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Cohran-Horwitz Method for Within-Lab Precision Acceptability in ISO 17025 Testing Laboratories

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Abstract: *The issue of reliability of retesting data is a growing concern among testing laboratories. This document describes how to establish the acceptability of retesting of retained items during quality assurance, determining competence and measurement uncertainty calculations. Two methods are discussed and numerical examples are also given.*

Keywords: Precision, Verification, ISO, Acceptability, Cohran Test, Horwitz Test, Outlier, Competence.

I. INTRODUCTION

There is, practically, always a certain variation among the measured values and also between the measured values and the actual or reference value. The variation is due to systematic error(bias) and random error. The precision ,which measures the random error,is divided into three levels;
Within-run Precision (Repeatability)
Between-run Precision (Intermediate Precision/Retesting/Within-laboratory Reproducibility) and
Between-lab Precision (Reproducibility).
This document focus only the second level of precision,that is within laboratory reproducibility, which the ISO 17025 testing laboratory has to perform for several purposes.

II. ISO REQUIREMENTS

The testing laboratory which comply ISO 17025 is required to conduct retesting mainly for two purposes;
For assuring quality of test result under clause 7.7.1 (g)
For competence requirements of personnel under clause 6.2.3 demonstrated skill and less frequently
For the verification of Test methods under clause 7.2.1.5
For Measurement Uncertainty under clause 7.6 read with ILAC P 14
The laboratories have to define the acceptance criteria for retesting ,analyze the data and evaluate them for improvements and/or corrective/preventive actions.

III. DEFINITIONS

The definitions used in this document are directly referred to ISO standards.

1. **Precision**: The closeness of agreement between **independent test results** obtained under **stipulated conditions**. “Independent test results” means results obtained in a manner not influenced by any previous result on the same or similar test object. Repeatability and reproducibility conditions are particular set of “extreme conditions”. Precision should be investigated using homogenous , authentic samples. If a homogenous sample is not available, then artificially prepared samples (eg., spiked samples) or a sample solution can be used. Precision may be considered at three levels: Repeatability, Intermediate precision and Reproducibility
2. **Repeatability**: Represents precision under same operating conditions over a short interval of time. This means in repeatability the independent test results are obtained with same method on identical test items in the same laboratory by the same operator using the same equipment within short intervals of time.
3. **Intermediate precision**: Precision represented as within laboratory variations such as different days, different analysts, different equipment

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4. **Reproducibility**: Represents precision between laboratories and are usually applied when standardizing methodology.
5. **Outlier**: A member of a set of values which is inconsistent with the other members of that set.

IV. ABBREVIATIONS

1. ISO -International Organization for Standardization
2. ILAC – International Laboratory Accreditation Cooperation
3. RSD-Relative Standard Deviation
4. PRSD-Predicted Relative Standard Deviation
5. SD-Standard Deviation
6. FSSAI-Food Safety and Standard Authority of India
7. AOAC-Association of Official Agricultural Chemists
8. MAL -Maximum Acceptability Limit

V. METHODOLOGY & DISCUSSION ON ACCEPTABILITY

The ISO 17025 testing laboratories occasionally conduct the retesting of retained items , but the data are not evaluated and checked for any possible outliers. This note explains a method to define the acceptability of data based on Cohrans and Horwitz equations.

Numerical examples are also provided for easy understanding.

The four major factors likely to influence the precision of a measurement method are

1. Time: whether the time interval between successive measurements is short or long.
2. Calibration: whether the same equipment is or is not recalibrated between successive groups of measurements.
3. Operator whether the same or different operators carry out the successive measurements.
4. Equipment: whether the same or different equipment (or the same or different batches of reagents) is used in the measurements.

All these factors remains constant during replicate analysis.However in within-laboratory precision, one or more of these factors may vary. This note deals with two such scenario;

1. Time different intermediate precision-where all influencing factors except Time remains constant and
2. Time and Operator different intermediate precision-where both Time and Analyst(Operator) changes.

The outliers in the data are checked by Cohrans test and the acceptability limit by Horwitz formula.

The standard deviation of data are not calculated by the usual conventional methods; insteaduse the following equations.

The time different standard deviation is calculated by

$$S_{[T]} = \sqrt{\frac{1}{t(n-1)}} \sum_{j=1}^{t} \sum_{k=1}^{n} (y_{jk} - \bar{y})^2$$

Where t-number of days and n-replicate per day.

The time and operator different standard deviation is calculated by

$$S_{[T.O]} = \sqrt{\frac{1}{TO} \sum w^2}$$

Where T- number of days O-number of operators w-range

5.1 Cohrans Test

For a given set of p standard deviations ,all calculated from the same number of replicate(n) results , Cohran's test statistic C is

$$C = s^2_{max} / \sum s^2$$

where s-standard deviation

It is assumed that data points in all groups are normally distributed, sample size in each group are same and Cohran's test is used for maximum variance only. The critical Cohrans value are given in Table-1.

