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#### Abstract

TNPSC-ASSISTANT DIRECTOR OF CO-OPERATIVE AUDIT STUDY MATERIAL AVAILABLE.


TNDB-(ASSESSOR/AE/JA) MATPRIALS WITH QUESTION BANK AVAILABLE UG-TRB/PG-TRB /TRB-POLYTDCHNIC/ DEO \& BEO MATERIALS ARE SENDING THROUGH COURIER.

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# TN-MAWS-SANITARY INSPECTOR <br> Analytical Chemistry: Classification of analytical Methods <br> Errors in Quantitative Analysis 

## Introduction:

The function of the analyst to obtain a result from measurement as very close to the true value as possible by the correct application of the analytical procedure used. The deviation occurs in the estimation means uncertainty analysis.

Quantitative analysis deals with the quantity or amount of the various components present. While doing the measurement or estimation in quantitative analysis, it requires excellent knowledge of chemistry. However, every measurement can be correct only within the possible limits and are always associated with certain degree of uncertainty. This uncertainty is called as error.

The measurements which are considered to be accurate at the highest level also consist of certain uncertainty. This uncertainty or error is often difficult to determine, it cannot be eliminated completely but can be minimized to an appreciable level. The reliability of result can be judged by two parameters, accuracy and precision. This chapter deals with some related terms, errors in analytical results to apply the statistical methods.

## Introduction to errors:

Measurements invariably involve errors and uncertainties and very few are mistakes on the part of analyst. Commonly errors are uncertainties caused by inaccurate calibrations or standardizations hence uncertainty results. We make mistakes in weighing sample and calculations also. It is impossible to perform a chemical analysis, that is completely free of errors or uncertainties. We try to minimize errors and estimate their size with good accuracy. Every measurement is influenced by many uncertainties which combine to give a scatter of results. In measurement uncertainties cannot be completely eliminated, measured data can give an estimate of true value. Experiment can be repeated might show this kind of error .The gross error is really a fault. It may be possible to find out such an error.

## Limitations of Analytical Methods:

Analyst use correct analytical procedure for obtaining the result very close to the true value as possible. The level of confidence that the analyst may enjoy the results will be very small unless he has knowledge of accuracy and precision of the method used, as being aware of sources of
error may be introduced. Sometimes, analyst have not sound knowledge of chemistry involved in quantitative analysis, there may be possibilities of interference of other ions, elements and compounds and statistical distribution of values.

## Classification of Errors:

"Error is a measure of the estimated difference between the observed or calculated value of a quantity and its true value". Every measurement has some degree of uncertainty which is called as error. An error that affects experimental results, discrepancy may occur. Errors are classified into two types:

1) Systematic Errors (determinate errors)
2) Random Errors (indeterminate errors)

## Systematic Errors (Determinate Errors):

The errors which have some cause to their occurrence and hence, can be determined are termed as determinate errors. These errors occur with definite regularity so they are also called as systematic errors. Since the source of occurrence of these errors is known, they can be detected, corrected for and can be eliminated or minimized. These are further classified as:

1) Operational and personal errors
2) Instrumental and reagent errors
3) Method errors
4) Additive and proportional errors
5) Operational and Personal Errors:

These errors are occur due to individual analyst. Analyst is responsible but not method or procedure of analysis. The errors are mostly physical in nature and occur when correct analytical technique is not followed.

For example, mechanical loss of material or compound in various steps of an analysis, means at the time of washing or over washing of precipitates, ignition of precipitates at incorrect temperatures, not proper cooling of crucibles before weighing, allowing hygroscopic materials absorbing moisture before or during weighing, reagents are not purified. In short operational error means:
a) Mechanical loss of material in various steps.
b) Insufficient cooling of crucible before weighing.
C) Incomplete or excessive heating of a precipitate
D) Under or over washing of a precipitate.

