



A Honeywell Company

Precision Statements in UOP Methods

UOP Method 999-13

Scope

This method is for developing precision statements as reported in UOP methods and relative bias of the same method between different laboratories. The calculation of precision, in terms of repeatability and intermediate precision (within a laboratory), reproducibility (between laboratories) and relative bias (between laboratories) is described. Precision statements in methods having a 98 or later suffix were developed by the procedure described; methods having an 88 through 97 suffix used UOP 888-88, while methods with suffixes earlier than 88 used UOP 666-82.

The features of UOP 999 are as follows:

- Minimum of 16 analyses required with emphasis on multiple concentration levels
- Better identification of the components of variation and repeatability estimates
- Alignment with ASTM repeatability, intermediate precision, and reproducibility definitions
- Relative bias between laboratories with 95% confidence interval

UOP 999 is the minimum guideline for estimating the initial precision for new or revised methods. Once a new or revised method is in use, a reference sample, if available, should be run on a regular basis. When 16 analyses have been completed, individual and range control charts are to be used to estimate the long-term UOP repeatability and are to be maintained on an ongoing basis. The example calculations in UOP 999 are made using Minitab[®], a statistical software package. The details of the calculations are in UOP 999-97 Supplement.

References

ASTM Practice E177, "Practice for the use of Terms Precision and Bias in ASTM Test Methods," www.astm.org

ASTM Practice E178, "Practice for Dealing with Outlying Observations," www.astm.org

ASTM Practice E691, "Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method," www.astm.org

"Errors of Routine Analysis," Student, Biometrika, XIX, 1927, pp. 151-164

"Precision Measurement and Calibration," NBS Special Publication 300, Vol. 1, Feb. 1969, U.S. Department of Commerce

Supplement to UOP 999-97

UOP Method 666-82, "Precision Statements in UOP Methods"

UOP Method 888-88, "Precision Statements in UOP Methods"

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Outline of the Method

Using the specified UOP test method, at least 16 tests are performed at a given laboratory or laboratories on the same representative sample, or on samples at multiple concentrations, using one of the nested sampling designs shown in the *Procedure* section. Exceptions to nested sampling design can be made at the discretion of the method coordinator. In each laboratory, the analysis is performed by at least two different analysts on each of two separate days, each analyst performing two tests per day. The estimated within-laboratory standard deviation (esd) and the estimated between-laboratory standard deviation (esd) are calculated using a stepwise nested analysis of variance (ANOVA) procedure (see Appendix 2 of the *Supplement* to this document).

The stepwise ANOVA procedure for the nested design is used to estimate the within-day test esd, day-to-day esd, analyst-to-analyst esd and lab-to-lab esd. The estimated components of variability from the stepwise ANOVA are used to calculate repeatability, intermediate precision, reproducibility, and relative bias as outlined in Table 1.

Repeatability is the expected maximum difference between two tests by the *same* analyst on the *same* day in one laboratory at the 95% confidence level. Repeatability is calculated using the Within-Day esd. Intermediate precision is the expected maximum difference between two tests by *different* analysts on *different* days in one laboratory at the 95% confidence level and is calculated using the Within-Laboratory esd. Reproducibility is the expected maximum difference between two tests by *different* analysts on *different* days in *different* laboratories at the 95% confidence level and is calculated using the Within-Laboratory esd plus the Between-Laboratory esd.

When all the tests are conducted in *only* one laboratory, then repeatability and intermediate precision may be calculated, but reproducibility cannot. For this case, applicable nested designs are shown in the *Procedure* section. When the testing is conducted across two or more laboratories, then the repeatability, the intermediate precision, the reproducibility and the relative bias can be calculated. For two or three laboratories, the applicable nested designs are found in the *Procedure* section. Table 2 in the *Procedure* section summarizes standard nested designs and their attributes with cross-reference to the design layout. If precision data are received from one or two laboratories, the repeatability and intermediate precision is the only precision information reported.

Calculations may also be performed on pairs of data, when such data are available, and the nested sampling designs shown in the *Procedure* section would be difficult or impossible to perform. See *Appendix 3*.

Definitions

95% Confidence Interval for Mean Difference, the interval about the average difference value that is believed to include the “true” population difference for approximately 95 out of 100 such estimates.

Analysis of Variance (ANOVA), a statistical procedure that divides the total variability for a set of data into meaningful component parts associated with specific sources of variation. The technique, in conjunction with the F-ratio, is used to provide a test of significance for component sources of variation and to obtain estimates of the standard deviations attributable to those sources.

Bias, deviation from a known or accepted value.

Day, refers to the span of time over which the analyses are performed on the same day by the same analyst in a laboratory and from which the within-day standard deviation is estimated.

