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PAPER-II

QUALITY CONTROL AND TRADITIONAL METHODS OF ANALYSIS-I

UNIT-I

A) QUALITY CONTROL IN ANALYTICAL CHEMISTRY

⇒ **Characteristics of an analysis:-**

✱ **Quality of an analytical Procedure:-**

The stages (or) steps in all overall Analytical Procedure can be summarised as Follows.

Definition of the Problem:-

Analytical information and level of Accuracy required Cost, Timing, Avaliability of laboratory instruments and facilities.

Choice of Techniques and method:-

selection of the best technique for the required analyser, such as chromatography, Infrared spectroscopy, titrimetry, Thermogravimetry.

Sampling:-

select a small sample of the material

to be analysed. where this is hetrogeneous special Procedures need to be used to ensure that a genuinely representative Sample is obtained.

Sample Pre-treatment (or) conditioning:-

Conversation of the Sample into a form suitable for detecting (or) measuring the level of the Analysis by the selected Technique and method. This may involve dissolving it, converting the analyte into a specific form (or) separating the analyte from other Components of the sample that could interfere with detection (or) quantitative measurments.

Qualitative Analysis:-

Tests on the sample under specified and controlled Conditions. Tests on reference materials for Comparison interpretation of the tests.

Quantitative Analysis:-

Preparation of standards containing known amount of the analyte (s) (or) of Pure reagents to be reacted with the analyte (s). Calibration of instruments to determine the response to the standard under controlled conditions.

Measurment of the instrumental response for each sample under the same conditions as for the standards. All measurments may be replicated to improve the reliability of the data. but, this has cost and time implecatio

Preparation of Report (or) Certificate of analysis

This should include a summary of the analytical procedure. The Results and their statistical assessment and details of any Problems encounted at any stage, during the analysis.

Review of the original Problem :-

The results need to be discussed with regard to their significance and their relevance in solving the original Problem.

Some times repeat analysis (or) new analysis may be under taken.

Limit of detection (LOD) :-

It is important to establish for analytical procedure.

In this, the small amount of analyte that can be detected and measured quantitatively. In statistical terms and for instrumental data, This is defined as the smallest amount of an analyte giving a detector response significantly, different from a blank (or) back ground response.

It is the lowest concentration level that can be determined by statistically difference from analyte blank.

Replicate blanks of one sample matrix are analysed to determine the mean blank value & its standard deviation.

Then a matrix is spiked with analyte near the detection ~~value, (or)~~ limit.

The LOD is the concentration calculated to give a response equal to the blank signal plus '3' standard deviations.

LOD = Blank sigal + 3 standard deviations

the concentrations that give the signal equal to '3' times the S.D of the back ground is generally taken as detection limit.

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Sensitivity :-

The ability to discriminate among similar concentrative of the analyte.

The ability to detect (qualitative) (or) determine (quantitative) small amount of analyte in a sample.

It can be expressed via, various parameters.

$$S = \frac{x}{c}$$

where,

x = variation of analytical sigal
c = Analyte

$$S = \frac{\delta x}{\delta c} = \frac{\Delta x}{\Delta c}$$

It is ability to distinguish two different concentrations and is determined by slope of the calibration curve. So measure the slope (or) sample of closely related high concentrations intermediate low concentrations.

The sensitivity & precision well govern (or) will give how many significant figures should be reported in a measurment.

⇒ **SAFETY:-**

safety in Acadamic chemistry laboratories Published by the American chemical society.

To guide discusses and Personal Protections are

a) laboratory Protocal
b) Recommended laboratory techniques
c) chemical Hazard's
d) Instructions on Reading
e) understanding material safety data sheet
F) safety equipment.
g) emergency Procedure.

Cost measurability:-

Analytical costs are expressed as a sum of money per result (or) samples are and less often in many hours.

The lower analytical costs are the higher will be cost effectivities which can be considered as an analytical Property.

Lowering cost usually sacrifying on some other analytical Property whether capitals basic (or) accessory.

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over head costs:-

It arises from laboratory set up and maintanance the Purchase and maintanance of equipment and the Salaries of staff. (managers, secretaries)

As a rule they are considered fixed costs. even through they can certainly vary to some extent.

selectivity:-

It denotes basic analytical methods (or) Procedures.

