PRESENTATION OF ANALYTICAL DATA

Aim of chemical analysis: *The aim of quantitative chemical analysis is to obtain the **actual** amount of the substance being estimated in the sample under consideration*. This is not a very easy task, since the actual quantity is unknown (if it is known, there is no need for an estimation!). For example, what is the percentage of iron present in a particular sample of haematite? This is not simply a case of taking a sample, doing an analysis and **claiming** that your estimation gives the actual value. Does the particular sample you have taken truly represent the whole bulk of the material? How can you be sure that the readings you have obtained on an instrument represent the true value? How reliable is the method of analysis you have chosen? How experienced and honest is the analyst? (The ability to do anything in life, however simple the job may be, improves with experience.)

Thus it is found that *however experienced and honest an analyst may be, there are several sources from which errors can creep into estimations*. It is very important to decide how correct the estimation is (how close to the actual value?). Another dilemma often faced by the chemist is that of the time available for an analysis and the cost of analysis. Should one use a fast and cheap method which is less reliable, or a reliable method which is costly and time consuming? The decision clearly depends on the **purpose** of the analysis (is it for a routine quality control analysis to determine whether the impurities fall within limits of the permissible range, or is it for obtaining an ultra pure sample for some critical application such as in spaceships or nuclear power plants?), and the time and funds available. It is therefore very important to understand how and why errors occur in estimations, and also contemplate methods for avoiding them, or at least to determine how much faith one can put on the results obtained by him.

Errors can be expressed either absolutely or relatively. When the error is expressed in the *same units as the measurement*, it is called **absolute error**. When the error is expressed as a *percentage* of the quantity being measured, it is called **relative error**. For example, suppose an analyst makes the same error of 0.002 g while weighing two different samples, one of mass 1.045 g and the other of mass 0.546 g. *The absolute error is 0.002 g in both cases*. But the relative errors in the two cases are:

(1) $\frac{0.002}{1.045} \times 100 = 0.19\%$ (2) $\frac{0.002}{0.546} \times 100 = 0.37\%$

Thus relative error can be used to indicate the seriousness of the error made. In the above example, the error is more serious in the second case.

Additive errors: Errors which are independent of the quantity being measured are called additive errors. For example loss in weight of a crucible on heating, errors in weights used etc.

Proportional errors: These errors increase in proportion to the measured quantity. For example hygroscopic precipitates, impurities in reagents or samples etc.

Significant digits: Different instruments used for measurement have *different accuracies*. For example, a scale marked in millimeters can be used for more accurate measurements than a scale marked in centimeters only. A chemical balance is capable of measuring weights in grams correct to four decimal places while an ordinary 50 cm^3 burette can read volumes in cm^3 correct to one decimal place only. When we say that the length of a pencil measured using a millimeter scale is 8.6 cm, the end of the pencil may not exactly coincide with the 8.6 cm mark; it may be slightly lower (but not lower than the 8.5 cm mark) or slightly higher (but not higher than 8.7 cm mark). Thus the last digit in the measurement is uncertain. Using this scale you cannot say that the pencil is 8.62 cm long, because there are no markings on the scale to read the last digit. If you say that the pencil is 8 cm long, you are losing information because the scale used is capable of more accurate measurement. Thus, **an analytical measurement should always be reported in such a way that it reflects the accuracy of the measuring instrument used, and only the last digit is uncertain**. The digits appearing in the result when reported in this manner are called significant digits. The rules are as follows:

(1) All non-zero digits are always significant. For example:
23.5 cm^3 (3 significant digits) 1.2136 g (5 significant digits)

(2) Zeros at the beginning are not significant. Zeros in the middle are significant. Zeros at the end are significant only if they represent accuracy of measurement. For example:

023.5 cm^3, 0.235 g, 0.0235 g, 0.00235 m (all have only 3 significant digits)
20.3 cm^3 (3 significant digits) 20.03 cm (4 significant digits) 2.103 m (4 significant digits)
18.9300 g has 6 significant digits if weighed on a chemical balance.

