

*Indian Standard***METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL)
FOR WATER AND WASTEWATER****PART 3 PRECISION AND ACCURACY***(First Revision)*

1. Scope — This standard prescribes the various methods to determine precision and accuracy of various test methods used in sampling and testing of water and wastewater.

2. Terminology

2.1 The definitions given in IS : 7022 (Part 1)-1973 'Glossary of terms relating to water, sewage and industrial effluents', Part 1; and IS : 7022 (Part 2)-1979 'Glossary of terms relating to water, sewage and industrial effluents', Part 2, and the following shall apply:

Precision — Closeness of agreement among the results obtained by applying the test procedure several time under prescribed conditions. The precision can be quantitatively measured with the help of the standard deviation.

Accuracy — Closeness of agreement between the true value and the results obtained by applying the test procedure very large number of times. The accuracy can also be measured with the help of the standard deviation. But with the difference that the deviations of the test results are calculated from the true and not from the average.

Repeatability — Closeness of agreement (as indicated by the corresponding standard deviation) among the successive results obtained by the same method on identical test material and under the same conditions (same operator, same apparatus, same laboratory and almost the same time). It is defined as that difference between two such single and independent test results as would be exceeded in the long run in only one case in twenty in the normal and correct operation of the test method.

Reproducibility — Closeness of agreement (as indicated by the corresponding standard deviation) among the test results obtained by the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories and/or different times). It is defined as that difference between two such single and independent results as would only be exceeded in the long run in one case in twenty in the normal and correct operation of the test method.

3. Determination of Precision and Accuracy

3.1 A method may have very high precision but recovery may be poor due to poorly standardized solutions, inaccurate dilution techniques, inaccurate balance-weights or improperly calibrated equipment. Likewise a method may be accurate but may lack precision because of low instrumental sensitivity, variable rate of biological activity or other factors beyond the analysis control.

3.2 It is possible to determine both precision and accuracy of a test method by analysing samples to which known quantities of standard substances have been added. It is possible to determine precision, but not accuracy of methods, such as suspended solids, BOD and numerous physical parameters because of the unavailability of standard substances that can be added in known quantities on which percentage recovery is based.

3.3 Test for recovery can be done with the sample analysis. Recovery methods are only tools to remove the doubt about the applicability of a method. The recovery procedure involves applying the method to reagent blank, to a series of known standards covering the expected range of concentration of the sample, in duplicate run and to recovery sample, prepared by adding known quantities of the substance to separate portions of sample, each portion equals the same volume (standard

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addition) taken for the run. The substance should be added in sufficient quantity to overcome the limits of error of the analytical method, but not to cause the total in the sample to exceed the range of the known standards used.

3.4 Correct results by subtracting reagent blank from each other determined value, and graphically present the resulting known standards. From this, determine the amount in the sample. Subtract this value from each of the analysis of the sample plus known added substance. The resulting amount of substance divided by the known amount added multiplied by 100 gives percentage recovery. This method can be applied not only to colorimetric and instrumental methods, but also to titrimetric, gravimetric and other types of analysis. Generally intricate and exacting procedures for trace substances that have inherent errors due to their complexity may give recoveries that would be considered poor and yet, from the practical view point of usefulness of the result, may be quite acceptable. Poor results may reflect either interference present in the sample or real inadequacy of the method of analysis in the range in which it is being used. Analytical skill is required to assure the validity of the methods. Recovery using colorimetric methods can be particularly deceptive, depending on the nature of the sample, its pretreatment and the concentration of the constituents being measured. Most analytical methods have satisfactory precision and accuracy over a limited range, with the lower range limit being controlling in trace analysis. A known addition to a sample may bring the concentration into the range where the method is reliable, if the addition is too large the apparent precision and accuracy apply at the higher concentration, and not the concentration originally present. Natural waters frequently contain complexing materials that combine with metals to the extent that the complexed metals will not react in some colorimetric methods. If nearly all of a metal is complexed, a known addition may be recovered completely but the method will still not recover the metal originally present in a complexed state. In such cases pretreatment to destroy the complex is necessary. The analyst must account for such pitfalls in designing recovery procedures.

4. Statistical Basis

4.1 It is assumed that differences exist between sets of measurements made by the same test operator on the same material at different times with the same or different apparatus or by different test operators on the same material in the same or different laboratories. The various systematic differences are further assumed to be additive functions of the magnitudes of measurements.

4.2 Usually two sources of variability can be discerned:

- a) The variability within a laboratory which is to a certain extent under the control of the test operator and consists of a number of components of varied magnitudes and importance; and
- b) The variability among laboratories, generally the largest source of variability and the one that cannot be controlled by the test operator.