Personal errors may arise from the constitutional inability of an individual to make certain observations properly. For example, while estimating the position of a pointer between two scale divisions, color of the solution at the end point of the titration, level of a liquid with respect to a graduation in a burette. For example, one person may read a pointer consistently high, another person may be slightly slow in activating a timer and third person may be less sensitive to color change. An analyst is insensitive to color changes tends to use excess amount of reagent in a volumetric analysis. Number bias is another type of source of personal error that varies from person to person. In short,
a) Poor color perception or color blindness.
b) Tendency of analyst to over or under titrate a solution.
C) Errors in reading a burette.
d) Failure to make homogeneous solution.

## 2) Instrumental and Reagent

This error arises due to use of non-ideal instrument. like faulty balances, improperly calibrated weights, graduated glassware and instruments, attack of reagents on glassware, use of impure reagents. These errors are eliminated by using correct and calibrated instruments and all glassware, use of A.R. grade reagents. Electronic instruments are under instrumental systematic errors. For example, error may occur as the voltage of a battery operated power supply than the electric supply decrease with use. Some instruments are not calibrated or incorrectly calibrated so can cause error. A pH meter used in acidic media is prone to an acid error. Electronic components shows variations due to change in temperature which leads to error. These type of errors can be detected as well as corrected. In short,
a) Incorrectly graduated burettes and pipettes.
b) Use of reagents, containing impurities.
c) Loss in weight of crucible upon strong heating.
d) Not properly calibrated instruments.

## 3) Method errors:

This type of error is due to incorrect sampling ,incomplete of reaction mechanism, In gravimetric analysis errors may arise owing to appreciable solubility of precipitates, coprecipitates and post precipitation, decomposition or volatilization of weighing forms on ignition, and precipitation of substances other than the intended. Another example of titrimetric analysis error may be due to failure of reaction proceeds towards completion, occurrence of induced and side reactions it may change the proper readings. Errors inherent in a method are very difficult to detect. In brief,
a) Decomposition or volatilization of a compound on ignition.
b) Co-precipitation and post precipitation.
c) Occurrence of induced and side reaction.
d) Failure of a reaction to proceed to completion.

This error is independent of the amount of the constituents present in the determination. Additive errors are loss in weight of crucible in which a precipitate is ignited and error in weights may be occurring. The error is due to taking the samples of different weights. The absolute value of proportional error depends on the amount of constituents present. The proportional error may arise from an impurity in any standard substance, which leads to incorrect molarity of a standard solution. The ignition of aluminium oxide at $1200{ }^{\circ} \mathrm{C}$, basically aluminium oxide is anhydrous and non-hygroscopic, ignition of various weights at lower temperature an error is occur called proportional error. Proportional errors increase or decrease according to the size of the sample taken for analysis, in brief,
a)Loss in weights.
b)Impurities present in standard samples.
c) Not proper sample size.

## Random errors (indeterminate errors):

These errors caused by the slight variations that occur in successive measurements done by the same analyst under identical conditions in which the analyst has no control. If sufficient number of observations are taken. This represents that:
a) Small error occur more frequently than large and
b) Positive and negative error of the same numerical value are equal.

If at least 50 number of repeatedly readings are taken of a continuous variable for example, end point of the titration, the results attained will be distributed about the mean. The mathematical model that satisfies a distribution of random errors is called normal distribution or Gaussian distribution. This curve is bell shaped that is symmetrical about the mean value.
For example: i) the equilibrium position of a balance varies slightly for every successive weighing. ii) The spectrophotometer or pH meter gives every time different readings.

## Accuracy:

In the analytical obtained data, an accuracy of data and measurement of the accepted correct value are considered. Accuracy is defined as the closeness of the measurement to the true value or accepted value. For analytical methods there are two ways of determining the accuracy namely absolute method and comparative method. It is expressed in terms of relative error and reliability of results only depends upon accuracy of the data.

## Methods of Expressing Accuracy

Accuracy is expressed in terms of absolute error or relative error.