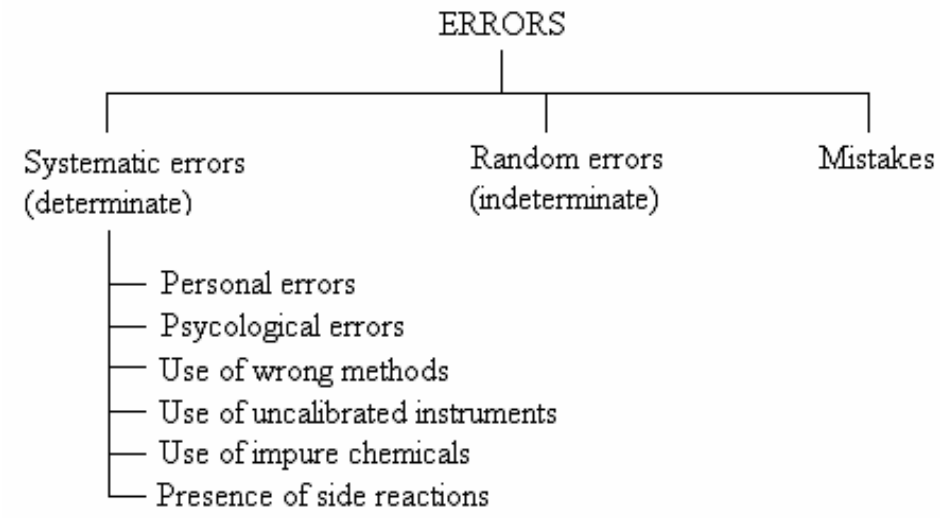
(3) When **adding** or **subtracting** numbers with different number of significant digits in them, the result must be reported with only as many **decimal places** as in the number having the smallest number of significant digits. For example:

18.2 g + 2.486 g + 0.2357 g = 20.9 g (not 20.9217 g)

(4) When **multiplying** or **dividing** numbers with different number of significant digits in them, the result must be reported with only as many **significant digits** as in the number having the smallest number of significant digits. For example:

$$\frac{V_1}{V_2} = \frac{96.685\,\text{mL}}{2.32\,\text{mL}} = 41.6$$ (and not 41.67 or 41.675)

Sources of errors: Errors in chemical estimations may be classified as follows:



Mistakes: Gross errors are called mistakes. For example, loss of some precipitate in a gravimetric experiment, or using a 10 cm^3 pipette instead of a 20 cm^3 pipette in a volumetric experiment etc. The result is totally useless and can only be discarded.

Systematic errors or determinate errors: These are errors for which the causes are known and the amount of error so produced can be determined. *Suitable methods can be adopted to avoid these errors since the reasons are known*. These fall under several categories.

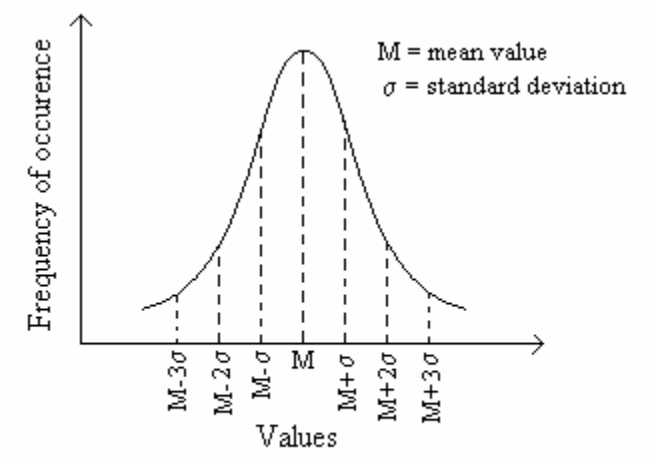
(1) *Personal errors*: The person doing the analysis (**analyst**) may suffer from physical defects like colour-blindness which may make him incapable of noting the colour change of the indicator in a titration. This problem can be solved either by replacing the analyst or by using some other method for estimation.
(2) *Psycological errors*: These are especially seen among students who are not confident of their own capabilities. Adjusting the end points to get concordant values, adjusting the results to agree with the result obtained by his friend etc. are examples.
(3) *Use of wrong methods*: Using ordinary filter paper when Whatman No.41 is recommended for a particular gravimetric analysis, using nitric acid instead of sulphuric acid recommended in the procedure for a titration, using tap water instead of distilled water, preparing a primary standard solution using NaOH or $KMnO_4$ etc are a few examples.
(4) *Use of uncalibrated instruments*: All precision measuring vessels and instruments like thermometers, burettes, pipettes, balances and weights, colourimeters and spectrophotometers,