(i) If a test statistic is less than or equal to its 5% critical value ,the item tested is accepted as correct.

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(ii) If the test statistic is greater than its 5% critical value and less than or equal to its 1% critical value ,the item tested is called a straggler and is indicated by a single asterisk.

(iii) If the test statistic is greater than its 1% critical value,the item is called a statistical outlier and is indicated by a double asterisk.

Table-1 Critical upper limit for(C_{UL}) Cohran's test

p	N=2		N=3		N=4		N=5		N=6	
	1%	5%	1%	5%	1%	5%	1%	5%	1%	5%
2	-	-	0.995	0.975	0.979	0.939	0.959	0.906	0.937	0.877
3	0.993	0.967	0.942	0.871	0.883	0.798	0.834	0.746	0.793	0.707
4	0.968	0.906	0.864	0.768	0.781	0.684	0.721	0.629	0.676	0.590
5	0.928	0.841	0.788	0.684	0.696	0.598	0.633	0.544	0.588	0.506
6	0.883	0.781	0.722	0.616	0.626	0.532	0.564	0.480	0.520	0.446
7	0.838	0.727	0.664	0.561	0.568	0.480	0.508	0.431	0.466	0.397
8	0.794	0.680	0.615	0.516	0.521	0.438	0.463	0.391	0.423	0.360
9	0.754	0.638	0.573	0.478	0.481	0.403	0.425	0.358	0.387	0.329
10	0.718	0.602	0.536	0.445	0.447	0.373	0.393	0.331	0.357	0.303
11	0.684	0.570	0.504	0.417	0.418	0.348	0.366	0.308	0.332	0.281
12	0.653	0.541	0.475	0.392	0.392	0.326	0.343	0.288	0.310	0.262
13	0.624	0.515	0.450	0.371	0.369	0.307	0.322	0.271	0.291	0.243
14	0.599	0.492	0.427	0.352	0.349	0.291	0.304	0.255	0.274	0.232
15	0.575	0.471	0.407	0.335	0.332	0.276	0.288	0.242	0.259	0.220
16	0.553	0.452	0.388	0.319	0.316	0.262	0.274	0.230	0.246	0.208
17	0.532	0.434	0.372	0.305	0.301	0.250	0.261	0.219	0.234	0.198
18	0.514	0.418	0.356	0.293	0.288	0.240	0.249	0.209	0.223	0.189
19	0.496	0.403	0.343	0.281	0.276	0.230	0.238	0.200	0.214	0.181
20	0.480	0.389	0.330	0.270	0.265	0.220	0.229	0.192	0.205	0.174
21	0.465	0.377	0.318	0.261	0.255	0.212	0.220	0.185	0.197	0.167
22	0.450	0.365	0.307	0.252	0.246	0.204	0.212	0.178	0.189	0.160
23	0.437	0.354	0.297	0.243	0.238	0.197	0.204	0.172	0.182	0.155
24	0.425	0.343	0.287	0.235	0.230	0.191	0.197	0.166	0.176	0.149
25	0.413	0.334	0.278	0.228	0.222	0.185	0.190	0.160	0.170	0.144

Where **p**-number of days/group/operator and **n**-number of replicates in each day/group

5.2 Horwitz Equation

Horwitz equation is an empirical relationship between the concentration of the analyte and the precision of the method. The relative standard deviation(RSD) varies with concentration , C , the dimensionless mass fraction.The approximate value for predicted relative standard deviation is calculated by the formula

Predicted RSD, **PRSD** $= C^{-0.15}$

The maximum acceptable limit of RSD shall be twice the PRSD from Horwitz equation.

The data are checked further by Horwitz equation for acceptability,define the criteria and evaluate the competence of a new personnel.

VI. NUMERICAL EXAMPLES

The following numerical examples illustrate how the acceptability of data are checked and how the competence of a new personnel is evaluated for the test parameter for which he/she is to be authorized.

Example-1 Time different intermediate precision.

Make successive analysis on same sample on successive days.

Sodium chloride content in Iodised salt was analysed in triplicate for seven days by single operator and data in Table-2.