## 1) Absolute Error:

The difference between measured(observed) value and true value including its sign is called as absolute error. The positive or negative sign indicates high or low value. If the measured result is low, the sign is negative.
Absolute error = [Observed or measured value] - [True value]
$\mathrm{E}=[\mathrm{O}-\mathrm{T}]$ (in units of measurements).
$\mathrm{E}=$ Absolute error,
$\mathrm{O}=$ Measured(observed)value and $\mathrm{T}=$ True value.
For example: a 4.52 g sample substance is reported as 4.32 g . the absolute error is -0.20 g .
$\mathrm{E}=[\mathrm{O}-\mathrm{T}]$
$\mathrm{E}=4.32-4.52$
$=-0.20 \mathrm{~g}$
In this case measured value is smaller than true value, so the result is negative.

## 2) Relative Error:

The absolute error value is divided by the true value is called relative error. It is more useful quantity than absolute error. Relative error is expressed in terms of percentage or parts per thousand (ppt)

$$
\begin{aligned}
& \text { Relative error }=\frac{\text { Absolute error }}{\text { True value }} \times 100 \text { in percentage } \\
& \text { Relative error }=\frac{\text { Absolute error }}{\text { True value }} \times 1000 \text { in parts per thousand }
\end{aligned}
$$

It has no unit.
For example, a measured value is found to give 7.44 g and true value is 7.55 g then absolute error can be calculated as,
$\mathrm{E}=[\mathrm{O}-\mathrm{T}]$
$\mathrm{E}=7.44-7.55$
Relative error $=\frac{\text { Absolute error }}{\text { True value }} \times 10$
Relative error $=\frac{-0.11}{7.55} \times 100$
Relative error $=1.4 \%$
Precision
Precision gives the reproducibility of measurements or the closeness of results that have been obtained in exactly the same way. In other words a measurement is determined by simply repeating the measurements on replicate samples. It can be defined as, "the degree of agreement between replicate measurements of the same quantity or reproducibility of number of similar measurements under identical conditions".

The difference between precision and accuracy can be understood by the following example. Suppose four students are asked to do some measurements. The result of their measurement is as shown

a) Student A shows good accuracy and good precision.
b) Student B shows poor accuracy and poor precise.
c) Student C shows good accuracy and poor precise.
d) Student $D$ shows poor accuracy and good precision.

## Methods of Expressing Precision:

Average deviation, standard deviation and relative mean deviation are the terms widely used to describe the precision.

## 1) Deviation( $\Delta$ ):

It is the difference between individual result and mean or average result called deviation. It is represented as,

$$
\begin{aligned}
& \qquad \Delta=|x-\bar{x}| \\
& x=\text { Individual result value } \\
& \stackrel{x}{x}=\text { Mean result value }
\end{aligned}
$$

## 2) Mean or Average Deviation ( $\bar{\Delta}$ )

The arithmetic sum of all the individual deviations divided by the number of set of data points is called mean deviation. It is denoted by $(\bar{\Delta})$.

$$
\bar{\Delta}=\frac{\Delta_{1}+\Delta_{2}+\Delta_{3}+\ldots . .+\Delta_{n}}{n}
$$

$\Delta_{1}, \Delta_{2}, \Delta_{3}, \Delta_{4} \ldots \ldots . . . . \Delta_{n}$ represents individual measurements, $n$ ' stands for number of measurements(data points)
3) Standard Deviations (SD)

It is defined as "the sum of the squares of the deviations divided the number of data points minus 1 , in the set" . Standard deviation is a statistical term:

$$
\mathrm{SD}=\sqrt{\frac{\Delta_{1}^{2}+\Delta_{2}^{2}+\Delta_{3}^{2}+\ldots .+\Delta_{0}^{2}}{\mathrm{n}-1}}
$$

$\Delta_{1}, \Delta_{2}, \Delta_{3}, \Delta_{4} \ldots \ldots \ldots . . . . . . \Delta_{n}$ represents individual measurements,
' $n$ ' stands for number of measurements, ( $n-1$ ) represents number of deviations.

## Example 1.

Analysis of iron ore sample gave the following percentage values for the iron content as 7.11,7.19,7.15,7.10,7.17,7.16,7.12.calculate the mean, average deviation and standard deviation.

