Statistical analysis of experimental data

I. Random Errors in Experimental Data

A. Indeterminate (or random) errors:

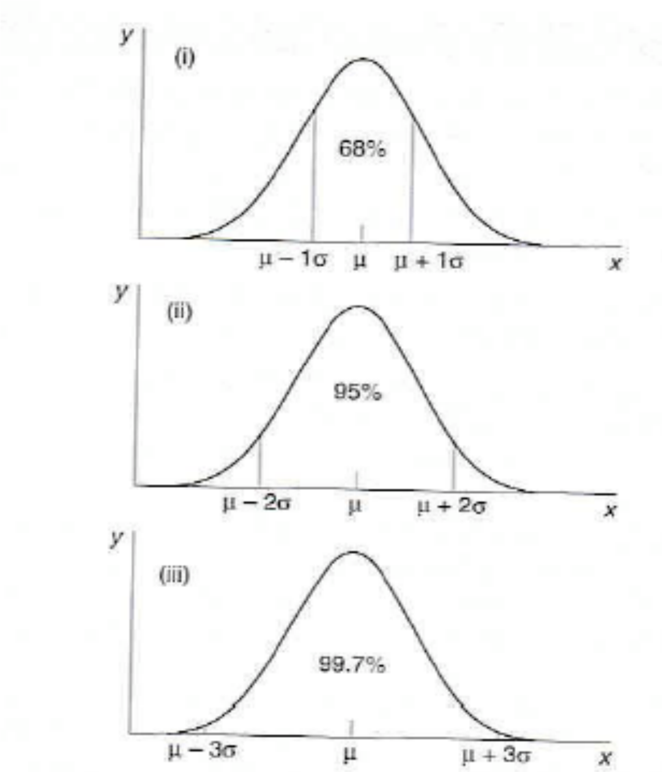
1. Usually are related to insufficiently controlled variations in experimental conditions.
2. Affect precision, but not accuracy.
3. Cannot be eliminated, but can be treated (statistically).
4. Are related to the small, random errors in an experiment that combine to give an overall error.
5. Because indeterminate error generally follows a normal distribution, calculations can be based upon characteristics of the normal distribution curve.

B. Properties of the Gaussian (normal) distribution.

The formula for the normal distribution is:

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

where, y = the frequency of a result, x
σ = the population standard deviation
μ = the population mean



a. **68.3% of the area between ±1 standard deviation (σ) unit of the mean (μ).**

b. **95.5% of the area between ±2 standard deviation (σ) unit of the mean (μ).**

c. **99.7% of the area between ± 3 standard deviation (σ) unit of the mean (μ).**

Spectrophotometric measurement (Abs) of a sample solution from 15 replicate measurements.

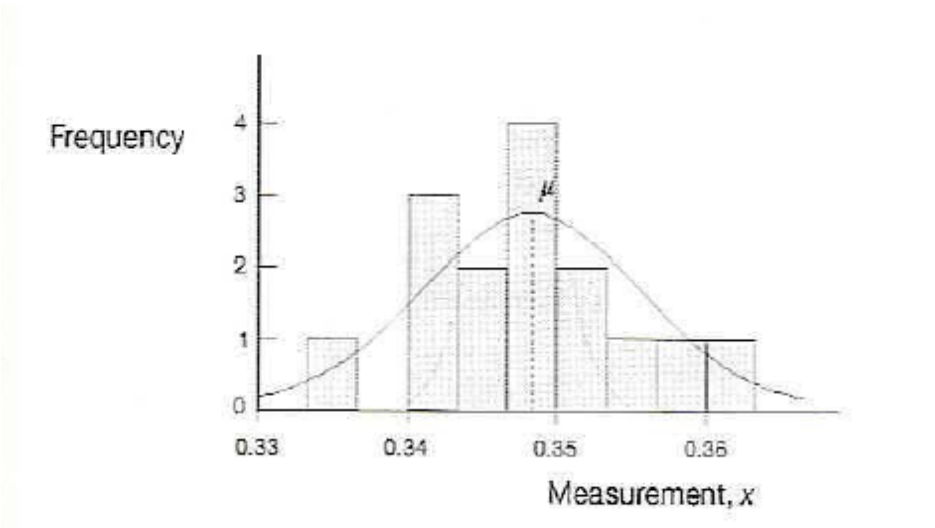
Measurement	Value	Measurement	Value
1	0.3410	9	0.3430
2	0.3350	10	0.3420
3	0.3470	11	0.3560
4	0.3590	12	0.3500
5	0.3530	13	0.3630
6	0.3460	14	0.3530
7	0.3470	15	0.3480
8	0.3460		

The following parameters are calculated for this set of measurements:

Parameter	**Value**
Sample #, n	15
Mean	0.3486
Median	0.347
Std Dev	0.00731
RSD %	2.096
Std error	0.00189
Max value	0.363
Min value	0.335

For this set of data the Gaussian curve is presented below:

Bell-shaped curve for the frequency of the measurements



C. Significance tests in Analytical Measurements

For the limited number of measurement we can not find the true population mean (μ) and true standard deviation (σ). However, we can determine sample mean and sample standard deviation values. The confidence interval: true mean (μ) is more likely lie within certain distance from measured mean ($\bar{x}$).