Table 1
Precision Statement Definitions
(The description of the terms is in the *CALCULATIONS*)

Quantity	Definition
Repeatability	Allowable difference between two tests performed by <i>same</i> analyst in one lab on <i>same</i> day at 95% confidence level.
Repeatability Equation	$t_{DF} \sqrt{2} s_{\text{Within-Day}}$
Intermediate Precision	Allowable difference between two tests performed by <i>different</i> analysts in one lab on <i>different</i> days at 95% confidence level.
Intermediate Precision Equation	$t_{DF} \sqrt{2} s_{\text{Within-Lab}}$
Within-Day Standard Deviation	$t_{DF} \sqrt{2} s_{\text{Within-Day}}$
Within-Lab Standard Deviation	$s_{\text{Within-Lab}} = \sqrt{s_{\text{Within-Day}}^2 + s_{\text{Day-to-Day}}^2 + s_{\text{Analyst-to-Analyst}}^2}$
Reproducibility	Allowable difference between two tests performed by <i>different</i> analysts in <i>different</i> labs on <i>different</i> days at 95% confidence.
Reproducibility Equation	$t_{DF} \sqrt{2} \sqrt{s_{\text{Within-Lab}}^2 + s_{\text{Between-Lab}}^2}$
Relative Bias	For specified sample, the average test difference between labs.
Within-Lab Mean Standard Deviation	$s_{X \text{ Within-Lab}} = \sqrt{\frac{s_{\text{Within-Day}}^2}{n_R n_{\text{Days}} n_{\text{Analysts}}} + \frac{s_{\text{Day-to-Day}}^2}{n_{\text{Days}} n_{\text{Analysts}}} + \frac{s_{\text{Analyst-to-Analyst}}^2}{n_{\text{Analysts}}}}$ $DF^* = n_{\text{Labs}} (n_{\text{Analysts}} - 1)$ where n_{Days} = No. days testing per analyst n_{Labs} = No. labs n_{Analysts} = No. analysts n_R = No. reps per day Note: See <i>SUPPLEMENT Appendix 2</i> for other than full model.
Relative Bias Confidence Interval	$x_{\text{Lab 1}} - x_{\text{Lab 2}} \pm t_{DF^*} \sqrt{2} s_{X \text{ Within-Lab}}$

Degrees of Freedom, the number of independent observations available to estimate the standard deviation. In general, when r constants for a model have been estimated from n data values, only $(n - r)$ degrees of freedom remain to estimate the model's variability.

Duplicate, the false replication of an analysis (i.e. one test immediately followed by another) in which *all* the sources of inherent variability are not operational.

Intermediate Precision, the allowable difference between two tests performed by different analysts in one laboratory on different days. Two tests should not differ by more than the stated allowable difference more than five percent of the time (for 95% confidence). This definition is the same as the term "UOP Repeatability" used in past UOP methods describing precision, and should be used when comparing data generated on other than the same day. Intermediate Precision may also be called Site Precision.

Mean Square (MS), an unbiased estimate of the population variance calculated by dividing the sum of squares (SS) by its degrees of freedom (DF).

Pooling, two or more variances (standard deviations squared) may be pooled by adding their variances weighted by ratio of the individual variance degrees of freedom divided by the sum of the degrees of freedom for all the variances.

Randomization, the operation of assigning a testing sequence in a purely chance manner by using a list of random numbers. Randomization increases the chance of obtaining a representative sample from the population and thereby assures and ensures a valid estimate of experimental error and associated significance tests.

Relative Bias, the average test difference between laboratories for the same sample analyses.

Repeatability, the allowable difference between two tests performed by the *same* analyst in one laboratory on the *same* day. The two tests should not differ by more than the stated allowable difference more than five percent of the time, thus giving 95% confidence in the repeatability. This definition more closely mirrors that of ASTM Repeatability, and should allow for closer comparison to independently reported ASTM repeatability statistics.

Replicate, the random repetition of an analysis over a specified period of time, such as a day, under identical conditions subject only to (but to all of) the random inherent variability of that time interval.

Reproducibility, the allowable difference between two tests performed by *different* analysts in *different* laboratories on *different* days. Two such tests should not differ by more than the stated allowable difference more than five percent of the time (for 95% confidence). This definition is the same as the ASTM convention; therefore, independently reported reproducibility statistics can be directly compared.

Test, the result of a single analysis performed in a laboratory by a specified UOP method. Determinations performed in duplicate (i.e. one test immediately followed by another) are discouraged, since little information is gained. However, when duplicates are routinely performed, a test is defined as the *average* of the two determinations.

Procedure

The laboratory supervisor under whose jurisdiction the method is performed is responsible for collecting the necessary nested data using the proper sampling procedure to assure uniformity between the samples analyzed, following the UOP method *exactly* as written, and reporting those data together with a record of the analyst, day, time and test number. Care must be taken to accurately record, on the form provided, the origin of each result, noting the analyst, test number, day and time of the test.

All the data collected must be reported and no effort should be made to eliminate data points by rejecting individual tests. Nor should the data be truncated by rounding. It is better to record too many digits than not enough. The resultant data are referred to as a “balanced nested” data set.

Choosing a Nested Design

Precision studies requiring no less than the minimum 16 separate analyses are characterized in Table 2 and shown in Figures 1A and 1B, Within-Laboratory and Within-plus-Between Laboratory Nested Sampling Designs. To estimate *only* the within-laboratory repeatability and intermediate precision for a single sample concentration in one laboratory using four analysts, use Form 1A-1 in

Appendix 1. When two sample concentrations in a single laboratory are to be used to estimate *only* the within-laboratory repeatability and intermediate precision, use Form 1A-2 in Appendix 1. To estimate repeatability, intermediate precision, reproducibility, and relative bias between two laboratories for a single sample concentration using two analysts per laboratory, use Form 1B-1 in Appendix 1. To estimate repeatability, intermediate precision, reproducibility, and relative bias between two laboratories at two sample concentrations using two analysts per laboratory, use Form 1B-1 in Appendix 1, at *each* laboratory. This requires 16 separate analyses at each laboratory for a total of 32 analyses.