## Solution:

Result

|  | Mean | Deviation $\Delta$ | $\Delta^{2}$ | Standard <br> devivation |
| :---: | :---: | :---: | :---: | :---: |
| 7.11 | $50.00 / 7$ | $7.11-7.14=-0.03$ | 0.0009 | $=\sqrt{\frac{0.0068}{6}}$ |
| 7.19 | $=7.14$ | $7.19-7.14=0.05$ | 0.0025 | $=\sqrt{6}$ |
| 7.15 |  | $7.15-7.14=0.01$ | 0.0001 | $=0.0336$ |
| 7.10 |  | $7.10-7.14=-0.04$ | 0.0016 |  |
| 7.17 |  | $7.17-7.14=0.03$ | 0.0009 |  |
| 7.16 |  | $7.16-7.14=0.02$ | 0.0004 |  |
| 7.12 |  | $7.12-7.14=-0.02$ | 0.0004 |  |
| 50.00 |  | 0.20 | 0.0068 |  |

Arithmetic mean $=\frac{50.00}{7}=7.14$
Meandeviation $=\frac{0.20}{7}=0.028$
Standard deviation $=\sqrt{6 i 6}$
$i \sqrt{\frac{0.0068}{6}}$

$$
=0.0336
$$

## 4) Relative Mean Deviation or Relative Standard Deviation:

It is obtained by multiplying the standard deviation by 100 and dividing the product by the mean or average value. It is expressed in percentage or parts per thousand.
The formula as follows:
Relative Mean Deviation $=\frac{\text { Average deviation }}{\text { Mean }(\text { Average }) \text { value }} \times 100$
or
Relative Mean Deviation $=\frac{\text { Average deviation }}{\text { Mean }(\text { Average }) \text { value }} \times 1000$

## Example 2.

A analyst were obtained the four measurements on repeating the same experiment:51.4,55.7,49.9,52.1.Calculate the mean deviation, standard deviation and relative mean deviation.
Solution:

| Measurement/results | Deviations |
| :---: | :---: |
| 51.4 | $51.4-52.25=-0.85$ |
| 53.7 | $53.7-52.25=1.45$ |
| 49.8 | $49.8-52.25=-2.45$ |
| 54.1 | $54.1-52.25=1.85$ |
| 209 | $=6.6$ |

Arithmatic Mean $($ Average $)=\frac{51.4+53.7+49.8+54.1}{4}$

$$
=52.25
$$

Meandeviation $=\frac{6.6}{4}=1.65$
Standard deviation $(S)=\sqrt{i 6 i}$
$i \sqrt{\frac{0.723+2.10+6.00+3.42}{3}}$
$i \sqrt{\frac{12.243}{3}}$

$$
S=2.02
$$

Relative Mean Deviation $=\frac{\text { Average deviation }}{\text { Mean }(\text { Average }) \text { value }} \times 100$
Relative Mean Deviation $=\frac{1.65}{52.25} \times 100$
¿3.16\%
Example 3.

One analyst were obtained the following results on repeating the same experiment four times as $29.8 \mathrm{mg}, 30.2 \mathrm{mg}, 28.6 \mathrm{mg}$ and 29.7 mg . Calculate the mean deviation, standard deviation and relative mean deviation.
Solution:

| Result | Deviations |
| :---: | :---: |
| 29.8 | $29.8-29.6=0.2$ |
| 30.2 | $30.2-29.6=0.6$ |
| 28.6 | $29.6-28.6=1.0$ |
| 29.7 | $29.7-29.6=0.1$ |
| 118.3 | 1.9 |
| Arithmatic mean $=\frac{118.3}{4}=29.6$ | Mean deviation $=\frac{1.9}{4}=0.475$ |

Standard deviation $=S=\sqrt{\frac{(0.2)^{2}+(0.6)^{2}+(1.0)^{2}+(0.1)^{2}}{4-1}}$

$$
S=0.686
$$

Relative mean deviation $=\frac{0.475}{29.6} \times 100=1.60 \%$

## Minimizatin if Errirs:

Systematic errors can be materially reduced by following methods,

1) Calibration of Apparatus and Application of Corrections

All instruments and glass wares should be calibrated. Calibrate the instruments against a standard. In some cases error cannot be removed, it is possible to apply a correction for the effect that produces, thus an impurity in a weighed precipitate may be determined and impurity weight deducted.
2) Running Blank Determination:

