Chapters 3 -5

Experimental Error & Calibration Methods

Experimental Error

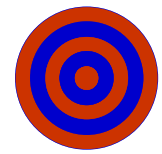
All measurements have error (uncertainty)

precision

- reproducibility

accuracy

- nearness to the "true value"
- data with unknown quality is useless!



•*How close your average value is to the correct one*

•*How close your values agree to each other*

•Out goal: accurate values that agree well with each other

Significant Figures

"The number of significant figures is the minimum number of digits needed to write a given value in scientific notation without loss of accuracy."

Counting Significant Figures

Rules for determining which digits are significant

1. All nonzero digits are significant.
2. All zeros between nonzero digits are significant.
3. All zeros at the end of a number on the right of a nonzero number on the right hand side of the decimal point are significant.
4. All other zeros are **not** significant.

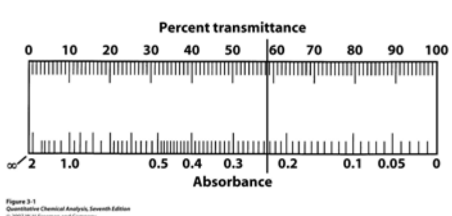
Ex. How many significant figures are understood in the following recorded measurement?

0.007805400 g

a) ten; b) four; c) seven; d) five

Significant Figures

When reading the scale of any apparatus, you should interpolate between the markings. It is usually possible to estimate to the nearest tenth of the distance between two marks.



Significant Figures in Arithmetic

Exact numbers

No uncertainty (or infinite number of significant figures); Ex. Counting indivisible things; Definitions in equations; exact relationships (conversion factors).

Rules for Rounding final data

1. If last digit of a # is 0-4, round down
2. If last digit of a # is 6-9, round up
3. If last digit of a # is 5, round to nearest even #

Don't round any # until calculation is complete…round at end.

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Significant Figures in Arithmetic

Addition and Subtraction

For addition and subtraction, the number of significant figures is determined by the piece of data with the fewest number of decimal places.

Ex. 3.4 + 0.021 + 7.310 = 10.731 = 10.7

$1.632 \times 10^5 + 4.107 \times 10^3 + 0.984 \times 10^6$ =? (P.41)

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Significant Figures in Arithmetic

Multiplication and Division

For multiplication and division, the number of significant figures used in the answer is the number in the value with the fewest significant figures.

Ex.

3.26×10^{-5}	4.3179×10^{12}	34.60
$\times$ 1.78	$\times\ 3.6 \times 10^{-19}$	÷ 2.462 87
5.80×10^{-5}	1.6×10^{-6}	14.05

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Significant Figures in Arithmetic

Logarithms and Antilogarithms

- In a <u>logarithm</u> of a #, keep as many digits to the right of the decimal (**mantissa**) as there are sig. figs in original #
- In an <u>antilogarithm</u>, keep as many digits as there are digits to the right of the decimal (**mantissa**) in the original #.

logarithm of n:

log **n** = **a** ⇔ **n** = 10^a **n** is the antilogarithm of **a**

log **339** = **2.530** ⇔ **339** = $10^{2.530}$

antilog(**2.53**) = $10^{2.53}$ = **3.4x10**^{1}

2 => character (corresponds to the exponent of the number written in scientific notation.)

.530 & .53 => mantissa

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p-Functions

$pX = -\log_{10}[X]$

examples:

pH

pOH

pCl

pAg

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Significant Figures and Graphs

- The rulings on a sheet of graph paper should be compatible with the number of significant figures of the coordinates.
- In general, a graph must be at least as accurate as the data being plotted. For this to happen, it must be properly scaled. Contrary to "popular belief", a zero-zero origin of a graph is very **<u>rare</u>**.

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Types of Error

no analysis is free of error or “uncertainty”

Systematic Error (determinate error)

The error is reproducible and can be discovered and corrected.

Random Error (indeterminate error)

Caused by uncontrollable variables, which can not be defined/eliminated.

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Systematic (determinate) errors

1. Instrument errors - failure to calibrate, degradation of parts in the instrument, power fluctuations, variation in temperature, etc.

Can be corrected by calibration or proper instrumentation maintenance.

2. Method errors - errors due to no ideal physical or chemical behavior - completeness and speed of reaction, interfering side reactions, sampling problems

Can be corrected with proper method development.

3. Personal errors - occur where measurements require judgment, result from prejudice, color acuity problems.

Can be minimized or eliminated with proper training and experience.