Table 2
Nested Designs for Different Precision Objectives

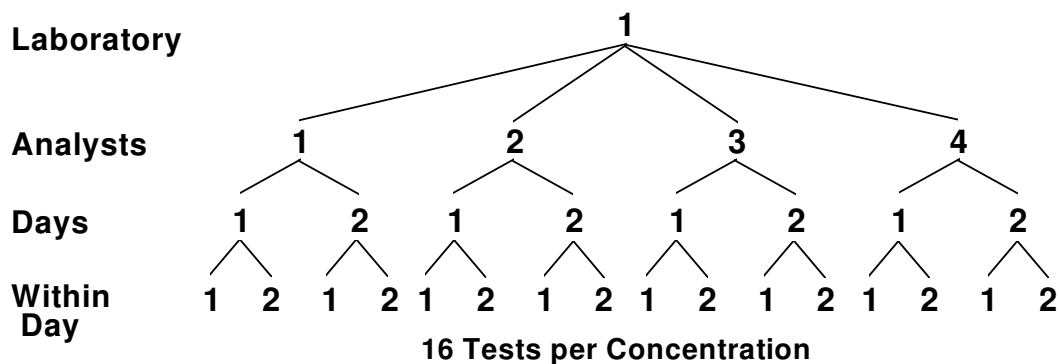
UOP 999 Precision Objective	No. Labs	No. Sample Concentrations	No. Analysts	No. Tests	See Figure
Estimate Only Repeatability Within Lab at 1 Concentration	1	1	4	16	1A-1
Estimate Only Repeatability Within Lab at 2 Concentrations	1	2	2	16	1A-2
Estimate Only Repeatability Within Lab at 3 Concentrations	1	3	2	24	1A-3
Estimate Repeatability, Reproducibility and Relative Bias using 2 Labs	2	1	2	16	1B-1
Estimate Repeatability, Reproducibility and Relative Bias using 2 Labs	2	2	2	32	1B-1 at each Lab
Estimate Repeatability, Reproducibility and Relative Bias using 2 Labs	2	1	3	24	1B-2
Estimate Repeatability, Reproducibility and Relative Bias using 3 Labs	3	1	2	24	1B-3

Note: For all the designs given in Table 2, each analyst performs 2 tests on each of 2 days.

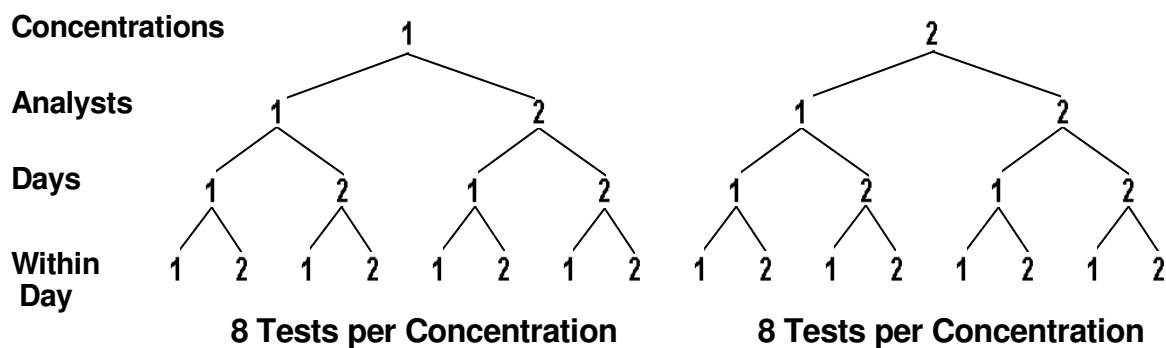
Figure 1A-3 shows a nested design requiring 24 analyses. This plan is for estimating *only* the within-laboratory repeatability and intermediate precision using three different concentration samples in a single laboratory with two analysts. Another nested design with 24 analyses is shown in Figure 1B-3, and is useful for estimating repeatability, intermediate precision, reproducibility, and relative bias between three laboratories for a single concentration sample using two analysts per laboratory. No corresponding data form was prepared for the nested designs requiring 24 analyses.

Within-Laboratory Nested Sampling Designs

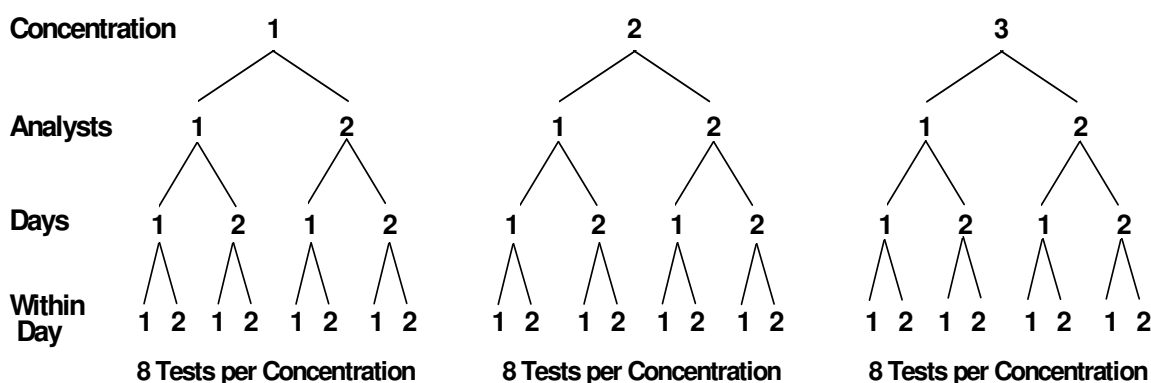
- Figure 1A-1: 1 Sample Concentration Level using 4 Analysts