To carry out the separate determination of back and blank experiment, and find out the effect of added impurities through the reagent and vessel.
3) Running a Control Determination:

Standard and pure substance is used in experiment in identical and suitable experimental conditions to minimize the errors. A standard substance which contains same weight of the constituents as it present in unknown sample. The weight of the constituent in the unknown can be calculated as,
' $x$ ' represents the weight of the constituent in unknown.
4) Independent Method of Analysis:

The accuracy in the results may be established by carrying the analysis in an entirely different manner. for example, iron may first be determined gravimetrically by precipitation and removing the interfering element by ignition to get iron oxide. another method to determine iron by titration method using standard solution of an oxidising agent. If the
results obtained by two different methods are concordant, probably the results are correct within small limits of error.
5) Running Parallel Determinations:

If larger variations in the results obtained from the determinations then it must be repeated until satisfactory concordant is obtained. duplicate and triplicate determinations should be sufficient, but this determinations does not justify the result is correct, constant error may be present this also shows the accidental errors.
6) Standard Addition Method:

The unknown amount of constituent is determined by adding to the sample then it is analysed for the total amount of constituent present. The difference between results for sample with and without added constituent are determined. If recovery is satisfactory confidently in the accuracy of the procedure is enhanced. Generally this method is used in physico-chemical procedures in spectrophotometry and polarography.
7) Internal Standard Method :

This method is used for spectroscopic and polarographic determinations. It involves adding a definite amount of reference material (internal standard) to series of known concentrations of the material to be measured. These results are plotted against the concentration values, it gives straight line graph. Unknown concentration can be determined by adding same quantity of internal standard and finding the ratio obtained which falls on the scale.
8) Amplification Methods :

In the determination, a small amount of material is to be measured this may be beyond the limit of apparatus. It may reject small amount, add the more molecules and measure the material within the scope of the apparatus and then minimize the error.
9) Isotopic Dilution:

The known amount of an element being determined, containing radioactive isotope mixed with sample and the element is isolated in pure form which is determined. The radioactivity of isolated material is measured and compared with added element then weight of the element in the sample can be determined.

## Significant Figures and Computation:

Significant figure is defined as "a digit which denotes the amount of the quantity in the place in which it stands". In simple words it is "the number of digits necessary to express the results which are measured with certain precision". (April 2016, Oct. 2014)

1) Every measurement has a certain degree of uncertainty associated with it. The reliability of the measurement can be indicated by expressing the measurement with only those digits that are certain and one additional digit, which is uncertain.

## Example:

If a burette reading is 17.3 ml , here 1 and 7 are the certain digits but the uncertainty lies with the digit 3 , i.e. the limit of error is +0.1 ml , therefore the burette reading can be 17.2 or 17.4 ml . Therefore, in this case, the significant figures are three 1,7 and 3 .
The numbers, $0.256,2.56$ and 256 all have three significant figures, where the digit 2 and 5 are certain, but digit 6 is an uncertain digit.
2) A zero may or may not be significant depending on its location in a number. A zero is not significant figure when it serves to locate the decimal point. A zero surrounded by other digit is always a significant figure.

## Example:

In the number 30.24; zero is a significant figure because zero is directly measured. Here the total number of significant figures is four, but if the same number is written as 0.03024 , still the significant figure is four, but the zero before 3 is not significant as it serves only to locate the decimal point.
3) Terminal or final zero may or may not be significant.

## Example:

If a container mentions its volume as 5.0 liter, here 5 and 0 both are significant, but if we express the same result as 5000 ml then, the last two zeros are insignificant; as the uncertainty in both the case is same.

## Rules of Siguifficunt Migures wnd Computations:

Following are the rules to follow to report the analytical data with the help of significant figures:

1) While expressing an experimental measurement, do not retain more than one doubtful digit. All those digits that are not significant shall be eliminated.
Example:
A burette reading which is between 30.5 ml and 30.7 ml should be expressed as 30.6 ml and not as 30.60 ml ; as it will indicate that the value lies between 30.59 and 30.61 ml .
2) While rounding off the quantities to the correct number of significant figure if the last digit is 5 or greater than increase the prevision digit by one. But if the digit is less than 5, then drop that digit.
Example:
If the number is 8.463 it will be rounded off to 8.5 , whereas, the number 32.274 is rounded off to 32.27
3) In addition or subtraction, there should be in each number only as many significant figures as there are in the least accurately known number.