⇒ It defined as ability to Produce exclusively depend on the analyte for its identification (or) quantification in sample.

⇒ It Provides direct Support for Accuracy.

⇒ It is extent method can measure the analyte of interest in the materials of sample being analysed without interference from the matrix.

⇒ In this method two different Parameters.

The total rated (TR) ratio of an interferen is concentration ratio of interferent (C_{int}) and concentration ratio of analyte ($C_{analyte}$)

$$T_R = \frac{C_{interference}}{C_{Analyte}}$$

The selectivity of method can be expressed as:

$$T_R = \frac{S_{analyte}}{S_{interference}}$$

The selectivity factor may be expressed as

$$S_F = \frac{(T_R)_1}{(T_R)_2}$$

Specific costs :-

These are to be paid by the laboratory's clients i.e by these who demand the information delivered. The difference b/w what the client actually pays & specific costs can be used as a criterion to establish the quality of an analytical procedure.

Specific costs can also be fixed (or) variable automation raises fixed costs (these of equipment) but decreases in variable costs (if reduce many hours).

Quality Control:-

It is a process of ensuring that

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the operation technique and activities used in analytical laboratory Provided results suitable for the interview Purpose.

It Comparises a system of planned activities in an analytical laboratory where by analytical methods are monitered at every stage to verify complain with validated Procedure and to take steps to eliminate course of unsatisfactor performance.

Results are considered to be of sufficiently high quality if

⇒ They meet specific requirements of required with in the contest of a defined analytical work Problem.

⇒ There is a confidence in their validates.

⇒ The work is cost effective

Ruggedness test :-

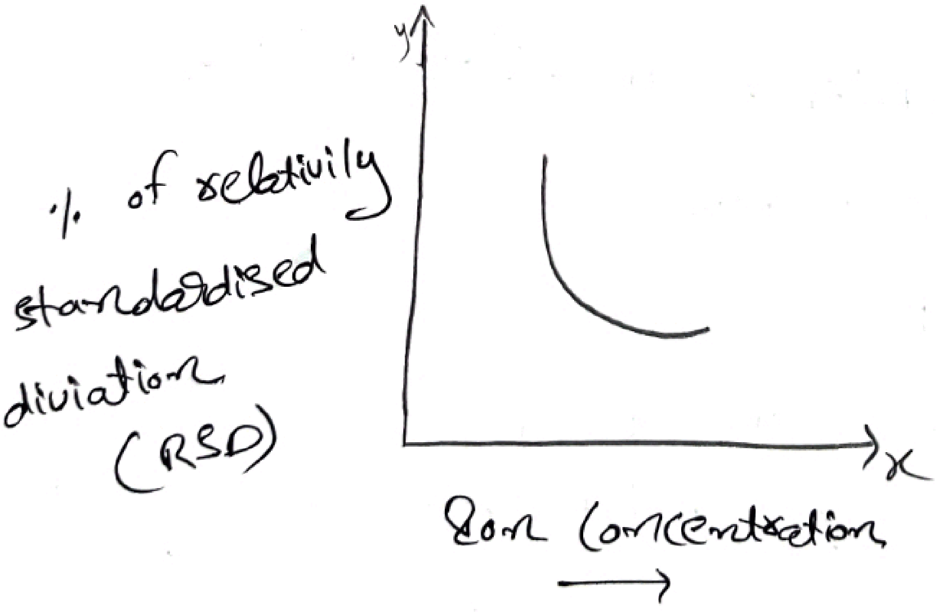
It refers to the Precision of one lab over multiple days, which may includes multiple analyte, multiple instruments different source of reagents, different chromatographic columns.

A Ruggedness Study will identify those

factors, that will contributes to variability of Results, and which should not change.

This is related to reliability of the method which refers to how sensitivity. It is to uncontrolled small changes in Parameters such as the size of the sample, temperature, pH of the solution, reagent concentration, time of the reaction etc...

Each Parameter should be tested separately unless statistically more sophesticated factorial analysis experiments for changing, several Parameters and to give differential values. these are analysed and the resultant value is compared with true values.