- Figure 1A-2: 2 Sample Concentration Levels using 2 Analysts



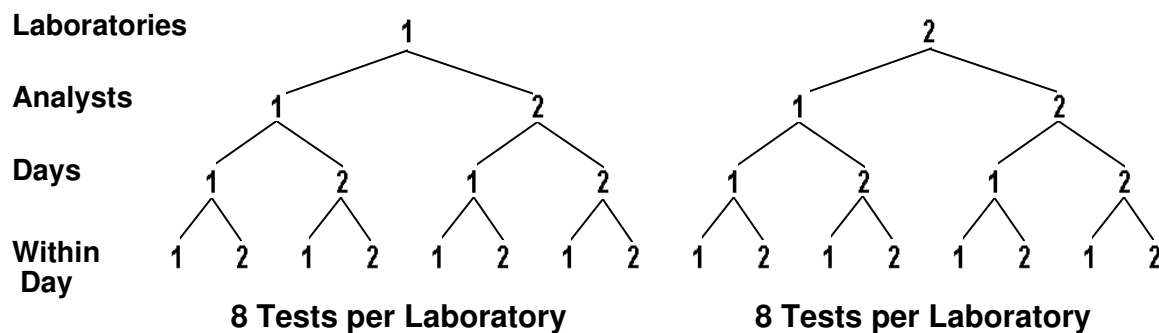
- Figure 1A-3: 3 Sample Concentration Levels using 2 Analysts



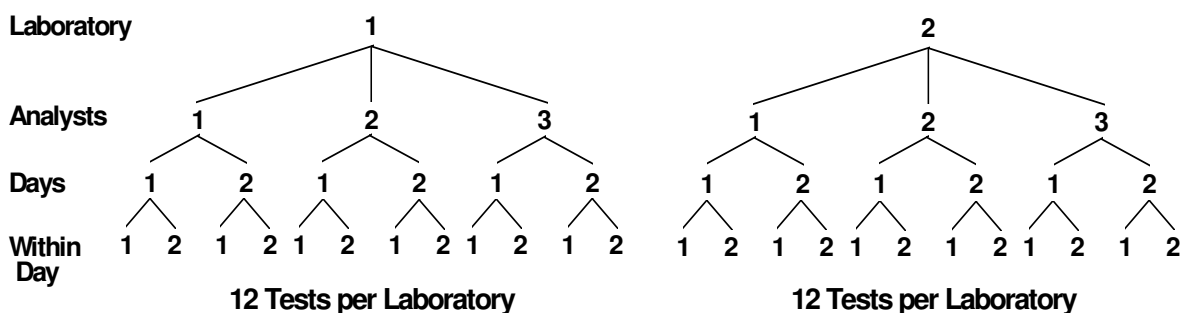
Note: Data forms corresponding to the Figure 1A-1 and Figure 1A-2 designs above are found in Appendix 1.

Within-plus-Between Laboratory Nested Sampling Designs

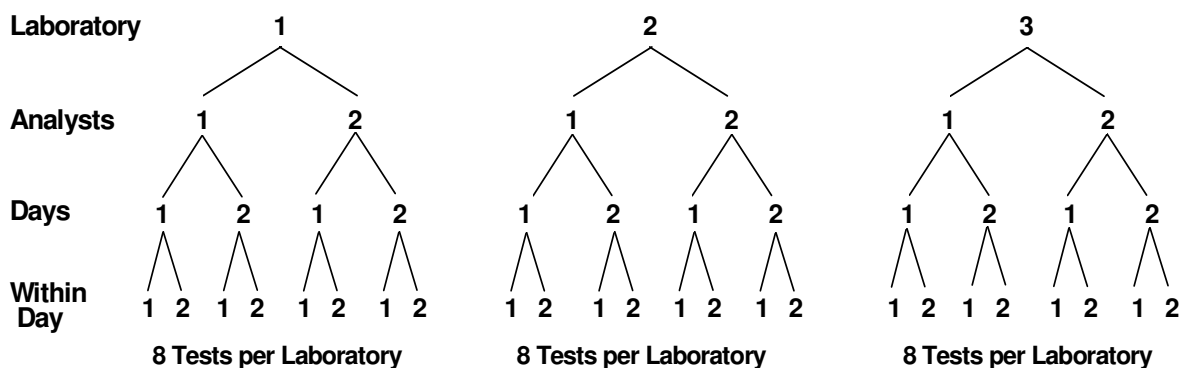
- Figure 1B-1: Single Sample



- Figure 1B-2: Single Sample using 3 Analysts



- Figure 1B-3: Single Sample for 3 Laboratories



Note: The data form corresponding to Figure 1B-1 design above is found in Appendix 1.

When a method claims applicability to a broad concentration range or to different sample types, the samples analyzed must cover the entire concentration range and/or matrices of interest.

Scheduling Representative Tests

To obtain a representative sampling for components of variance estimation, the tests run in each laboratory should be carried out over a period spanning more than one week. Furthermore, the testing intervals for the analysts should overlap each other. In addition, the two analyses carried out each day or shift by the analyst should be performed, if possible, at different times during the day or shift.

The replicate analyses carried out during the course of a day, to provide a realistic estimate of the within-day precision, must be capable of being considered to be a random sample of the day for the statistical estimates to work as intended. For the standard nested design, some replicates should be run one after another in the AM and/or PM. Other replicates should be run with the maximum time span between the within-day tests made by the same analyst where possible. See *Example Calculation No. 1* Form 1B-1 in *Supplement* to this document showing the more-or-less random times that the within-day replicate analysis were run by the same analyst.