## Example:

Consider the following operations:

| 1 | 2 | 3 |
| ---: | ---: | ---: |
| 34.1 | 0.0052 | 10.213 |
| +3.41 | +5.1176 | +0.0048 |
|  |  |  |
| 37.9 | 14.629 | 18.23 |
|  | 9 |  |

In the first example, all three numbers having identical number of significant figure i.e. three, but 34.1 have the least decimal place i.e. one. Therefore, the number of significant figure in this case is one. In the second example all have same number of decimal places but the first number has only two significant digits. Here the result can be expressed upto 4 decimal places. In the third example, the significant number of all is different but the last number has only two decimal places therefore the result will be expressed upto only two decimal places.
4) When carrying out the addition or subtraction, of several measurements, each number taken for addition or subtraction should contain only as many significant digits as is present in the number which has least accuracy.

Example 1:
If we have to add the following numbers $0.0211+64.55+2.08725$; here since the second number i.e. 64.55 contains two digits after decimal point, hence it is least accurate amongst the three, so for addition, we consider digits upto 2 decimal points here $0.02+64.55+2.09=66.66$.
Thus, the result expressed i.e. 66.66 contains only 4 significant digits as is present in the least accurate number.
Example 2:
Sum of $65.3+0.261+41.71=107.271$ but since the digit 65.3 contains only one decimal place, the result should be expressed with only one decimal place, however while doing so we can round off the digit of the next digit if it is greater than five. Hence, the result is expressed as 107.3.

Same is applicable to subtraction also. However, please note that significant figure in the answer can change but they should retain the decimal place.
Example 3:
Consider the subtraction of $14.3497-00.0044$.

$$
\frac{\square 4.3453}{00.0044} 0.0044
$$

Here see that although, both the subtracting numbers contains 6 significant digits and 4 decimal places, the result retains the decimal place of 4 digits but the significant digits are only two. This shows that significant digits in the answer can change.
5) In multiplication or division, we should retain in each factor one significant digit more than that present in the number having largest uncertainty. However, the product (or answer) should contain same number of significant figure that are present in the component having largest uncertainty.

## Example:

$13.4 \times 0.22961=3.07667$
Out of these two components, 13.4 have 3 significant figures but have larger uncertainty, Therefore the other component can retain $3+1=4$ significant figures. Hence we can retain the second component up to 0.2296 . The answer of multiplication is 3.07667 but according to the rule, the answer should contain same number of significant digit as there are in the least uncertain number (i.e. 13.4 which contains 3 significant digits).
The answer should be expressed as 3.08 .
Consider another example, multiplication of $1.43 \times 1.398 \times 0.6853 \times 11.6724$ in this case, 1.43 is the number having least accuracy, It has 3 significant digits.
$\therefore$ For the purpose of multiplication, the other number can have $3+1=4$ significant digits. 1.43 $\times 1.398 \times 0.6853 \times 11.67=15.98802$
The product should also be expressed in 3 significant digits.
The answer is 16.0.
The same rule as above is to be followed for division of numbers.

## Distribution Random Errors:

The spread of a series of results obtained from a given set of measurements can be ascertained from the value of the standard deviation. However, this term does not indicate how the results are distributed.