conductivitymeters, polarimeters and viscometers have to be calibrated properly by using known standards before use. This is to ensure that the readings shown indded represent the actual values. It is also necessary to have a knowledge of the accuracy obtainable using each instrument (you can weigh 18.3126 g on a chemical balance, but can you deliver 18.3126 mL HCl from a burette, or 20.3 mL from an ordinary pipette?).

(5) *Use of impure chemicals*: When we weigh out 1.2056 g of sodium carbonate to prepare a standard solution, we believe that the material will react in stoichiometric proportions. But suppose that the sodium carbonate contains 8% sand or some other inert material? Impurities present may also create havoc by catalyzing unwanted reactions, causing unexpected colours or absorptions in colourimetry and spectrometry, or causing side reactions to occur.

(6) *Presence of side reactions*: We expect a reaction to take place according to the chemical equation representing that reaction and calculate quantities accordingly. But if side reactions occur and are not accounted for, these calculations can go wrong.

Random errors: However carefully we may try to avoid errors and however experienced an analyst may be, still one gets slightly different results when the same estimation is repeated several times, for unknown reasons. (Even if your teachers may demand it, do you honestly get the same results when you repeat your titrations or carry out duplicates in your gravimetric analyses?) These are known as random errors and cannot be entirely avoided. *But random errors show certain statistically predictable patterns when the analysis is repeated a large number of times*. When the error is truly random, there is equal probability for positive and negative deviations to occur. (The difference between the determined value and the actual value is called **deviation**. There is equal chance for the estimated value to be greater than or less than the actual value). In such cases, when the numbers of occurrences of each value are plotted against the values obtained, a bell-shaped curve is obtained. This is called a **Gaussian curve** or a **normal distribution curve**.



The Normal Distribution Curve

Properties of the Gaussian curve:

(1) Small errors (deviations) occur more frequently than large errors.
(2) Large errors occur only rarely.
(3) Positive and negative errors are equally likely to occur. Therefore the curve is symmetric.
(4) 68% of all values lie between M+σ and M-σ. 95% of all values lie between M+2σ and M-2σ. 99% of all values lie between M+3σ and M-3σ. These percentages are known as **confidence limits**.

Let there be '*n*' observations or measurements, and the values obtained be x_1, x_2, x_3 … x_n. Then,

Mean *is the mathematical average*. Sum of the individual values divided by the total number of observations. Mean = $\bar{x} = \frac{x_1 + x_2 + x_3 + ... + x_n}{n} = \frac{\sum x_i}{n}$. **Median** *is the middle value* when all values are arranged in the ascending order. **Mode** *is the most frequently occurring value*. The differences between the mean value and the individual values are called **deviations** (*d*).

$$d_1 = (x_1 - \bar{x}), \quad d_2 = (x_2 - \bar{x}), \quad d_3 = (x_3 - \bar{x}) \quad \text{etc.}$$

Mean deviation *is the average of the individual deviations*, $\frac{d_1 + d_2 + d_3 + ... + d_n}{n} = \frac{\sum d_i}{n}$. Since positive and negative deviations are equally likely, they may cancel each other and therefore the mean

deviation may become zero, giving the wrong impression that there are no deviations at all. Therefore the squares of the deviations are considered. *The mean of the squares of the deviations is known as* **variance**. Variance = $\frac{d_1^2 + d_2^2 + d_3^2 + ... + d_n^2}{n} = \frac{\sum d_i^2}{n}$. *It is a measure of the spread of the values about the mean value*.

