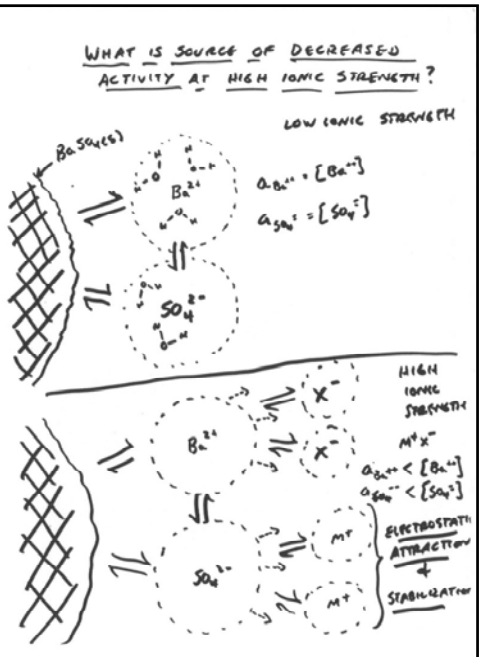
ELECTROSTATIC !

$$F = \frac{1}{4\pi\epsilon_o}\frac{q_1 q_2}{r^2}$$

q_1, q_2: charges on ions
r : distance between charges
ϵ_o: permitivity







☞ the effect can be expressed to be dependent on the ionic strength (μ) :

$$\mu = \sum \tfrac{1}{2} C_i z_i^2$$

C_i = concentration of ion i
z_i = charge of ion i

example 1 : ionic strength of 0.1M NaCl

$\mu = \tfrac{1}{2}[Na^+](+1)^2 + \tfrac{1}{2}[Cl^-](-1)^2$
$= \tfrac{1}{2}[0.1M](+1)^2 + \tfrac{1}{2}[0.1](-1)^2$
$= 0.1M$

Ionic strength of singly charged species is equal to the analytical concentration

example 2 : ionic strength of 0.1M $La_2(SO_4)_3$

$\mu = \tfrac{1}{2}[La^{+3}](+3)^2 + \tfrac{1}{2}[SO_4^{-2}](-2)^2$
$= \tfrac{1}{2}[0.2M](9) + \tfrac{1}{2}[0.3](4)$
$= 1.5\ M$

EXAMPLES

8.7 d) 0.06 M $La(NO_3)_3$ + 0.03M $Fe(NO_3)_2$
Calculate μ

$C_{La^{3+}} = 0.06\ M$
$C_{NO_3} = 3(.06) + 2(.03) = .24\ M$
$C_{Fe^{2+}} = 0.03\ M$

$\mu = \sum_i \frac{1}{2} C_i z_i^2 = \frac{1}{2}\sum(c_i z_i^2)$

$= \frac{1}{2}\left(\underbrace{0.06(3)^2}_{La} + \underbrace{.24(-1)^2}_{NO_3^-} + \underbrace{(.03)(2)^2}_{Fe^{2+}}\right)$

$= 0.45\ M$

Activity

$$a_x = \gamma_x[x]$$

a_x = activity of species x
γ_x = activity coefficient
[x] = molar concentration of species x

Equilibrium constants are only truly constant if we express them with activities

Remember: $aA + bB \rightleftharpoons cC + dD$

We write this as :

$$K_{eq} = \frac{[a_c]^c \times [a_d]^d}{[a_a]^a \times [a_b]^b}$$

Substituting

$$K_{eq} = \frac{\gamma_c[C]^c \times \gamma_d[D]^d}{\gamma_a[A]^a \times \gamma_b[B]^b} = \frac{\gamma_c\gamma_d}{\gamma_a\gamma_b} \times \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$= \frac{\gamma_c\gamma_d}{\gamma_a\gamma_b} \times K'_{eq}$$

If we knew activity coeficients, we could calculate predict K_{eq}'

The Debye-Hückel Equation

- used to describe the activity coefficient assuming purely electrostatic forces of ions.

for derivation, see: A.W. Adamson, *"A Textbook of Physical Chemistry"*, 2nd ed., Academic Press, NY, 1979.