## A normal distribution curve

If a large number of replicate readings, at least 50, are taken of a continuous variable, e.g. a titrimetric end point, the results obtained will usually be distributed about the mean in a roughly symmetrical manner. The mathematical model that best satisfies such a distribution of random errors is called the normal (or Gaussian) distribution. This is a bell-shaped curve that is symmetrical about the mean, as shown
The curve satisfies the equation,
$f(x)=\frac{1 \sigma}{\sqrt{2 \pi}} \exp \left[\frac{-(x-\mu) 2}{2(\sigma) 2}\right]$
It is important to know that the Greek letters $\sigma$ and $\mu$ refer to the standard deviation and mean respectively of a total population, whereas the Roman letters are used for samples of populations, irrespective of the values at the population and the population standard deviation. With this type of distribution about $68 \%$ of all values will fall within one standard deviation on either side of the mean, $95 \%$ will fall within two standard deviations and $99.7 \%$ within three standard deviations. Example:
Analysis of an iron ore sample, the standard deviation is $\pm 0.045 \%$. If the assumption is made that the results are normally distributed, then $68 \%$ (approximately 7 out of 10 results) will be between $\pm 0.045 \%$ and $95 \%$ will be between $\pm 0.090 \%$ of the mean value. It follows that there will be a $5 \%$ probability ( 1 in 20 chance) of a result differing from the mean by more than $\pm$
$0.090 \%$ and a 1 in 40 chance of the result being $0.090 \%$ higher than the mean.

## Reliability of Results:

Analysis of the results can be considered in two main categories: (a) the reliability of the results and (b) comparison of the results with the true value or with other sets of data. A most important consideration is to be able to arrive at a sensible decision as to whether certain results may be rejected. It must be stressed that values should be rejected only when a suitable statistical test has been applied or when there is an obvious chemical or instrumental reason that could justify exclusion of a result. Too frequently, however, there is a strong temptation to remove what may appear to be a 'bad' result without any sound justification.

Therefore, the results must be screened by proper statistical test its rejection. Following rules must be followed to determine whether or not a rejection of result is justified.

A more reliable method for rejection of measurements is the 'Q' test. For small data sets ( $3 \leq \mathrm{n} \leq 10$ ), which are often encountered in chemical analysis, a simple method to determine, if an outlier rejection is the Q test. In this test, a value for Q is calculated and compared with a table of $Q$ values that represent a certain percentage of confidence that the proposed rejection is valid. If the calculated $Q$ value is greater than the value from the table, then the suspect value is rejected and the mean recalculated. If the Q value is less than or equal to the value from the table than the calculated mean is reported. Q is defined as follows:

$$
\begin{gathered}
Q=\frac{[\text { Questionable value }- \text { Nearest value }]}{[\text { Largest value }- \text { Smallest value }]} \\
\mathrm{Q}=\frac{\text { gap }}{\text { range }}
\end{gathered}
$$

Q-Critical values for different sample size

| Sample size | Critical value |
| :--- | :--- |
| 4 | 0.831 |
| 5 | 0.717 |
| 6 | 0.621 |
| 7 | 0.570 |
| 8 | 0.524 |
| 9 | 0.492 |
| 10 | 0.464 |
|  |  |

## Example:

The following values were obtained for the determination of cadmium in a sample of dust: 4.3, $4.1,4.0,3.2 \mathrm{\mu g} \mathrm{~g}^{-1}$. Should the last value 3.2 be rejected?

## Solution:

The Q test may be applied to solve the problem.

$$
\begin{aligned}
& \frac{[\text { Questionable value }- \text { Nearest value }]}{[\text { Largest value }- \text { Smallest value }]} \\
Q & =\frac{[3.2-4.0]}{[4.3-3.2]} \\
Q & =\frac{[0.8]}{[1.1]}
\end{aligned}
$$

In the calculated value of Q exceeds the critical value the questionable value may be rejected. In this example $Q$ calculated is 0.727 and $Q$ critical is 0.831 for a sample size of 4 . Hence the result $3.2 \mu \mathrm{~g} \mathrm{~g}{ }^{-1}$ should be retained. But if three additional measurements were made, with the results $4.3,4.1,4.0,3.2 .4 .2,3.9,4.0 \mu \mathrm{~g} \mathrm{~g}{ }^{-1}$
then,

$$
Q=\frac{[3.2-3.9]}{[4.3-3.2]}
$$

$$
Q=\frac{[0.7]}{[1.1]}
$$

$$
=0.636
$$

The value of Q critical is 0.570 for a sample size of 7 , so it is justified to reject the value $3.2 \mu \mathrm{~g}$ $\mathrm{g}^{-1}$. Note that the value Q has no regard to algebraic sign.