Data Examination

It is conceivable that some of the data may be unusable, which then unbalances the nested design. When the ANOVA is complicated by missing data, it is best to consult a statistician.

The within-day replicate data should be plotted as a function of the Lab or Concentration, Analyst, and Day identification, to determine whether the data appears reasonable prior to any statistical analysis. The within-day replicate plot should be examined for unusual analysis results due possibly to a recording error or error in carrying out the test. Figure 2 in the *Example Calculation No. 1* section of the *Supplement* shows an example of this type of plot. The decision to reject test data should be made in consultation with a statistician.

The within-day replicate data should be statistically analyzed using a simple range chart to detect abnormalities (see *Example Calculation No. 1* section, Figure 3 of the *Supplement*).

Analysis and Components of Variance

The total analytical variability may be separated into specific causes or sources of variability by statistically analyzing the chemical and/or physical analysis results using the stepwise ANOVA procedure. The components of variance that must be estimated from the data are as follows:

1. Within-day variance component measuring variation between tests performed on a single day, by one analyst, in one laboratory. This estimated within-day component ($S^2_{\text{Within-Day}}$) is used to calculate the repeatability.
2. Day-to-day variance component measuring variation among single tests performed on different days, by one analyst, in one laboratory. This estimated component ($S^2_{\text{Day-to-Day}}$) could be zero, under ideal conditions.
3. Analyst-to-analyst variance component measuring variation between single tests performed on one day, by different analysts, in one laboratory. This estimated component ($S^2_{\text{Analyst-to-Analyst}}$) could be zero, under ideal conditions.
4. A laboratory-to-laboratory variance component measuring the variation among single tests performed on one day, by one analyst, in different laboratories. Combined with the three other components of variation, this is used to develop the reproducibility statement. Similarly, the laboratory-to-laboratory estimated component ($S^2_{\text{Lab-to-Lab}}$) could be zero, under ideal conditions.

The first three components are added to estimate the total variation in any of the testing laboratories, and are used to develop the intermediate precision statement.

The nested design stepwise ANOVA procedure is described in Appendix 2 of the *SUPPLEMENT* to this document. In the *Supplement* the nested design stepwise ANOVA procedure is applied to copper analysis data and tin analysis data in two separate examples.

Once the components of variance are estimated, they are used to calculate repeatability, intermediate precision, reproducibility, and relative bias with its confidence interval. When a method claims applicability to a broad concentration range or to different sample types, the samples analyzed must cover the entire concentration range and/or matrices of interest. Furthermore, a separate precision statement is developed for each target concentration or matrix, unless statistical tests indicate that the components of variance by concentration and/or matrices are not significantly different and hence, may be combined.

The ANOVA and other computations discussed in this document can be carried out using the Minitab® software. The use of this software is recommended since it is relatively easy to use.

Calculations

The details of the precision calculations are in the *Supplement* to UOP 999-97.

Repeatability Calculation

Repeatability is defined as the allowable difference between two tests performed by the *same* analyst in one lab on the *same* day at the 95% confidence level. It is calculated as follows:

$$\text{Repeatability} = t_{DF} \sqrt{2} s_{\text{Within-Day}} \quad (1)$$

where:

t_{DF} = t distribution value with DF degrees of freedom for two-tail 95% confidence, Table 3

DF = (Total number of tests / No. tests by analyst per day) x (No. tests by analyst per day - 1) Usually DF equals 8 where the total number of tests is 16 with each analyst performing 2 tests during the course of a day or shift.

$s_{\text{Within-Day}}$ = Within-day estimated standard deviation with DF degrees of freedom

$\sqrt{2}$ = Value when multiplied by $s_{\text{Within-Day}}$ estimates the standard deviation for the difference between two tests made anytime during the day by the same analyst.

Intermediate Precision (Site Precision) is defined as the allowable difference between two tests performed by *different* analysts in one lab on *different* days at the 95% confidence level. It is calculated as follows:

$$\text{Intermediate Precision} = t_{DF} \sqrt{2} s_{\text{Within-Lab}} \quad (2)$$

where:

t_{DF} = t distribution value with DF degrees of freedom for two-tail 95% confidence, Table 3

$s_{\text{Within-Lab}}$ = Within-Lab estimated standard deviation with DF degrees of freedom containing the within-day variability and, if present, the day-to-day and analyst-to-analyst variability; or,

$$= \sqrt{s_{\text{Within-Day}}^2 + s_{\text{Day-to-Day}}^2 + s_{\text{Analyst-to-Analyst}}^2} \text{ with DF degrees of freedom}$$

DF = Estimated by the Satterthwaite equation as discussed in Appendix 2 of the *Supplement*. The Satterthwaite equation weights the degrees of freedom of the within-day, day-to-day and analyst-to-analyst components of variance. For standard

nested design with 16 tests, the Satterthwaite calculated DF for $s_{\text{Within-Lab}}$ is between 2 and 8 depending on the ANOVA MS and degree of freedom values.

$\sqrt{2}$ = Value when multiplied by $s_{\text{Within-Lab}}$ estimates the standard deviation for the difference between two tests made by *different* analysts in one lab on *different* days.

