

PRECISION STATEMENTS IN UOP METHODS

UOP Method 888-88

SCOPE

This method is for developing precision statements as reported in UOP methods. The calculation of precision, in terms of repeatability (within a laboratory) and reproducibility (among laboratories), is described. Precision statements in methods having an 88 or later suffix were developed by the procedure described, while earlier methods utilized UOP 666-82.

OUTLINE OF METHOD

Using the specified test method, 8 tests (see Note 1) are performed at a given laboratory on the same representative sample. The analysis is performed by two different analysts on each of two separate days, each analyst performing two tests per day (for a graphic illustration see Fig. 1). The estimated standard deviation (esd) within a laboratory is calculated by a prescribed procedure (Table 1) that includes the analyst-to-analyst esd, the day-to-day esd and the test-to-test esd of the method. Repeatability (which is the precision of the difference between two tests in the one laboratory at the 95% confidence level) is calculated from the within-laboratory esd. Where practicable, the same 8-test procedure is followed at multiple laboratories. Then the among-laboratory esd is calculated by the prescribed procedure (Table 1). The reproducibility (which is the precision of the difference between two tests done at different laboratories at the 95% confidence level) is calculated using this among-laboratories esd. If the UOP Method is practiced at one or two of the company laboratories, the repeatability calculated from the within-laboratory esd is the only precision information reported.

DEFINITIONS

Test, the result of a single analysis performed in a laboratory by a specified UOP method. When duplicates are routinely performed, a test is the average of the two determinations.

Repeatability, the allowable difference between two tests performed by different analysts in one laboratory on different days. Two randomly chosen tests should not differ by more than the stated allowable difference more than five percent of the time, by chance (for 95% confidence).

IT IS THE USER'S RESPONSIBILITY TO ESTABLISH APPROPRIATE PRECAUTIONARY PRACTICES AND TO DETERMINE THE APPLICABILITY OF REGULATORY LIMITATIONS PRIOR TO USE. EFFECTIVE HEALTH AND SAFETY PRACTICES ARE TO BE FOLLOWED WHEN UTILIZING THIS PROCEDURE. FAILURE TO UTILIZE THIS PROCEDURE IN THE MANNER PRESCRIBED HEREIN CAN BE HAZARDOUS. MATERIAL SAFETY DATA SHEETS (MSDS) OR EXPERIMENTAL MATERIAL SAFETY DATA SHEETS (EMSDS) FOR ALL OF THE MATERIALS USED IN THIS PROCEDURE SHOULD BE REVIEWED FOR SELECTION OF THE APPROPRIATE PERSONAL PROTECTION EQUIPMENT (PPE).

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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, by chance (for 95% confidence).

PROCEDURE

The laboratory supervisor under whose jurisdiction the method is performed is responsible for collecting the necessary precision data, following the UOP method *exactly* as written, and reporting those data together with a record of the analyst, day and test number. Care must be taken to accurately record, on the form provided, the origin of each result, noting the analyst, test number and day of the test (Appendix, Table 1). All the data collected must be reported and no effort should be made to eliminate data points by rejecting individual tests. The resultant data are referred to as a “balanced nested” data set.

The components of variance identified for the statistical analysis are listed below. The method of calculations is shown in *CALCULATIONS* and an illustrative example is given in *EXAMPLE CALCULATION*. The components of interest that must be determined are:

1. A test-to-test component measuring variation between tests performed on the one day, by one analyst, in one laboratory.
2. A day-to-day component measuring variation among single tests performed on different days, by one analyst, in one laboratory.
3. An analyst-to-analyst component measuring variation among single tests performed on one day, by different analysts, in one laboratory.

The above three components are utilized to measure the total variation in any given laboratory.

4. A laboratory-to-laboratory component measuring the variation among single tests performed on one day, by one analyst, in different laboratories.

Statistical tests can be performed to reject tests that have resulted from systematic errors (outliers).

When a method claims applicability to a broad concentration range or to different sample types, data should be collected to fully cover the entire range. Analyze representative samples that span the range of concentrations or matrices of interest. A separate precision statement is developed for each target concentration or matrix, unless statistical tests demonstrate that the data can be combined (i.e., the data are statistically homogeneous). A simplification to the nested data analysis is described in the *APPENDIX*.