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Control Charts :-

The Principle of a control chart is a visual representation of quality useing as a bases the desired quality and the limit.

A Control Chart is a used for Justification of quality of Product Producing by a Company (or) plant.

It is develped as a system for keeping track of quality during large scale operation especially It is useful as individual inspection of each item is not Possible and in some cases the quality test is distruck to and hence Cannot be applied for each specimen Produce by company.

The control chart method is also useful in monitoring of Performance of analytical method in laboratories where the same type of sample are analysed Continuosly day after day over long period of time.

The Control Chart method is a high degree of efficiency periodically to give a determination of quality of sample.

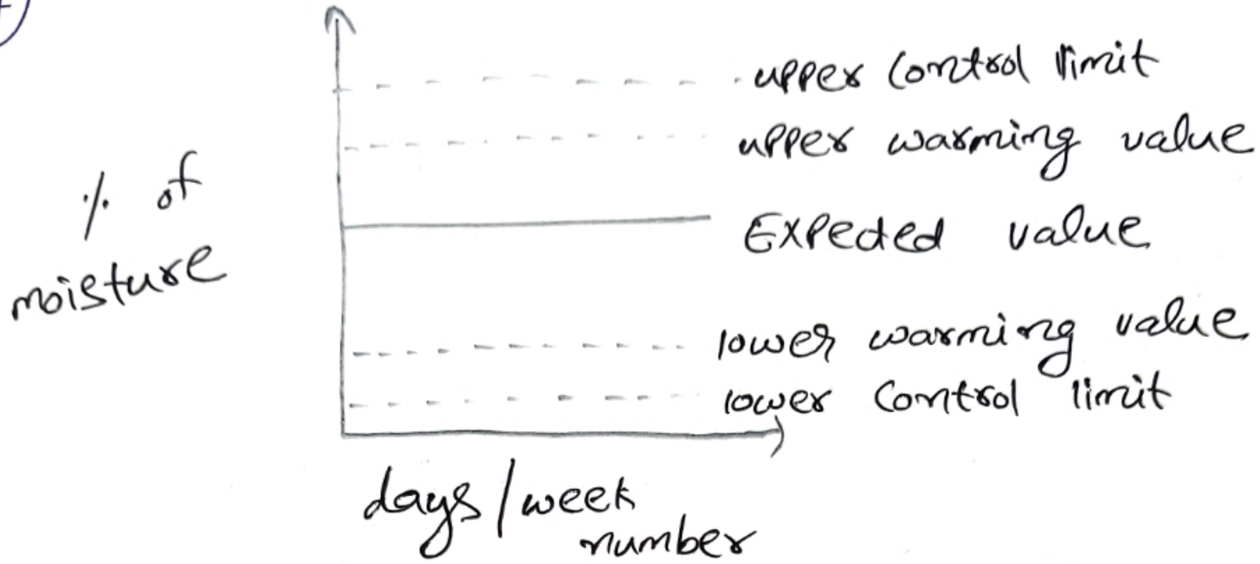
The following type of control charts are used in analytical quality assurance.

1) Shewhart chart (or) conventional chart
2) X - charts (blank value charts)
3) Recovery rate control charts
4) Range control charts (R- charts)
5) $\overline{X}$ - R combination chart
6) Standard deviation chart.
7) difference charts
8) Cusum charts

let us suppose the company manufacturing some material as a part of quality control programme the analytical laboratory performs each day a certain analysis. samplying coming out of the blank for any parameter like % of moistu mass of the sample can be used for Justificati of quality of sample.

The following shows the identificatio of quality of sample in control chart method.

i.e



The Plant (or) Company should also use a control chart method based on the laboratory reports for the monitoring, For the quality of Products. the Percentage moisture in the Standard Sample is indicated on the chart by horizontal line. The standard sample is analysed everyday and the average of weekly results what ever may be drawn on the chart.

The control limits, shown above & below. the standard values are designated to have responsible to take either the Product (or) the method selected for estimation of Particular Components. As long as results fall within the limits. we can say the Product (or) method is under control. Finally the analysed sample is compared with standard value by useing different chart methods

This method is suitable method for Justification of quality of sample.

