Plagiarism - Report

Originality Assessment

12%

Overall Similarity

Date: Dec 30, 2023
Matches: 249 / 2140 words
Sources: 11

Remarks: Low similarity detected, check with your supervisor if changes are required.

Verify Report:

ANALYTICAL METHOD VERIFICATION –A TITRIMETRIC CASE STUDY

Dr Abhilash Babu G

Research Officer & ISO 17025 Assessor

Government Analysts Laboratory , Vanchiyoor PO , Trivandrum-35 , Kerala , India

ABSTRACT

The ISO 17025 testing laboratories have to verify the selected methods before introducing them for routine analysis.This application note provides an illustration for the verification of titrimetric methods.The Grubbs , Cohrans and Horwitz formula are used in this study.

KEYWORDS: Verification, Precision,Competence,Cohran Test,Horwitz Formaula , Standard Deviation

I.INTRODUCTION

Laboratories complying to ISO 17025 are required under clause 7.2.1.5 – to verify that it can properly perform methods before introducing them by ensuring that it can achieve the required performance.The ISO 17025 standard defines verification in Clause 3.8 as ‘verification : provision of objective evidence that a given item fulfils specified requirements’.Three examples for this definition are also given in the clause.However, Example 2: Confirmation that performance properties or legal requirements of a measuring system are achieved is being taken for this study.

When a method is tobe verified,laboratory is required to demonstrate that it can achieve certain specific performance characteristics,but not all, established during the validation specified in clause 7.2.2.3.The minimum objective evidence for verification include specificity,repeatability intermediate precision LoD and LoQ obtained from actual laboratory data with the matrices to which the method

being applied.

II.METHODS & MATERIALS

AOAC guidelines lists some performance characteristics for method verification.All are not equally applicable for all kinds of test methods.In titration methods, the specificity of reaction , repeatability and within laboratory precision can be considered.

Specificity : Specificity is the ability to measure accurately and specifically the analyte of interest in the presence of other components that may be expected to be present in the sample matrix.It includes the methodology such as identification , assay and purity tests.

The specificity depends on the basic principles of reaction and instrumentation.

If the lab 6 samples are identical to those in the standard method and if any difference in the instrumentation do not impact specificity, no verification is needed.For example , in argentometric titration of chloride determination , the basic principle is to produce a precipitate of AgCl and hence no verification is required.

If the lab samples differ from those in the standard method, verification same as those required for validation is to be performed.

If the differences between instruments could affect specificity, the verification activity needed only deal with the unique aspects of instrument.For example, the different resolution or detection systems in ICP-OES may result in different interferences.

Repeatability: 2 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 9 operator using the same equipment within short intervals of time.

Intermediate Precision:Precision represented as within laboratory variations such as different days,different analysts,different equipment.In this study time different intermediate precision is discussed.

Acceptability of Data: The acceptability criteria for repeatability and intermediate precision are determined by applying Grubbs , Cohran and Horwitz formula.

Grubbs Method

This method involves determining the outlier using Grubbs equation.

Grubbs test is a simple technique to quantify the outlier in the set of data points.It is based on a normal distribution and a test statistic is calculated from the most extreme data point using the formula

Gexp = (Xmax – Xmean) / s (for highest data point) Gexp = (Xmean – Xmin) / s (for lowest data point)

A value can be regarded as an outlier if the statistic G value (Gexp) is greater than critical value G(α,n)

(Table-1).Then the mean and standard deviation are recalculated excluding the outlier.

n

G(α,n) for α = 1 %

G(α,n) for α = 5%

n

G(α,n) for α = 1 %

G(α,n) for α = 5 %

3

1.15

1.15

15

2.71

2.41

4

1.49

1.46

16

2.75

2.44

5

1.75

1.67

17

2.79

2.47

6

1.94

1.82

18

2.82

2.50

7

2.1

1.94

19

2.85

2.53

8

2.22

2.03

20

2.88

2.56

9

2.32

2.11

21

2.91

2.58

10

2.41

2.18

22

2.94

2.60

11

2.48

2.23

23

2.96

2.62

12

2.55

2.29

24

2.99

2.64

13

2.61

2.33

25

3.01

2.66

14

2.66

2.37

α - probability of incorrectly rejecting the suspected outlier

n- 1 number of samples in the data set.

Table-1 Critical values for Grubbs Test

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

$$C = s2max / \sum s2$$ 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-2.

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

(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.

The time different standard deviation is calculated by

S[T] =

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

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

Table-2 Critical upper limit for(CUL) Cohran’s test (Where p-number of days/operator and n-number of replicates in

each day/group)

Horwitz formula

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

$$\text{Predicted RSD, PRSD} = C - 0.15$$

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

III.DISCUSSION

The method verification is done as follows.