1. Is the difference significant?

$$t = \frac{\bar{x} - \mu}{s}\sqrt{n}$$

one variable t- test (student's test)

s is the standard deviation
n is the number of parallel measurements

If | t | value exceeds a certain critical value, then the H_0 is rejected.

t-test table

Values of t for ν Degrees of Freedom for Various Confidence Levels[a]

ν	Confidence Level, 90%	95%	99%	99.5%
1	6.314	12.706	63.657	127.32
2	2.920	4.303	9.925	14.089
3	2.353	3.182	5.841	7.453
4	2.132	2.776	4.604	5.598
5	2.015	2.571	4.032	4.773
6	1.943	2.447	3.707	4.317
7	1.895	2.365	3.500	4.029
8	1.860	2.306	3.355	3.832
9	1.833	2.262	3.250	3.690
10	1.812	2.228	3.169	3.581
15	1.753	2.131	2.947	3.252
20	1.725	2.086	2.845	3.153
25	1.708	2.060	2.787	3.078
∞	1.645	1.960	2.576	2.807

v is the degree of freedom and equal to **n-1**

For the two sets of data with n_1 and n_2 measurements a two-sided t-test is used in analytical chemistry. The following formula is used to calculate the t-value:

$$t = \frac{|\bar{x}_1 - \bar{x}_2|}{s_d}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

Where $\overline{X_1}$ and $\overline{X_2}$ are average values for the first and second set of data. And S_d is the a *polled* standard deviation making use of both sets of data:

$$s_d = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2}}$$

2. Comparison of standard deviations of two samples (F-test).

Assume following sets of measurement from two different labs of the same sample (Titanium content %):

Lab 1	Lab2
0.470	0.529
0.448	0.490
0.463	0.489
0.449	0.521
0.482	0.486
0.454	0.502
0.477	
0.409	

Standard deviation values obtained from labs are 0.0229 and 0.0182 respectively.

The value of F is:

$$F_{calculated} = \frac{s_1^2}{s_2^2} = \frac{0.0229^2}{0.0182^2} = \frac{0.000524}{0.000331} = 1.58$$

Degrees of freedom are 7 and 5, respectively. Based on the table below, we have the critical value of F (at 95 % confidence level) of 4.88. The calculated value is lower than tabulated, and therefore testing results are not significantly different between two labs.

"F" test table

Values of *F* at the 95% Confidence Level

	$\nu_1 = 2$	3	4	5	6	7	8	9	10	15	20
$\nu_2 = 2$	19.0	19.2	19.2	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4
3	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.70	8.66
4	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.86	5.80
5	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.62	4.56
6	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	3.94	3.87
7	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.51	3.44
8	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.22	3.15
9	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.01	2.94
10	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.85	2.77
15	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.40	2.33
20	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.20	2.12
30	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.01	1.93

3. Should I retain an outlier: Q-test?

Assume we obtained Cu content (ppm) in a penny by ASV:

5.30 5.00 5.10 5.20 5.25 6.20 5.15

1. Arrange data in the order of increasing values:

5.00 5.10 5.15 5.20 5.25 5.30 6.20 (quesionalble)

2. Calculate the **range**: difference between lowest and highest number.

6.20 – 5.00 = 1.20

3. Calculate the **gap**: difference between questionable point and nearest value.

6.20 – 5.30 = 0.90

4. Calculate the Q value

$$Qcalculated = \frac{gap}{range} = \frac{0.90}{1.20} = 0.75$$

5. Compare with the table value (see below).

$\mathbf{Q_{90}}$	0.507	$\mathbf{Q_{calculated}}$	**0.75**	$Q_{calc} > Q_{table}$	Discard
$\mathbf{Q_{95}}$	0.568			$Q_{calc} > Q_{table}$	Discard
$\mathbf{Q_{99}}$	0.680			$Q_{calc} > Q_{table}$	Discard

Q-test table

Rejection Quotient, *Q*, at Different Confidence Limits[a]

No. of Observations	Confidence level		
	Q_{90}	Q_{95}	Q_{99}
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
15	0.338	0.384	0.475
20	0.300	0.342	0.425
25	0.277	0.317	0.393
30	0.260	0.298	0.372