4.3 Estimates of variability within a laboratory and among laboratories caused by different personnel, equipment and environmental factors in following a prescribed method of test can be obtained in terms of standard deviations.

5. Determination of Repeatability and Reproducibility

5.1 Repeatability — The primary use of repeatability is to allow an operator to check his technique by making a further test. In this case, the repeatability is the critical difference between the two results which, if exceeded, probably indicates poor technique, and if not exceeded, indicates the acceptability of the test results. The value of repeatability may be taken as equal to 2.77 times the standard deviation of the test results arising under the repeatability conditions.

5.2 Reproducibility — The primary use of reproducibility is to enable two or more laboratories to countercheck their results. In this case, the reproducibility is the critical difference between two such results which, if exceeded, casts doubt on the test results, and if not exceeded, indicates acceptability of the test results. The value of reproducibility may be taken as equal to 2.77 times the standard deviation of the test results arising under the reproducibility conditions.

5.3 For further details on computation and application of repeatability and reproducibility, refer to IS : 5420 (Part 1) - 1969 'Guide on precision of test methods: Part 1 Principles and applications' and IS : 5420 (Part 2) - 1973 'Guide on precision of test methods: Part 2 Interlaboratory testing'.

6. Graphical Representation

6.1 This is one of the simplest methods for showing the influence of one variable on another. Graphs are desirable and advantageous in colorimetric analysis because they show any variation of one variable with respect to other within specified limits.

6.1.1 General method — Ordinary rectangular graph paper is satisfactory for most purposes. For some graph, semilogarithmic paper is preferable.

The five rules generally followed for choosing co-ordinate scales are useful. Although these rules are flexible, they are satisfactory. When doubt arises, use common sense. The five rules are:

- 1) Plot the independent and dependent variables on abscissa and ordinate in a manner that can be comprehended easily.
- 2) Choose the scales so that the value of either ordinate can be found quickly and easily.
- 3) Plot the curve to cover as much of the graph paper as possible.
- 4) Choose the scales so that the scope of the curve approaches as nearly as possible.
- 5) Other things being equal choose the variables to give a plot that will be nearly a straight line as possible.

Entitle a graph to describe adequately what the plot is intended to show. Present legends on the graph to clarify possible ambiguities. Include in the legend complete information about the conditions under which the data were obtained.

6.1.2 Method of least squares — If sufficient points are available and the functional relationship between the two variables is well defined, a smooth curve can be drawn through the points. If the function is not well defined, as is frequently the case when experimental data are used, use the method of least squares to fit a straight line to the pattern.

Any straight line can be represented by the equation $X = my + b$. The slope of the line is represented by m and the slop intercept by ' b ' which is a constant. The method of least squares has the advantage of giving a set of values for these constants not dependent on the judgement of the investigator. Two equations in addition to the one for a straight line are involved in these calculations.

$$m = \frac{n \sum xy - \sum x \sum y}{n \sum y^2 - (\sum y)^2}$$

$$b = \frac{\sum y^2 \sum x - \sum y \sum xy}{n \sum y^2 - (\sum y)^2}$$

n being the number of observations (sets of x and y values) to be summed. To compute the constant by this method, first calculate $\sum x^2$, $\sum y^2$, $(\sum y)^2$ and $\sum xy$. Carry out these operations to more places than the number of significant figures in the experimental data because the experimental values are assumed to be exact for the purpose of calculation.

Example: Given the following data to be graphed, find the best line to fit the points.

Absorbance	Solute Concentration (mg/l)
0.10	29.8
0.20	32.6
0.30	38.1
0.40	39.2
0.50	41.3
0.60	44.1
0.70	48.7

Let y equals absorbance values that are subject to error and x the accurately known concentration of solute. Then

x	y	y^2	xy
29.8	0.10	0.01	2.98
32.6	0.20	0.04	6.52
38.1	0.30	0.09	11.43
39.2	0.40	0.16	15.68
41.3	0.50	0.25	20.65
44.1	0.60	0.36	26.46
48.7	0.70	0.49	34.09
$\Sigma 273.8$	2.80	1.40	117.81

Substituting the summations in the equations for m and b and $n = 7$, there are seven sets of x and y values.