1.Suitability of Test Conditions: Reagents ,glasswares and equipments

AR Grade potassium chromate,silver nitrate and CRM Grade Sodium chloride,calibrated glasswares and

calibrated electronic balance with accuracy ensured by intermediate checks are used.

2.Specificity : Since the basic reaction is the formation of the precipitate of AgCl , no verification is required.

3.Repeatability : A Iodised salt sample was homogenized and analysed seven times in a day.The data evaluation is given in Table-3 and Table-4.

Sl No

Weight of Sample (g)

Make up Volume (ml)

Volume Pipette(ml)

Volume Burette(ml)

Sodium chloride Content

1

1.1137

100

10

18.8

98.4986

2

1.1353

100

10

19.5

100.2223

3

1.0440

100

10

17.6

98.3677

4

1.0783

100

10

18.2

98.4855

5

1.1124

100

10

18.8

98.6403

6

1.1175

100

10

19.0

99.2079

7

1.2359

100

10

21.0

99.1462

mean

1.119586

100

10

18.98571

98.93836

Standard Deviation , S = 0.655403

Grubbs Test Gmax = 1.959014 Gmin = 0.870697 Gcritical = 1.94

As Gmax > Gcritical Data 2 is an outlier

Table-3 Repeatability Data Evaluation

Recalculated data

Sl No

Weight of Sample

Volume Make up

Volume Pipette

Volume Burette

Sodium chloride

1

1.1137

100

10

18.8

98.4986

2

1.0440

100

10

17.6

98.3677

3

1.0783

100

10

18.2

98.4855

4

1.1124

100

10

18.8

98.6403

5

1.1175

100

10

19.0

99.2079

6

1.2359

100

10

21.0

99.1462

mean

1.116967

100

10

18.9

98.72437

Standard Deviation S = 0.361678

Grubbs Test Gmax = 1.336917 Gmin = 0.986145 Gcritical = 1.82

No outlier.Data set acceptable.

Table-4 Repeatability Data Evaluation (Recalculated)

4.Within laboratory Precision

The same homogenized sample was analysed for next six days in triplicate.The data evaluation is given in Table-5.

Day

Weight of Sample

Volume Burette

Result(X)

(X-M)

(X-M)2

Cohrans Value

Day-1

1.7126

28.8

98.1244

-0.07613

0.005796

0.6511

With P=6,N=3 and α =0.05 Cohran 8 Critical Value = 0.72

No outlier .All data set acceptable.

1.0923

18.3

97.7574

-0.44313

0.196367

1.1644

19.7

98.7198

0.519267

0.269638

Mean (M)

1.3231

22.26667

98.20053

Sum Difference2 = 0.471801

Day-2

1.0151

17.3

98.4538

1.014133

1.028466418

1.0492

17.7

98.4462

0.006533

4.26844E-05

1.2819

21.4

97.4190

-1.02067

1.041760444

Mean(M)

1.1154

18.8

98.43967

Sum Difference2 = 2.070269547

Day-3

1.2615

21.1

97.6066

-0.22603

0.051091068

1.1665

19.6

98.0518

0.219167

0.048034028

1.0736

18.0

97.8395

0.006867

4.71511E-05

Mean(M)

1.1672

19.5667

97.83263

0.099172247

Day-4

1.2064

20.3

98.1255

0.2989

0.089341

1.0918

18.3

97.7429

-0.0837

0.007006

1.0637

17.8

97.6114

-0.2152

0.046311

Mean(M)

1.120633

18.8

97.8266

0.142658

Day-5

1.2411

20.9

98.2012

-0.03603

0.001298

1.1735

19.9

98.8888

0.651567

0.424539

1.2186

20.4

97.6217

-0.61553

0.378881

Mean(M)

1.211067

20.4

98.23723

0.804719

Day-6

1.0934

18.4

98.1332

0.19215

0.036921622

1.2106

20.3

97.78508

-0.15597

0.024326641

1.0483

17.6

97.90487

-0.03618

0.001308992

Mean(M)

1.117433

18.76667

97.94105

0.062557256

Total Mean

1.146347

19.26667

98.05544

∑(X-M)2 = 3.179376

SD-Time S[T] = 0.514731

RSD[T] = 0.5249

Table-5 Intermediate Precision Data Evaluation

Predicted RSD (Horwitz equation), PRSD = 1.003

The maximum acceptability limit (2PRSD) , MAL = 2.006 (approx 2).Since RSD[T] < MAL , all data are also acceptable as per Horwitz calculation.