Detection of Systematic Errors

1. Analysis of standard samples

2. Independent Analysis: Analysis using a "Reference Method" or "Reference Lab"

3. Blank determinations

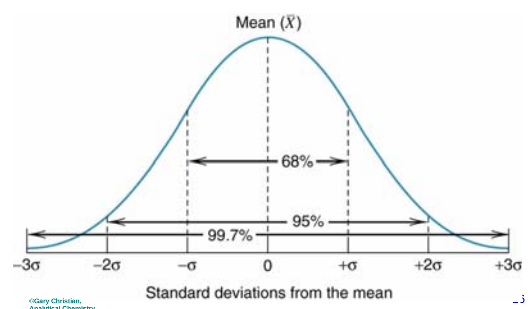
4. Variation in sample size: detects constant error only

Random (indeterminate) Error

- No identifiable cause; Always present, cannot be eliminated; the ultimate limitation on the determination of a quantity.
- *Ex. reading a scale on an instrument caused by the finite thickness of the lines on the scale; electrical noise*
- The accumulated effect causes replicate measurements to fluctuate randomly around the mean; Give rise to a normal or Gaussian curve; Can be evaluated using statistics.

Random errors follow a Gaussian or normal distribution.

We are 95% certain that the true value falls within 2σ (infinite population), IF there is no systematic error.



Normal error curve.

How do we determine error?

Accuracy – closeness of measurement to its true or accepted value

Systematic or determinate errors **affect accuracy!**

Precision – agreement between 2 or more measurements of the sample made in exactly the same way

Random or indeterminate errors **affect precision!**

Mean: Average or arithmetic mean

Median: arrange results in increasing or decreasing order

Precision: S, RSD, Cv

Accuracy: Error, Relative Error

Accuracy

Absolute error (E) – diff. between true and measured value

$E = xi - xt$

where xi = experimental value, xt = true value

Ex.

xi = 19.78 ppm Fe & xt = 20.00 ppm Fe

E = 19.78 – 20.00 ppm = -0.22 ppm Fe

(-) value too low, (+) value too high

Relative error (Er) – expressed as % or in ppt

Er = $\frac{x_i - x_t}{x_t} \times 100$ (as %); Er = $\frac{x_i - x_t}{x_t} \times 1000$ (as ppt)

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Analytical Procedure

2-3 replicates are performed and carried out through the entire experiment

-results vary, must calculate "central" or best value for data set.

Mean – "arithmetic mean", average

Median – arrange results in increasing or decreasing order, the middle value of replicate data

Rules:

For odd # values, median is middle value

For even # values, median is the average of the two middle values

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

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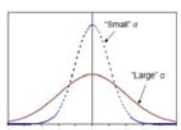
Precision

Standard Deviation (S) for small data set

$$S = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

Standard deviation (σ) of population: for infinite/large set of data

$$\sigma = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \mu)^2}{n}}$$



Where μ is mean or average of the population (most popular value) 21

Precision

Variance (S^2) = square of the standard deviation

n-1 = degrees of freedom

Another name for precision…..

$$S = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

Relative Standard Deviation (RSD)

RSD (ppt) = ($\frac{S}{\bar{X}}$) x 1000

commonly expressed as parts per thousand (ppt)

When express as a percent, RSD termed the coefficient of variation (Cv).

Cv (%) = ($\frac{S}{\bar{X}}$) x 100

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The exact value of μ for a population of data can never be determined (it requires an infinite # of measurements to be made).

Confidence Limits: interval around the mean that probably contains μ.

Confidence Interval: the magnitude of the confidence limits

Confidence Level: fixes the level of probability that the mean *is* within the confidence limits

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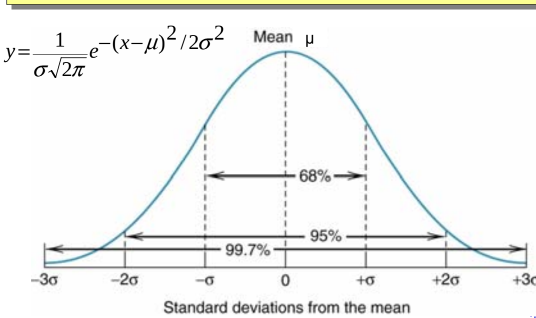
Random errors follow a Gaussian or normal distribution.

We are 95% certain that the true value falls within 2σ (infinite population), IF there is no systematic error.

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



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Normal error curve.

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Pooled Standard Deviation

To achieve a value of s which is a good approximation to σ, i.e. $N \geq 20$, it is sometimes necessary to *pool* data from a number of sets of measurements (all taken in the same way). Suppose that there are *t* small sets of data, comprising *N*1, *N*2,….*N*t measurements.

The equation for the resultant sample standard deviation is:

$$s_{pooled} = \sqrt{\frac{\sum_{i=1}^{N_1}(x_i - \bar{x}_1)^2 + \sum_{i=1}^{N_2}(x_i - \bar{x}_2)^2 + \sum_{i=1}^{N_3}(x_i - \bar{x}_3)^2 + ...}{N_1 + N_2 + N_3 + ...-t}}$$

(***Note:*** one degree of freedom is lost for each set of data)

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Comparison of Two Standard Deviations (precision) using F-test

$$F_{calculated} = \frac{s_1^2}{s_2^2}$$

Rules: $F_{calculated}$ always >=1

If $F_{calculated} > F_{table}$ (95%), difference is significant

P. 63, Table 4-4

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Table 4-3 Masses of gas isolated by Lord Rayleigh

From air (g)	From chemical decomposition (g)
2.310 17	2.301 43
2.309 86	2.298 90
2.310 10	2.298 16
2.310 01	2.301 82
2.310 24	2.298 69
2.310 10	2.299 40
2.310 28	2.298 49
—	2.298 89
Average	
2.310 11	2.299 47
Standard deviation	
$0.000\ 14_3$	0.001 38

SOURCE: R. D. Larsen, J. Chem. Ed. 1990, 67, 925; see also C. J. Giunta, J. Chem. Ed. 1998, 75, 1322.