$$m = \frac{7(117.81) - 2.80(273.8)}{7(1.40) - (2.80)^2} = 29.6$$

$$b = \frac{1.4(273.8) - 2.80(117.81)}{7(1.40) - (2.80)^2} = 27.27$$

To plot the line, select three convenient values of y , say 0, 0.20, 0.60 and calculate the corresponding values for x

$$x_0 = 29.6(0) + 27.27 = 27.27$$

$$x_1 = 29.6(0.2) + 27.27 = 33.19$$

$$x_2 = 29.6(0.6) + 27.27 = 45.03$$

When the points representing these values are plotted on the graph a straight line is formed, which best fit for the given data. The plot will be as follows:

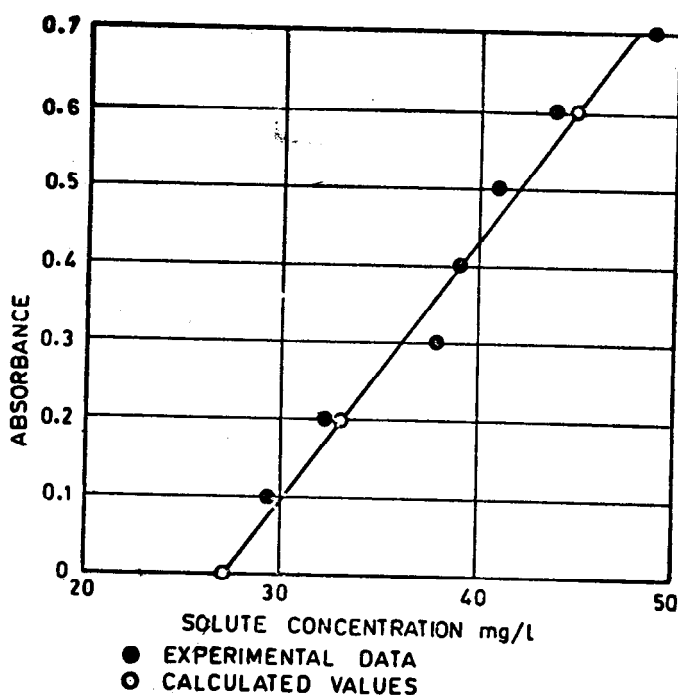


FIG. 1 LEAST SQUARE METHOD EVALUATION

6.1.3 Self evaluation — A good analyst tampers confidence with doubt. Such doubts stimulate a search for new and different methods of confirmation for reassurance. Frequent self appraisals should embrace every step from collecting samples to reporting results.

The analysts' first critical scrutiny should be directed at the entire sample collection process to guarantee a representative sample for analysis and to avoid any possible losses or contamination during collection. Attention should be given to the type of container and to the manner of transport of storage.

A periodic reassessment should be made of available analytical methods with an eye to applicability for the purpose and situation. In addition, each method selected must be evaluated by the analyst for sensitivity, precision and accuracy because only in this way it can be determined whether the analysts' technique is satisfactory and whether directions have been interpreted properly. Self evaluation on these points can give the analyst confidence in the value and significance of reported results.

The benefits of less rigid intralaboratory as well as interlaboratory evaluations deserve serious considerations. The analyst can regularly check standard or unknown concentrations with and without interfering elements and compare results on the same sample with results obtained by others. Such programmes can uncover weaknesses in the analytical chain and permit improvements to be instituted without delay. The results can disclose whether the trouble stem from faulty sample treatment, improper elimination of interference, poor calibration practices, sloppy experimental technique, impure or incorrectly standardized reagents, defective instrumentation or even inadvertent mistakes in arithmetic.

Other checks on analysis are ionic balance, conductivity measurements, ion exchange methods and recovery of added substance in the sample.

All these approaches are designed to appraise and upgrade the level of laboratory performance and this inspires greater faith in the final reported results.

EXPLANATORY NOTE

This standard is one of the series of standards on 'Methods of sampling and test for water and wastewater. The earlier version, namely, IS : 3025-1964 'Methods of sampling and test (physical and chemical) for water used in industry' had dealt with some methods of test for water and wastewaters. This standard has now been revised and published in various parts, each part covering a particular characteristic. This standard (Part 3) covers the precision and accuracy of the physical and chemical test methods employed for water and wastewater. IS : 3025-1964 had not covered this aspect earlier, and it has been introduced now as a new method.

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TO
IS 3025 (Part 3) : 1987 METHODS OF SAMPLING AND
TEST (PHYSICAL AND CHEMICAL) FOR WATER AND
WASTEWATER

PART 3 PRECISION AND ACCURACY TEST

(First Revision)

(Page 1, clause 3.2) — Add the following at the end of the clause:

'Care should be taken to see that sensitivity of method and instruments are at least ten times higher than the specified values.'

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