The root of the variance, or root mean square deviation, is known as **standard deviation**, denoted by 'σ' or '*s*'. Since *n* observations have only *(n-1)* degrees of freedom, statisticians prefer division by *n-1* rather than *n*. Therefore:

$$\sigma \text{ or } s = \frac{\sqrt{d_1^2 + d_2^2 + d_3^2 + ... + d_n^2}}{n-1} = \frac{\sqrt{\sum d_i^2}}{n-1}$$

Minimisation of errors: Systematic errors may be reduced to a certain extent by adopting the following techniques.

(1) By properly calibrating all weights, apparatus and instruments. Even automatic or electronic equipments require calibration periodically.
(2) The effects caused by the presence of impurities or side reactions etc. may be eliminated by running a blank determination using all reagents and procedures exactly as in the case of the sample.
(3) Lack of sensitivity of the method or instrument may be compensated to a certain extent by running a control determination using a standard sample with exactly known content along with the unknown sample. Then even if the observed value deviates from the actual content, the deviations will be similar for the standard and the unknown sample, so that

$$\frac{\text{observed result for standard}}{\text{observed result for unknown}} = \frac{\text{actual weight in standard}}{\text{actual weight in unknown}}$$

(4) See whether similar results are obtained when different methods of analysis are used.
(5) By running parallel determinations using different sample sizes, it can be determined whether the errors are constant or proportional in nature.
(6) By adding a standard substance of known value, such as addition of TMS in NMR spectroscopy
(7) Amplification methods. For example when the quantity being estimated is too small in gravimetric analysis, a very bulky precipitating reagent may be employed to obtain a sufficiently large mass to be measured.
(8) Isotopic dilution. Since the presence of even trace amounts of radioactive materials can be accurately determined, a minute but known amount of a radioactive isotope may be added to the sample, which will then undergo all transformations exactly like the sample, but will maintain the original isotope to sample ratio.

Accuracy and precision: We say that a result is accurate when the actual value and the estimated value are very nearly the same ie. there are no errors, systematic or random, in the result. *Precision* means getting similar results when the experiment is repeated several times. A precise result shows that the analyst is capable of perfectly duplicating his estimations without random errors. But it does not guarantee accuracy since systematic errors may be present (reproducing the same wrong result!). Precision can mean accuracy only in the absence of systematic errors.

Coefficient of variation or C.V. (same as relative standard deviation or RSD): *The standard deviation expressed as a percentage of the mean value is called the coefficient of variation* (or CV or RSD). It is used to compare the variability of the same character in two different groups (see example 1), or that of two different characters in the same group (see example 2).

Example 1: The mean value for the hydrolysis constant of ethyl acetate was obtained as 7.32 with a standard deviation of 0.26. That for methyl acetate was found to be 12.78 with a standard deviation of 0.31. Which result shows more variance?

$$\text{CV for ethyl acetate} = \frac{\text{SD}}{\text{mean}} \times 100 = \frac{0.26}{7.32} \times 100 = 3.55\%$$

$$\text{CV for methyl acetate} = \frac{\text{SD}}{\text{mean}} \times 100 = \frac{0.31}{12.78} \times 100 = 2.43\%$$

Thus the hydrolysis constant for ethyl acetate shows more variation.