Reproducibility Calculation

Reproducibility is defined as the allowable difference between two tests performed by *different* analysts in *different* labs on *different* days at the 95% confidence level. It is calculated as follows:

$$\text{Reproducibility} = t_{\text{DF}} \sqrt{2} \sqrt{s_{\text{Within-Lab}}^2 + s_{\text{Between-Labs}}^2} \quad (3)$$

where:

t_{DF} = t distribution value with DF degrees of freedom for two-tail 95% confidence, Table 3

$s_{\text{Within-Lab}}$ = Within-Lab estimated standard deviation with DF degrees of freedom containing the within-day variability and, if present, the day-to-day and analyst-to-analyst variability; or,

$$= \sqrt{s_{\text{Within-Day}}^2 + s_{\text{Day-to-Day}}^2 + s_{\text{Analyst-to-Analyst}}^2} \text{ with DF degrees of freedom}$$

$s_{\text{Lab-to-Lab}}$ = Lab-to-lab estimated standard deviation accounting for average differences between the laboratories in the study

DF = Estimated by the Satterthwaite equation as discussed in Appendix 2 of the *Supplement*. The Satterthwaite equation weights the degrees of freedom of the within-day, day-to-day, analyst-to-analyst and lab-to-lab components of variance. For standard nested design with 8 tests at 2 labs, the Satterthwaite calculated DF for $s_{\text{Within-Lab}}^2 + s_{\text{Lab-to-Lab}}^2$ is between 1 and 8 depending on the ANOVA MS and degree of freedom values.

$\sqrt{2}$ = Value when multiplied by $\sqrt{s_{\text{Within-Day}}^2 + s_{\text{Between-Lab}}^2}$ estimates the standard deviation for the difference between two tests made by *different* analysts in *different* laboratories on *different* days.

**Two-Tailed Student's t Values
for 95% Confidence**

Table 3

Degrees of Freedom	t-Value	Degrees of Freedom	t-Value	Degrees of Freedom	t-Value
1	12.7062	12	2.1788	23	2.0687
2	4.3027	13	2.1604	24	2.0639
3	3.1824	14	2.1448	25	2.0595
4	2.7765	15	2.1315	26	2.0555
5	2.5706	16	2.1199	27	2.0518
6	2.4469	17	2.1098	28	2.0484
7	2.3646	18	2.1009	29	2.0452
8	2.3060	19	2.0930	30	2.0423
9	2.2622	20	2.0860	60	2.0003
10	2.2281	21	2.0796	120	1.9799
11	2.2010	22	2.0739	Infinity	1.9600

**Relative Bias and
95% Confidence Interval Calculation**

Relative bias is defined as the average test difference between laboratories for the same sample analyses. For three laboratories the relative biases are calculated as follows:

$$\text{Bias}_{\text{Lab 1} - \text{Lab 2}} = \bar{X}_{\text{Lab 1}} - \bar{X}_{\text{Lab 2}} \quad (4)$$

$$\text{Bias}_{\text{Lab 1} - \text{Lab 3}} = \bar{X}_{\text{Lab 1}} - \bar{X}_{\text{Lab 3}} \quad (5)$$

$$\text{Bias}_{\text{Lab 2} - \text{Lab 3}} = \bar{X}_{\text{Lab 2}} - \bar{X}_{\text{Lab 3}} \quad (6)$$

where:

$$\bar{X}_{\text{Lab 1}} = \text{Lab 1 Average of } n \text{ tests}$$

$$\bar{X}_{\text{Lab 2}} = \text{Lab 2 Average of } n \text{ tests}$$

$$\bar{X}_{\text{Lab 3}} = \text{Lab 3 Average of } n \text{ tests}$$

For the nested design shown in Figure 1B-3, n is 8 at each laboratory.

The uncertainty of the laboratory biases is given by the 95% confidence interval for those differences:

$$\bar{X}_{\text{Lab 1}} - \bar{X}_{\text{Lab 2}} \pm t_{\text{DF}} \cdot \sqrt{2} s_{\bar{X} \text{ Within-Lab}} \quad (7)$$

$$\bar{X}_{\text{Lab 1}} - \bar{X}_{\text{Lab 3}} \pm t_{\text{DF}} \cdot \sqrt{2} s_{\bar{X} \text{ Within-Lab}} \quad (8)$$

$$\bar{X}_{\text{Lab 2}} - \bar{X}_{\text{Lab 3}} \pm t_{\text{DF}} \cdot \sqrt{2} s_{\bar{X} \text{ Within-Lab}} \quad (9)$$

where:

$$s_{\bar{X} \text{ Within-Lab}} = \sqrt{\frac{s_{\text{Within-Day}}^2}{n_R n_{\text{Days}} n_{\text{Analysts}}} + \frac{s_{\text{Day-to-Day}}^2}{n_{\text{Days}} n_{\text{Analysts}}} + \frac{s_{\text{Analyst-to-Analyst}}^2}{n_{\text{Analysts}}}}$$

$\text{DF}^* = n_{\text{Labs}}(n_{\text{Analysts}}-1)$ degrees of freedom for full model (see Model 1, Appendix 2 in the *SUPPLEMENT*)

t_{DF^*} = t distribution value with DF^* degrees of freedom for two-tail 95% confidence, Table 3

n_{Labs} = Number of laboratories

n_{Analysts} = Number of analysts per lab

n_{Days} = Number of days testing per analyst

n_R = Number of replicates per day per analyst

$\sqrt{2}$ = Value when multiplied by $s_{\bar{X} \text{ Within-Lab}}$ estimates the standard deviation for the average difference of $n_{\text{Analysts}} n_{\text{Days}} n_R$ tests made at each of two laboratories.

In the event that bias exists in the data, efforts are expected to be made to find the source of the bias and then to eliminate the bias, if possible. Relative Bias is used internally for method development and is not reported in the published method.