Table 4-3
Quantitative Chemical Analysis, Seventh Edition

Are the two standard deviations sig. different?

Fcalculated = $0.00138^2/0.00014_3^2$

$= 93._1$

Significant? Yes according to Table 4-4

# of degrees of freedom?

n-1

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Table 4-4 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

Table 4-4
Quantitative Chemical Analysis, Seventh Edition

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Error Propagation

Uncertainties from Random Error in Addition and Subtraction

$$y = a(\pm e_a) + b(\pm e_b) - c(\pm e_c)$$

Absolute uncertainty

$$e_y = \sqrt{e_a^2 + e_b^2 + e_c^2}$$

Percent relative uncertainty $\%e_y = \frac{e_y}{y} \times 100$

Ex.

$$y = 5.75(\pm 0.03) + 0.833(\pm 0.001) - 8.02(\pm 0.001)$$

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Error Propagation

Uncertainties from Random Error in multiplication and Division $y = \frac{a \times b}{c}$

Percent relative uncertainty

$$\%e_y = \sqrt{(\%e_a)^2 + (\%e_b)^2 + (\%e_c)^2}$$

Relative uncertainty

$$\frac{e_y}{y} = \sqrt{(\frac{e_a}{a})^2 + (\frac{e_b}{b})^2 + (\frac{e_c}{c})^2}$$

Ex. $y = 251(\pm 1) \times \frac{860(\pm 2)}{1.673(\pm 0.006)}$

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Error Propagation

Uncertainties from Random Error in Exponents and logaithms, etc.

$$y = \log x$$

$$e_y = \frac{1}{\ln 10} \times \frac{e_x}{x} \approx 0.434 \frac{e_x}{x}$$

$$y = 10^x$$

$$\frac{e_y}{y} = (\ln 10) e_x \approx 2.303 e_x$$

Ex. P.48

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Error Propagation

Random uncertainty

Table 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
$y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\frac{e_x}{x}$
$y = x_1 \cdot x_2$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
$y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

a. x represents a variable and a represents a constant that has no uncertainty.

b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x/x$.

Systematic uncertainty

Add the uncertainties of each term in a sum or difference

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Basics of Quality Assurance

Table 5-1 Quality assurance process

Question	Actions
Use Objectives Why do you want the data and results and how will you use the results?	• Write use objectives
Specifications How good do the numbers have to be?	• Write specifications • Pick methods to meet specifications • Consider sampling, precision, accuracy, selectivity, sensitivity, detection limit, robustness, rate of false results • Employ blanks, fortification, calibration checks, quality control samples, and control charts to monitor performance • Write and follow standard operating procedures
Assessment Were the specifications achieved?	• Compare data and results with specifications • Document procedures and keep records suitable to meet use objectives • Verify that use objectives were met

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Calibration using Standard Addition

- Often components present in an analyte sample (other than the analyte itself) also contribute to an analytical signal, causing matrix effects.
- It is difficult to know exactly what is present in a sample matrix, so it is difficult to prepare standards.
- Possible to minimize these effects by employing standard additions

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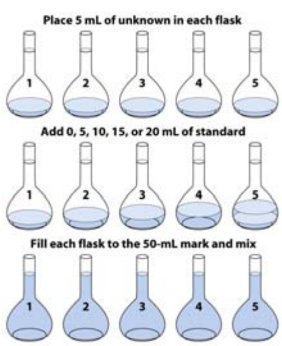
How does Standard Addition work?



- Add a known amount of standard to the sample solution itself.
- Perform the analysis.
- The resulting signal is the sum of the signal for the sample and the standard.
- By varying [standard] in the solution, it is possible to extract a value for the response of the unknown itself.

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How does Standard Addition work?

$$\frac{\text{Conc. of analyte in initial solution}}{\text{Conc. of analyte + Std. in final solution}} = \frac{\text{Signal from initial solution}}{\text{Signal from final solution}}$$

$$\frac{[X]_i}{[S]_f + [X]_f} = \frac{I_X}{I_{S+X}}$$

$$[X]_f = [X]_i \left(\frac{V_0}{V}\right)$$

$$[S]_f = [S]_i \left(\frac{V_S}{V}\right)$$

The quotient V_0/V (initial Vol./final Vol.), which relates final concentration to initial concentration, is called dilution factor.

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