Quality :-

Quality signifies excellance of a Product (or) services which is measured based on costumers experience with the Product are serivices against his (or) her requirements.

Quality Control :-

It deals with a system which accepts (or) rejects any activities which effect the quality and quality deficiency and imports Consistance in the quality of the Product (or) services.

Quality Control in an analytical laboratory :-

This refers to various operations that need to be under taken in the laboratory to ensure that the data Produced (or) generator will of acceptable degree of Accuracy and Precision. The laboratory management must know the limit of accuracy of the data and hence this should be the objective of quality Control inorder to achieve this objective the quality Control function should used various Parameters like

⇒ Trainee man Power
⇒ use of appropriate laboratory Standards
⇒ use of appropriate and calibrate instruments.
⇒ safety operations
⇒ use of suitable equipment
⇒ To maintain quality laboratory equipment and laboratory analysis cost.

If we does not use quality operating systems then should not analysed the sample with Accuracy and should not maintain data of sample with qualitatively. The sample should be quality analysed it depends upon the above factors

Youden Plot :-

⇒ youden plot method for the execution, evaluation of inter laboratory programmes is sitted to laboratory monitering.
⇒ since it is a statistical method for obtaining information about a precision & systamatic errors.
⇒ only two additional samples must be analysed

⇒ The inter laboratory test is eluted graphically by plotting to result as a Youden plot.

⇒ However application of Youden Plots are not only limited laboratory monitering by means of inter laboratory test.

Ranking Test :-

The Test used to determine several samples differ on the basis of a single characteristic a control need it be identified.

⇒ Analysis are produce sample simultaneous including [a standard (or) control] Code no's are asked to rank all samples, According to the intensity of the specified characteristics.

⇒ The analysis are asked to rank coded Sample according to their Prefarence.

⇒ The rank of sample numerical order, Accor-ding to the preference characteristics of Properties

⇒ when more than 3 samples are required to be compound ranking method is suitable.

⇒ The method can be used for the comparing one treatment with others.

→ For a Sample to be Considered atleast one of the rank either test Sample (or) any other marked Sample must be lower than the higher limit in the upper plane.

Hadonic Rating :-

It results, pleasure (or) unpleasure experience, The Hadonic rating measures to Consum acceptability of Consumer Product.

→ To Result the numerical values are design.

→ Hadonic rating evaluated by Rank Test. In this each sample arranged in ↑ & ↓ Numerica order ranking assign.

→ The Purpose of rating obtained knowledge on how well Produce Prefer for the uses.

eg:

Specific Sample (Δ) = monthly Sample Size

$$\Delta = a\sqrt{2n}$$

where,

n = Monthly Production

a = Constant range depend on a nature of Product.

units for measure rating :-

overall rating is the ~~ratio~~ No. of demerits for the detector f divided by no. of units of Products in the sample.

$$R = \frac{\text{No. of demerits for the detectors}}{\text{No. of units after Products in the sample}}$$

limitations of analytical methods :-

For limitation of analytical methods. there are two ways to determine accuracy.

a) Absoulte method

b) Comparative method

⇒ Most Problems Cannot be approached by such methods.

⇒ Requires great mathematical knowledge and skills to solve more ofter then not.

⇒ with the fuse development in computational capacity this methode have become rather slow in comparisons.

Accuracy :-

Accuracy is one of the method for

for the determination of the sample and to get a values and to get a less error in a analysis of a sample.

In accuracy concept, a suitable method is apply for the determination of the sample and the resultant values very close to the standard value and accuracy is increase

Accuracy is depend upon,

i, creativity of analyst
ii, useing of chemical reagents
iii, used operators
iv, Calculations.

For analytical methods, there are two ways to determine accuracy. They are

Absoulte method:-

- ⇒ The substance must be known purity.
- ⇒ It is a method is likely to be largely controlled by the separation involves.
- ⇒ The degree of Accuracy required depends on the context of analytical system, problem never must be shown.

Comparative method :-

⇒ It involves secondary (2°) standard

⇒ By repeating an analysis a no. of times and computing an Average value for the result.

⇒ Accuracy cannot be estimated with a true (or) acceptable value is known.