Example 2: The pressure of a gas measured at a certain temperature gives an average value of 821 mm Hg with a SD of 6 mm. The volume of the gas measured at the same temperature is 117.5 mL with a SD o 4.8 mL. Which shows more vaiance?

$$\text{CV for pressure} = \frac{\text{SD}}{\text{mean}} \times 100 = \frac{6}{821} \times 100 = 0.73\%$$

$$\text{CV for volume} = \frac{\text{SD}}{\text{mean}} \times 100 = \frac{4.8}{117.5} \times 100 = 4.09\%$$

Thus the volume of the gas shows more variation.

Scatter diagrams and correlation coefficients: Usually, the values of a dependant variable '*y*' are plotted against the values of an independent variable '*x*' on a graph to bring out the nature of the relationship between *y* and *x* in a function *y = f(x)*. The relationship may be linear if y is directly or inversely proportional to x, or it may be exponential etc. However, because of the presence of random errors in experimental results, all the data points may not fall exactly on the ideal curve, but may be scattered randomly in the proximity of it. Therefore these plots are known as **scatter diagrams**. In figure 1, imagine that the curve is not there, but only the points. Does it appear that there is any relationship between them?

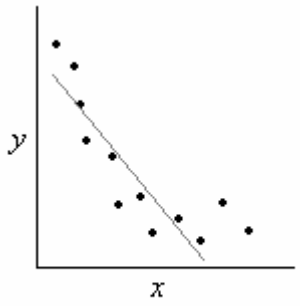


Figure 1. Scatter diagram

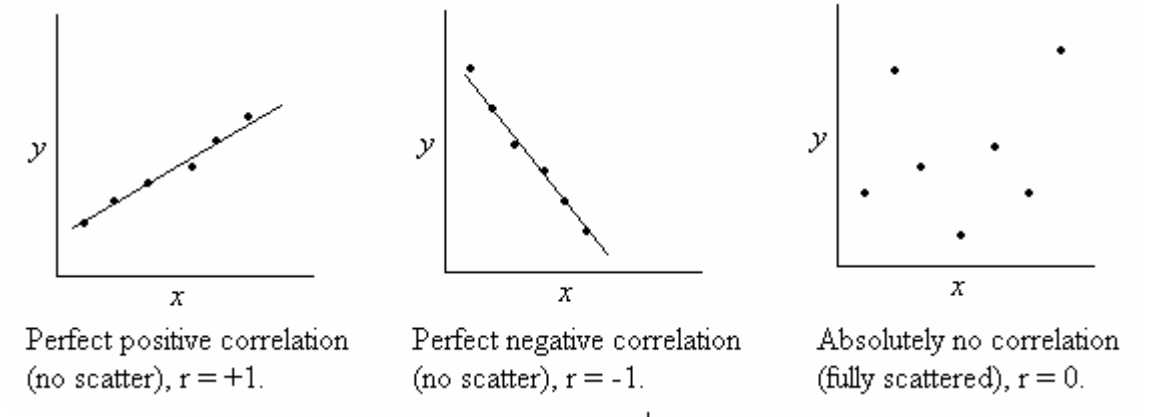
In such cases, a value called **correlation coefficient** can be computed statistically that will help us decide whether there is actually a linear relationship between *x* and *y* or not. To obtain the correlation coefficient, the values of x and y in each measurement is recorded in a tabular form as follows:

