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Performance characterstics, Quality parameters and Techniquies of Analytical Instrumentation : A Review

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Abstract: The assurance of quality in analytical measurements is the driving force behind several current initiatives that are addressing different aspects of the overall problem. This review paper outline the framework of current developments in "Quality" that link with the need to understand and quality the performance of instruments.
Keywords- Performance characterstics ,Uncertainty, Quality standards, Performance Qualification.

Introduction-

The aim of an analytical procedure is to discover some specific information about the sample under investigation, and ultimately to make a decision about the sample. Such information may be as follow:

(a) Qualitative

where the analysis identify a particular quantity of the sample, yielding a numerical value, e.g concentration of oil in sea water.

(b) Qualitative

where the analysis identify a particular quality of the sample. e.g the presence of a particular molecular bonding structure.

The role of quality assurance is to be ensure and demonstrate that the instrument is and will continue to be , 'fit for purpose'. The demand of a modern technological society have highlighting the need for greater assurance in analytical measurements. [1]

The analyst must be able to decide if the system, the equipment and the method are 'fit' for the purpose for which it is going to be used. The ultimate purpose of a quality system for an analytical laboratory is therefore to ensure and to demonstrate that the laboratory will continue to meet predefined standards. The multipurpose use of the word 'standard' may be lead to confusion in relation to quality system, and in analytical chemistry the term 'standard' appears in respect to at least three different types of situation as follow:

1. Chemical standard e.g a sample of known concentration.
2. Performance standard, e.g being able to measure concentration.
3. Quality standard, e.g adopting recognized methods of organization and working.[1,2]

Traceability to standards in an essential concept within any quality system. The following are of particular significance.

1. It is important to be trace the lines of responsibility in management and how information flows through the system
2. In an analysis , it is also important to trace how the final analytical results can be related to chemical or physical certified reference materials (CRMs).

The operation aspects that are used to deliver a quality system will include the following-

(a) Quality control

Quality control encompasses those activities, carried out within the system, that are designed to keep the system operating within the accepted standard of service. Quality control of the analytical process requires the systematic monitoring of method and instrument performance.

(b) Quality assurance

Quality assurance is that set of activities which confirm that the quality control process is performing adequately and that the system is operating within the accepted quality standard.

(c) Quality management

The quality management of everything within the system must also reflect the needs of the quality system without an adequate standard of quality management, the other elements of the system can fail to link a satisfactory whole.

(d) Quality manual

The details of all essential procedures within the quality system must be documented in a quality manual. This reference document defines the quality system at all levels, and sets out in detail, all of the essential procedures.[1,3]

Basic of analytical Instruments

Various types of instruments can be used in the process of analysis. Some are basic measuring instruments, while other performe an inherent analytical function. The most important distinction between an analytical instrument and a basic instrument is that:

1. An analytical instrument performs an experiment as part of the detection process.
2. The conditions of that experiment can be controlled by the operator to suit the particular analytical situation.

However, because the user of the measuring instrument does not have the opportunity of changing the conditions of that experiment, they remain basic measuring instruments. It is common for analytical instruments systems to contain basic measuring process as sub units. [6]

An example of analytical instrument is a spectrophotometer, which measures the absorbance of radiation passing through a sample. The wavelength of light is used in the spectrophotometer can be systematically changed to provide an output spectrum (absorbance vs wavelength).

A spectrophotometer will include a detector unit for the measurement of light intensity.[1,7]

Data Output

A simple measuring instrument typically produces a result on a one dimensional (1-D) scale. For example, a thermometer gives a number on a temperature scale. Whereas in an analytical instrument, however, the conditions of the experiment can be changed and these conditions can add extra dimensions to the output data. The production of multidimensional data ia a characterstic of an analytical instrument. However ,with the development of computer technology it is now normal practice to display the 2-D data on a visual display unit screen. The development of modern computer systems has now also enabled the easy visualization of three dimensional (3-D) data by using 3-D computer display and printouts.[8]

Error - The error is the difference between the observed value and true value.
Error = Observed value - True value
Classification of Error- Error are classified into following two types:

(a) Bias or systematic error :

Where the error (magnitude and sign) remains the same if the measurement under the same conditions.