⇒ Hence statistical tests indicating the accuracy of a result with a given Probability are widely used.

Precision :-

It is a closeness of Agreement between replicated measurments is called "Precision."

⇒ Accuracy expressed the corredness of measurments and Precision express the reproducibility measurments.

⇒ Precision always accompanies accuracy but high degree precision does not imply Accuracy.

⇒ The Precision of results obtained with in one working session is known as Repeat ability (or with in run) precision.

⇒ The Precision of result obtained over a series of working sessions is known as reproducibility (or b/w runs) precisions.

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Errors :-

The error denote the estimated the uncertinity in measurments.

uncertainity :-

A perameter is the range of values with in which the values of quantity being measured.

definition :-

It is defined that the difference between standard value and measured value.

$$\boxed{\text{Error} = S.V - M.V}$$

$$\boxed{\%\ \text{of Error} = \frac{S.V - M.V}{S.V} \times 100}$$

Absoulte error :-

It is defined that the difference between experimental value and true value is known as "Absoulte error".

$$\boxed{\text{Absoulte error} = E.V - T.V}$$

Relative error :-

The percentage of absoulte error is

known as relative error.

$$R.E = \left(\frac{e.v - T.V}{T.V}\right) \times 100$$

Errors in chemical analysis :-

The difference b/w the true value and the value obtained by the practical value is called as Errors.

classification of errors :-

Experimental results may conviently by divided into following four types.

They are :

1) systematic errors
2) Random errors
3) Gross errors
4) other errors

Systematic errors :-

These are also called as determinate errors, which can be avoided (or) whose magnitude sample determination important them are.

1) operational & personal errors
2) instrumental errors
3) errors of method
4) Additive (or) Proportional error

operational & Personal errors :-

These includes due to factors which individual analysis is responsible and are not connect with the method (or) Procedure.

⇒ These are mostly Physical in Nature.

⇒ occur when sound analytical technique is not followed.

Eg: Mechanically loss of material in various steps of analysis, over washing of ppt, ignitition of ppt and cooling & before weighing & used harmful impurity.

Instrumental errors :-

These are caused by Non-ideal instrumental behaviour.

From the faulty construction of balance in use of improperly calibrated weights.

Eg: Different arise from useing graduate glassware, from concentrate on inner surface mostly electronic instruments are subjected to I.S.E.

Errors of the method :-

These are arised from Non-ideal chemic Physical behaviour of analyte system.

⇒ These are originate from in correct sample and incomplete solubility of PPt, Post PPt, Co-PPt.

⇒ Non-specified reagent is possible.

⇒ occurrance of the side reaction, that interfere with measurment process.

Additive (or) Proportional errors:-

The absoulte value of additive error is independent of the amount of the constituent present in the determination.

eg:- Loss in weight of crusible in which a PPt is ignited & error in weight, the error is related by taking a sample of the different weights.

Random errors (or) indeterminent errors:-

These errors are the slight variation that occur in successive measurment made by the same observer under nearly identical conditions. They are due to causes over which the analyst has no control in capable of analysis.

Gross errors:-

Common Gross errors due to careless of analyst are

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⇒ use of numerically incorrect conversion factor.

⇒ wrong selection of the method.

⇒ unsuitable storage of the sample.

other errors :-

→ Errors in radiometric analysis

⇒ Errors in chromatography

⇒ Photometric errors.

MINIMIZATION OF ERRORS :-

systematic errors can be reduced by the following methods.

1) Calibration of operator & Application of correction
2) Running a blank determination
3) Running a controlled determination
4) use of independent method of analysis
5) Standard addition method
6) Internal standard method (or) Calibration curve method.

7) Isotopic dilution

① Calibration of operator and application of corrections :-

All instruments should be calibrated in suncases, where as error cannot be eliminated

It is possible to apply a correction from the effect that it produces. Thus an impurity in a weight precipitation. Many determined and it can be reduced.

② **Running a blank determination:-**

This consist in carrying out a separatio determination without sample under exactly same reagents are used for analysis of sample, which reagents are used in standard sample.

