

PRECISION STATEMENTS IN UOP METHODS

UOP Method 666-82

SCOPE

This method is for developing precision statements as reported in UOP Methods. Precision data in all new methods or in methods with a 67 suffix or later were developed by the described procedure.

OUTLINE OF METHOD

Using a specified method of test, either a minimum of 5 duplicate sample analyses or a minimum of 5 replicate analyses are performed. Results are tabulated and the estimated standard deviation (esd) and allowable difference are calculated.

PROCEDURE

The laboratory supervisor under whose jurisdiction the method was developed is responsible for collection of the necessary precision data. All data should be obtained by the same operator. It should preferably be of the in-line sample, duplicate result type but may also be developed from replicates on the same sample.

Obtain analyses on a minimum of 5 duplicate samples (pairs) or 5 replicates of the sample. Six or more pieces 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 esd's 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

A. Estimated Standard Deviation (esd) from Pairs (Mean Range)

Calculate the average difference (mean range) as follows:

$$\text{Average difference} = \frac{\sum A}{B}$$

where:

A = difference between two results comprising a pair

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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B = number of pairs

Calculate the esd as follows:

$$\text{esd from pairs} = \frac{C}{d}$$

where:

C = average difference, defined above

d = divisor, obtained from Table 1

Example Calculation

Sample Data, Percent Platinum

Sample No.	Trial 1	Trial 2	Difference
1	0.3824	0.3837	0.0013
2	0.3880	0.3865	0.0015
3	0.4075	0.4085	0.0010
4	0.3905	0.3915	0.0010
5	0.3780	0.3800	0.0020

1. Calculate the average difference (Mean Range) from the data.

$$\frac{0.0013 + 0.0015 + 0.0010 + 0.0010 + 0.0020}{5} = 0.00136$$

2. Find the appropriate “d” (5 pairs of data) from Table 1. Divide the average difference by “d” to obtain the esd.

$$\text{esd} = \frac{0.00136}{1.19} = 0.0011\% \text{ Pt}$$

Table 1

Divisors to Calculate esd from Mean Range

Number of Pairs of Data	Divisors, “d”	Degrees of Freedom, “n”
5	1.19	4.6
6	1.18	5.5
7	1.17	6.4
8	1.17	7.2
9	1.16	8.1

B. Estimated Standard Deviation from Replicates

Calculate the esd from replicates as follows:

$$\text{esd from replicates} = \sqrt{\frac{\sum D^2}{N-1}}$$

where:

D = deviation of an individual value from the average of all values

N = number of replicates

Example Calculation

Sample Data

Trial	% Pt
1	0.3824
2	0.3837
3	0.3850
4	0.3820
5	0.3835
6	0.3840

1. Calculate the average value from the data.

$$\text{Average} = \frac{0.3824 + 0.3837 + 0.3850 + 0.3820 + 0.3835 + 0.3840}{6} = 0.3834$$

2. Calculate the deviation of each value from the average.

Trial	Deviation
1	0.3834 - 0.3824 = 0.0010
2	0.3837 - 0.3834 = 0.0003
3	0.3850 - 0.3834 = 0.0016
4	0.3834 - 0.3820 = 0.0014
5	0.3835 - 0.3834 = 0.0001
6	0.3840 - 0.3834 = 0.0006

3. Calculate the sum of the squares of each deviation.

Trial	Square
1	(0.0010) (0.0010) = 0.00000100
2	(0.0003) (0.0003) = 0.00000009
3	(0.0016) (0.0016) = 0.00000256
4	(0.0014) (0.0014) = 0.00000196
5	(0.0001) (0.0001) = 0.00000001
6	(0.0006) (0.0006) = 0.00000036
Sum of the Squares = 0.00000598	

4. Calculate the esd by substituting into the above equation

$$\text{esd} = \sqrt{\frac{0.00000598}{5}} = \sqrt{\frac{5.98 \times 10^{-6}}{5}} = \sqrt{1.196 \times 10^{-6}} = 1.09 \times 10^{-3} = 0.0011\% \text{ Pt}$$

C. Allowable Difference (95% Probability)

Calculate the allowable difference (95% probability) from the esd obtained from either pairs or replicates using the appropriate multiplier from Table 2.

Table 2
Multiplier to Calculate Allowable Difference
(95% Probability)

Degrees of Freedom, "n"*	Multiplier	Degrees of Freedom, "n"*	Multiplier
4	3.92	10	3.15
4.6	3.75	11	3.11
5	3.64	12	3.08
5.5	3.55	13	3.05
6	3.46	14	3.03
6.4	3.41	15	3.01
7	3.34	20	2.95
7.2	3.32	30	2.89
8	3.26	40	2.86
8.1	3.25	120	2.80
9	3.20	∞	2.77

*n = Number of replicates less one, where replicates are used to calculate the esd. Table 1 gives "n" for determining the multiplier where pairs are used.

Example Calculations

If the esd calculated from 5 pairs = 0.0011% Pt and "n" from Table 1 = 4.6, then the multiplier from Table 2 is 3.75 and the allowable difference (95% probability) = (0.0011) (3.75) = 0.0041% Pt.

If the esd calculated from 6 replicates = 0.0011% Pt and "n" from Table 2 = 5, then the multiplier from Table 2 is 3.64 and the allowable difference (95% probability) = (0.0011) (3.64) = 0.0040% Pt.

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 6 replicate determinations (or, if pairs were used, 'based on 5 pairs of analyses'), the estimated standard deviation (esd) for platinum at the 0.38 wt-% level was calculated to be 0.0011%.

Duplicate results by the same operator should not differ by more than 0.0040 wt-% (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 6 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).”

Component	Level, wt-ppm	esd, wt-ppm	Allowable Difference, wt-ppm
Benzene	88	1.1	4.0
Toluene	27	0.3	1.1

NOTES

1. If it is absolutely impossible to develop precision data, a statement such as the following should be included:

“An estimated standard deviation is not reported since insufficient data are available at present to permit this calculation with at least 4 degrees of freedom.”

Such a statement should be accompanied by an estimate such as:

“It is estimated that duplicate analyses should agree within 0.2 wt-%.”

2. The calculations described in this method provide a qualitative estimate as to the precision of the method, however, the results obtained from these computations should not be considered exact statistical statements.

3. Precision data are only an indication of how well the method can be repeated. There is no direct relationship between repeatability and accuracy.