CALCULATIONS

Analysis of Variance Calculations for the Nested Sample

An analysis of variance (ANOVA) for the balanced nested design (Fig. 1) is exemplified in Table 1. The ANOVA yields estimates of the components of variance (test-to-test, day-to-day, analyst-to-analyst and laboratory-to-laboratory). These components are used to estimate the within- and among-laboratory variances required in the approximate expressions for repeatability and reproducibility.

The ANOVA described in Table 1 does not involve difficult calculations, however, it is tedious. Consequently, a computer program (see *EXAMPLE CALCULATION* and Note 2) can be used to perform the data reduction.

It is conceivable that some of the data may be unuseable, unbalancing the sampling design. When the ANOVA is complicated by missing data, the analysis given in Table 1 must be modified. Although the computer program can still handle the analysis, more care is needed in the interpretation. Also, the estimate of some variance components may be negative. In this case the corresponding component (day, analyst or laboratory) is not significant and this simplifies the model and the ANOVA. The detailed ANOVA to handle these two situations is performed in consultation with a statistician.

Repeatability

Calculate the repeatability from the value of the total within the laboratory esd, as indicated in the following equation:

$$\text{Repeatability} = t_{DF} \sqrt{2} \sqrt{\sigma_W^2}$$

where:

t_{DF} = student-t value (two-tailed), Table 2, for the number of degrees of freedom (DF) taken as DF_T , calculated as shown in Table 1

σ_W = within laboratory esd, calculated as indicated in Table 1

$\sqrt{2}$ = value which permits comparison of two data.

Reproducibility

Calculate the reproducibility of the method from the among- and within-laboratory esd's, as indicated in the following equation:

$$\text{Reproducibility} = t_{DF} \sqrt{2} \sqrt{\sigma_B^2}$$

where:

σ_B = among laboratory esd calculated as indicated in Table 1

t and $\sqrt{2}$ are as previously defined

When there are only two laboratories, $DF_L = 1$. Consequently, the *Reproducibility* calculation will usually be unrealistically large (see *EXAMPLE CALCULATION*). Therefore, the calculation of reproducibility will be practical only if at least three laboratories perform the tests.

EXAMPLE CALCULATION

The hypothetical data of Table 3 have been used to perform the ANOVA and calculate the repeatability values indicated. The results of the calculations are summarized in Table 4 and shown graphically in Fig. 2. The program is shown in the *APPENDIX*, Table 2.

REPORT

The statements included in the *PRECISION* section of a UOP method depend upon whether data were collected from only one or two laboratories, or from three or more laboratories.

One or Two Laboratories

The within-laboratory esd, the number of data used to calculate it and the repeatability are clearly stated. Then a reproducibility statement is added to clearly show that there is insufficient data for determining the reproducibility. For example:

Repeatability

“Based on two tests performed by each of two analysts, on each of two days (8 tests) in each of two laboratories, the within-laboratory esd was calculated to be 0.0012 at a copper concentration of 0.3916 mass-%. Two tests performed in the one laboratory by different analysts on different days should not differ by more than 0.0039 (95% probability) at the stated level.”

Reproducibility

“There is insufficient data to calculate the reproducibility of the test at this time.”

Multiple Laboratories (Three or More)

The within-laboratory esd, the among-laboratory esd and the number of data used in the calculations are clearly stated. Then the reproducibility and repeatability are stated. For example:

Repeatability

“Based on two tests performed by each of two analysts, on each of two different days (8 tests per lab) and using data collected from each of 5 laboratories, the within-laboratory esd was calculated to be 0.0025 and the between-laboratory esd was calculated to be 0.0027 at a copper concentration of 0.3916 mass-%. Two tests performed in the one laboratory by different analysts, on different days, should not differ by more than 0.0074 (95% probability) at the stated level.”

Reproducibility

“Two tests performed in different laboratories by different analysts, on different days should not differ by more than 0.0106 (95% probability) at a concentration of 0.3916 mass-%”

NOTES

1. It is essential that two analysts perform two tests on each of two separate days to perform the statistical analysis required. However, much more reliable statistics result if more data are available. Therefore, it is recommended that as many tests as possible be performed. The data should always be collected according to the nested sampling method described (i.e., from tests done on different days by different analysts), and reported in the format shown in *APPENDIX*, Table 1.