$$-\log\gamma_x = \frac{0.509 * Z_x^2\sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}$$

where

- γ_x activity coefficient for ion x
- Z_x charge on ion x
- μ ionic strength ($\Sigma \frac{1}{2} C_i Z_i^2$)
- α_x effective hydrated ion diameter (nm)

When μ is small (ie <0.01), then an approximation is given by:

$$-\log\gamma_x = 0.509 * Z_x^2\sqrt{\mu}$$

The Debye-Hückel Limiting Law

8-8b) Calculate γ for Pb^{2+} at $\mu = 0.012M$

$$-\log\gamma_x = \frac{0.51 Z_x^2\sqrt{\mu}}{1+3.3\alpha_x\sqrt{\mu}}$$ Use extended

$$= \frac{0.51(2)^2\sqrt{0.012}}{1+3.3(0.45)\sqrt{0.012}}$$

$= .2664$ ← .45 nm from Table in Book

$\gamma_x = 10^{-0.2664}$

$= 0.54$ ← 0.54 | 1

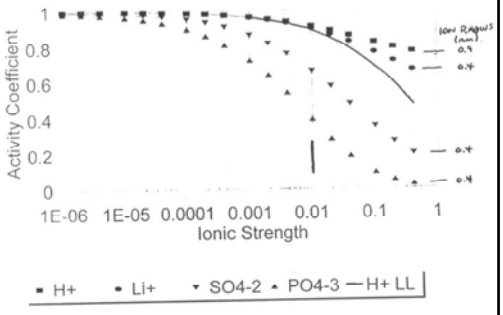
Extended Debye-Hückel Equation in Harris

$$\log\gamma = \frac{-0.51z^2\sqrt{\mu}}{1+\left(\frac{\alpha\sqrt{\mu}}{305}\right)}$$

γ = activity coefficient
z = charge on ion
μ = ionic strength (M)
α = hydrated radius (pm - 10^{-12})

Limiting Law ($\mu < 0.01M$)

$$\log\gamma = -0.51z^2\sqrt{\mu}$$



Net effects

higher ionic strength → smaller γ
higher charged ions → smaller γ
larger ion radius → larger γ

At small ionic strength, we can use the *The Debye-Hückel Limiting Law* to calculate activity coefficients; at higher ionic strength, we use the extended DH equation to take into account the effective diameter of the ions.

- activity coefficients must be measured experimentally for ionic strengths > 0.1M. This is due to a breakdown in the DH theory, namely the assumption that only electrostatic forces affect γ.

- γ may be >1 at high concentrations

Why would you expect a breakdown of DH theory at high ionic strength??

➥ it must mean that the electrostatic attractive and repulsive forces of ions are not the only forces at play. What else can happen at high concentrations.

Consider the average volume of an ion in a 1M solution.

$$V_{ion} = \frac{1L}{6.022\times10^{23} molecules} = 1.7\times10^{-24} L \approx 1.7\times10^{-27} m^3$$

What is radius of a sphere of this volume?

$V_{ion} = 4/3\pi r^3$

$$r = \sqrt[3]{\frac{3V_{ion}}{4\pi}} = \sqrt[3]{\frac{3\cdot1.7\times10^{-27} m^3}{4\pi}} = 7.4\times10^{-10} m$$

r_{sphere} = 0.74 nm = 740pm

$1m = 10^{-12}$ m

What is diameter of a hydrated ion?

A - 0.25-1.1nm (250-1100pm)

Therefore, at high concentrations, ions cannot form a complete hydrated shell. Other ions are present in that shell. Ions are close packed, "touching" one another.

Hydrogen bonding, orbital overlap. These other forces come into play and cause a breakdown of the DH theory. It also means that non-ionic species can have non-unity activity coefficients at high concentrations.

