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.

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

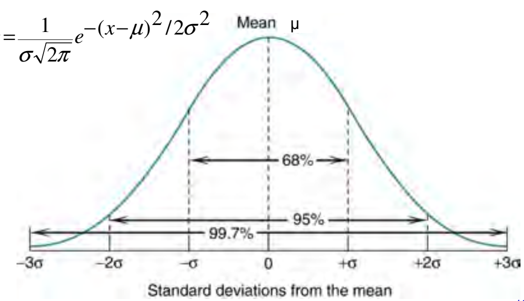
Random (indeterminate) Error

- 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.

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



Normal error curve.

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.

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

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

When performing calculation involving mixed operations (addition/subtraction and multiplication/division)

1. Perform addition/subtraction, determine absolute error of result, and then relative error of result
2. Perform multiplication/division operation using relative errors

Error Propagation

Uncertainties from Random Error in Exponent:

For $y = x^a$ $x \pm \%e_x$

$$\%e_y = a(\%e_x)$$

$y = x^3$ $x = 5.981 \pm 2.13\%$

$\%e_y = 3(2.13\%) = 6.39\%$

$y = 214.0 \pm 6.39\%$

Error Propagation

Uncertainties from Random Error for logarithms:

For y = log(x) $x \pm e_x$

$$y = \log x$$

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

y = log(x) $x = 3.17 \pm 0.28$

$e_y = (.43429) \cdot (0.28)/(3.17) = 0.038_4$

$y = 0.501 \pm 0.038$

Error Propagation

Uncertainties from Random Error for natural logarithm:

For y = ln(x) $x \pm e_x$

$$e_y = \frac{e_x}{x}$$

y = ln(x) $x = 7.432 \times 10^{-5} \pm 0.917 \times 10^{-5}$

$e_y = (0.917 \times 10^{-5})/(7.432 \times 10^{-5}) = 0.123_3$

$y = -9.507 \pm 0.123$

Error Propagation

Uncertainties in logarithms and antilogarithms, etc.

$$y = \log x$$

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

$$y = 10^x$$

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

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Example

For pH= 5.21 +/- 0.03, find [H⁺] and its uncertainty.

$$[H^+] = 10^{pH} = 10^{(5.21 \pm 0.03)}$$

For $y = 10^x$,

$$\frac{e_y}{y} = (\ln 10)e_x \approx 2.303e_x = 2.303 \times 0.03 = 0.069$$

$$y = 10^{-5.21} = 6.17 \times 10^{-6} \Rightarrow e_y = 4.26 \times 10^{-7}$$

Error Propagation

Random uncertainty

Table 3-1 Summary of rules for propagation of uncertainty

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

Systematic uncertainty

Add the uncertainties of each term in a sum or difference

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

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

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

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

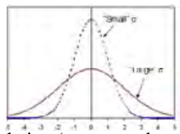
Precision

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)

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)

$$\text{RSD (ppt)} = \left(\frac{S}{\bar{X}}\right) \times 1000$$

commonly expressed as parts per thousand (ppt)

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

$$\text{Cv (\%)} = \left(\frac{S}{\bar{X}}\right) \times 100$$

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

How sure are we that the "true value" is close to our measurement average?

The confidence interval (CI) is an expression stating that the true mean, µ, is likely to lie within a certain distance from the measured mean.

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

Where, t is student's t. (p.57)

Comparison of Means with Student's t-test

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

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.

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

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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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

Table 5-1
Quantitative Chemical Analysis, Seventh Edition

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