Report

The statements included in the *Precision* section of a UOP method are dependent upon whether data were collected from only one or two laboratories, or from three or more laboratories. See Appendix 2 for deciding how many digits to record based on the pooled within-day esd. A **Bias** paragraph may be included after the **Reproducibility** paragraph only if a comparison can be made between the results obtained by the method and known or accepted values. Refer to ASTM Practice E 177, “Practice for the use of Terms Precision and Bias in ASTM Test Methods,” for examples of possible bias statements.

One or Two Laboratories

The within-day and within-laboratory esd and the repeatability are clearly stated. Then a reproducibility statement is added to clearly show that there is insufficient data for reporting the reproducibility. For example:

Repeatability and Intermediate Precision

A nested design was carried out for copper analysis with four analysts. Each analyst carried out tests on two separate days and performed two tests each day. The total number of tests performed was 16. The average copper concentration of all 16 analyses was 0.392 mass-%. Using a stepwise analysis of variance procedure the within-day estimated standard deviation (esd) was 0.0009. Two tests performed in one laboratory by the same analyst on the same day should not differ by more than 0.003 with 95% confidence. Using a stepwise analysis of variance procedure the within-lab estimated standard deviation (esd) was 0.0014. Two tests performed in one laboratory by different analysts on different days should not differ by more than 0.005 with 95% confidence.

Reproducibility

There is insufficient data to report the reproducibility of the test at this time.

Multiple Laboratories (Three or More)

The within-day esd, within-laboratory esd and between-laboratory esd are clearly stated. Then the repeatability and reproducibility are stated. For example:

Repeatability and Intermediate Precision

A nested design was carried for tin analysis. Forty eight analyses were performed in three laboratories at two concentrations with two analysts per laboratory, with each analyst carrying out tests on two separate days and performing two tests each day. The average tin concentration of 24 analyses at each concentration was 0.377 mass-% and 0.596 mass-%, respectively. Using a stepwise analysis of variance procedure the within-day estimated standard deviation (esd) was 0.0007. Two tests performed in one laboratory by the same analyst on the same day should not differ by more than 0.002 with 95% confidence. Using a stepwise analysis of variance procedure the within-lab estimated standard deviation (esd) was 0.0018. Two tests performed in one laboratory by different analysts, on different days, should not differ by more than 0.005 with 95% confidence.

Reproducibility

A nested design was carried out for tin analysis. Forty eight analyses were performed in three laboratories at two concentrations with two analysts per laboratory, with each analyst carrying out tests on two separate days and performing two tests each day. Using a stepwise analysis of variance procedure the between-lab estimated standard deviation (esd) was 0.0019. The average tin concentration of 24 analyses was 0.377 mass-% and 0.596 mass-%, respectively. Two tests performed in one laboratory by different analysts, on different days, should not differ by more than 0.008 with 95% confidence.

Suggested Supplier

Minitab Inc., 1829 Pine Hall Road, State College, PA 16801-3008 (814-238-3280)
www.minitab.com

Appendix 1

Reporting Precision Data Form 1A-1

For Estimating Repeatability for Laboratory at Single Sample Concentration

Laboratory Location _____

Supervisor _____ Component, Units _____

Sample Concentration _____ Sample Identification _____

Analyst Initials	Date and Time	Within-Day Test Replicate No.	Test Results
1 _____	_____	1	_____
	_____	2	_____
1 _____	_____	1	_____
	_____	2	_____
2 _____	_____	1	_____
	_____	2	_____
2 _____	_____	1	_____
	_____	2	_____
3 _____	_____	1	_____
	_____	2	_____
3 _____	_____	1	_____
	_____	2	_____
4 _____	_____	1	_____
	_____	2	_____
4 _____	_____	1	_____
	_____	2	_____

Appendix 1

Reporting Precision Data Form 1A-2

For Estimating Repeatability for Laboratory at Two Sample Concentrations

Laboratory Location _____

Supervisor _____ Component, Units _____

Sample Concentrations _____ Sample Identifications _____

Sample Concentration	Analyst Initials	Date and Time	Within-Day Test Replicate No.	Test Results
1 _____	1 _____	_____	1	_____
		_____	2	_____
1 _____	1 _____	_____	1	_____
		_____	2	_____
1 _____	2 _____	_____	1	_____
		_____	2	_____
1 _____	2 _____	_____	1	_____
		_____	2	_____
2 _____	1 _____	_____	1	_____
		_____	2	_____
2 _____	1 _____	_____	1	_____
		_____	2	_____
2 _____	2 _____	_____	1	_____
		_____	2	_____
2 _____	2 _____	_____	1	_____
		_____	2	_____

Appendix 1

Reporting Precision Data Form 1B-1

For Estimating Repeatability, Reproducibility and Relative Bias between Labs

Laboratory Location _____ UOP Method No. _____

Supervisor _____ Component, Units _____

Sample Concentration _____ Sample Identification _____

Analyst Initials	Date and Time	Within-Day Test Replicate No.	Test Results
1 _____	_____	1	_____
	_____	2	_____
1 _____	_____	1	_____
	_____	2	_____
2 _____	_____	1	_____
	_____	2	_____
2 _____	_____	1	_____
	_____	2	_____

Laboratory Location _____ UOP Method No. _____

Supervisor _____ Component, Units _____

Sample Concentration _____ Sample Identification _____

Analyst Initials	Date and Time	Within-Day Test Replicate No.	Test Results
1 _____	_____	1	_____
	_____	2	_____
1 _____	_____	1	_____
	_____	2	_____
2 _____	_____	1	_____
	_____	2	_____
2 _____	_____	1	_____
	_____	2	_____

Appendix 2

Number of Significant Digits to Record

Given the pooled Within-Day estimated standard deviation, the minimum number of digits to record the analytical data is shown below:

Within Day esd	Round Data to Nearest	Example
0.0001 to 0.00099	Ten-thousandth	0.3545
0.001 to 0.0099	Thousandth	0.355
0.01 to 0.099	Hundredth	0.36
0.1 to 0.99	Tenth	0.4
1 to 9.99	Integer	1238
10 to 99.99	Ten	1240

When the Within-Day esd is not known from similar procedures, it is better to record the data using too many digits than to find out later that more digits are needed.