2. The program used for data analysis is resident in the SAS[®] software at the Engineered Materials Research Center, Computer Applications Department and is run on the VAX-8600 Computer. The specific procedure used is “NESTED”, which is described in SAS User’s Guide: Statistics Version 5 Edition, pp 569-573 and references therein.

REFERENCE

UOP Method 666

Table 1

**Balanced Nested Analysis of Variance
(Balanced Components of Variance)**

For, r, tests done on each of, d, days by each of,
a, analysis in each of, λ, laboratories

Source of Variation	Degrees of Freedom, DF	Sum of Squares	Mean Square	Expected Mean Square	F Test Statistic
Total	$\lambda \text{ adr}-1$	SS_{Total}			
Laboratories	$\lambda -1 = DF_L$	SS_L	$\frac{SS_L}{DF_L} = MS_L$	$\sigma_T^2 + r\sigma_D^2 + dr\sigma_A^2 + \text{adr}\sigma_L^2$	MS_L/MS_A
Analysts in Laboratories	$\lambda (a-1) = DF_A$	SS_A	$\frac{SS_A}{DF_A} = MS_A$	$\sigma_T^2 + r\sigma_D^2 + dr\sigma_A^2$	MS_A/MS_D
Days in Analysts in Laboratories	$\lambda a(d-1) = DF_D$	SS_D	$\frac{SS_D}{DF_D} = MS_D$	$\sigma_T^2 + r\sigma_D^2$	MS_D/MS_T
Tests in Days in Analysts in Laboratories	$\lambda \text{ ad}(r-1) = DF_T$	SS_T	$\frac{SS_T}{DF_T} = MS_T$	σ_T^2	
SS_{Total}	$=$	$\sum_{i=1}^{\lambda} \sum_{j=1}^a \sum_{k=1}^d \sum_{\ell=1}^r (Y_{ijk\ell} - \bar{Y})^2$	where:	$\bar{Y} = \frac{1}{\lambda \text{ adr}} \sum_i \sum_j \sum_k \sum_{\ell} Y_{ijk\ell}$	
SS_L	$= \text{adr}$	$\sum_i (\bar{Y}_i - \bar{Y})^2$	where:	$\bar{Y}_i = \frac{1}{\text{adr}} \sum_j \sum_k \sum_{\ell} Y_{ijk\ell}$	
SS_A	$= \text{dr}$	$\sum_i \sum_j (\bar{Y}_{ij} - \bar{Y}_i)^2$	where:	$\bar{Y}_{ij} = \frac{1}{\text{dr}} \sum_k \sum_{\ell} Y_{ijk\ell}$	
SS_D	$= r$	$\sum_i \sum_j \sum_k (\bar{Y}_{ijk} - \bar{Y}_{ij})^2$	where:	$\bar{Y}_{ijk} = \frac{1}{r} \sum_{\ell} Y_{ijk\ell}$	
SS_T	$=$	$\sum_i \sum_j \sum_k \sum_{\ell} (Y_{ijk\ell} - \bar{Y}_{ijk})^2$			

Table 1 (continued)

**Balanced Nested Analysis of Variance
(Balanced Components of Variance)**

**For, r, tests done on each of, d, days by each of,
a, analysts in each of, λ, laboratories**

The components of variance can be estimated by beginning with the bottom line of the Analysis of Variance and working line by line to the top of the table, equating each Mean Square with its Expected Mean Square:

- 1) First the test-to-test component (σ_T^2) is estimated by MS_T (as defined in the table proper)
- 2) Then the day-to-day component (σ_D^2) is estimated as $(MS_D - MS_T)/r$
- 3) Next the analyst-to-analyst component is estimated as $(MS_A - MS_D)/(dr)$
- 4) Last the laboratory-to-laboratory component is estimated as $(MS_L - MS_A)/(adr)$

The “within-laboratory” variance of a single random test, done on a random day, by a random analyst, at a given laboratory, is given by:

$$\sigma_W^2 = \sigma_T^2 + \sigma_D^2 + \sigma_A^2$$

and the “among-laboratory” variance of a single random test, done on a random day, by a random analyst, at a random laboratory, is then given by:

$$\sigma_B^2 = \sigma_W^2 + \sigma_L^2$$

Finally:

Repeatability	=	$t_{DF_T} \sqrt{2} \sqrt{\sigma_W^2}$	where: DF_T is given in the table proper
and			
Reproducibility	=	$t_{DF_L} \sqrt{2} \sqrt{\sigma_B^2}$	where: DF_L is given in the table proper and: t_{DF} is given in Table 2

Table 2
Two-Tailed Student-t Values

Degrees of Freedom, DF	$t_{95\%}$	Degrees of Freedom, DF	$t_{95\%}$
1	12.706	19	2.093
2	4.303	20	2.086
3	3.182		
4	2.776	21	2.080
5	2.571	22	2.074
		23	2.069
6	2.447	24	2.064
7	2.365	25	2.060
8	2.306		
9	2.262	26	2.056
10	2.228	27	2.052
		28	2.048
11	2.201	29	2.045
12	2.179	30	2.042
13	2.160		
14	2.145	40	2.021
15	2.131	60	2.000
		120	1.980
16	2.120	∞	1.960
17	2.110		
18	2.101		

Table 3
Hypothetical Copper Analysis Data

<u>Lab (i)</u>	<u>Analyst (j)</u>	<u>Day (k)</u>	<u>Test No. (ℓ)</u>	<u>Test Yijkℓ</u>
(1)	1	1	1	0.3901
			2	0.3922
		2	1	0.3897
			2	0.3898
	2	1	1	0.3916
			2	0.3911
		2	1	0.3913
			2	0.3906
(2)	1	1	1	0.3920
			2	0.3927
		2	1	0.3916
			2	0.3901
	2	1	1	0.3931
			2	0.3936
		2	1	0.3939
			2	0.3928

Table 4
EXAMPLE CALCULATION

SAS
Coefficients of Expected Mean Squares

<u>Source</u>	<u>Lab</u>	<u>Analyst</u>	<u>Day</u>	<u>Error</u>
Lab	8	4	2	1
Analyst	0	4	2	1
Day	0	0	2	1
Error	0	0	0	1

SAS
Analysis of Variance Y

<u>Variance Source</u>	<u>DF</u>	<u>Sum of Squares</u>	<u>Mean Squares</u>	<u>Variance Component</u>	<u>Percent</u>
Total	15	0.0000273775	0.000001825167	0.0000024125 ⁵	100
Lab	1	0.0000112225	0.0000112225	9.587500E-07 ⁴	39.7409
Analyst	2	0.000007105	0.0000035525	6.150000E-07 ³	25.4922
Day	4	0.00000437	0.0000010925	2.537500E-07 ²	10.5181
Error	8	0.00000468	5.850000E-07	5.850000E-07 ¹	24.2487

Mean	0.3916375
Standard Deviation	0.00764852927
Coefficient of Variation	0.195296142

¹ = estimate of σ_T^2
² = " " σ_D^2
³ = " " σ_A^2
⁴ = " " σ_L^2
⁵ = " " $\sigma_B^2 = 1 + 2 + 3 + 4$
" " $\sigma_W^2 = 1 + 2 + 3$
= 0.00000145375