(b) Imprecision or Random error

Where the sign and magnitude of the error change randomly between the measurement. It is easier to detect and also allow for, the effect of random errors than the effect of systematic errors. A well designed analytical procedure will, where possible convert systematic errors into random errors. It is also possible that a particular factor, which gives a systematic error in one laboratory, may become a random error between different laboratories (who use slightly different procedure).

Various positive terms are used to give estimates of the maximum errors that are estimated to be present in a measurement as follow:

1. Trueness- Which is an estimation of the systematic error in the measurement.
2. Precision- Which is an estimation of the random error in the measurement.
3. Accuracy- Which is an estimation of the maximum total error in the measurement.[9]

Error can be classified on the basis of their expected probability distribution around the true value. The two distribution that are used most commonly are

1. Normal distribution/ Gaussion distribution
2. Rectangular distribution

(a) Normal distribution/ Gaussion distribution

Random error in experimental results are usually assumed to follow a normal distribution. The probability of obtaining a particular value of experimental error is given by the following parameters.[1,10]

Mean value =μ_o (error = 0)
Standard deviation = σ
Variance = σ^2

The mean value μ_o the true value of the result, and the spread of possible results is given by the standard deviation σ of the distribution. The standard deviation is also the root mean square value for the distribution. In practice, for an analytical measurement, the value of μ_o is not normally known, and can also be estimated from the experimental results themselves.

The true standard deviation, σ can be estimated by either of the following appearance –

1. Consideration of the detailed process of measurement.
2. The recording the standard deviation, s, of the experimental results.

(b) Rectangular distribution

There are some situations where the probability of a particular error does not follow a normal distribution. It is possible that all values of error within a specified range are equally likely to accure. The probability distribution of this situation has a rectangular shape. e.g rectangular distribution of error might arise is in a performance check for the wavelength accuracy of a spectrophotometer.[1,11]

Uncertainty

This is an estimate of the possible magnitude of the error. The magnitude of 'Uncertainty' must be derived on the basis of knowledge of the way in which the measurement was performed and the reliability of the equipment that was used.[2]

Expression of uncertainty

The methods of qualifying the uncertainty of a particular error will depends on the probability distribution that the error is expected to follow-

1. For the normal distribution, the uncertainty can be expressed as a standard deviation, e.g noise <0.02 (sol).
2. For the rectangular distribution, the uncertaintywill be given by the limits of the distribution.

The standard deviation, u(x) in a variable x, is defined as one standard deviation in the value of x.when several uncertainty factors are combined together, the result is a combined standard uncertainty, $u_c(x)$. it is often importantto give the uncertainty in the value of a variable as a fraction of the value itself. The fraction uncertainty is frequently expressed as a percentage, as follows :

$$\text{Coefficient of variation(CV\%)} = \frac{100 \times \text{standard deviation}}{\text{Mean}}$$

The range for the final results should be quoted as an expanded uncertainty, U, defined as a multiple of the combined uncertainty as follows:

Where k is the coverage factor.

The use of the expanded uncertainty is designed to cover a greater proportion of the possible variation in results.[12]

Combined uncertainty

when two or more factors (a,b,c etc) give a combined results, t the uncertainty in the final result u(t), can be estimated from the individual standard uncertainties [u(a), u(b), u(c) etc]. The method of combining the uncertainties depends on the form of the relationship.[1,3]

Instrument performance characterstics

We know that an analytical instrument performes an experiment. It is important to know the performance characterstics of the instrument for the following reasons-

1. we can be sure that the instrument is conducting the experiment under the required conditions.
2. we can interpret the result on tha basis of knowledge of the response of the instrument.
3. we can estimate the uncertainties in the result. There sre four types of performance characterstics for an analytical instrument. These are required to describe how well the experiment is being conducted.