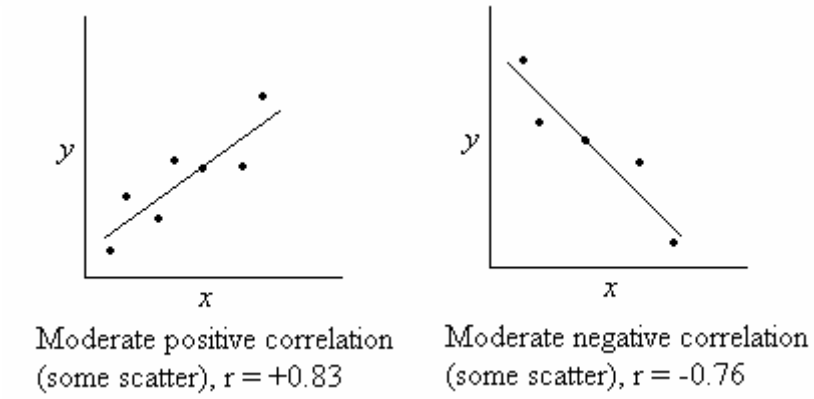
Serial No.	x	$\bar{x}$	$(x-\bar{x})$	$(x-\bar{x})^2$	y	$\bar{y}$	$(y-\bar{y})$	$(y-\bar{y})^2$	$(x-\bar{x})\times(y-\bar{y})$
1	x_1				y_1				
2	x_2				y_2				
3	x_3				y_3				
4	x_4	$\frac{\sum x_i}{n}$			y_4	$\frac{\sum y_i}{n}$			
5	x_5				y_5				
6	x_6				y_6				
7	x_7				y_7				
8	x_8				y_8				
	$\sum x_i$			$\sum (x-\bar{x})^2$	$\sum y_i$			$\sum (y-\bar{y})^2$	$\sum (x-\bar{x}) \times (y-\bar{y})$

Then the correlation coefficient '*r*' is computed according to the equation:

$$r = \frac{\sum (x-\bar{x})(y-\bar{y})}{\sqrt{\sum (x-\bar{x})^2 \sum (y-\bar{y})^2}}$$

The value of the correlation coefficient '*r*' will lie between -1 and +1. *The value +1 shows complete positive correlation* (ie. directly proportional; all points lie on a line with positive slope) and *a value of -1 shows complete negative correlation* (ie. inversely proportional; all points lie on a line with negative slope). A *value close to zero indicates no correlation at all*.





The closer the value of *r* to +1 or -1, better the correlation.

Comparison of results: Statistical figures obtained from a set of results are only of limited value by themselves. It is only by comparing them with the true value, or with other sets of data, that it is possible to determine whether an analytical procedure has been accurate or superior to another method. The *t*-test, *F*-test and χ^2-test (pronounced "khy square test") are the common methods used for comparing results.

[Meaning of 'degrees of freedom' as used in statistics: A set of '*n*' values has '*n*' degrees of freedom ie. all the *n* values can be arbitrary; but quantities like $\sum(x-\bar{x})^2$ etc. computed from the *n* values have only (*n-1*) degrees of freedom. This is because for any defined value of $\bar{x}$, only (*n-1*) values can be assigned freely, the n^{th} being automatically obtained from the other values.]

(a) **The Student's *t*-test**: This test was devised by W.S.Gosset, who used 'Student' as his pen name. The *t*-test is used to compare the *mean from a set of values* with a *standard value* and say whether the difference between the two values is significant. It is also used to compare the means $\bar{x}_1$ and $\bar{x}_2$ of two different sets of data and determine whether the difference between the two values is significant. If there is considerable probability that the difference can occur by chance, then the difference is not significant. If there is only less than 1% chance of such occurrence (or less than 5% or 10% chance, depending on the confidence limit selected), then the difference is very significant (there is 99% probability that they are really different, and indicates some bias in the results). The *t*-test is usually applied for a small sample size (number of observations < 30). The value of '*t*' is obtained from the equation

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

where $\bar{x}$ is the mean of the set of observations, 'μ' is the standard value, '*n*' is the number of observations and '*s*' is the standard deviation. The calculated value of '*t*' is compared with values of '*t*' in a standard table (the *t*-table, similar to a logarithm table) against the number of degrees of freedom for the set of data.

Example: Estimation of nickel in a sample by 12 students gave a mean value of 8.37 with a SD of 0.17. If the correct nickel content is known to be 7.91, find whether this difference is significant. [The difference between the mean value and the estimated value is 8.37 – 7.91 = 0.46. The test is to determine whether such a difference can occur by chance or not.]

$$t = \frac{(8.37 - 7.91)\sqrt{12}}{0.17} = 9.4$$

From t-tables for 11 degrees of freedom we can see that:

t = 1.80 (for 10% probability)
t = 2.20 (for 5% probability)
t = 3.11 (for 1% probability)

Since the calculated value of t (9.4) is much greater than 3.11, there is only less than 1% chance for the difference in values to arise out of chance. Therefore the difference is significant, indicating some bias in the procedure or methods used by these students. [Had the calculated t been less than 1.80, there would have been a 10% probability for the difference to occur by chance.]