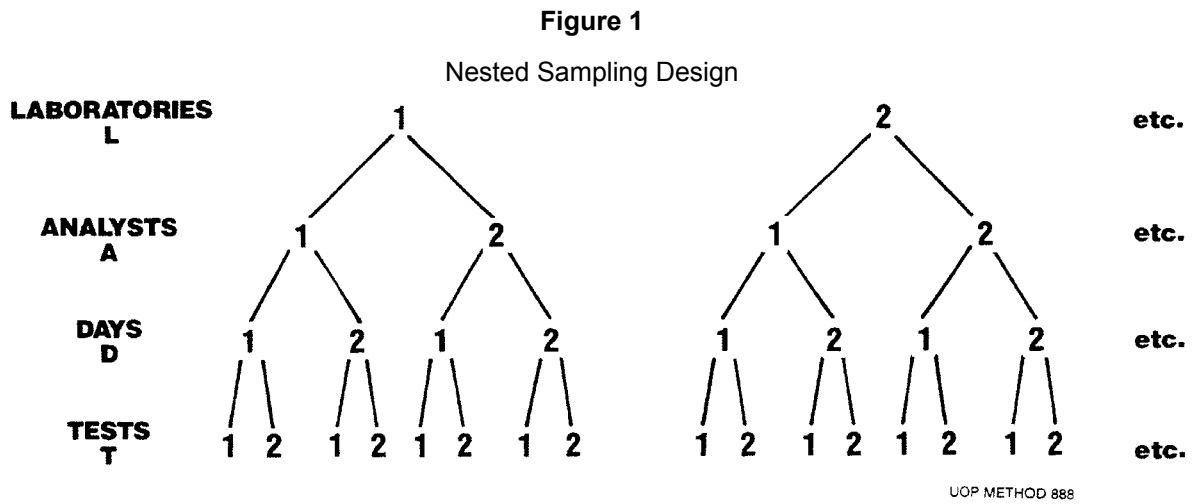
Table 4 (continued)
EXAMPLE CALCULATION

$$\begin{aligned}
 \text{Then Repeatability (a)} &= t_{DF_T} \sqrt{2} \sqrt{\sigma_W^2} \\
 &\text{where: } DF_T = 8 \\
 &= 2.306 \sqrt{2} \sqrt{0.00000145375} \\
 &= 0.0039 \\
 \\
 \text{and Reproducibility (b)} &= t_{DF_L} \sqrt{2} \sqrt{\sigma_B^2} \text{ where: } DF_L = 1 \\
 &= 12.706 \sqrt{2} \sqrt{0.0000024125} \\
 &= 0.0279
 \end{aligned}$$

-
- (a) Also, a 95% confidence limit for the difference between two tests repeated by the one analyst, on the one day are available from the estimate of σ_T^2 . In the example:

$$\begin{aligned}
 &t_{DF_T} \sqrt{2} \sqrt{\sigma_W^2} \\
 &\text{where: } DF_T = 8 \\
 &= 2.300 \sqrt{2} \sqrt{5.85E-07} \\
 &= 0.0025
 \end{aligned}$$

- (b) The t value has only 1 DF and the resulting Reproducibility is far too large to be useful here. For Reproducibility to be more reliable, more than 2 laboratories should be in the test, preferably many more.



$$Y_{ijkl} = M + L_i + A_{ij} + D_{ijk} + T_{ijkl}$$

where:

M = the mean of all tests, i.e., the true result

L_i = a constant for the test done by the i^{th} laboratory

A_{ij} = a constant for the test done by the i^{th} lab using analyst j

D_{ijk} = a constant for the test by the i^{th} lab, analyst j on day k

T_{ijkl} = a constant for the i^{th} lab, j^{th} analyst, k^{th} day and for test ℓ