Type | - The conditions under which the instrument can perform the experiment.
Type || - The response of the instrument to the results of that experiment.
Type | (u) – The uncertainty in the experimental conditions.
Type || (u) – The uncertainties in the response of the instrument.[1]

Generic response characterstics

The following generic characterstics are used to quantify the response to analytical signals in many types of instruments.

Responsivity

The ratio of the output signal divided by the input signal. The common mathematical form of a straight line is given by the following equation:

Y = mx + c
It is possible to define the straight line by using only the following two variables:
(a) the slope, m, which is given by m = dy / dx.
(b) the intercept, c, which is the offset on the y- axis.
The equivalent equation for the straight line response of an instrument with a non zero offset is as follow
$S_0 = R' S_A + S_D$
For the ideal instrument response , the offset, S_D , should be zero.
The slope of the line is the differential responsivity R' , which is given by the following[1,4]
Differential Resposivity (R') = change in S_0/ change in S_A = d S_0 / d S_A
The differential responsivity is defined at specific points on the graph. However, responsivity is defined simply as follow:
Resposivity (R) = Output signal (S_0) / Input signal (S_A)
Responsivity is usually the key parameter for an instrument system.

2 Linearity

The extent to which the resposivity remains constant for different values of the input. The ' Linearity' range is a performance characterstic that identifies the range of values of S_A over which the response is 'linear' . This gives an effective operational range for the instrument of (S_A max – S_A min) .

For modern system , the offset error is normally very small and its effect on the linearity only occurs at very low signsl levels. Hence , the dividing parameter for the linearity range is normally the point ,at high signal levels, at which the response changes by 5%. For example, the range of a spectrophotometer is often expressed as the maximum absorbance value up to which the system remains linear.

The linear dynamic range is the ratio which compare the largest signal , S_A max and the smallest signal S_A min, within the linear range that can be measured with acceptable accuracy.[1,6]

The dynamic range of the input signal (D R_A)is given by the following:

$DR_A = S_A$ max / S_A min

The linear dynamic range is an important factor in instruments that are expected to operate at both trace and assay levels of analysis. A large linear dynamic range reduce the need to dilute the more concentrated samples.

Offset

The value of the output signal when the input signal is zero. Offset may occurs due to the following –