③ **Running a controlled determination:-**

This consist a carrying out a determinati under as nearly as possible for identical experimental condition upon a quantity of a standard substance which contain the same consistuents as in the unknown sample.

i.e

$$\frac{\text{Result found for standard sample}}{\text{Result found for unknown sample}} = \frac{\text{wt of constituents in standard sample}}{a}$$

use of independent method of analysis :-

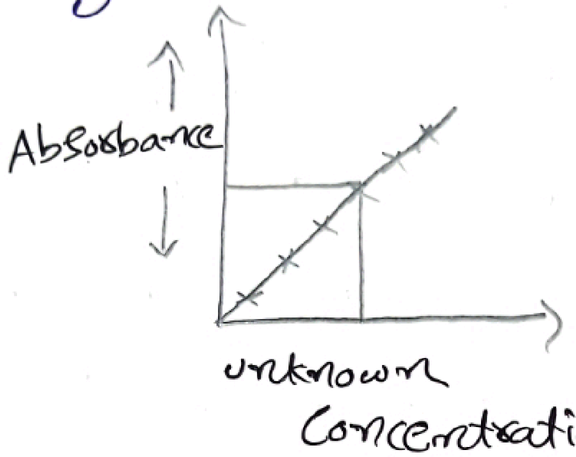
In this , we are usscing two (or) more methods for example Iron make first determined gravimetrically by Precipitated as Iron trioxides ($Fe(OH)_3$). After removing interfering eliments followed by ignition of the Precipitation through Iron oxides. It may be determined, titrimetrically by reduction to Fe (II) states and titration with a standard solution of oxidising agent such as Potassium dichromate.

standard addition method :

A known amount of constituent being determined is added to the sample, which is then analysed for the total amount of constituent present. The difference b/w the analytical results for the sample with and without added constituents.

Internal standard method (calibration curve method)

This is Particularly in spectroscopy and chromatography determination. It involve the addition of fixed amount of a reference material to a seriee of known concentration, of the material to be determined then measuring the physical parameter.



Isotopic dilution :-

A known amount of the element being determined containing a radioactive Isotopes is mixed with sample and the element is isolated in pure form, which is weighed.

The radioactivity of isolated material is measured and compared with that of added element. The weight of eliment in the sample can be calculated.

Propagation of errors :-

statistical result is not only one measurment. It also used to measuring of the substance values including with other measurments.

Mostly it is express based on "determine error" in this addition and substraction (or) multiplication and division.

Eg: To determine Potassium thiocyanide (KSCN) molecular weight based on atomic weight is, K atomic weight is 39.10 instead of 39.01 and S atomic weight is 32.06 instead of 32.60 and C, N atomic weight are accurately taken

According to Potassium (K) the determination of molecular weight then the determinate error = -0.09.

According to sulphar (S) the determination of molecular weight then the determinate error = +0.54

∴ Potassium thiocyanide (KSCN) molecular weight then the determinate error is +0.45.

Significant figures:-

The No. of digits necessary to express the results of a measurment only one of the consists of with the measured precision.

The term digits denote ten numerical includings to zero's.

Significant figure is a digits which

denotes the amount of the quantity in the Place in which it stands the digit zero is a significant figure except where it is the first figure in a number,

eg: 1.2686 g
1.0062 g

The zero is significant and each quantity containing five significant figures but in the quantity 0.0025 kg. The zero's are not significant because the value can be written as 2.5g.

Computation :-

Retain has many significant figures in a result has will give only one uncertain figure.

eg: ① A volume which is known to between 10.5 ml to 10.7 ml should be written as 10.6 ml but not 10.60 ml.

eg ② 5.2600g should not written as 5.260g (or) 5.26g

the rounding of quantities to the correct number of significant figures add one to the last figure retained.

eg: 8.856 has been round upto 8.86

In addition (or) substraction, computation has follows.

$$168.11 + 7.045 + 0.6832$$

$$\Rightarrow 168.11 + 7.04 + 0.68$$

$$\Rightarrow 175.83$$

In multiplication (or) division, computation has follows

$$1.26 \times 1.236 \times 0.6834 \times 24.8652$$

Note:- To maintain three significant figures in multiplication (or) division.

$$\rightarrow 1.26 \times 1.236 \times 0.683 \times 24.86$$

$$\Rightarrow 26.448.$$