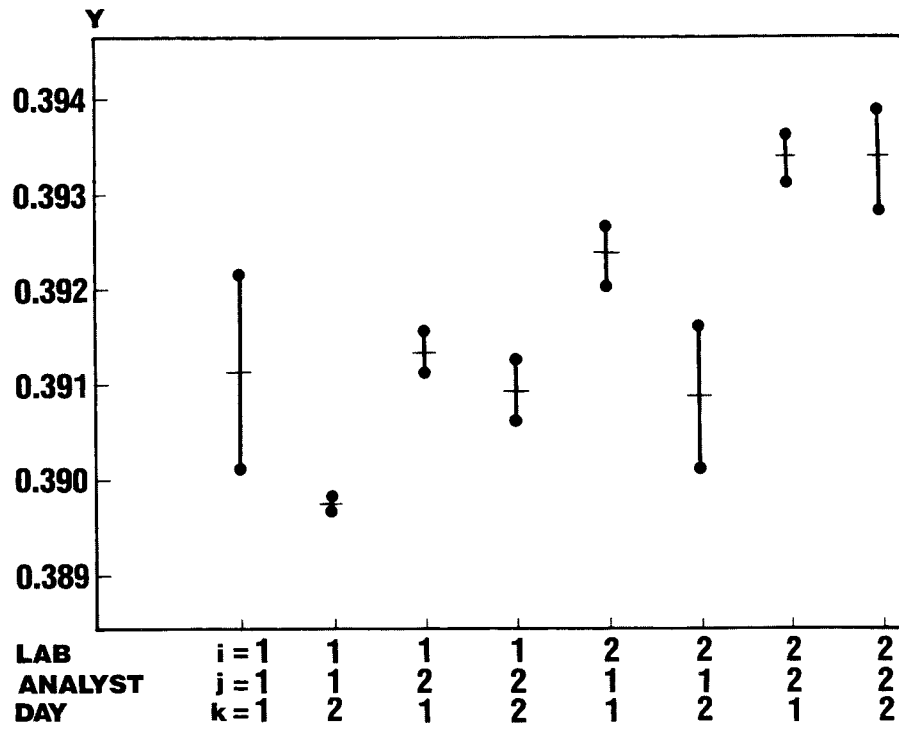


Figure 2

Hypothetical Copper Analysis Data

APPENDIX

Simplification of Nested Data Analysis

A simplification of the method may be possible by eliminating the within-laboratories nesting, so that Sources of Variation involving Days or Analysts are pooled in an all-inclusive “within-laboratories” source. The data produced at each laboratory should be that of the analysts routinely performing the test, on different days. The within-laboratory esd will then be simply the standard deviation of the tests, within the laboratory and without regard to the particular analyst or day. Distinction between tests performed at different laboratories is still considered.

The simplified analysis, leading to the calculation of Repeatability and Reproducibility, is given in *APPENDIX*, Table 3.

Table 1A

Example of Form for Reporting Precision Data

Laboratory Name _____

Supervisor _____

<u>Analyst</u>	<u>Date</u>	<u>Test Number</u>	<u>Test Results</u>
1 _____	_____	1	_____
		2	_____
1 _____	_____	1	_____
		2	_____
2 _____	_____	1	_____
		2	_____
2 _____	_____	1	_____
		2	_____

Table 2A**Example of SAS® Computer Program**

```
DATA COPPER;
INPUT LAB ANALYST DAY TESTNO Y;
```

```
CARDS;
```

```
1 1 1 1 0.3901
1 1 1 2 0.3922
1 1 2 1 0.3897
1 1 2 2 0.3898
1 2 1 1 0.3916
1 2 1 2 0.3911
1 2 2 1 0.3913
1 2 2 2 0.3906
2 1 1 1 0.3920
2 1 1 2 0.3927
2 1 2 1 0.3916
2 1 2 2 0.3901
2 2 1 1 0.3931
2 2 1 2 0.3936
2 2 2 1 0.3939
2 2 2 2 0.3928
```

```
PROC NESTED;
  CLASS LAB ANALYST DAY;
  VAR Y;
```

Table 3A**Simplified Analysis of Variance****For r_i Tests Done in the i^{th} Laboratory, $i = 1, \dots, \lambda$**

$n = \sum_{i=1}^{\lambda} r_i$ will denote the total number of tests in all λ laboratories

<u>Source of Variation</u>	<u>DF</u>	<u>Sum of Squares</u>	<u>Mean Square</u>	<u>Expected Mean Square</u>	<u>F Test Statistic</u>
Total	$n - 1$	SS_{Total}			
Among Labs	$\lambda - 1$	SS_L	$\frac{SS_L}{\lambda - 1} = MS_L$	$\sigma_W^2 + c\sigma_L^2$	MS_L/MS_W
Within Labs	$n - \lambda$	SS_W	$\frac{SS_W}{n - \lambda} = MS_W$	σ_W^2	

σ_W^2 is estimated by MS_W

and σ_L^2 by $(MS_L - MS_W)/c$

$$\text{where: } c = \frac{1}{n} \sum_i r_i^2$$

The “among-laboratory” variance of a single random test is again given by:

$$\sigma_B^2 = \sigma_W^2 + \sigma_L^2$$

$$\text{Repeatability} = t_{DF} \sqrt{2} \sqrt{\sigma_W^2} \quad \text{where: } DF = n - \lambda$$

$$\text{Reproducibility} = t_{DF} \sqrt{2} \sqrt{\sigma_B^2} \quad \text{where: } DF = n - 1$$

The t_{DF} are again obtained from Table 2.