1. An interfering signal from some other component of the sample.
2. A standing signal in the instrument system.[7]

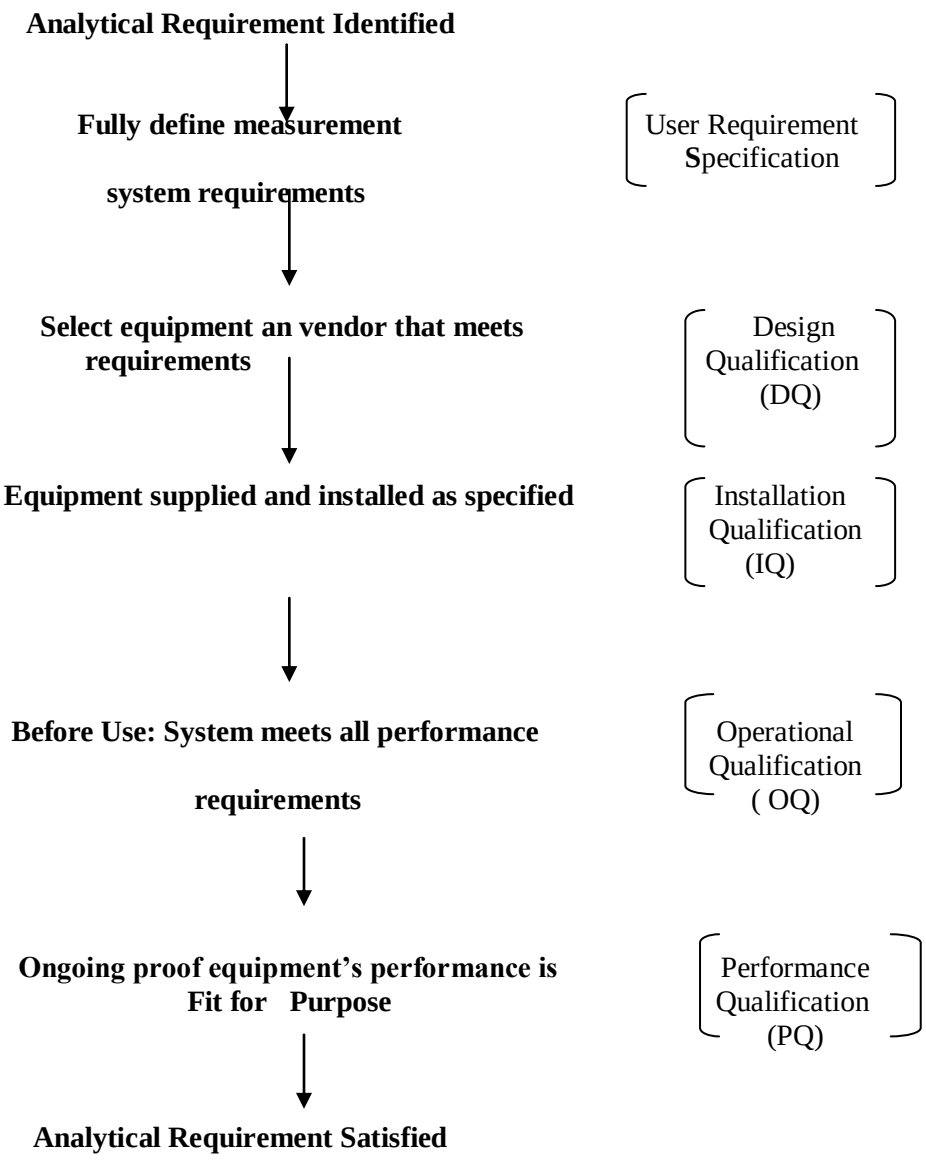

Fig. 1 Relevance of Each Stage of Equipment Qualification to Satisfying an Analytical Requirement.

Performance Qualification (PQ)

PQ should be viewed as a process rather than an event and should be an integral part of the SOPs and other Quality Assurance documentation that governs the conductivity instrumentation's use. There are three main areas to effective PQ of conductivity instrumentation:

1. *Simple, visual inspections* should be performed on a regular basis. For laboratory and portable instruments this will be covered by recording that the equipment has been checked daily or prior to each use.

2.*System Suitability Checks with Control Standards* should be performed with eachbatch of test samples. The routine use of Control Standards will also ensure compliance with the principles of good laboratory practice(8) and is an essential element of effective Quality Control of conductivity measurements.

3.Periodic Re-Qualification of the conductivity measuring equipment. The use of Control Standards provides a straightforward, holistic check of the entire measurement system's performance. The Re-Qualification frequency depends upon the robustness of the measuring system, the criticality of the test measurements and the ramifications of any decisions made based upon the test measurements. It is recommended that Re-Qualification should be performed at least annually and more frequently for conductivity equipment used for critical measurement applications. [12]

Drift

The gradual random change of the output signal with time when the input signal remains constant. The offset setting in instrument system is particularly susceptible to drift. Some example are following where drift can affect the offset.

1. A drift in the offset of a pH measurement requires the resulting of the 'set Buffer' control.
2. A drift in the ' 0 volt' output from a DC amplifier requires a readjustment of the 'set- zero' control.[1,5]

Noise

The rapid random change of the output signal with time when the input remains constant . Noise is a fundamental problem in any form of measurement and appears in a variety of form, i.e drift, interference and both short term and long term noise. The total amount of noise that is present in a particular instrument system will depend on the range of frequencies to which the system responds, with the response range of a system being called its bandwidth, Δ f.