## Solved Examples

## Example 1:

The results of an analysis are found by analyst to give 36.89 \% of a metal compared to the true value of $36.98 \%$. What is the relative error in parts per thousand?

## Solution:

$$
\begin{aligned}
& \begin{aligned}
\text { Absolute error }= & {[\text { Observed value }- \text { True value }] } \\
& =36.89-36.98 \\
& =-0.09 \% \\
\text { Relative error } & =\frac{\text { Absolute error }}{\text { True value }} \times 1000 \\
& =\frac{-0.09}{36.98} \times 1000 \\
& =-2.7 \mathrm{ppt}
\end{aligned}
\end{aligned}
$$

## Example 2:

The percentage of chloride in $\mathrm{CaCl}_{2}$ was reported by different persons as $32.64,32.54,32.61$ and $32.53 \%$. Calculate the mean deviation, standard deviation and relative mean deviation in the results.

## Solution:

| Result | Deviation |
| :---: | :---: |
| 32.64 | $32.64-32.58=0.06$ |
| 32.54 | $32.54-32.58=-$ |
| 32.61 | 0.04 |
| 32.53 | $32.61-32.58=0.03$ |
|  | $32.53-32.58=-$ |
|  | 0.05 |
| $\Sigma=130.32$ | $\sum=0.18$ |

$$
\begin{gathered}
\text { Arithmetic mean }=\frac{130.32}{4}=32.58 \\
\text { Mean deviation }=\frac{0.18}{4}=0.045
\end{gathered}
$$

$$
\begin{aligned}
& \text { Standard deviation }=\sqrt{\frac{(0.06)^{2}+(0.04)^{2}+(0.03)^{2}+(0.05)^{2}}{4-1}} \\
& =\sqrt{\frac{0.0086}{3}}=0.0536 \\
& \text { Relative mean deviation }
\end{aligned}=\frac{\text { Mean deviation }}{\text { Mean of the result }} \times 100
$$

## Example 3:

Following results were obtained in the replicate determination of the lead content of a blood sample: $0.752,0.756,0.752,0.751$ and 0.760 ppm of Pb . Calculate the mean and standard deviation of the data.

## Solution:

| Results | Deviations |
| :---: | :---: |
| 0.752 | $0.752-0.754=0.02$ |
| 0.756 | $0.756-0.754=0.02$ |
| 0.752 | $0.752-0.754=0.02$ |
| 0.751 | $0.751-0.754=0.03$ |
| 0.760 | $0.760-0.754=0.04$ |
|  |  |
| $\Sigma=3.771$ | $\sum=0.13$ |

$$
\begin{gathered}
\text { Arithmatic mean }=\frac{3.771}{5}=0.754 \\
\text { Mean deviation }=\frac{0.13}{5}=0.026 \\
S=\sqrt{\frac{(0.02)^{2}+(0.02)^{2}+(0.02)^{2}+(0.03)^{2}+(0.04)^{2}}{5-1}}
\end{gathered}
$$

Standard deviation $(S)=0.03$

## Example 4:

Four different samples of silver alloy were analyzed for silver and were found to contain 16.37, 16.29, 16.39 and $16.35 \%$ of silver. Calculate the mean deviation, standard deviation and relative mean deviation.

## Solution:

| Results | Deviations |
| :---: | :---: |
| 16.37 | $16.37-16.35=$ |
| 16.29 | 0.02 |
| 16.39 | $16.29-16.35=$ |
| 16.35 | 0.06 |


|  | $16.39-16.35=$ |
| :---: | :---: |
| 0.04 |  |
|  | $16.35-16.35=$ |
| 0.00 |  |
| $=65.3$ <br> 8 | $\Sigma=0.12$ |

Arithmetic mean $=\frac{65.38}{4}=16.345$

$$
\text { Mean deviation }=\frac{0.12}{4}=0.03
$$

Standard deviation $=\sqrt{\frac{(0.02)^{2}+(0.06)^{2}+(0.04)^{2}+(0.00)^{2}}{4-1}}$

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