8-13 a) Calculate solubility of $Ag(IO_3)$ in 0.0167M $Ba(NO_3)_2$

i) molar concentration

ii) activities

$\mu = \frac{1}{2}(.0167(2)^2 + 2(.0167)) = 0.05M$ ✓

$K_{sp} = 3.1\times10^{-8}$

i) $Ag(IO_3) \rightleftharpoons Ag^+ + IO_3^-$

$[Ag^+] = [IO_3^-] = S$ $\quad K_{sp} = [Ag^+][IO_3^-] = S^2$

$S = \sqrt{K_{sp}} = \sqrt{3.1\times10^{-8}} = 1.8\times10^{-4} M$

TABLE 8.1

ii) $\gamma_{Ag^+}(\mu=0.05) = 0.8$

$\gamma_{IO_3^-}(\mu=0.05) = 0.82$

$a_{Ag^+} = \gamma_{Ag^+}[Ag^+]$

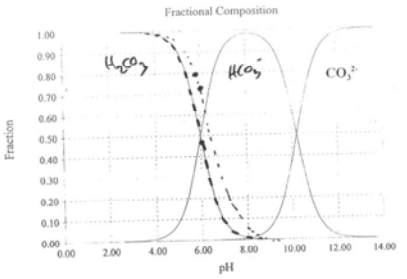
$K_{sp} = a_{Ag^+} a_{IO_3^-} = \gamma_{Ag^+}\gamma_{IO_3^-}[Ag^+][IO_3^-]$

$= \gamma_{Ag^+}\gamma_{IO_3^-} S^2$

$a_i = \gamma_i [i]$

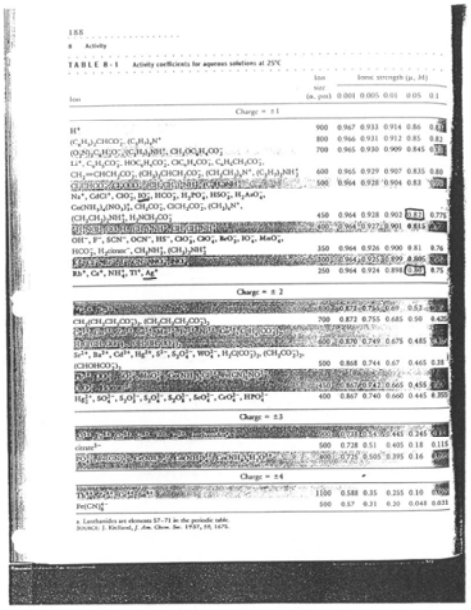
$$S = \sqrt{\frac{K_{sp}}{\gamma_{Ag^+}\gamma_{IO_3^-}}} = \sqrt{\frac{3.1\times10^{-8}}{.8\cdot.82}} = 2.2\times10^{-4}$$

20% more soluble



Ionic Strength = 0.1

---- ignore activity coefficients



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8 Activity

TABLE 8-1 Activity coefficients for aqueous solutions at 25°C

Ion	Ion size (a, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
Charge = ±1						
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_2H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $OC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$,						
$CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_3NH^+$	600	0.965	0.929	0.907	0.835	0.80
[illegible]	500	0.964	0.928	0.904	0.83	0.80
Na^+, $CdCl^+$, ClO_3^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$,						
$Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$,						
$(CH_3CH_2)_3NH^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
[illegible]	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_2^-, ClO_3^-, BrO_3^-, IO_3^-, MnO_4^-,						
HCO_3^-, H_2citrate$^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
[illegible]	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75
Charge = ±2						
[illegible]	900	0.872	0.755	0.69	0.53	0.45
$CH_3(CH_2CH_2CO_2^-)_2$, $(CH_3CH_2CH_2CO_2^-)_2$,	700	0.872	0.755	0.685	0.50	0.425
[illegible]	600	0.870	0.749	0.675	0.485	0.40
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_3^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$,						
$(CHOHCO_2^-)_2$	500	0.868	0.744	0.67	0.465	0.38
[illegible]	450	0.868	0.743	0.668	0.46	0.375
Hg_2^{2+}, SO_3^{2-}, $S_2O_4^{2-}$, $S_2O_5^{2-}$, $S_2O_6^{2-}$, SeO_3^{2-}, CrO_4^{2-}, HPO_3^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3						
[illegible]	900	0.718	0.54	0.445	0.245	0.18
citrate^{3-}	500	0.728	0.51	0.405	0.18	0.115
[illegible]	400	0.730	0.505	0.395	0.16	0.095
Charge = ±4						
[illegible]	1100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.031

a. Lanthanides are elements 57–71 in the periodic table.
SOURCE: J. Kielland, *J. Am. Chem. Soc.* 1937, 59, 1675.