Noise and drift are both random fluctuations- they carry no information. We will use the term signal to apply to all fluctuations including both wanted and unwanted informations. Different types of unwanted signals are often categorized as being noise, drift and interference.

Rapid random fluctuations with a frequency higher than about 5 Hz are usually described as ' short term noise'. Noise in the intermediate range (0.01 -5.0 Hz) is often called 'long term noise' . we classified noise into following categories –

1. White noise

The key features of ' white noise' are as follow-

1. It has components with equal amplitude at all frequencies (as white light).
2. These frequency compound are in random phase.

2. Johnson (thermal) noise

Thermal noise accures in all electronic components, including detectors. Except at the absolute zero of temperature, the electrons (and holes) will have thermal kinetic energies which create random motion of the electrical charge, statistical fluctuations in this charge distribution will thus lead to a random potential difference appearing across the terminals of the component . The rms voltage, $V_{N,rms}$ generated by thermal noise is given by the following-

$\mathbf{V_{N,\,rms}} = \sqrt{(\,4\,KTR\Delta\,F\,)}$
Where Δf is the bandwidth of the system that is recording this voltage.
R = Resistance of the conductor, k = Boltzmann constant, T = Temperature.

3. Shot noise

Electric current is measured as the charge passing a given point at a given instant [1 amp (A) = 1 coulomb (c) passing per second (s)].

However , the charge is carried by individual electrons (each with a discrete charge of -1.6×10^{-19} c) and is not uniformly distributed in the same way . The passage of individual electrons gives rise to fluctuations in the current flow.

The rms current noise , I_{rms} is giving by the following-
$I_{N,\,rms} = \sqrt{(2I_0\,e\,\Delta f)}$
Where Δf = bandwidth of the system that is recording this current.
I_0 = Steady current through the device.[1,2]

Dynamic Range

The ratio of the largest signal that can be measured to the smallest signal.

Selectivity

The differential response to a wanted analyte compared to that of an unwanted analyte.[5] *Selectivity = Responsivity to wanted analyte / Responsivity of unwanted analyte.*

Details of the measuring environment –

Particularly for portable and online conductivity measurement, it is essential to specify the equipment's operating environment in the URS so that a suitable measuring system can be identified. The

URS should address the following areas:

1. The physical space that the equipment will be required to operate in.
2. Operating temperature and humidity.
3. The required level of waterproofing, ideally specifying the level of Ingress Protection (IP) Rating required.
4. The equipment's required level of electrical safety certification.
5. For online conductivity sensors, the dimensions of the measurement stream must be specified so that a suitable sensor and housing can be identified.[11]

Conclusion

The benefits of performing Equipment Qualification are highlighted and guidance is given on the selection of Control Standards and why the equipment vendor performing stages of Equipment Qualification can be of benefit to the user. The relationship between Equipment Qualification and Method Validation is discussed, including how these activities play a major role in determining the quality control measures that should be applied to routine analysis. Equipment Qualification plays a fundamental role in a laboratory's quality system as it assists the development and validation of suitable test methods and helps identify the Quality Control and Quality Assurance measures that will be required to ensure that test measurements are fit for purpose. Equipment Qualification ensures that measuring equipment is capable of generating test measurements that are fit for purpose.

Equipment Qualification's components of fully defining the equipment's required performance, ensuring that suitable equipment is selected and ensuring that the equipment's performance is consistently of the required standard have many benefits for the analyst:

- Attaining the correct result and proof of the correct result (in conjunction with other QA and QC measures)
- Reduced incidence of test measurements that are not of the required quality.
- Rapid identification and rectification of any problems that may occur with the measuring equipment during its entire working life.
- Subsequent long term savings of both time and money.

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