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Day (P)	Run-1(R_1)	Run-2(R_2)	Run-3(R_3)	Mean (M)	SD (s) (per day)	Variance(S^2) (per day)	Cohran's value(C)
1	98.498	100.222	98.368	99.029	1.0349	**1.0710**	0.3697
2	98.124	97.757	98.720	98.200	0.4860	0.2362	
3	99.454	98.446	97.419	98.440	1.0175	1.0353	
4	97.607	98.052	97.839	97.832	0.2226	0.0496	
5	98.126	97.743	97.611	97.827	0.2675	0.0716	
6	98.201	98.889	97.622	98.237	0.6343	0.4023	
7	98.133	97.785	97.905	97.941	0.1768	0.0312	
Mean of mean = 98.215					Mean =0.5485	$\sum s^2 = 2.8972$	

.**Acceptability of Data (Table-2)**

With **P=7** and **N=3** and α =0.05 ,the upper critical limit $\mathbf{C_{UL} = 0.561}$

As $\mathbf{C < C_{UL}}$ with 95% confidence , all data set are correct and acceptable as per Cohrans test method.

The time different standard deviation $S_{[T]} = 0.6505$

The time different RSD , $RSD_{[T]} = 0.6623$

Predicted RSD (Horwitz equation), PRSD = 1.027

The maximum acceptability limit (2PRSD) , MAL = 2.054 (approx 2).

Since RSD <MAL , all data are also acceptable as per Horwitz calculation.

Competence evaluation of new operator for test parameter

Consider , a new personnel is assigned to do the test (sodium chloride content in Iodised salt).He performed the test in triplicate.

Data : 98.04 , 97.66 , 97.91

Mean : 97.87 SD = 0.1931 RSD = 0.1973

Since the RSD of new operator is less than the MAL defined earlier (that is 2.054) , the new operator is competent.

Example-2 Time and Operator different Intermediate Precision

The test portion of a sample wasanalysed5 times in one day was again analysed by a different analyst on the next day. In a month 12 pairs of such data were obtained. The saponification value in % is calculated and data given in Table-3.

Acceptability of Data (Table-3)

Sample no.	First Day	Next Day	Range (w)	W^2	Cohran Value	Critical Cohran value
1	252.599	253.222	0.623	0.388	0.548	0.541
2	251.368	251.515	0.147	0.022		
3	251.614	251.686	0.072	0.005		
4	**251.646**	**254.168**	**2.522**	**6.360**		
5	251.466	250.409	1.057	1.117		
6	250.597	251.042	0.445	0.198		
7	250.423	250.786	0.363	0.132		
8	251.919	250.915	1.004	1.008		
9	250.705	250.049	0.656	0.430		
10	250.452	249.961	0.491	0.241		
11	250.811	249.979	0.832	0.692		
12	249.970	250.981	1.011	1.022		
	Mean 251.131	Mean 251.226		$\sum w^2$=11.615		

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The Cohrans' test indicates that the range for sample 4 is outlier.

The values for this sample is removed for the computation of the [Time + Operator]- different intermediate standard deviation.

New Mean = 251.0215

New $\sum w^2 = 5.255$ New Cohran Value (for 1.117) = 0.213 Critical Cohran value(p=11 n=2) = 0.570

No outlier.All the 11 data are acceptable.

New Time -Operator dependent SD , $S_{[T.O]} = 0.4887$

New RSD = 0.1947

Predicted RSD = 0.871

Maximum acceptability Limit (2PRSD, MAL) = 1.742 approx 1.7

Since RSD <MAL , all data are also acceptable as per Horwitz calculation.

Competence evaluation of new operator for test parameter

Consider , a new personnel is assigned to do the test (saponification value of oil).He performed the test in triplicate.

Data : 253.157 , 252.885 , 254.096

Mean : 253.379 SD = 0.6354 RSD = 0.2508

Since the RSD of new operator is less than the MAL defined earlier (that is 1.742) , the new operator is competent.

VII. CONCLUSION

The testing laboratories can use the above methods for determining the acceptability of data points for intermediate precision calculations. The evaluated data can be used for measurement uncertainty ,verification , competence requirements and quality control. The illustrations relate to food testing laboratories provide a better understanding of the application of methods.

VIII. CONFLICT OF INTEREST

The author has no technical ,financial and intellectual conflict of interest.

REFERENCES

[1]. ISO 5725 series
[2]. ISO 17025:2017
[3]. IS 15393 series
[4]. ISO 3534 series
[5]. IS 7920
[6]. IS 15202
[7]. AOAC Guidelines for Single Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals
[8]. AOAC Appendix F: Guidelines for Standard Method Performance Requirements
[9]. AOAC Method Verification Protocols
[10]. ILAC Protocol14
[11]. IS 253
[12]. FSSAI Manual of Oils and Fats
[13]. 13 .Eurachem Guide : The Fitness for Purpose of Analytical Methods
[14]. JCGM 100:2008 GUM
[15]. IUPAC Technical Report *Pure Appl.Chem.,* Vol. 74 , No. 5 ,pp. 835-855 2002
[16]. AMC Technical Brief No. 17 July 2004 @ Royal Society of Chemistry
[17]. Analytical Quality Control and Method Validation Procedures foe Pesticide Residue Analysis in Food and Feed SANTE/11312/2021