(b) **The *F*-test**: This is to compare the *precision* of the results obtained from two different sets of observations.

$$F = \frac{s_1^2}{s_2^2}$$

where s_1 and s_2 are the standard deviations from the two sets. The larger value of s is used in the numerator so that the value of F is always >1. The calculated F value is then compared with values from a standard *F*-table.

Example: Estimation of the iron content of a sample in one laboratory gave a SD of 0.210 from 11 determinations. Estimation in another lab gave a SD of 0.641 from 13 determinations. Is there any significant difference between the precisions obtained in these two labs?

$$F = \frac{(0.641)^2}{(0.210)^2} = \frac{0.411}{0.044} = 9.4$$

From *F*-tables, we get:

F = 2.19 (10% chance)
F = 2.75 (5% chance)
F = 4.30 (1% chance)

Since the calculated F value of 9.4 is greater than 4.3, the levels of precision obtained by the two labs are entirely different.

(c) **The χ^2-test**: This test is used to determine whether a distribution obtained is significantly different from a theoretical distribution.

$$\chi^2 = \sum \frac{(O - E)^2}{E}$$

where O is the observed frequency and E is the expected frequency. All probabilities have to be considered and summed up as in the following example.

Example: When a coin was tossed 100 times, heads came up 25 times. Is there any bias in the coin?

Heads came up 25 times also means that tails came up 75 times. We expect heads to come up 50 times. Therefore

$$\chi^2 = \frac{(25 - 50)^2}{50} + \frac{(75 - 50)^2}{50} = \frac{625 + 625}{50} = 25$$

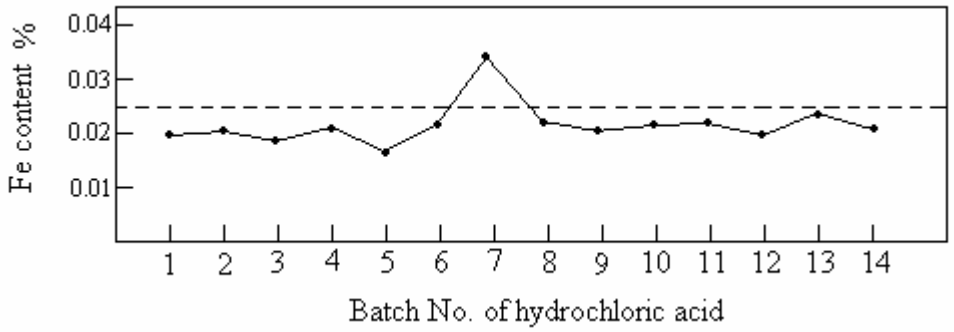
From χ^2-tables we get:

χ^2 = 6.63 (1% chance)

$$\chi^2 = 10.83 \text{ (0.1\% chance)}$$

Since the calculated χ^2 is much greater than 10.83, there is significant bias in the tossing of the coin.

Control charts: In industrial process control labs and quality control labs, the same type of analysis on similar samples has to be carried out on a routine basis. It is recommended that the results be plotted on a chart on a regular basis. Any large deviation from the general trend can be immediately detected, which may point to some extraordinary situation that needs correction.



Suppose that the maximum permissible level of iron as impurity in hydrochloric acid is 0.025%. A control chart maintained by the quality control lab indicates that generally the product is acceptable, but something seriously went wrong with batch no.7, and a detailed investigation of the possible causes were initiated. It was some temporary malfunctioning of the system, or the use of low quality raw materials in a single batch, since later batches were not affected.