Thus, in this test method, the acceptability 1 criteria can be fixed at a RSD of 2.0 which can be used for evaluating the competence of another operator.

The verification study can be summarized in Table-6.

Attributes

Reference Method IS 253

Within Lab

Remarks/Comment

Equipments

1.Volumetric Flask , 100 ml

2.Burette , 50 ml

3.Pipette , 10 ml

4.Electronic balance

1.Volumetric Flask , 100 ml (Calibrated)

2.Burette , 50 ml (Calibrated)

3. Pipette , 10 ml (Calibrated)

4.Electronic balance , readability 0.0001 g

(calibrated)

Verified

Reagents

1.Potassium chromate

2.Silver nitrate

3.Silver nitrate solution

(approx. 0.1 N)

4.Sodium chloride

1.Potassium chromate , AR Grade

2.Silver nitrate , AR Grade

3.Silver nitrate solution , 0.1 N standardized

using Sodium chloride solution

4.Sodium chloride , CRM

Verified

Specificity

(Basic Principle)

Precipitation of silver chloride

Since basic reaction 11 is the same , no verification required

N/A

Repeatability

--

Data acceptable Grubbs Method

Verified

Intermediate Precision

--

Data acceptable Cohran Test

Verified

Acceptability Limit

--

RSD = ± 2 (apporx.) Horwitz Method

Verified

Sl. No

Table-6 Verification Documentation

IV.CONCLUSION

The ISO 17025 standard requires the laboratories to verify methods but does not provide any guidelines to fulfils it.This paper suggest a method to verify titration method.The analytical data are successfully evaluated for method verification under clause 7.2.1.5 of ISO 17025 standard.This is done in simple and easily understandable way.The laboratories can follow the evaluation method used in this study not only for method verification,but also for measurement uncertainty and ensuring validity of their test results.

V.CONFLICT OF INTEREST

The author has no conflict of interest.

VI.REFERENCE

1. ISO 17025:2017 standard
2. IS 253:2014 Reaffirmed 2021
3. AOAC Guidelines for Single Laboratory Validation of Chemical Methods for Dietary Supplements and Botanicals
4. AOAC Appendix F: Guidelines for Standard Method Performance Requirements
5. AOAC Method Verification Protocols
6. ILAC Protocol14
7. Eurachem Guide : The Fitness for Purpose of Analytical Methods
8. Analytical Quality Control and Method Validation Procedures foe Pesticide Residue Analysis in

Food and Feed

SANTE/11312/2021

9. 2 Dr Abhilash Babu G ‘Acceptability criteria for replicate tests in ISO 17025:2017 Testing Laboratories’ Quest Journal of Research in Agriculture and Animal Science Volume 10 Issue 12 (2023)

10. A Guide to Analytical method Validation Waters.com

11. ISO 5725 Series

12. ISO 3534

13. IS 15393 Series

14. Dr Abhilash Babu G ‘Cohran-Horwitz Method for Within lab Precision Acceptability in ISO 17025 Testing Laboratories’ www.doi.org/10.48175/IJARSCT-14335

Sources

1	https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3658022/ INTERNET 3%
2	https://www.questjournals.org/jraas/papers/v10-i12/10124044.pdf INTERNET 2%
3	https://www.ijarsct.co.in/Paper14335.pdf#:~:text=If the test statistic is greater than its,outlier and is indicated by a double asterisk. INTERNET 2%
4	https://chem.libretexts.org/Courses/Northeastern_University/08:_Gravimetric_Methods/8.2:_Precipitation_Gravimetry INTERNET 1%
5	https://www.aoac.org/wp-content/uploads/2019/08/app_f.pdf INTERNET 1%
6	https://www.aoac.org/wp-content/uploads/2019/09/ALACC-method-verification.pdf INTERNET 1%
7	https://studylib.net/doc/18377106/how-to-meet-iso-17025-requirements-for-method-verification INTERNET 1%
8	https://machinelearningmastery.com/critical-values-for-statistical-hypothesis-testing/ INTERNET 1%
9	https://documentserver.uhasselt.be/bitstream/1942/11253/1/repeatability10[1].pdf#:~:text=Repeatability is the precision obtained, under the 'same',intervals of time; these are termed repeatability conditions. INTERNET <1%
10	https://www.eurachem.org/index.php/publications/guides/mv INTERNET <1%
11	https://www.scribd.com/doc/129620200/Alacc-Guide-2008 INTERNET <1%

EXCLUDE CUSTOM MATCHES	OFF
EXCLUDE QUOTES	OFF
EXCLUDE BIBLIOGRAPHY	OFF