Copper data from *Example Calculation No.1* section of the *Supplement* is shown below. The data in the rightmost columns has been intentionally truncated and rounded to the nearest thousandth. The estimated Within-Day standard deviation is 0.000765 for the data rounded to the nearest ten-thousandth and 0.000866 for the data rounded to the nearest thousandth. When the data is truncated and rounded to the nearest thousandth the resulting Within-Day standard deviation is 13% higher. The table above shows the data should be recorded to the nearest ten-thousandth.

Lab	Analyst	Day	Within Day Average of 2	Within Day Replicate Std. Dev.	Degrees of Freedom	Within Day		Truncated Data Within Day	
						Rep 1	Rep 2	Rep 1	Rep 2
1	1	1	0.39115	0.00148492	1	0.3901	0.3922	0.390	0.392
1	1	2	0.38975	0.00007071	1	0.3897	0.3898	0.390	0.390
1	2	1	0.39135	0.00035355	1	0.3916	0.3911	0.392	0.391
1	2	2	0.39095	0.00049497	1	0.3913	0.3906	0.391	0.391
2	1	1	0.39235	0.00049497	1	0.3920	0.3927	0.392	0.393
2	1	2	0.39085	0.00106066	1	0.3916	0.3901	0.392	0.390
2	2	1	0.39335	0.00035355	1	0.3931	0.3936	0.393	0.394
2	2	2	0.39335	0.00077782	1	0.3939	0.3928	0.394	0.393
Overall Average =				0.3916375		$s_p = \sqrt{\frac{\sum_{i=1}^8 s_i^2}{8}} = 0.00076485$ Based on data rounded to ten-thousandth $s_p = 0.000765$		Based on data rounded to thousandth $s_p = 0.000866$ 13% Higher due to truncated rounding	
Pooled Within Day Rep Std. Dev. =				0.00076485					
Pooled Within Day Rep Mean Square =				0.000000585					
Pooled Within Day Std. Dev. Degrees of Freedom =				8					

Appendix 3

Precision Statements Calculated from Pairs of Data

It is preferred that precision statements be generated using data from the nested sampling designs shown in the *Procedure* section of the body of the method. However, there may be some instances in which such data may be difficult or impossible to obtain. If multiple pairs of data are available, e.g., from duplicate analyses, such data may be used to generate an alternative precision statement. The procedure for calculating precision statements from pairs of data is given hereinafter.

Procedure

Obtain analyses on a minimum of 5 duplicate samples (pairs) of the sample. Six or more pairs of data are preferable since the calculation will be more precise. When a method claims applicability to a broad concentration range or to different sample types, several estimated standard deviations should be determined to fully cover the entire range. Calculate an estimated standard deviation and an allowable difference at the 95% probability level as shown in *Calculations*.

Calculations

Estimated Standard Deviation (esd) from Pairs

Calculate the average difference (mean range) using Equation A1:

$$\text{esd} = \sqrt{\frac{\sum d^2}{2k}} \quad (\text{A1})$$

where:

d = difference between two results comprising a pair (absolute value)

k = number of pairs

Allowable Difference from Pairs

Calculate the allowable difference (95% probability) from the esd obtained from pairs using Equation A2 and the appropriate multiplier from Table A1.

$$\text{Allowable difference} = E M \quad (\text{A2})$$

where:

E = esd, from Equation A1

M = multiplier, obtained from Table A1

Table A1
Multiplier to Calculate Allowable Difference

Number of		Number of	
<u>Pairs</u>	<u>Multiplier</u>	<u>Pairs</u>	<u>Multiplier</u>
5	3.75	15	3.03
6	3.55	20	2.95
7	3.41	30	2.89
8	3.32	40	2.86
9	3.25	120	2.80

Report

Two statements are included in the precision statement of the method; the first will state the calculated esd, and the second the allowable difference at the 95% probability level. For example,

“Based on six pairs of analyses, the estimated standard deviation (esd) for platinum in the range of 0.36 – 0.40 mass-% was calculated to be 0.0011 mass-%.

Duplicate results by the same operator should not differ by more than 0.004 mass-% (95% probability) at the stated level.”

When more than one esd is required, due to different sample type or concentration ranges, the data should be presented in a table format. For example,

“Based on six replicate determinations, the estimated standard deviation (esd) was calculated for the impurities listed in the table below. Duplicate results by the same operator should not differ by more than the allowable difference shown (95% probability).”

Table A2			
<u>Precision, mass-ppm</u>			
<u>Component</u>	<u>Concentration</u>		<u>Allowable Difference</u>
	<u>Range</u>	<u>esd</u>	
Benzene	88 - 91	1.11	4.0
Toluene	27 - 29	0.29	1.1